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Abstract-Number: *23*

RECYCLING OF SPENT REFRACTORIES

Bradley M.
LKAB Minerals Ltd, Flixborough, United Kingdom

Recycled refractories have been around for over 20 years although the focus and demand for these has really only taken off in the last few years. It would be environmentally unthinkable and extremely expensive for end users of refractories to send thousands of tonnes of used refractories to landfill. In addition, continued restrictions on the export of key refractory raw materials, from China in particular, has resulted in a drive to incorporate increasing amounts of recycled refractories into a variety of finished products to ensure price stability & long term supply.
A wide range of used refractories can be reclaimed including firebrick, mid-alumina brick, bauxite brick, alumina-carbon, alumag and mag- carbon.
A structured system must be in place to ensure used refractories can be segregated, transported away from the steel plant, and sorted to ensure any contaminants have been removed (e.g. slag, cement, wood). Once a clean pile has been created, the material can be tested to ensure consistency and then transported to processing plant in order to get it to sizes that a refractory customer can use. LKAB Minerals has spent several years developing suitable systems for recovering & processing recycled refractories in partnership with end users and reclaimers.
Typical applications for alumino-silicate recycled materials include medium range castables and precast shapes. Recycled alumag and mag-carbon can be used for tundish spray and furnace gunning repair products. Other possible uses of recycled refractories have been reported such as a bauxite replacement in secondary ladle treatment and crushed magnesite-carbon refractories being used as a slag conditioner in EAF.

Abstract-Number: *32*

MINERALS MATTER: REFRACTORY RAW MATERIAL SUPPLY TRENDS AND DEVELOPMENTS

O'Driscoll M.
IMFORMED Industrial Mineral Forums & Research Ltd, Leatherhead, United Kingdom

The lifeblood of successful refractories production and their application is the satisfactory development and supply of refractory raw materials. In turn, the development and supply of refractory raw materials is subject to the prevailing market performance of the key refractory markets - iron and steel, cement, glass, non-ferrous metallurgy - as well as the specification demands placed upon raw materials by the refractory manufacturers, ultimately driven by technical requirements from the end user market. Key factors among raw material requirements by refractory producers are raw material source, quality, supply, availability, logistics, and cost. Other factors such as potential alternative materials also feature in certain circumstances, although, above all, the refractory purchaser's watchword is “consistency”.
Market supply, quality, and cost characteristics differ between refractory minerals, and other factors may influence the supply and demand of certain or some minerals at any given time. This paper aims to review the latest supply trends and developments in key refractory raw materials and provide a mineral outlook for the refractories market.

Abstract-Number: *34*

IMPROVEMENT OF BOF LINING LIFE AFTER REVAMPING AT ISDEMIR WORKS

Kilic S.[1], Uzun O.[1], Yamanoğlu B.B.[2]
[1]İSDEMİR A.Ş., Refractory, Hatay, Turkey, [2]İSDEMİR A.Ş., Steelmaking shop, Hatay, Turkey

İsdemir was founded as an integrated steel plant in 1975 and located on southernmost corner of Turkey. Steel production process was done with three 130 tonne capacity converters until 2007. The total capacity was 2 million tons of steel per year. With “Modernisation and Transformation Investments” had been started in 2007, 2 million tons of established capasity expanded to 5,2 million tons and besides long products, Isdemir also started to produce flat products like hot steel roll. After complementation of “Modernisation and Transformation Investments” in 2012, Isdemir expanded its capacity, increased its product range and became available to produce such quality products that meet the market needs all in one.
During the modernisation period all three basic oxygen furnace capasities increased from 130 tone to 200 tone and new advanced technologies was integrated to 200T converters such as bottom stirring, sublance sampling, automation control (level 2-3-4) systems.

In this bulletin, current converter refractory lifetime and the main factors that affecting the converter refractory lifetime of modernised and optimised 200 ton Isdemir converters are examined. (graphics is given attc.)

Abstract-Number: *36*

COKE DEPOSITION IN THE REFRACTORY LINING OF FLUID CATALYTIC CRACKING UNIT (FCCU) - A CASE STUDY

Maity M.
Saudi Basic Industries Corporation (SABIC), Jubail, Saudi Arabia

The cracking reactions of heavy hydrocarbon feed in Fluid catalytic Cracking Unit (FFCU) of petrochemical plants, result in release of carbonaceous gases. These carbonaceous gases penetrate the porous refractory and condense as coke into the refractory matrix. Deposition of coke inside the refractory castable lining is a common problem and causes premature failures. Both the dense and the semi-insulating castables used as lining exhibit this build-up of coke in their pores. The coke impregnation inside the refractory significantly changes the thermo-mechanical properties and performance of lining. The entrapment of carbon significantly increases the casing temperature because higher thermal conductivity of carbon filled refractory material.
An investigation was conducted to check the extent of penetration of carbon in the refractory of a FCCU reactor vessel. The results revealed that the refractory lining is impregnated with carbon for a depth more than 80 % of total thickness. The detailed observations and results of refractory sample post-mortem analysis will be discussed.

Abstract-Number: *37*

THE NEW INNOVATION ON LIFE-TIME OF MSCO STEELMAKING LADLES BY USING IMPROVED SMART AMC REFRACTORIES

Bavand-Vandchali M.[1], Naiemi M.[2], Soufian G.[3]
[1]*Science and Research branch, Eslamic Azad University, Tehran, Iran, Islamic Republic of,* [2]*Mehrgodaz Refractory Co., Esfahan, Iran, Islamic Republic of,* [3]*Mobarakeh Steel Co., Esfahan, Iran, Islamic Republic of*

Carbon-containing refractory bricks (CCRBs) are one of the most important materials for the iron and steel industry worldwide. One modern steel-making company alone needs to use advanced refractories of which 70-80% are CCRBs such as MgO-C (MC) and Al2O3-MgO-C (AMC) bricks. Recently, AMC refractories are main candidate to use in different areas of steelmaking ladles, because of lower thermal conductivity, higher erosion and corrosion resistance in compare to MC refractories. Using these bricks, steelmaking ladles life-time and durability of this important equipment´s that have significant role in steel production capacity has increased.
In the present work, a new innovation of improved experienced in Mobarakeh Steel Complex (MSCo.) steelmaking ladles by using high performance smart AMC bricks will be reported. Firstly, some influential parameters governing on steelmaking ladles such as thermal, chemical and thermo-mechanical stresses and their effects on AMC refractories life-time was evaluated. Based on the above factors influencing, optimized selection of raw materials, formulation, mixing and forming condition was considered. Also, considering the importance of the in-situ spinel phase formation mechanism in the refractory bodies and its role in the properties improvement of smart AMC bricks, the microstructure of refractories was engineered by best selection and optimization of alumina and magnesia types, percent and their particle sizes. Finally, higher stability of bricks because of high thermal cycles in the steelmaking ladles, were also enhanced by mechanical strength at high temperatures.
The results indicate the new smart AMC refractories at least 30% improve in quality and performance in compare to previous bricks in MSCo.

Abstract-Number: *42*

INFLUENCE RESEARCH OF FERROSILICON ADDITION AMOUNT ON SIALON SYNTHESIS AND PROPERTIES OF SIALON BOND CORUNDUM REFRACTORIES

Primachenko V.V., Martynenko V.V., Babkina L.A., Savina L.K.
Ukrainian Research Institute of Refractories named after A.S. Berezhnoy, Kharkiv, Ukraine

Sialon bond corundum refractories are one of perspective refractories kinds, combining high strength, thermal shock resistance and resistance to oxidization, metal melts, alkaline corrosion and others.
Influence of ferrosilicon addition on β´ sialon synthesis and properties of the sialon bond corundum refractories has been investigated. It was shown that introduction of ferrosilicon addition intensifies β´sialon synthesis, thus an optimal amount of ferrosilicon content is 3 %, that allows to get maximally dense and strong samples containing 88-90 % β´sialon.
At manufacturing of the sialon bond corundum refractories, sialon forms “in situ”. It was shown that introduction 0.6 % ferrosilicon in a batch for these refractories production provides more complete flowing of β´ sialon formation reaction in the batch, that it is confirmed by carrying out X-ray and electronic-microscopic researches. Research of samples microstructure by petrographic analysis method showed that, in the samples with ferrosilicon addition β´ sialon hems, which provide denser contact of filler grains with bond matrix, are observed on the surface of corundum grains.With the using of this addition, sialon bond corundum products with low porosity, high thermal shock resistance and increased cold crushing strength (by ~ 25-27 % higher, than for products without addition) were develop.
This advanced refractories will find application in ferrous and non-ferrous metallurgy (on a contact with melts of non-ferrous metals, iron, steel and slags) and machine-building (structural elements of muffles).

Abstract-Number: *43*

THE EFFECT OF DIFFERENT BINDING AGENTS ON THE MATRIX PHASE DEVELOPMENT AND HIGH TEMPERATURE SAGGING OF A 80WT% AL_2O_3 REFRACTORY CASTABLE

Medrano L.L.O., Baldo J.B.
The Federal University of São Carlos, Materials Engineering, Sao Carlos, Brazil

In this work it was comparatively evaluated the effects on the matrix phase development and high temperature strength, of calcium aluminate cement (CAC), colloidal silica (SC) and hydratable alumina (HA), when used as binding agents for refractory castables of the 80wt% Al_2O_3 class. The phase development was followed by X-ray diffraction and the strength evolution was measured by means of the sag test after exposure for 4 hours at 1250 and 1450°C. The results indicated that for temperatures less than 1250°C, the castable assumes a more stable volumetric behavior when CAC is used as binder. On the other hand, when the castable is bonded by colloidal silica the results did not match what was reported in the literature. Conversely, for exposure at 1450°C/4h, the castable bonded by means of hydratable alumina behaved significantly better than the other two castables.

Abstract-Number: *44*

DYNAMIC PURGE PLUG; A NEW DIMENSION TO STEEL LADLE GAS PURGING TECHNOLOGIES

Velgay E.N.
Metamin Mumessillik Sanayi ve Ticaret A.S., Management, Istanbul, Turkey

With increasing demands for special qualities of steel by end consumers, in steelmaking, secondary metallurgy is becoming more and more important for steelmakers in the pursuit of producing clean, pure and homogeneous molten steel. This necessity has turned the steel ladle from a simple transport item into a reaction vessel [1]. Gas purging in steel ladles is a key element in the process of secondary steelmaking.
The aim of this paper is to provide detailed information on our recently developed product; dynamic purge plug which is designed to prevent the main thread to a ladle gas purging plug; steel infiltration.
Comparative analyses are carried out to illustrate distinctions of dynamic plug amongst several types of conventional purge plugs; both directional and non-directional. Additionally, industrial trial results are shared and performance related benefits of dynamic plug are discussed through present study.
Keywords: Gas purging plug, molten steel stirring technologies, steel ladle.
References:
1. Chaudhuri, S., Stein, D.: Application of new gas purging systems in ladle metallurgy. Interceram, Vol. 41, No. 5, 1992, pp. 313-316

Abstract-Number: *45*

UNDERSTANDING THE PROCESS MODEL FOR BUILDING TECHNOLOGICAL AND KNOWLEDGE RELATIONSHIPS BETWEEN COMPANIES IN THE ADVANCED NATIONS AND THE IRANIAN COUNTERPARTS WITHIN THE REFRACTORY INDUSTRY POST SANCTIONS

Razeghi Y.[1], Nejati Gilani S.[2], Sadoogh M.[2]
[1]*Shahid Beheshti University, Tehran, Iran, Islamic Republic of,* [2]*Management Innovation Leaders, Yazd, Iran, Islamic Republic of*

This study examines the process of rebuilding relationships between organisations in the advanced economies and the Iranian manufacturers within the refractory industry after the international sanctions have been lifted. The areas concerned include technological and knowledge transfer, and strategic partnerships. The knowledge and technological partnerships have historically existed between multinational firms and Iranian counterparts during the pre-sanctions period. However, this relationship which was built on trust, experience and cultural understanding has deteriorated during the past decades. Rebuilding these bridges will require special attention to details of change and transformational processes. Iran's rich deposits of minerals and energy resources will require new knowledge and technological advances in order to become fully operational. In the past, European countries developed effective relationships within the Iranian market, but lately this has been replaced by the Korean, Chinese and Russian industries. Kanter et al (1992) mentions the change as “the shift in behavior of the whole organization, to one degree or another”. Gouillart and Kelly (1995) further highlight the transformation process is “the orchestrated redesign of the genetic architecture of the corporation, achieved by working simultaneously - although at different speeds”. According to above authors, this transformation process is equivalent to a living organism which is created, then grows through stages of developments successfully or poorly, matures, and then dies. They further reiterate that these processes are affected by environmental turbulence including cultural, economic and technological. This highlights the main criteria of the connectivity relationship which must develop between businesses of different cultures and backgrounds. Knowledge communities and business communities must develop effectively if they are to become strategic partnerships.
Given the fact that the sanctions against Iran are currently being discussed and negotiated and that it is hoped that sanctions will step by step be reduced, this will pave the road for new opportunities for strategic partnerships.
Our study provides an overall framework for understanding the processes required for rebuilding the broken partnerships and building new ones with the Iranian refractory industry.

Abstract-Number: *49*

THE EFFECTS OF DIFFERENT TYPE OF BONDS ON BAUXITE REFRACTORIES

Mirhadi B.[1], Souri A.[2], Mirhabibi A.[1], Nabipour A.[1]
[1]*Iran University of Science & Technology, School of Metallurgy and Materials Engineering, Tehran, Iran, Islamic Republic of,* [2]*Malayer University, Malayer, Iran, Islamic Republic of*

Despite of introducing a destructive glassy phase which reduces the hot strength, different types of clay binders are used to produce bauxite refractories for many years. In this study, the effects of amount and type of clay binders such as an Iranian clay and RR40 clay has studied in order to reduce the amount of destructive glassy phase and increase hot strength of these kinds of refractories. Based on the results of this study, it has been noticed that the refractories which has been bonded by different amounts of Iranian clay binder have unacceptable high temperature characteristics, but by using different amounts of RR40 as a clay binder those properties are improved. Refractories which made of Guyanian bauxite showed a better properties than those were made by Chinese bauxite with the same amounts of RR40 clay binder. As mentioned above, such glassy phase in high amount is present in these refractories even by using pure clay binders such as RR40 clay binder, so in order to lower its amount, it is better to replace some clay binder by removable binders such as organic ones. It is found that the refractories which made of both organic and RR40 clay binders, provided that the sintering process performs perfectly in terms of time and temperatures have shown better properties. As a result hot strength has improved by the decrease in glass phase amount.

Abstract-Number: *50*

INVESTIGATION OF INTERFACIAL REACTION OF FE-C ALLOYS ON SPINEL SUBSTRATES AND SILICON CARBIDE SUBSTRATES

Okuno H.[1], Isoda Y.[2], Fukami N.[1], Miyoshi N.[3], Ogawa T.[4], Shinozaki N.[5]
[1]Taiko Refractories Co.,Ltd., Technical, Kitakyushu, Japan, [2]Kyushu Institute of Technology, Graduate School of Engineering, Kitakyushu, Japan, [3]Kyushu Institute of Technology, Center for Instrumental Analysis, Kitakyushu, Japan, [4]Mechanics and Electronics Research Institute Fukuoka Industrial Technology Center, Material Technology, Kitakyushu, Japan, [5]Kyushu Institute of Technology, Graduate School of Life Science and Systems Engineering, Kitakyushu, Japan

During the process of steel-making, the refractory is eroded when it was in contact with the molten metal and slag, due to the interfacial reaction. One of the reasons for the occurrence of the erosion is that the molten metal and slag will penetrate into the internal pores of the refractory. Since the penetration is strongly dependence on the wettability and reactivity between the melt and the refractory, it is very important to study these basic properties in order to obtain a better understanding of the refractory's erosion mechanism. Generally, the main component of the refractory consists of Al_2O_3, MgO, $MgAl_2O_4$, SiO_2, CaO, ZrO_2, SiC, C, Cr_2O_3 and so on. For instance, Al_2O_3, $MgAl_2O_4$, SiC and C are often used as the refractory materials of the trough transferring the molten iron discharged from the blast furnace. So far, many studies have reported the wettability and interfacial reaction between kinds of single-component ceramic substrates and the molten iron or slag. However, few researchers have investigated the wettability and interfacial reaction of Fe-C alloys on the spinel substrate or the silicon carbide substrate.
In this study, the wettability and interfacial reaction of Fe-C alloys on the spinel substrate and the silicon carbide substrate were investigated using the sessile drop method at 1473~1773 K and the distribution of the penetrated Fe-C alloys was analyzed at the interface.
The spinel substrate (Al_2O_3-28.3mass%MgO) and the SiC substrate (purity over 99.7mass %) were employed in this study. The penetration depth of the Fe-C components in the substrates and the distribution of MgO, Al_2O_3 and SiC were investigated by varying the holding time at 1473~1773 K. The EDS analysis showed that for the Fe-C alloys / spinel substrate system, the penetration of the Fe-C alloys in the spinel substrate was not found, thus, it could be concluded that the reaction between the spinel substrate and the Fe-C alloy was less likely to occur. For the Fe-C alloys / the SiC substrate system, due to the dissociation reaction of SiC occurring continually, the Fe-C alloy was easily penetrated into the SiC substrate with Si and C dissolving into the Fe-C alloy. Moreover, with increasing the holding time at high temperature, the amount of penetration increased.

Abstract-Number: *51*

INFLUENCE OF DISPERSANTS TYPE AND AMOUNT ON THE STRUCTURE RHEOLOGICAL PROPERTIES OF VIBROCAST GRAIN MIXES FROM CAO-STABILIZED ZRO_2

Primachenko V.V., Martynenko V.V., Shulik I.G., Kushchenko P.A., Shyshkovskiy D.A.
Ukrainian Research Institute of Refractories named after A.S. Berezhnoy, Kharkiv, Ukraine

Use of vibrocasting method for zirconia products manufacture allows making of complicated configuration products, in particular crucibles for melting of platinum group metals. Application of high-efficiency dispersants, which allow substantial decreasing in moisture of forming mix, plays considerable role for vibrocasting technology.
In this work, an influence of three modern dispersants (Castament FS 10 + FW 10 and Castament FS 65) on the flowability under vibration of grain mix from CaO-stabilized ZrO_2 has been researched. It was shown that, the mix flowability is substantially better with using of Castament FS 65 instead Castament FS 10 + FW 10 in an optimal amount at equal moisture. An influence of the mix holding time (up to 216 hours) with the use of Castament FS 10+FW 10, and also Castament FS 65 on the change of mix flowability under vibration, as well as its plastic strength, has been investigated too. It was determined that, in the mix with the use of Castament FS 10 + FW 10 a coagulate-condensation structure appears with the increasing of its strength as far as the increase of mix holding time. With Castament FS 65 introduction an appearing in the mix structure substantially differs from previous - it is weak and practically fully is destroyed under vibration for 7-8 minutes even after mix holding for 120 hours. These researches allowed setting “life” of mix. As a result of the carrying out researches, due to the use of Castament FS 65, the mix moisture for making of products from CaO-stabilized ZrO_2 by the vibrocasting method was decreased to 3.0-3.2 % as compared to 4.0-4.2 % for the analogical mixes, containing Castament FS 10 + FW 10.

Abstract-Number: *52*

PHASE EVOLUTION OF HIGH-ALUMINA PHOSPHATE-BONDED REFRACTORY CASTABLES

da Luz A.P.[1], Gomes D.T.[2], Pandolfelli V.C.[1]
[1]*Federal University of Sao Carlos, Materials Engineering Department, São Carlos, Brazil,* [2]*Petrobras, Rio de Janeiro, Brazil*

Different routes can be used to induce *in-situ* generation of monoaluminium phosphate [$Al(H_2PO_4)_3$ or MAP] in castable compositions. MAP is one of the most applied chemical binder in the refractory field, due to its suitable solubility in water, bonding strength and reaction with basic and amphoteric raw materials at low temperatures. Considering these aspects, this work evaluates the effect of adding $Al(OH)_3$ to H_3PO_4-containing refractory formulations, aiming to point out the main phase transformations taking place during drying (at 110ºC) and firing steps (up to 800ºC) of the prepared samples. Various experimental tests (flowability, setting time, cold mechanical strength, thermogravimetric measurements, X-ray diffraction) were carried out. According to the attained results, the most promising binding system was obtained by mixing H_3PO_4 solution with 48 wt% of concentration + $Al(OH)_3$ particles prior to castables homogenization/preparation procedure. The formation of a higher content of $MgHPO_4.3H_2O$ and $AlPO_4.H_2O$ hydrates seemed to act speeding up the castable's setting time. Based on the crystalline phases contained in the fired samples, Al_2O_3, $AlPO_4$ (monoclinic or hexagonal), farringtonite [$Mg_3(PO_4)_2$] and $M_2P_2O_7$ were the main compounds derived from the interaction of the hydrated phosphates with the refractory raw materials during heating. Furthermore, the samples prepared with 48 wt% solution of H_3PO_4 showed cold flexural strength and hot modulus of rupture values around 15 - 30 MPa after firing them in the temperature range of 500ºC to 815ºC.

Abstract-Number: *53*

DESIGN OF HIGH-ALUMINA MGO-BONDED REFRACTORIES BASED ON THE BNG (BOUNDARY NUCLEATION AND GROWTH) MODEL

Santos Jr. T.[1], da Luz A.P.[1], Pagliosa C.[2], Pandolfelli V.C.[1]
[1]*Federal University of Sao Carlos, Materials Engineering Department, São Carlos, Brazil,* [2]*Magnesita Refratarios S.A., Research and Development Center, Contagem, Brazil*

MgO is a very attractive raw material for refractories. Nevertheless, its use has been mainly directed to the development of high-magnesia and magnesia-carbon bricks due to the marked hydration likelihood of this oxide, and the related drawbacks (volumetric expansion, cracks formation) associated to this transformation. This work aims to evaluate some critical aspects that affect the MgO reaction with water (magnesia source, particle size, concentration of available sites for nucleation, influence of a hydrating additive - acetic acid, and others) during curing and drying of Al_2O_3-MgO binder-free refractory castables. The attained experimental results were correlated to the boundary nucleation and growth model proposed in the literature. According to the *in situ* elastic modulus measurements carried out at 110ºC, the MgO particle size and reactivity present an important effect on the nucleation and growth of brucite crystals, highlighting that a proper site activation (saturation) should be induced during the castables' curing process in order to effectively allow the use of magnesia as a binder source for refractories. A faster $Mg(OH)_2$ nuclei generation also helps to minimize the further growth of these crystals, leading to a decrease of the samples' porosity and, consequently, a continuous increase of the overall refractory' stiffness (E values).

Abstract-Number: *57*

THE EFFECT OF PENTAVALENT OXIDES ADDITIVES ON THE PHYSICAL AND MECHANICAL PROPERTIES OF α ALUMINA CERAMICS

Naga S.M.[1], Hassan A.M.[2], Awaad M.[1]
[1]*National Research Centre, Ceramics, Cairo, Egypt,* [2]*Zagazig University, Faculty of Engineering, Materials Engineering Dept., Zagazig, Egypt*

The effects of Ta_2O_5 and Nb_2O_5 addition on the densification behavior, microstructure and mechanical properties of Al_2O_3 ceramics were investigated. The Ta_2O_5 and Nb_2O_5 additions to the alumina matrix were varied from 0.25wt% to 0.75 wt%. The powders of each composition were uniaxially pressed at 220 MPa into discs and rectangular bars, which were then pressureless-sintered at 1650 °C for 1 h. The phase constitution and microstructure of the sintered ceramic bodies were characterized with a X-ray diffractometer and a scanning electron microscope. The mechanical properties of the ceramic bodies were evaluated on the basis of their Vickers hardness (HV1), bending strength and fracture toughness. It was found that Ta_2O_5 addition enhanced the mechanical properties of alumina bodies in comparison to Nb_2O_5 addition. The maximum bending strength, fracture toughness and Vickers hardness of the bodies with 0.75wt% Ta_2O_5 were 14.2, 6.1 and 3% higher than that of 0.75 wt% Nb_2O_5 doped Al_2O_3 samples.

Abstract-Number: *59*

CHARACTERIZATION OF THE COMPRESSIVE CREEP BEHAVIOR OF CLAY REFRACTORY MATERIALS - DEVELOPMENT OF A "TIME LAW"

Pilate P.[1], Lardot V.[1], Cambier F.[1], Bröchen E.[2]
[1]*BCRC, Belgian Ceramic Research Centre (member of EMRA), Mons, Belgium,* [2]*FGF, Forschungsgemeinschaft Feuerfest, Höhr Grenzhausen, Germany*

A classical 40-45 % alumina clay refractory material was characterized by its chemical and crystallographic compositions, apparent density and open porosity, refractoriness under load and bending strength versus temperature. Creep tests were realized, using the differential method. In this work, a new approach was used to interpret the results and to develop a new creep model for this kind of refractory material.
In the range of temperature used in this work (1250-1350°C) and under a constant pressure of 0.2 MPa (according to EN and ISO Standards), the result of the tests is a densification (shrinkage and porosity decrease). Authors stated that the creep is not only a function of the time but also of the microstructure. During the creep test, the microstructure evolves continuously and the relation between the creep deformation, the creep rate and time is probably complex. Actually, it does not exist adequate tools to exactly describe the microstructure of refractory materials, notably the vitreous phase and its location. Then it is not possible to relate the creep behavior to the evolution of the microstructure and it is interesting to develop model(s) and law(s) describing the macroscopic behavior of the material. The premise that the creep rate is directly linked to the inverse of the displacement, allows the development of new formulas which mathematically allow describing the creep curves:
$\varepsilon = (a \exp -Q/RT)\, t^{1/2}$ and $V = (1/2\, a \exp -Q/RT)\, t^{-1/2}$. The model allows describing both the first and the second steps of the creep curve. It also leads to calculate single activation energy which is valid during the whole time of deformation. The obtained value is very similar to that one calculated with a more classical method, during the stationary (linear) step. Comparison between the experimental values and calculated ones from the model shows a good correlation. The scattering of the results is explained by the heterogeneity of the material which induces difference in samples. It can be also explained by the effect of temperature which probably induces a modification of the vitreous phase composition.
Results will be discussed and compared to previous literature and previous creep models.
This work was realized in the framework of a CORNET project: CREEPREF and was thankfully funded by AIF (Germany, project IGF-Nr 74 EN) and SPW (Belgium-Wallonie, project Nr 1117538).

Abstract-Number: *61*

MONOLITHIC SOLUTION FOR LINING CEMENT KILNS: INNOVATIVE CONCEPT & COMPARISON VERSUS BRICKS

Soudier J.[1], Klippel U.[1], Malkmus P.[2], Dromain C.[1]
[1]*Calderys, Research & Development, Saint Quentin Fallavier, France,* [2]*Calderys, Research & Development, Neuwied, Germany*

Cement rotary kilns require high performing refractories able to withstand very high temperatures, high thermo-mechanical stresses, and chemical attack from hot or liquid clinker. Consequently the lining of the upper transition, burning and lower transition zones consists very often in magnesia spinel bricks. Magnesia can withstand high temperature, the incorporation of spinel grains is known to improve capability to resist to high thermo-mechanical solicitations such as thermal cycling or geometrical deformation during operation.
However, there are sections where bricks cannot be installed easily; mainly due to strong shell geometrical deformation; or do not perform as expected due strong lining deformation during operation. This is typically the case for the tires areas. It is also more and more the case that magnesia-spinel bricks suffer from strong chemical attack resulting from penetration of alkali salts or sulfurs and chlorides coming from intensive use of alternative fuels.
In the upper cases of difficulty for brick installation, high shell and lining deformation during operation and strong chemical attack, monolithic refractories could be an advantageous solution. Refractory castables can be installed on any geometry, can accommodate thermal cycling and hot deformation during operation, and can as well exhibit totally different pores size and capillary structure than bricks, resulting in different behavior in front of salts attack. In particular magnesia based castables could be valuable candidates.

The present paper describes in a first part how formulation design of dense, cement free, magnesia based castables has been optimized in terms of thermal-cycling resistance and macro crack propagation resistance when submitted to deformation. In particular it has been investigated how the mentioned optimizations can be achieved by incorporation of compounds such as alumina, AM spinel or Zirconia, exhibiting either thermal expansion mismatch versus magnesia matrix, or phase transformations, that results in micro-cracks formation during first lining heating up or first cooling down.
In a second part, properties of such optimized castables are compared to standard magnesia-spinel bricks, both in terms of thermo-mechanical behavior and in terms of resistance to clinker, alkali, sulfurs and chlorides contact.

Abstract-Number: *62*

PREMATURE WEAR IN THE HEARTH OF A BLAST FURNACE AND ITS DIMINUTION BY THE APPLICATION OF TITANIUM DIOXIDE

Fünders D.[1], Harmuth H.[2], Pötschke J.[2]
[1]*GSR - Gesellschaft für Synthetische Rohstoffe, Moers, Germany,* [2]*Montanuniversitaet Leoben, Chair of Ceramics, Leoben, Austria*

Adding titanium dioxide to the slag may repair premature wear in the hearth of a blast furnace (BF) under service. Titanium carbonitrides are formed and deposit preferential in the damaged zones.
The paper presents the thermodynamic calculation of possible carbonitride formation and makes a suggestion why they accumulate mainly in the damaged zones.
Calculation shows, that drops of pig iron passing through the slag are forming iron-titanium carbonitrides on their surface. They accumulate at the interface between slag and hot metal.
Due to intensive cooling of the worn out location its hot face temperature is somewhat lower than the hot metal itself. In addition the melt is saturated with carbon, reacting with the graphite of the wall, which lowers the oxygen activity in the melt near the refractory hot face. Both effects result in a Marangoni flow of both melts hot metal and slag, respectively, towards the lining hot face. Hence titanium carbonitride is transported toward the damaged zones. The Marangoni flow is calculated quantitatively. Even by using unfavorably specifications the Marangoni flow at least results to about 10cm/s. This is a lower limit and should be higher under service conditions.

Abstract-Number: *63*

LATEST DEVELOPMENTS IN RH DEGASSER SNORKELS

Kumar S., Kremer A.
GSB Group GmbH, Bochum, Germany

The RH vacuum degassing technology has been upgraded by many equipment builders through many improvements since its introduction in 1959 in Stahlwerk “Henrichshütte” in Germany. In addition to its primary purpose of eliminating harmful gases, RH degasser has included various operations such as refining special steel by parallel use of oxygen blowing RH-OB for making ultra low carbon. Both in BOF and EAF steel making route the RH degasser has become indispensable in the secondary metallurgy area.
The snorkels are one of the critical part of RH degasser and its service life is the key for uninterrupted effective functioning of the equipment as well as the refractory cost. Performance improvement in RH Snorkels is the ongoing challenge and the latest developments carried out over the past years. The determination factors for the performance are the wear of inner bricks as well as outer castable, crack formation and peeling effect of outer castable. Also the deformation of the core steel shell plays a vital role in determining the service life.
Scope: This paper provides brief information about the key factors affecting the performance of the RH Snorkels. The paper also underpins the importance of steel construction involved snorkel manufacturing, highlighting the benchmarking performance of selected steel mills in Europe and recent developments with regard to the RH Snorkels including complete monolithic lining as well as introduction of chrome free bricks for snorkel application.
Keywords: RH Vacuum Degassing, RH Snorkels, Refractory, Steel shell core, Deformation, Castables, Crack, Benchmarking.

Abstract-Number: *64*

EFFECT OF MICROSTRUCTURE ON SLAG CORROSION RESISTANCE OF MAGNESIA CARBON BRICKS

Miyamoto Y., Hino Y., Matsunaga H., Watanabe K.
JFE Steel Corporation, Steel Research Laboratory, Chiba, Japan

Magnesia carbon bricks possess superior corrosion resistance against steelmaking slags, and thus have been used for the lining of converters. As it is thought that the microstructure and chemical composition of bricks affect their corrosion resistance, one important factor for obtaining improved corrosion resistance is to understand the relation between the corrosion resistance and microstructure of bricks. In this study, a slag corrosion test and microstructure observation were carried out, and the relation between the microstructure and corrosion resistance and the factor that affects corrosion resistance were discussed.
Six samples with carbon contents of 20mass% were used in a slag corrosion test using a high-frequency induction furnace. A hexagonal sleeve of sample bricks was formed and was set in the furnace. 6.8kg of metal and slag were melted, and the wear thickness of each sample was compared. The experimental temperature was 1953K and the holding time was 3hours. (T.Fe of the slag was 20.8mass% and the basicity of the slag was 3.0 as slag composition.) The magnesia particle size, graphite particle size and periclase grain size in magnesia particle were measured by microscopy.
As a result, the corrosion reisistance of magnesia carbon brick with large periclase grains was better than that of bricks with small grains. From this, it was predicted that the periclase grain size, namely, the ultimate particle size of periclase, rather than the magnesia particle size, i.e., the secondary particle size or graphite size, would largely affect corrosion resistance. Therefore, it is predicted that use of magnesia raw material with a larger ultimate particle diameter in magnesia carbon bricks is preferable for improving the corrosion resistance of bricks.

Abstract-Number: *65*

PENETRATION OF COAL TAR INTO GLAZE COATED COKE OVEN DOOR BLOCKS

Nishiguchi H., Sakawa K., Yamashita K., Iida M.
Shinagawa Refractories Co.,Ltd., Bizen, Japan

Glaze coated coke oven door block after commercial application was investigated. According to the chemical analysis of the block, carbon that hadn't been included in the initial block was detected. The result shows that coal tar was penetrated into the block in spite of glaze coating treatment of its surface. Prior to the commercial application, however, effectiveness of glaze coating on inhibition of coal tar penetration had been demonstrated by heating experiment of tar-topped specimens. Taking these facts into account, it is hypothesized that coal tar ingredients, i.e. hydrocarbon, penetrated into the block as gas phase, the so-called coke oven gas, during operation.
From the view point of changes in physical properties after commercial application, decrease in apparent density and apparent porosity, increase in bulk density and cold crushing strength were recognized. The tendency is considered attributable to the densification of structure by filling pore with penetrated coal tar ingredients deposit.
The coal tar penetration and consequential densification was more remarkable in far side from the coking chamber. The difference in carbon penetration degree, i.e. densification degree, between chamber side and outer side can be explained by transfer and condensation of coal tar ingredients as follows. In coking period, coke oven gas is pressed into the door blocks by in-chamber pressure followed by condensation of coal tar ingredients at outer side due to the lower temperature. In discharging period, however, pressure decrease in chamber side induced by door removal causes gas flow from inside of the block to the outside which causes escape of coke oven gas from the block.
Nevertheless, the block maintained smooth surface of glaze coated layer. The smoothness is advantageous in gas emission from coking chamber as well as in reduction of work load for door cleaning. Hence, it is concluded that glaze coating is effective to keep the door block surface smooth even if the coal tar penetrated into the block.

Abstract-Number: *66*

EFFECT OF MICROSILICA ADDITION ON THE PROPERTIES OF BAUXITE-ANDALUSITE BASED CASTABLES AT THE PRESENCE OF COLLOIDAL SILICA BINDER

Zhang J.[1], Yan S.[1], Liu X.[1], Jia Q.[1], Li X.[2], Guo H.[2]
[1]*Zhengzhou University, Zhengzhou, China,* [2]*Henan Hongda Luliao Co. Ltd, Zhengzhou, China*

Bauxite-andalusite based castables were prepared using homogenization bauxite (Al_2O_3≥80%) and andalusite as aggregates, andalusite fines, corundum fines, ultrafine Al_2O_3 and microsilica as matrixes, and using colloidal silica as binders. The influences of microsilica on the bulk density, apparent porosity, green strength, cold modulus of rupture, cold compressive strength, hot modulus of rupture and thermal shock resistance of castables at the presence of colloidal silica binder were firstly investigated. After that, the structural evolution and morphologies of castables were studied with the aids of X-ray diffraction and scan electron micrograph. The final results show that the specimens exhibited a higher of bulk density values and the defects of porosity content decreases through replacing some colloidal silica by microsilica; which exhibited higher green strength, cold CCS, cold MOR, hot MOR values and better thermal shock resistance compared to the only colloidal silica bonded castables.

Abstract-Number: *67*

INVESTIGATION OF CORROSION OF N-SIC MATERIAL BY THE MELT OF COPPER AND THE COPPER SLAG

Yurkov A.[1], Danilova O.[2], Dovgal A.[2], Doroganov V.[3], Evtushenko E.[3]
[1]*JSPC 'Voljsky abrasive works', Moscow, Russian Federation,* [2]*JSPC 'Voljsky abrasive works', Voljsky, Russian Federation,* [3]*Belgorod State Technological University named after Shukhov, ceramics and glass, Belgorod, Russian Federation*

Silicon Carbide refractories may be used in contact with copper and copper slags. The object for the investigation of corrosion by the melt of copper and the copper slag was the N-SiC siphon block of the slag collector in the runner of the cathode shaft furnace for the re melting of cathode copper. It is exposed to the permanent flow of copper with small amount of slag. Slag on the surface of the melt is stopped by siphon block and it suffers the most extensive corrosion wear, but the same time it is a good object for investigation, because different parts of this plate are exposed to intensive corrosion by different corrosive agents.
General observations show, that the corrosion of N-SiC by slag is sufficiently more extensive and the wear is about 3 mm per month, while the wear by the flowing copper is below 1 mm per month.
The observation of the cross section of the exposed N-SiC plate on macro level shows 4-5 zones of different color. Microstructural observations shows almost no changes of the material in direct contact with molten copper without exposure of air, that suggests slow dissolution of Silicon Carbide and Silicon Nitride in the flowing melt of copper. The same may be said about the “back” part of the plate, dipped in the copper (not exposed to permanent flow) - there is no wear and there is almost no observable changes in the structure of N-SiC refractory.
The upper part of N-SiC plate (above the level of the melts of copper and slag) slowly oxidizes, that is accompanied by volume increase of the plate due to the positive volume effect of oxidation of Silicon Carbide and Silicon Nitride. The expansion by 2 mm of the upper part (not exposed to the erosion by slag and copper) of 70 mm N-SiC plate (~2,9%) within 8 months and by 5 mm (~7%) of the part, dipped in copper, suggests inner changes in the material. This kind of interaction might be estimated by oxidation resistance test ASTM C863, where the volume increase is a criterion.
The most severe wear of NiC refractory is by slag. Not an easy question on priority - if these phosphates and silicates of Aluminium, Zink and Copper interact directly with Silicon Carbide and Silicon Nitride, or first takes place the oxidation of Silicon Carbide and Silicon Nitride to Silica, and the resulting Silica reacts with Phosphates and Silicates of Aluminium, Zink and Copper with following dissolution of reactants in the flowing melt.

Abstract-Number: *69*

ALF_3 MECHANISM AND ITS INFLUENCE ON THE CALCINED ALUMINA PROPERTIES

Riello D.[1], Zetterström C.[2], Parr C.[2], Braulio M.A.L.[3], Gallo J.B.[3], Pandolfelli V.C.[1]
[1]*Federal University of São Carlos, São Carlos, Brazil,* [2]*Kerneos SA, Vaulx-Milieu, France,* [3]*Alcoa SA, Poços de Caldas, Brazil*

α-Al_2O_3 is one of the most used oxides for advanced ceramics due to its excellent properties such as chemical inertness, hardness and wear resistance. Calcination is an important step in the alumina processing, affecting its surface area, soda content, impurities, crystal morphology and the alpha-phase amount. Over the previous decades attempts have been made to understand this step in the presence of mineralizers. Aluminum fluoride, AlF_3, is the most common additive used for decreasing the conversion temperature, bringing important benefits for the industry. It is known from the literature that a mineralizer speeds up the mass transport from the transition phase to the α-Al_2O_3 one, but the actual reaction mechanism is not well understood. Besides

decreasing the conversion temperature, AlF_3 also affects the physico-chemical properties of the calcined alumina changing its morphology and inducing the crystal growth. In this study small contents of AlF_3 (0.45 and 0.6 %wt) were added by a dry mixing procedure to different precursors (hydroxide and transition alumina) and the morphology, primary crystal size and surface area of the calcined powder were evaluated. The likely AlF_3 reaction mechanism was investigated by DSC, SEM and XRD. The gas-solid reaction via the generation of a transition compound (Al-O-F) was finally evidenced and the results pointed out that the alpha conversion can be easily concluded in less than 30 minutes if enough fluoride and temperature are provided. Additionally, the influence of the homogenization step in the alpha transformation was studied.

Abstract-Number: *71*

NONLINEAR TEMPERATURE PROFILING IN CALORIMETRIC THERMAL CONDUCTIVITY DETERMINATIONS

Bullock L.C., Mustafa C., White R.N.
Lucideon, Testing, Stoke-on-Trent, United Kingdom

Current thermal conductivity techniques that employ temperature gradients and calorimetry make the assumption that thermal conductivity is independent of temperature. As such the Laplace equation holds for thermal conductive heat transfer across a variety of refractory and insulation products. Several types of refractory and insulation materials were tested to a modified version of the panel method to determine the departure from linearity of the temperature profiles of a number of materials; along with the effect of fitting to these profiles to define an integral mean thermal conductivity. These determinations were compared with the results of established calorimetric thermal conductivity techniques.

Abstract-Number: *72*

SLAG ENTRAINMENT IN STEEL LADLES IMPACTING REFRACTORY WEAR

Huang A.[1,2], Harmuth H.[2], Doletschek M.[2], Vollmann S.[2]
[1]*Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallurgy, Wuhan, China,*
[2]*Montanuniversitaet Leoben, Chair of Ceramics, Leoben, Austria*

It is well known that at high purging rates slag entrainment may occur in steel ladles and by this cause wear of the side walls also below the steel/slag interface. Therefore measures to estimate a critical purging rate are needed in order to avoid this kind of wear. Three different approaches are presented in this work. One is the choice of suitable figures of merit like the Capillary Number and the Weber Number to establish a criterion for slag entrainment. A second route is a computational fluid dynamics (CFD) simulation, and a third the application of a water model. All three possibilities have been studied and are compared in the presented research work.
While the application of figures of merit is the most simply option, CFD simulation is a very challenging task due to multi-scale phenomena. To decrease the computational effort an analytical framework was set up which enables the calculation of the boundary conditions if only a part of the steel- and slag-volume is represented in the model chosen. Then, a Large Eddy Simulation combined with a multiphase Volume of Fluid model was applied. As a result, also the droplet size distribution could be calculated, and the mechanism of slag entrainment was revealed. Slag entrainment starts with a severe deformation of the steel/slag interface especially at the edge of the open eye formed by the spout. There some slag is pulled downwards in the direction of the fluid flow, and detachment of droplets starts at the lower end of this part of the slag.
As a result it was observed that the capillary number well agrees with the onset of slag entrainment as identified by the simulation and the water model. Additionally the latter two methods give the possibility to obtain information about the mechanism of slag entrainment, the droplet size and the amount of entrained slag.

Abstract-Number: *73*

EUROPEAN REFRACTORIES RECYCLING - CURRENT TRENDS AND PROSPECTS

Roberts J.
Roskill Information Services, London, United Kingdom

Europe has long been a leader in recycling of used refractory products but in the last decade recycling has gained traction, due to factors such as sustainability and environmental issues, and security of raw materials.
In 2008 the European Commission launched the Raw Materials Initiative, which aimed to establish an integrated strategy for ensuring access to raw materials of key importance to Europe's industries. Part of the initiative was to promote recycling and use of secondary raw materials. The EU refractories industry is heavily reliant on imports of refractory raw materials such as dead burned and fused magnesia, graphite, bauxite, zircon and fused zirconia.
Refractory recycling in Europe thus serves two main purposes; it reduces waste and landfill, and provides a stable supply of key raw materials. The European Refractory Producers Federation (PRE) estimates that 20% of used refractories are recycled into refractory applications, 27% is reused in non-refractory applications, 35% is dissolved during use, and 18% is landfilled.
Roskill estimates that European refractories production was 3.8Mt in 2013, indicating that around 750,000t of used refractories were recycled into materials for refractory applications. Germany is the leader in the refractory recycling market, producing approximately 215,000tpy of secondary materials for refractories or around a third of the European total. Germany creates around 350,000tpy of refractory waste according to Statisches Bundesamt.
The main secondary raw materials produced from recycled refractories are magnesia, dolomite, silica, alumina, zirconia and silicon carbide. The EU-28 countries produce a significant proportion of world output of calcined alumina, sintered dolomite, and silica, but are reliant on imports for refractory magnesia, zircon and zirconia, and silicon carbide.
This paper will discuss the supply situation for production of secondary refractory minerals, and contrast this with virgin production of these minerals and the competitiveness of secondary minerals in the EU refractories market.
In addition the paper will address the main refractory products and applications that secondary minerals are used in and their cost compared to virgin materials. The paper will also provide a medium-term outlook for refractories recycling and secondary minerals production in Europe, and how this could affect demand for virgin raw materials over the next decade.

Abstract-Number: *74*

NOVEL MULTILAYER REFRACTORIES DERIVED OF CAST CERAMIC GREEN TAPES AND PRECERAMIC PAPERS

Hammerbacher R.[1], Dermeik B.[1], Travitzky N.[1], Lange F.[2], Roosen A.[1]
[1]*University of Erlangen-Nuremberg, Department Material Science, Glass and Ceramics, Erlangen, Germany,* [2]*Siemens AG, Mülheim an der Ruhr, Germany*

A new approach to enhance the thermal shock and corrosion resistance of refractories based on multilayer structures of cast ceramic green tapes, preceramic papers, or a combination thereof. For this study, tapes of different powders with particle sizes up to 1 mm and thicknesses between 0.1 and 4 mm were cast. Due to different powder fractions of Al_2O_3, $MgAl_2O_4$, MgO and Mullite in the individual tapes the porosity, sintering shrinkage and coefficients of thermal expansions could be varied. In order to fabricate multilayer structures different tapes are stacked and joint in the green state via lamination techniques such as thermo-compression and cold low pressure lamination. For further improvement of the properties of multilayer refractories, ceramic green tapes were laminated with preceramic papers. These papers may be high loaded with different ceramic powders (e.g. Al_2O_3) and fibers and therefore influence sintering behaviours such as shrinkage, microstructure and thus properties of resulting ceramic structures.
The study presents the manufacturing process of ceramic green tapes and of multilayer products including preceramic papers. Thermal and mechanical properties of the sintered structures were characterized extensively. The effect of laminate design on the properties of such multilayer refractories is discussed.

Abstract-Number: *75*

INFLUENCE OF ANTIFREEZING AGENT ADDITION ON ALUMINATE CEMENT BONDED REFRACTORY CASTABLE USED AT NEGATIVE TEMPERATURE

Wang S.Y., Zhang X., Cao X.Y., Wang Z.M.
Sinosteel Luoyang Institute of Refractories Research, Luoyang, China

Refractory castable can hardly achieve normal workability at negative temperature. By adding antifreezing agent and then casted at negative temperature (-5℃, -10℃ and -15℃), series of properties of aluminate cement bonded refractory castable were studied, including the flowability, strength after natural curing, strength and PLC after heat treatment respectively at 110℃×24hr, 1200℃×3hr and 1450℃×3hr as well as HMOR at 1300℃.

Normal workability of castable at negative temperature can be ensured by adding antifreezing agent, that is, little influence on flowability and demoulding strength after natural curing. However, there was certain degree decrease on strength after heat treatment. Otherwise, a little decrease on HMOR was found due to some low melting point inorganic salt introduced by antifreezing agent. Further simulation field test proved aluminate cement bonded refractory castable can achieve normal workability by adding antifreezing agent at negative temperature.

Abstract-Number: *77*

INFLUENCE OF NANOPARTICLES AND SEMICONDUCTOR ON THE MECHANICAL AND THERMO-MECHANICAL PROPERTIES OF CARBON BONDED ALUMINA REFRACTORIES

Mertke A., Aneziris C.G.
TU Bergakademie Freiberg, Keramik, Glas-, und Baustofftechnik, Freiberg, Germany

Modern steel casting plants require functional refractory components such as monobloc stoppers, submerged entry nozzles, and ladle shrouds. The functional flow control components in steel casting plants are often made of carbon bonded alumina refractories containing approximately 30 % residual carbon after coking. A high disadvantage of this type of refractory is the possible oxidation of carbon. In this work different additives (carbon nanotubes, alumina nanosheets and semiconductive silicon) were added to the system Al_2O_3-C to investigate its influence on the mechanical and thermo-mechanical properties. Simultaneously, the carbon content was reduced to approximately 20 %. By optimizing the mixing and curing conditions of the samples and with adding of all the additives, high residual strengths could be recorded after thermal shock treatment. Before thermal shock the samples had a cold modulus of rupture (CMOR) of 14.5 MPa. After the first thermal shock the CMOR decreases to 12.1 MPa and increases after the fifth thermal shock to 13.9 MPa. Finally the samples had a strength loss of only 4.3 % after the fifth thermal shock (reference without additives 35.6 %). To determine the possible reason for this result an scanning electron microscope was used. An increase of SiC-whisker formation could be seen with the addition of all additives.

Abstract-Number: *78*

MOLAR VOLUME MODEL AND DATABASE FOR MOLTEN SLAGS

Thibodeau E., Jung I.-H.
McGill, Mining and Materials Engineering, Montreal, Canada

Molar volume is one of the most fundamental physical properties necessary for engineering material processes. In the present study, all the literature experimental data for the molar volume of molten oxide slags of the CaO-MgO-Al2O3-SiO2-FeO-Fe2O3-MnO-PbO-Na2O-K2O-Li2O system were critically evaluated. A new structural molar volume model based on silicate melt structure was developed to reproduce all the reliable experimental data within experimental error limits. This new model can successfully reproduce the molar volume in all slag composition ranges while previous linear molar volume models are only applicable in certain ranges.

Abstract-Number: *79*

STUDY ON THE PREPARATION AND PROPERTIES OF ALUMINA HEAT INSULATION MATERIAL WITH HIGH PURITY

Wang G.[1], Yuan B.[1], Wu H.[2], Dong B.[1], Han J.[1], Chen K.[1], Li H.[1]
[1]*State Key Laboratory of Advanced Refractories, Sinosteel Corporation Luoyang Institute of Refractory Research Co., Ltd., Luoyang, China,* [2]*State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China*

With the widely using of transparent alumina ceramic and sapphire, the demand of the furnace for them was promoted steadily, and the furnace lining materials were upgrading. Having low thermal conductivity and the same composition with transparent alumina ceramic and sapphire, high-purity alumina porous ceramic was expected to be used to lower the high energy consumption without contamination. In this paper, porous alumina ceramics with porosity of 75.3-81.9% and impurity of less than 0.1% were prepared by foaming method combined with gelcasting, using high-purity alumina powders as raw materials. By changing the solid

content and amount of foaming agent can tailor the microstructure and properties of porous ceramics. The compressive strength of the porous ceramics ranged from 22.4 to 48.1MPa, thermal conductivity at 1000℃ ranged between 0.41-0.65W / (m • K).

Abstract-Number: *81*

DEVELOPMENT OF QUICK DRYING CASING MATERIAL FOR A BLAST FURNACE

Kajihara M., Komatsu T., Fujiwara H.
Nippon Crucible Co.,Ltd., Toyota plant, Aichi, Japan

Generally, middle or large sized blast furnace has four or more main troughs. The main trough repair is systematically performed in rotation. While the blast furnace operates stably, the main trough repair requires for 7 to 10 days before the restart of the furnace operation. Casting material is usually applied for the trough repair. After the repair with the casting material, drying is required in order to remove the moisture inside of the installed casting material. An automatic dryer is used for drying. The moisture within the casting material is gradually evaporated by slow heating. A sound structure without crack and peeling has to be made before the operation starts.
In contrast, a small sized blast furnace usually has one or two main troughs. Long time repair for the middle or large sized blast furnace during the stable operation is possible. But long time repair is not possible for the small furnace. The repair has to be completed within a short time, because the furnace needs to be restarted soon.
If the operation is unstable for the middle or the large sized furnace, the repair has to be finished as soon as possible. Then the main trough should be restarted soon. In this case, the drying process, which is the longest process for the repair, has to be shortened. Therefore, we have developed casting material that has quick drying character for the trough at the blast furnace and we would like to present the paper.
As a result of quick drying casting material installation at the actual trough, the drying time was reduced by half or more than the conventional casting material. We succeeded to form sound structure as well as maintaining the lining life for the casting material.

Abstract-Number: *85*

IMPROVEMENT OF THE CORROSION RESISTANCE FOR SPINEL GRAPHITE MATERIALS

Liu G., Li H., Yang W.
Luoyang Institute of refractory research, Luoyang, China

Monolithic stopper is a key functional refractory for continuous casting, which control the molten steel flow from the tundish to the mold. When used to cast high-Mn steel, spinel-graphite monolithic stopper was seriously eroded. Micro spinel particle, zirconia or chromium oxide was added into the spinel-graphite material and physical properties were measured. The developed materials were also made into the monolithic stopper to cast high-Mn steel. The results show that the corrosion resistance of developed monolithic stopper was improved. By analyzing the microstructure of the used specimen, the corrosion mechanism by high-Mn steel was also concluded.

Abstract-Number: *86*

THERMOMECHANICAL AND THERMO-HYDRAL SIMULATIONS OF THE FIRST DRYING STAGE OF A REFRACTORY CONCRETE PART

Valentin O.[1], Lemaistre H.[2], Nazaret F.[1], Meunier P.[2]
[1]Aurock, Albi, France, [2]Calderys France, Saint Quentin Fallavier, France

The drying of refractory castables is a process consisting of the removal of water after manufacturing through a temperature increasing. The typical phenomena dread is the spalling due to the rapid increase of internal pressure of vapour. Excessive cares are taken to avoid the spalling at first heating. Typically, the schedules of heating are modified using slower heating rate and longer dwell, but this ascribed significantly the whole process time.
Since the 1960s, drying experiments are conducted with simultaneous measures of mass (loss of water), pressure and temperature changes to characterize the phenomena directly on specimens. Models and simulation have then been developed to anticipate the

spalling risk. The stress sources in the refractory concrete parts during drying have two origins: the first issue is the gradients of thermal expansion from the heterogeneous temperature fields, the second is the rise in pore pressure resulting from the vaporization of water. To anticipate the failure, the description of mechanical behaviour of materials can be complex because it may include viscoplasticity with damages and cracks propagation phenomena. The thermohydral drying phenomena with pore pressure prediction is described using multi-phase or single-phase mass transport models. The most realistic and modern approach is to consider a general multi-phase mass transport and heat transfer fully coupled with mechanics, unfortunately the complexity of models and computer codes is then difficult to merge with the industrial requirements.
In this work, a simplified single-phase model, similar to Bazant's one, was implemented in a commercial FEA code. The permeability function and key parameters of the model for various refractory materials were identify by the way of a numerical design toolbox. Finally, a thermomechanical and a thermohydral simulations were carried out independently on a complex industrial part. The method is to share the stress sources in the global analysis of the structure. This parting in two simulation models of reduced complexity, instead of a sophisticated fully coupled model, allows to simplify the choice of a safe and time-saving industrial drying cycle.

Abstract-Number: *87*

SLIP CASTING AND REORHOLOGY CONTROL OF SIALON CERAMICS

Ozawa M.[1], Nasu T.[2], Suzuki S.[2]
[1]Nagoya University, Nagoya, Japan, [2]Nagoya Institute of Technology, Nagoya, Japan

Sialon ceramics are solid solutions of Si3N4, Al203 and AIN and can be applied gradually to refractory parts such as break rings of horizontal continuous casts from a blast furnace because of their favorable corrosion resistance and thermal shock resistance. Sia1on ceramics as structural materials are densified by hot press (HP) methods. But with these methods, it is difficult to prepare complex and large shapes with sia1on materials. It would be advantageous if sia1on ceramics could be prepared by a slip casting method. In this work, a series of sialon ceramics, Si6-zAlzOzN8-z were prepared from aqueous slurries by a slip casting method were investigated as a function of Z values from 0 to 4. Aqueous slurries are examined whether the solid content and organic additives have influenced on green bodies composed of Si3N4, Al2O3 and AIN and also on resultant sintered sialon bodies. The microstructure of samples were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The bending strength, fracture toughness, thermal expansion coefficient and density were evaluated. Present sialon ceramics and processing by slip casting are useful for their applications as refractory parts such as a continuous cast from a blast furnace.

Abstract-Number: *88*

STRUCTURE EVOLUTION DURING DEHYDRATION PROCESS AND ITS EFFECT ON MECHANICAL PROPERTIES OF CAC-BONDED ALUMINA CASTABLES

Wang Y.[1], Chen P.[1], Zhu B.[1], Li X.[1], Ma Z.[2]
[1]Wuhan University of Science and Technology, State Key Lab of Refractories and Metallurgy, Wuhan, China, [2]Zhejiang Zili Company Limited, Shangyu, China

Using tabular alumina, α-Al2O3 and secar71 cement as the main raw materials, alumina castables were prepared and then heated at different temperature of 110°C, 200°C, 900°C, 1000°C and 1500°C. The phase composition, microstructure and mechanical properties of castables at different dehydration had been investigated. The results showed that plate-like C3AH6 and particle AH3 are formed at 110°C. As the heating treatment temperature rising, the plate-like structure of C3AH6 will be transformed into irregular structure which should relate to the dehydration process accompanying with hydroxy loss. The strength of castables decreases and reaches the minimum value at 900°C. The phases of CA_2 and C_3A with particle shape appear at 1000°C and then the strength of castables increases. At 1500°C, tabular CA_6 is formed and the strength arrives at the maximum value. The expansion coefficient of castables decreases before 320 °C due to the formation of loose structure resulted by dehydration reaction, as temperature rising, the expansion coefficient will be increased gradually, which was reached its maximum value at about 1200°C. It was found that at this temperature a large amount of CA_2 are formed through solid state reaction. As the temperature rising further, the expansion coefficient can be kept in a relative lower level, which should attribute to the effect of system densification even though the generation of CA_6 in the castables.

Abstract-Number: *90*

WEAR OF MAGNESIA BRICKS IN THE PERMANENT LINING OF A LADLE TANK DEGASSING UNIT

Harmuth H.[1], Auer T.[2], Bertignol M.[2]
[1]*Montanuniversitaet Leoben, Chair of Ceramics, Leoben, Austria,* [2]*Böhler Edelstahl GmbH & Co KG, Kapfenberg, Austria*

A degassing ladle was lined with magnesia carbon bricks in the wear lining, followed by a magnesia back filling mix and magnesia bricks in the permanent lining. The latter ones initially showed a CaO/SiO_2 ratio of 0.59 (by weight) and 94.5 mass% MgO. When relining the magnesia carbon material the hot face of the permanent lining bricks showed a loss of bond resulting in an easily erodible surface. This necessitated a too frequent replacement of the permanent lining. A post mortem investigation therefore was performed in order to investigate the wear mechanism and find countermeasures.
According to the CaO/SiO_2 ratio forsterite and monticellite occurred as bonding phases. A microscopical investigation clearly showed decomposition of these phases, monticellite being more stable than forsterite. Further also a beginning reduction of magnesia was observed, and magnesia fines in the matrix have partly been consumed. Thermochemical considerations helped to explain these experimental findings. During operation the total pressure is reduced to less than 10^{-3} atm. Therefore also the partial pressure of CO which is one major gas species due to the application of magnesia carbon bricks decreases. As the oxygen partial pressure is proportional to the square of the carbon monoxide partial pressure, it will be significantly lowered and more reducing conditions prevail. This causes a significant SiO partial pressure in equilibrium with the silicate phases; it decreases with increasing CaO/SiO_2 ratio of the silicates. As a result a higher CaO/SiO_2 ratio is expected to improve the stability.
As a countermeasure therefore a magnesia refractory with a CaO/SiO_2 ratio of 2 was used. This increased the life time of the permanent lining by a factor of more than four. Dicalciumsilicate which is partly acting as a bonding phase remains stable. As a conclusion magnesia refractories with a high CaO/SiO_2 ratio are recommended for application in ladle tank degassing units, at least for the case of a permanent lining associated with magnesia carbon bricks in the wear lining.

Abstract-Number: *92*

REFRACTORY WEAR IN LEAD, ZINC AND COPPER FURNACES

Gregurek D.[1], Majcenovic C.[1], Wenzl C.[2], Spanring A.[2]
[1]*RHI AG, TC Leoben, R&D, Leoben, Austria,* [2]*RHI AG, BU Nonferrous Metals, Vienna, Austria*

In non ferrous metals industry, particularly in lead, zinc and copper furnaces the refractory lining is exposed to several stresses which are rather complex in their interaction. Generally, the main wear parameters influencing the refractory lining life in metal production furnaces (i.e. QSL reactor, KIVCET furnace, Ausmelt/Isa smelter, Kaldo furnace, short rotary kiln, Peirce Smith converter, flash smelter, anode furnace and Waelz kiln) can be subdivided into chemical, thermal and mechanical stresses occurring either as a single wear factor or - more often - as combination. In the present work the main chemical wear parameters in these furnaces, such as corrosion by silica-rich slag, as well as high sulfur supply, iron oxide attack, redox effects and in particular cases hydration, are briefly introduced and discussed. Additionally, the extraordinarily high SiO_2 supply caused by changes in the process route and/or the uncontrolled addition of silica sand results in a severe formation of forsterite and consequently in a volume expansion, leading due to “forsterite bursting”. All these previously mentioned chemical wear phenomena lead to a severe degeneration of the brick microstructure and a decreased lining life. Therefore, understanding of wear mechanisms through “post mortem investigation” and field trials at customers are highly important to ensure suitable product recommendations for industrial applications.

Abstract-Number: *95*

SUSTAINABLE INSULATION TECHNOLOGY FOR ENERGY SAVING IN INDUSTRIAL KILNS

Klischat H.-J., Beimdiek K.
Refratechnik Cement GmbH, Research & Development, Göttingen, Germany

Recently, the reduction of energy and heat losses have been enforced significantly, not only driven by economic reasons but also by legislation and sustainability demands (carbon footprint, reduction of greenhouse gas emission, etc.). A major parameter is the application of a thermal insulating lining in a cement kiln system to reduce heat losses by installation of refractories with lower thermal conductivity. Due to latest developments, insulating castables and medium-weight products as a back-up lining or even as a working lining have become increasingly important, as they offer a higher flexibility regarding installation than pre-shaped products or bricks. For a successful installation, not only the thermal conductivity itself has to be considered, but as a whole other important

properties as well, like mechanical strength, alkali resistance, thermal application temperature limit, the adjustment of the temperature gradient in the lining, and corrosion prevention. The latter is especially important in case of temperatures at the metallic kiln shell below the dew point of water, where an electrolytic corrosion reaction by the always present alkali and chloride ions is accelerated. All properties can be influenced by selection of raw materials (vermiculite, expanded clay, lightweight fireclay amongst others), and by the usually cementitious binding system. The selection of the insulation and medium-weight concretes comprises the operating conditions of the kiln, the enclosure of the anchoring system, and the achievement of homogeneous structural and mechanical properties. Additionally, the sigma-phase embrittlement of metallic anchors can be significantly minimized, reduced or even avoided by a corresponding choice of the refractories. Furthermore, the installation technique, e. g. casting, rodding, or gunning, is of crucial importance for the lining properties and its performance. Various concretes are assessed regarding their insulation and corrosion prevention properties so that a lining with optimum performance can be selected, respecting an optimum technical and ecological performance of the refractory installation.

Abstract-Number: *96*

INFLUENCE OF SPECIMEN SHAPE AND THE SPECIMEN/PRESSURE PLATE INTERFACE ON THE COLD CRUSHING STRENGTH

Gruber D.[1], Sharma V.[1], Urbanek G.[2], Harmuth H.[1]
[1]*Montanuniversitaet Leoben, Chair of Ceramics, Leoben, Austria,* [2]*RHI AG, Leoben, Austria*

Several standards, for example ISO 10059-1/-2, EN993-5, ASTM C133 or GOST 4071-80 are describing the determination of the cold crushing strength. The specimen shape and measures to treat the influence of friction between sample and pressure plate differ significantly from each other. Three commonly used refractories (magnesia, magnesia carbon, chromia alumina) have been selected to test different specimen shapes and pressure plates with different hardness and surface qualities. Furthermore the influence of surface flaws due to the cutting procedure and the application of a wood fiberboard interlayer between sample and pressure plate were investigated.
Supplementary to the experiments a Finite element model was set up in the commercial FE package ABAQUS to simulate the stresses in the samples and the pressure plates to quantify the impact of friction, shape and surface flaws. Mode I and Mode II failure models allow a forecast whether tensile or shear failure will be the dominating failure mechanism.
The results from the simulations are showing clear influences from the friction between the sample and pressure plate and the deformation of the pressure plate. Results from laboratory experiments show the same tendency as the simulation results although the laboratory strength values are affected be the heterogeneity of commercial refractories. To reduce the influence of the friction between the sample and the pressure plate a length to diameter ratio of at least 2:1 is advantageous.

Abstract-Number: *97*

EXPLORING THE MIXING PROPERTIES OF CERAMIC MATERIALS

Zhou Y.[1], Freeman C.L.[2], Yuan L.[1], Tong L.[1], Liu X.[1], Wang J.[1], Wei H.[1]
[1]*Ruitai Materials Technology Co.,Ltd, Beijing, China,* [2]*University of Sheffield, Sheffield, United Kingdom*

In the essay, the code GULP (General Utility Lattice Program) is used for calculating the lattice energy of different compositions and configurations. And lattice statistics method is employed to explore the formation of solid solutions in different systems (MgO/CaO, $MgCO_3$/$CaCO_3$,Ca_2SiO_4/Mg_2SiO_4).Through the calculation of final energy with different configurations in different systems, we get the enthalpy of mixing curves with different compositions at 300K and 1000K. Firstly, our calculation shows that due to the radii of Ca is larger than Mg, it is more favorable to dope Mg into the position of Ca. Secondly, our calculation shows that the stable structure with the lowest energy configuration of (Mg,Ca)O and $(Ca,Mg)_2SiO_4$ is that the segregation of Ca^{2+} and Mg^{2+} in different layers.

Abstract-Number: *99*

SINTERING PROPERTIES AND MICROSTRUCTURE OF MICROPOROUS CORUNDUM WITH NANO-SIZED ALUMINA SOL ADDITIVE

Fu L.[1], Gu H.[1], Huang A.[1], Ma L.[2], Li Z.[3], Lu D.[1], Zhao Y.[2]
[1]*Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallurgy, Wuhan, China,* [2]*Zhejiang Zili Corporation Limited, Shangyu, China,* [3]*The Limited Company of Jingxin High Temperature Material, Yangzhou, China*

A lightweight wear lining for industrial furnace is an important direction in field of refractory materials. In order to achieve guaranteed slag resistance of prepared lightweight wear lining, fabrication of refractory aggregates with high closed porosity and small pore size has attracted increasing attention. Nano-sized additives had been added to increase closed porosity of sintered materials in this paper, due to its superplastic. After sintered at 1800 °C, microporous corundum aggregates were obtained with α-Al_2O_3 micro-powder as main raw material by adding nano-sized alumina sol and its effects on the sintering properties and microstructure of microporous corundum aggregates was investigated. Experimental results show that, the introduction of nano-sized alumina sol leads to an increase in the closed porosity and decrease in bulk density of materials. Despite a slight increase in pore size, the quantity of intracrystalline pores significantly increases. However, due to the in-situ decomposition of alumina sol, with excessive nano-sized alumina sol, the closed porosity of materials reduces instead. Microporous corundum with 3.39 g/cm^3 bulk density, 7.2% apparent porosity, 7.8% closed porosity and 0.53 µm median pore diameter can be obtained with 3wt% nano-sized alumina sol additive.

Abstract-Number: ***100***

LADLE WELL FILLER - THE KEY TO HIGH FREE OPENING RATES

Bombeck M.[1], Janssen M.[1], Breitzmann M.[1], Deinet T.[2], Dannert C.[2]
[1]*Purmetall GmbH, Oberhausen, Germany,* [2]*Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany*

The trouble-free opening of the slide gate on a steel casting ladle, as the cast is initiated, has a significant impact on the quality of the steel, as well as the safety of the process in the steelworks. The ladle well filler, in turn, facilitates the successful opening of the slide gate. The inner nozzle and the well block situated in the casting ladle are filled with ladle well filler prior to casting. The function of the ladle well filler is well known. Yet the interaction of the ladle well filler in combination with various steel grades ready for casting had not been systematically researched, until now. Newly developed grades of steel are showing issues affecting the independent opening of the slide gate precisely at the time of casting. Due to lacking scientific data, problem solving is often reduced to a time-consuming „trial and error“ approach, using conventional or slightly altered ladle well fillers. The affects of minerals, crystallography, granulometric and chemical composition, as well as mineral deposit and source on the effectiveness of the ladle well filler remain mostly unknown. Purmetall, and three other research partners are in the process of deciphering this mystery within the framework of a European research project. The aim of the project is to discover the fundamental reactions of the ladle well filler to various process and material related factors. In the future, this will enable the development of ladle well fillers made with available raw materials and targeted to provide reliable opening rates, which are simultaneously designed to work with particular grades of steel and manufacturing processes,
Since the project's launch, 24 months ago, radical new insights have been gained into the process conditions inside the ladle well filler during steel manufacturing. Sophisticated measuring techniques delivered findings that were far removed from the theoretical expectations.
These results were subsequently transferred to the lab environment, in order to research the function mechanism of conventional types of ladle well filler.

Abstract-Number: ***109***

CORROSION OF ALUMINA REFRACTORY BY INGOT CASTING STEELS

Fruhstorfer J.[1], Schöttler L.[2], Dudczig S.[1], Fricke R.[1], Schmidt G.[1], Aneziris C.G.[1]
[1]*Technische Universität Bergakademie Freiberg, Institute of Ceramic, Glass and Construction Materials, Freiberg, Germany,* [2]*Deutsche Edelstahlwerke GmbH, Siegen, Germany*

The requirements on steel and its purity increased over the last decades. Recently, research focuses again on improving refractories for steel ingot casting. However, these steels vary widely in composition. For future corrosion tests of different refractory materials, a highly corrosive steel grade should be determined. Therefore, the corrosion of alumina as reference material in contact with four different highly alloyed steels was investigated.

Large and small pure alumina crucibles were cast and slip cast, respectively. The tested steel grades were 1.3520 (Mn 1.1 %, Cr 1.5 %), 1.3816 (Mn 19.1 %, Cr 18.1 %), 1.4542 (Mn 0.7 %, Cr 15.3 %, Ni 4.5 %, Cu 3.2 %) and 1.6587 (Mn 0.6 %, Cr 1.5 %). The corrosion tests in the large crucibles were conducted with 20 - 25 kg steel in an induction melting furnace, whereby the casting temperature of the specific steel grade was held for 1 h. The corrosion was evaluated by SEM with EDX, XRD and visually. Furthermore, 20 - 25 g of the steel types were treated similarly in the small crucibles in an electrically heated furnace.
The large crucibles had an open porosity of ≈ 16.6 % and a total one of ≈ 20.2 %. Unlike the steel 1.3520, which showed visually neither infiltration nor corrosion, the other steels reacted with the refractory. The steel 1.3816 built an about 0.5 mm thick reaction layer of manganese aluminate spinel. The steels 1.4542 and 1.6587 exhibited a double layer of 3.5 mm which consisted of an outer manganese aluminate and an inner chrome-containing layer. However, 1.6587 was also eroded after the test possibly due to the high casting temperature of 1580 °C. Therefore, it was the most corrosive steel grade. However, all four steel grades showed visually neither infiltration, corrosion nor erosion when melted in the small crucibles due to the low open porosity of only ≈ 3 % of the small crucibles. Consequently, besides a suitable chemical composition of the refractory, porosity should be minimized for achieving an excellent corrosion resistance.

Abstract-Number: *112*

IMPROVEMENT OF THERMAL SHOCK RESISTANCE OF LOW CARBON CARBON-CONTAINING REFRACTORIES

Li H., Liu G.Q., Ma T.F., Yang W.G.
Luoyang Institute of Refractory Research, Luoyang, China

Carbon-containing refractories were the typical materials of the functional components such as ladle tube, submerged entry nozzles or monolithic stoppers, which were commonly used for steel continuous casting. In recent years, the development of clean steel is very rapid. In order to meet the needs of casting clean steel, the development of low-carbon refractories is put on the agenda. But poor thermal shock resistance of low-carbon refractories has been known as the major drawback, which limits its broad applications. Sheet nanocarbon-Al2O3 composite powders and resin analyst were introduced into low carbon Al2O3 graphite refractories. Phase compositions and microstructure of the materials were investigated by XRD, SEM, FESEM, respectively. The results show that sheet nanocarbon-Al2O3 composite powders and resin analyst can effectively improve the thermal shock resistance of low carbon carbon-containing refractories.

Abstract-Number: *114*

CONTROLLED FORMATION OF CERAMIC PHASES IN MGO-C REFRACTORIES WITH AL AND SI ADDITIVES

Li Y., Zhu T., Sang S.
Wuhan University of Science and Technology, Wuhan, China

MgO-C refractories are widely used in steelmaking process due to their outstanding performance of thermal shock resistance and corrosion resistance. Usually, some additives such as Al, Si, etc. were incorporated into MgO-C refractories to avoid oxidation and to *in-situ* form ceramic phases for reinforcing such refractories. In the past decades, with the progress in clean steel technology and requirements of CO_x emission reducing and resource/energy saving, the conventional high carbon MgO-C refractories (normally 12-18 wt% C) have to be replaced by low carbon ones (less than 5 wt% C, even 3 wt% C). In this case, *in-situ* formed ceramic phases in the refractories have to be controlled in order to achieve the performance as expected, especially thermal shock resistance. In present paper some research work will be carried out to optimize their microstructure and improve their mechanical and thermo-mechanical properties, where Al and Si additives, Ni containing catalytic precursor and firing temperature are investigated to control *in-situ* formed ceramic phases (their amounts, distribution and morphologies) in MgO-C refractories. Also, the growth mechanisms of all the ceramic phases are discussed thermodynamically.

Abstract-Number: *115*

REFRACTORY USAGE AND PERFORMANCE IN PRIMARY ALUMINIUM PRODUCTION

Wright W.W., Walton M.C.
RefMet, Melbourne, Australia

Refractories have significant usage in the construction of cells for the production of aluminium via the electrolysis process. The aluminium reduction cell is not the typical refractory system observed in most thermal industries. It uses hundreds if not thousands of vessels instead of the typical one or two primary vessels of other industries. These vessels typically last from 5 to 8 years and have a normal change-out rate of 10 to 20% per year. It instinctively allows greater opportunity for the trialing of alterative designs and materials within an Al reduction plant, however a significant risk is present with the typical time required to establish success of 5 to 8 years. This period is required due to the closed nature of the cell during operation. This means a plant will be faced with a choice between being conservative and waiting 5 to 8 years or fast tracking changes at greater risk to capture value today, accepting that problems may occur later. The ability to fast track trials is critical today with the low metal prices that have been observed in the last few years.
This paper will discuss the sub-cathodic area of the Al cell in reference to the above dilemma. It will highlight the factors that need to be balanced. These include available volume (especially important in old technology with small sub-cathodic depths), containment of hostile liquids and vapours, correct energy balance, isotherm location and construction options. This paper will highlight and discuss how these factors interact, and will outline the success and failure criteria for these materials at both short and long timeframes to best manage the risk of these changes.

Abstract-Number: *116*

REFRACTORY CASTABLES FOR MAIN RUNNERS - DEVELOPMENTS FOR NEW CHALLENGES IN BLAST FURNACE CASTHOUSE OPERATION

Díaz García P.[1], Covián M.[2], Ruisánchez Rodríguez E.[3]
[1]Pasek Minerales, S.A.U., R&D, Salinas, Spain, [2]Pasek España, S.A.U., technician, Salinas, Spain, [3]Pasek Minerales, S.A.U., Commercial, Salinas, Spain

Dunite is a plutonic rock with a basic chemical classification, being olivine and serpentine its principal components. Not long ago from a Geological perspective, primary minerals came up fused to the Earth Crust, in partial contact with sea water, performing as a result a hydrothermal process on these minerals; the resultant water fixation inside the mineral structure corresponds to Dunite's LOI content.
In today's Steel industry, basic mixes act as a protective coating for the permanent refractory lining (for example on tundish working linings). These kinds of mixes are usually designed as an addition of natural forsterite raw materials to a matrix of dead burnt magnesite, because its combination allows to reach stable solid solutions at high temperatures.
Because of the progressive increase of steel quality, contamination from refractory material to the steel needs to be minimized, especially in terms of hydrogen and carbon pick up.
Thermodynamic studies about the thermal behaviour of Dunite hydrated phases have shown that due to its mineral complexity its dehydration process takes place in several stages between 400 and 900ºC. This water elimination does not happen instantaneously, but progressively.
Exhaustive analysis carried out while evaluating the use of Dunite for this purpose reached the conclusion that the best results are achieved using Dunite's calcined version, for two main reasons:

- In order to prevent the hydrogen pick up due to dehydration at high temperatures, especially in cold start practices.
- In order to be able to increase the percentage of Dunite in the mix, and therefore reduce its cost.

In this paper, we will describe PASEK's steel making basic materials technology experience when using Calcined Dunite (instead of magnesite and / or olivine) in percentages of over 20%; this mixes are high quality refractory materials with similar performance levels and constitutes an effective way to reduce their costs. Solid phase's relationship and interactions, mineralogy discussion, laboratory and industrial behaviour of finished products will also be presented.

Abstract-Number: *118*

EFFECT OF IN-SITU FORMATION OF AL_5O_6N ON THE MECHANICAL PROPERTIES OF AL_2O_3-C REFRACTORIES

Li X.[1], Deng X.[1], Zhao Z.[1], Zhu B.[1], Chen P.[1], Ma Z.[2], Wang X.[3]
[1]Wuhan University of Science and Technology, State Key Lab of Refractories and Metallurgy, Wuhan, China, [2]Zhejiang Zili Company Limited, Shangyu, China, [3]Shandong Shengquan Chemical Co., Ltd, Shandong, China

Al_2O_3-C refractoreis are widely used as functional elements like nozzles, well blocks, sliding gate plates and stoppers in the continuous casting process of steel production. The function of these refractories is to control flow field and velocity, decrease the addtion of impurity and prevent the oxidation of moletn steel. The thermodynamics analysis of Al-Si-O-C-N system showed that the phases of SiC and AlN could be generated at 1473K in reducing atmosphere while the phase of AlON could not be formed until the temperature rising to 1846K. The experiments on the matrix of Al_2O_3-C refractories revealed that metallic Si takes place the carbonization reaction to form SiC phases while both metallic Al and AlN would be oxidized to phases of Al_2O_3 at 1773K in reducing atmosphere. When the heat-treated temperature increases to 1873K, Al_2O_3 has a further reaction with AlN to generate AlON phases. FTIR Results also showed that the absorption peaks of Al-O-N bond can not be found in the matrix of refractories until at the temperature of 1873K. SiC phases exist as the shape of whisker and there is a liquid drop at the top of the whisker. However, AlON phase present particle shape, which behaved the solid-phase reaction mechanism.

Abstract-Number: *119*

A WATER MODELLING COMPARISON OF HYBRID PLUG, SLOT PLUG AND POROUS PLUG DESIGNS

Trummer B.[1], Fellner W.[2], Viertauer A.[3], Kneis L.[4], Hackl G.[2]
[1]RHI AG, Product Management Sec Met Concepts, Vienna, Austria, [2]RHI AG, R&D Modelling and Simulation, Leoben, Austria, [3]RHI AG, Product Management Steel Technology, Vienna, Austria, [4]RHI AG, Product Management Sec Met Purging, Vienna, Austria

Soft bubbling with purging plugs is an essential state of the art process step in secondary metallurgy. Soft bubbling is carried out at very low flow rates with inert gases like argon or nitrogen.
In this paper the results of a water model investigation comparing the bubbling behavior of a hybrid plug and a porous plug at very low flow rates are described.
Implications on soft bubbling in the ladle are presented and conclusions regarding the soft bubbling efficiency of hybrid plug versus porous plug design are given.

Abstract-Number: *120*

MICRO-ZONING OF REFRACTORIES IN STEEL LADLES - A LOGICAL APPROACH FOR EFFECTIVE PERFORMANCE CUSTOMIZATION

Schemmel T., Sengupta U., Jansen H.
Refratechnik Steel GmbH, Duesseldorf, Germany

Steel ladle contributes a major share of consumption of refractories in steel making. Utilization of total working lining is one of the main focus areas to get low consumption of refractories, higher rate of ladle circulation at shop floor with minimum wastage of resources. An attempt to achieve performance customization by designing of micro-zoning in ladle has been carried out in the present investigation. Designing of micro-zoning is based on identification of micro-zones with respect to residual thickness after full life, correlation of erosion profile with operational parameters and selection of suitable quality to have higher/optimized life with minimum wastage of refractories. Erosion of refractory in ladle takes place mainly by corrosion imparted by slag and metal, abrasion at elevated temperature by turbulence of bath melt and/or thermal cycling etc. at different area of working lining during application influenced by the operational parameters eg share of secondary operation, LF arcing time, bottom purging pressure, holding period, heat size variation, steel and slag chemistry etc. Different operational factors play different stresses at different area of lining. This paper deals in the concept of micro-zoning and its design of ladle working lining to have performance customization. The micro-zoning is to design in such a way that the ladle should not be prematurely put down for high erosion at one area having left-over life potential at other zones. Correlation of operational parameters with lining thickness, brick shape and its quality are utmost important factors to design micro-zoning with the help of erosion profile of working lining in layer wise and zone wise manner. It is tailor made concept and differs from plant to plant for obvious reason. Detail discussion on designing by selection of suitable quality of refractories at different micro-zones, its lining practice vis-à-vis different operational parameters was done. It has been observed that suitable micro-zoning practice in ladles have resulted higher life by 20 to 25 % with improved cost-performance ratio at different plants with different ladle capacities and operational practice. A few case studies have been described to justify

the concept. Finally, the service performance with respect to life time and performance customization leading to improved cost-performance ratio was correlated with micro-zoning design and operational parameters during application.

Abstract-Number: *121*

EVALUATION OF NEW CHROMIA FREE REFRACTORIES BY FIELD TEST IN A SLAGGING GASIFIER

Gehre P.[1], Klinger M.[2], Aneziris C.G.[1]
[1]*TU Bergakademie Freiberg, Institute of Ceramic, Glass and Construction Materials, Freiberg, Germany,* [2]*TU Bergakademie Freiberg, Institute of Energy Process Engineering and Chemical Engineering, Freiberg, Germany*

During gasification, a refractory lining protects the gasifier shell from high temperatures and pressures, thermal shock and cycling, and corrosion due to molten coal or biomass slag. The poor service life of the refractory lining in range of three up to 24 month plays an important role in the limitation of the gasifier availability. In order to put gasification technology forward, new corrosion resistant refractories based on alumina as well as magnesia were developed to replace the state of the art high chrome oxide materials. Beside the investigation of material properties, the structure and the phase composition, static cup tests at 1450 °C in reducing atmosphere with coal and gasifier slags as corrosion medium have been performed. Compared to high chromia materials, the new developed refractories provide a much higher thermal shock resistance, which will reduce the refractory loss caused by spalling during service. The analysis of the slag-refractory-interface in SEM after corrosion test revealed two different mechanisms, which causes a reduction of slag infiltration depth as well as dissolution of the refractories matrix by slag: in situ formation of protective layer on the top of the refractory and the increase of the slag viscosity by influencing its chemistry caused by interaction with the refractory. The high corrosion resistance of the most promising refractory material has also been proven by operation in a 5-$MW_{(th)}$ entrained-flow gasifier at 1700 °C.

Abstract-Number: *122*

ADDITIVE MANUFACTURING AS A NOVEL APPROACH FOR PRODUCING CERAMIC PARTS

Schwentenwein M., Glaser M.
Lithoz GmbH, Vienna, Austria

With their ability to produce functional parts directly from CAD data, additive manufacturing (AM) technologies have an enormous potential for the fabrication of prototypes, small-scale series or intricate and complex shapes. The ultimate advantage of AM over traditional manufacturing methods is the freedom of design; it is possible to introduce new features in the design of parts without the limitations of conventional forming techniques.
While these kinds of technologies have already been established in plastics processing and metalworking over the last decade, their usage for the fabrication of ceramic materials or refractories used to be rare due to technological limitations.
In this paper a novel AM-approach is presented: Lithography-based Ceramic Manufacturing (LCM) is a so-called slurry-based process, where the ceramic powder is dispersed in an organic matrix which comprises a photoinitiator, monomers and additives to give the slurry. The fabrication of the parts is based on the layer-by-layer curing of the photosensitive slurry by a mask exposure process which generates a photopolymer matrix that temporarily acts as scaffold and binder for the ceramic particles. This polymer matrix is later on pyrolyzed at elevated temperatures to generate a ceramic body which is subsequently sintered to result in the final ceramic structure. In this manner LCM enables the production of strong, dense and accurate ceramic parts without any constrictions by geometrical limitations. Different materials that could already be structured successfully are manifold and among others include alumina, zirconia, magnesia or various silica-based compounds. In the sintered state, the parts produced by this technology show almost identical mechanical properties as conventionally formed ceramics; for example in the case of alumina a theoretical density of over 99.3 % and 4-point bending strength of over 430 MPa has already been realized. These characteristics are perfectly acceptable for the use of such compounds as functional parts in numerous areas of application. This makes the LCM-process an innovative and capable production method, especially for complex shaped structures, customized parts or small series production.

Abstract-Number: *124*

INFLUENCE OF CREEP ON THE THERMOMECHANICAL BEHAVIOR OF A RH-SNORKEL

Jin S.[1], Harmuth H.[1], Gruber D.[1], Rössler R.[2]
[1]*Montanuniversitaet Leoben, Leoben, Austria,* [2]*voestalpine Stahl GmbH, Linz, Austria*

Snorkel linings of RH vessels are frequently exposed to high temperatures and suffer severe thermomechanical loads. Under such conditions creep will play a role and also affect the joint opening of the working lining. To investigate the impact of creep on the thermomechanical behaviour of RH snorkels, classical and Drucker-Prager creep models have been applied. The latter one additionally allows shear failure. A RH snorkel comprising a magnesia chromite brick lining was studied including the operation procedure of preheating, submerging and idle time. Two specific testing approaches, viz. modified shear test and creep test, were employed to gain the input parameters for the modelling. Significant different results out of the two creep modeling approaches were observed on the creep strain and stress distribution. This emphasizes the need for further identification and verification of suitable creep models.

Abstract-Number: *125*

POLITICAL & ECONOMIC CHALLENGES FACING INDIAN REFRACTORY INDUSTRY

Chattopadhyay A.K.[1,2], Dasgupta A.[2]
[1]*National Refractories, Kolkata, India,* [2]*Indian Refractory Makers Association, Kolkata, India*

By 2020, India is expected to produce 125-130 million tonnes of crude steel. Apparently, it seems that it will herald good times for Indian refractory industry but there are many riders associated with it. Firstly, around 30-35% of steel production will still be through induction furnace route where very low quality refractories (mostly silica ramming mass) is used. This is because large scale acquisition of land is now difficult in India along with getting iron ore and coal linkages. There is intense internal competition as well as threat of cheaper imports which is almost 30% of the market share. The domestic manufacturers too, operate at 50-60% capacity and many are forced to sell products below sustenance level to manage the everyday overheads. Even the payments are delayed mostly in public sector steel plants by 6 months-year (or unilaterally deducted) although the refractory makers have to pay upfront for raw materials, energy and human resource. With the onset of Total Refractories Management, the onus is on the refractory makers to supply, install and maintain the refractory linings. On one hand, it beckons new business opportunity but on the other hand the refractory makers are kept in the dark by many users about various operating parameters, production target etc which affect the refractory lining life. Lastly refractory industry's turnover is miniscule compared to its users which results in poor negotiating power. As a result, their issues are not highlighted in the proper forums and suffer from indifference from the policy makers. Although refractory cost is only 2-3% of steel making, in case of downturn, refractory industry is targeted first for cost cutting. The Governmental policy too does not favour the domestic refractory industry as import duty of raw materials as well as finished product is pegged at same rate. The present paper deals with these issues and also makes a comparative study of linkage between refractory industry and steel industry in India, China and Japan.

Abstract-Number: *127*

EFFECT OF RARE EARTH OXIDES ADDITION ON THE SINTERING PROPERTIES OF MAGNESIA

Ma Y., Wang Z.F., Wang X.T., Liu H.
The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China

Magnesites with two different impurity contents were calcined at 950 °C to obtain light-burned MgO powder. The mixed MgO powder with Y_2O_3, CeO_2 and La_2O_3 added was finely ground, and then dry pressed. The samples were sintered between 1600°C to 1700 °C. The effects of the variety and content of rare earth oxides as well as the fire temperature on the sintering properties, phase composition, and microstructure of the sintered magnesia were investigated. The results showed that the addition of the present three types of rare earth oxides was beneficial to the sintering densification of magnesia. The bulk density and linear shrinkage ratio increased with increasing amount of rare earth oxides. The promoting effect of Y_2O_3 on the sintering of magnesia was significantly higher than that of CeO_2 or La_2O_3. The present rare earth elements were mainly located at the grain boundary. Especially, the Yttrium elements existed in the network distributing silicate phases. In addition, the rare earth oxides added samples with lower impurity content possessed higher bulk density and lower apparent porosity.

Abstract-Number: ***128***

EFFECT OF SPINEL CONTENT OF LIGHTWEIGHT AGGREGATES ON THE REACTION CHARATERISTICS OF PERICLASE-SPINEL REFRACTORIES WITH CEMENT CLINKER

Yan W., Lin X., Chen Q., Li N.
Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallurgy, Wuhan, China

Periclase-spinel refractories have been widely used as workinng lining of burning zone of cement rotary kiln due to their high chemical stabilities and thermal shock resistances. However, the shell temperature at the external surface of the cement rotary kiln could exceed 350-400°C in service leading to severe heat loss because these periclase-spinel refractories are manufactured by using dense aggregates as main raw materials. To address this issue, it is necessary to develop new kinds of periclase-spinel refractories with lower thermal conductivities by substituting porous refractory aggregates for the traditional dense ones.
Whether the periclase-spinel refractories fabricated using porous aggregates as raw materials could substitute the traditional dense ones depends on their corrosion resistance and kiln coating adherence. While the corrosion resistance and kin coating aherence depend on the reactions between cement clinker and refractories. The phase compositions and pore charateristics strongly affect the reactions, and then affect the penetration of liquid phase, which would further affect the kiln coating adherence.
In prensent work, five lightiweht periclase-spinel refractories are fabricated using same matrix and different periclase-spinel aggregates varing with spinel content. A static crucible test and a sandwich test will be adopted to determine corrosion resistance and kiln coating adherence, respectively. The effect of spinel content of lightweight aggregates on the reaction charateristics of periclase-spinel refractories with cement clinker will be investigated through X-ray diffractometer (XRD), scanning electron microscopy (SEM) and FactSage® software, etc.

Abstract-Number: ***130***

EVALUATION OF DEHYDRATION MECHANISM DURING HEATING OF HYDRATED CALCIUM ZIRCONIUM ALUMINATE PASTE

Madej D., Szczerba J.
AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Krakow, Poland

Calcium zirconium aluminate has been recently discovered that exhibits hydraulic properties. The hydration behaviour of $Ca_7ZrAl_6O_{18}$ at room temperature and 60°C was reported elsewhere [1-2]. This paper presents the results of an experimental study investigating the characterization of the dehydration process of hydrated calcium zirconium aluminate paste exposed to high temperature environments.
The hardened paste prepared at a w/s (water/solid) ratio of 1.5 and cured for 24h at room temperature was subjected to temperature of 100, 200, 300, 500, 900, and 1100°C. The hydrated and dehydrated materials were investigated by simultaneous DTA-TG-EGA, LT-XRD, HT-XRD, FT-IR, and SEM/EDS techniques. According to data of DTA-TG investigation the decomposition of $CaO\text{-}Al_2O_3\text{-}H_2O$ phases occurred in the three steps up to about 350°C in the paste cured at room temperature for 24h. The dehydration of gibbsite, $Al(OH)_3$ and hydrogatnet, $Ca_3[Al(OH)_6]_2$ proceeded in two steps even though the steps were overlapping in the paste cured at room temperature for 24h and additionally heat treated at 100°C for 24h. The conversion reaction of metastable hexagonal hydrated phases, i.e., CAH_{10} and C_2AH_8 to the cubic form C_3AH_6 due to higher temperature was proved by means of DTA-TG-EGA, LT-XRD and FT-IR methods. Calcium aluminates, $Ca_3Al_2O_6$, $Ca_{12}Al_{14}O_{33}$, and $Ca_5Al_6O_{14}$ were formed as dehydration products of calcium aluminate hydrates. The results of IR spectroscopic measurements revealed that pentacalcium trialuminate, $Ca_5Al_6O_{14}$ has appeared as a preliminary amorphous calcium aluminate phase. Qualitative and quantitative EDS X-ray microanalysis using SEM was employed for evaluating the chemical composition of dehydrated product as an unknown ternary phase of the Ca-Zr-Al-O group compound forming a ring around the internal core of the unhydrated $Ca_7ZrAl_6O_{18}$ grains.

References:

[1] D. Madej, J. Szczerba, W. Nocuń-Wczelik, R. Gajerski, Hydration of $Ca_7ZrAl_6O_{18}$ phase, Ceramics International 38 (2012) 3821-3827
[2] D. Madej, J. Szczerba, W. Nocuń-Wczelik, R. Gajerski, K. Hodur, Studies on thermal dehydration of the hydrated $Ca_7ZrAl_6O_{18}$ at different water-solid ratios cured at 60°C, Thermochimica Acta 569 (2013) 55-60

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Abstract-Number: *131*

STUDY OF THE PLASTICITY INDUCED BY THE ZIRCONIA PHASE TRANSFORMATION IN HIGH ZIRCONIA REFRACTORIES

Gouraud F.[1], Antou G.[1], Germaneau A.[2], Doumalin P.[2], Dupre J.C.[2], Huger M.[1], Chotard T.[1]
[1]SPCTS UMR CNRS 7315, Centre Européen de la Céramique, Limoges, France, [2]Institut Pprime CNRS, Futuroscope Chasseneuil Cedex, France

The high quality level required for new glass applications implies the development of new high zirconia (HZ) fused cast refractories. The use of these refractories requires a good control of the manufacturing process to avoid critical flaws due to severe thermo-mechanical stresses. To optimize the manufacturing process, a French research program called ASZTech aims to improve the existing model and to implement from specific experiments a realistic description of zirconia transformations.
Previous studies have led to considerable progresses in the understanding of the mechanical behavior of these HZ refractories during the critical step of cooling down after casting. However, few studies are available about the consideration of the plasticity associated to the zirconia transformation (TRIP) and the role played by this TRIP on the residual stresses induced by the process. The present work deals in one hand, with the investigation of the plasticity which can be induced by an external applied stress during the tetragonal to monoclinic transformation of zirconia and in the other hand with the characterization of the residual stresses in bricks at the end of the elaboration process.

Abstract-Number: *132*

THERMO-OPTICAL MEASURING METHODS FOR HIGH TEMPERATURE CHARACTERIZATION OF REFRACTORIES

Raether F., Baber J., Git P.
Fraunhofer Center for High Temperature Materials and Design (HTL), Bayreuth, Germany

Modern high temperature processes require an accurate design of the refractory lining. Finite element simulations are an appropriate tool to calculate temperature distributions and stresses. Lifetime models are developed to predict service life of the components. However, accurate data on high temperature properties are urgently needed as input parameters for modeling to improve the precision of the model predictions.
A coarse microstructure is typical for most refractory products. This makes it difficult to apply customary high temperature measuring methods with a small probe volume. Spatial variation of the material properties causes large uncertainty in the measured results. So, measuring methods with a sufficient sample volume of - at least - some tens of cubic centimeters are required. On the other hand, temperature fields in the probe volume have to be well defined since properties vary with temperature. Chemical reactions between measuring instruments and samples frequently affect measuring results. Therefore, non-contact measuring methods are to be preferred.
At HTL a special class of Thermo-optical measuring (TOM) methods has been developed which meets these requirements [1-3]. Measurements are performed in lab furnaces up to temperatures of 2400°C in controlled atmospheres and temperature fields. Excitation and detection of measuring signals is performed non-contact using light or acoustic waves. Lasers, special optical technics and acoustic couplings are used to enable measuring through small windows in the furnaces without distortion of the temperature field. Measuring quantities are thermal diffusivity, emissivity, coefficient of expansion, elastic modulus, thermal shock resistance, uniaxial viscosity, viscous Poisson ratio etc. Recent developments of two TOM devices, TOM_air and TOM_wave, are presented which enable higher accuracy and offer new measuring opportunities.

References:

[1] Raether, F., Springer, R., Beyer, St.: Optical dilatometry for the control of microstructure development during sintering. Mat. Res. Innovations, **4** (2001) 245-250
[2] Baber, J., Klimera, A., Raether, F.: In situ measurement of dimensional changes and temperature fields during sintering with a novel thermooptical measuring device. J. Eur. Ceramic Soc., **27** (2007) 701-705
[3] Raether, F.: Current state of in-situ measuring methods for the control of firing processes. J. Am. Ceram. Soc., **92** (2009) 146-152

Abstract-Number: *133*

PROPERTIES OF MGO-SPINEL BRICK AND ITS APPLICATION IN RH DEGASSER IN CHINA

Fang B.X.[1], Zhang W.G.[2], Ma Z.[1], Luo M.[1], Tai L.[2], Zhu Y.N.[1], Shen M.K.[1]
[1]Zhejiang Zili Co., Ltd., Shaoxing, China, [2]Baoshan Iron & Steel Co., Ltd., Shanghai, China

MgO-spinel brick is produced by fused Magnesite, MgO-Al_2O_3 based spinel and several metal powders as the main raw materials. It behaves denser microstructure, higher mechanical strength, better thermal shock resistance, better slag penetration resistance and similar slag erosion resistance compared with magnesite-chrome brick. However, MgO-spinel brick has larger permanent linear expansion ratio and larger hot linear expansion ratio than magnesite-chrome brick due to the in situ spinel formation reaction during the heat treatment.
Because of good service performance and no environment pollution of MgO-spinel brick, it is used as the working layer of RH vacuum degasser to replace magnesite-chrome brick in more and more large and medium-sized steel plants in China.
MgO-spinel brick still exposes spalling problem during the use because of high coefficient of thermal expansion. Improving the spalling resistance of MgO-spinel brick is the research focus in future.

Abstract-Number: *134*

WAYS TO OVERCOME THE PREHEATING EXPLOSION OF ALUMINA SPINEL-FORMING CASTABLE

Yeh S.-R.[1], Lin W.-T.[1], Liu P.-C.[2], Chen H.[1]
[1]Good Furnace Refractory Industrial Co., Ltd., Taipei, Taiwan, Republic of China, [2]Good Furnace Refractory Industrial Co., Ltd, Taipei, Taiwan, Republic of China

Alumina Spinel-forming castable is widely used for steel-making ladle because of its excellent slag resistance and volume stability at high temperature. However, its preheating explosion is always a trouble to any user of steel-making ladle and R & D staff in charge of developng alumina spinel-forming castable in any refractory company. It is important to find a way to settle the preheating explosion of alumina spinel-forming castable. This study tests and evaluates several methods to prevent the preheating explosion of alumina spinel-forming castable. The experiment result shows that using aluminum lactate, adding more alumina cement with inorganic sodium salt, and selecting engineered alumina cement with organic fiber are the possible ways to overcome the preheating explosion of Alumina Spinel-forming castable. But, to prevent using MgO powder containing the hydration of MgO is more important than adding any anti-explosion additive because the hydration of MgO, or called $Mg(OH)_2$, can produce the water vapor during the preheating process, especially at a temperature higher than 350°C, and the water vapor is not easy to release from alumina spinel-forming castable. It's the key point to cause the preheating explosion of alumina spinel-forming castable.

Abstract-Number: *137*

DEVELOPMENT OF AL_2O_3-CR_2O_3 REFRACTORIES BY REACTION SINTERING OF HYDRATED ALUMINA AND CHROMIC OXIDE

Tripathi H.S., Nath M., Ghosh A.
CSIR-Central Glass & Ceramic Research Institute, Refractories Division, Kolkata, India

Dense Al_2O_3-Cr_2O_3 refractories containing 10-50 mol% Cr_2O_3 were developed by reaction sintering of hydrated alumina and chromic oxide in the temperature range 1500-1700°C. Effects of furnace atmosphere on the densification behaviour of Al_2O_3-Cr_2O_3 were evaluated by dilatometry. Formation of solid solution of $(Al_{2-x}Cr_x)_2O_3$ where $0 \le x \le 2$ were monitored by using X-ray diffraction. It was observed that inert/reducing sintering atmosphere favours the densification compared to oxidising atmosphere. Samples sintered at 1600ºC shows higher hot MOR than the samples sintered at 1700ºC. Microstructures of the sintered samples were correlated with the various properties. Corrosion test were carried out with borosilicate glass in static conditions and due to imperceptible corrosion, glass-refractory interface were investigated using XRD and electron microscopy with EDX analysis.

Abstract-Number: *138*

REVISION OF THERMODYNAMIC DATABASE FOR UNARY, BINARY AND TERNARY ZRO2 CONTAINING SYSTEMS

Kwon S.Y., Hudon P., Jung I.-H.
Mcgill University, Mining and Materials Engineering, Montreal, Canada

Recently new thermodynamic property and phase diagram information have been published for ZrO2 containing systems which are of important to the corrosion of ZrO2 refractories in high temperature processes. In this study, new critical evaluation and optimization of unary ZrO2, binary and ternary ZrO2 containing systems within the CaO-MgO-Al2O3-FeO-Na2O-SiO2-ZrO2 system were performed, and the optimized thermodynamic model parameters are incorporated to the commercial FactSage database to improve the accuracy in thermodynamic calculations for ZrO2 refractories. New evaluated phase diagram and thermodynamic data will be presented along the critical evaluations of all available experimental data.

Abstract-Number: *139*

POST MORTEM STUDY OF UNFIRED AL-ZN INCORPORATED AL_2O_3-C SLIDE PLATES

Liu X., Ma T., Liu Z., Huang Y., Jia Q.
Zhengzhou University, High Temperature Ceramics Institute, Zhengzhou, China

Al-Zn incorporated Al_2O_3-C slide plate is newly developed unfired and low carbon type characterized by high hot modulus of rupture (52MPa at 1400°C), good thermal shock resistance and oxidation resistance. Post mortem investigations have been carried out on Al-Zn incorporated Al_2O_3-C slide plates after used in 90-120t ladles casting low carbon steel for 2 consecutive heats. The bore enlargement is less than 2mm/heat, and roughening on the sliding surface is slightly. The evolution of used slide plate specimens in composition and microstructure from hot end (edge of bore) to cold end have been studied by means of XRD, SEM and EDS. The results show Al in situ formed nonoxide bonding at the hot end, create strengthening and toughening effect; and there is no slag attack, oxidation and penetration during casting are the main factors for damage.

Abstract-Number: *140*

OPTIMISATION OF PROCESS PARAMETERS IN SYNTHESIS OF SINTERED MAGNESIA DOPED ZIRCONIA NOZZLES

Durmus C.[1], Ozgen S.[2], Koroglu V.[1]
[1]*Metamin Mumessillik Sanayi ve Ticaret A.S., Istanbul, Turkey,* [2]*Technical University of Istanbul, Department of Materials and Metallurgy, Istanbul, Turkey*

Zirconia based nozzles have special applications in steel casting processes. In this study, the process parameters in manufacturing of zirconia nozzles are optimised to improve microstructural and mechanical properties for improved service performance.
The process stages of zirconia stabilisation, granulation, and sintering conditions are investigated to adjust these parameters for the optimum results. Natural dead burnt magnesite was used as the stabilising agent to decrease the cost in manufacturing.
Spray drying was used to improve the flowability of fine zirconia powders. Flow properties, compressibility and morphology were characterized to improve the suitability of granulated powder for industrial die-pressing. The effects of sintering conditions on the physical properties of nozzles were investigated. The characterisation of zirconia nozzles were carried out by microstructural and phase analyses. Also the physical properties such as bulk density, porosity, mechanical strength and hardness are monitored. The optimised process parameters are then applied at the manufacturing stage to analyse the results in the service performance.

Abstract-Number: *141*

ACOUSTIC EMISSION OF THE BENDING FRACTURE OF MGO-C BRICKS IN THE 3-POINT BENDING TEST

Kageyama K.[1], Saito Y.[2], Goto K.[1]
[1]*Nippon Steel & Sumitomo Metal, Refractory Ceramics Div., Futtsu, Japan,* [2]*Nippon Steel & Sumitomo Metal, Oita works, Oita, Japan*

The fracture behavior of carbon-containing refractories during thermal-shock testing is evaluated in various ways. There are many reports on the evaluation of thermal shock resistance by visual analysis of crack morphologies, and a few reports discuss non-destructive evaluation methods to analyze the cracking behavior. In this study, the fracture behavior of MgO-C brick was analyzed in

the 3-point bending test by acoustic emission. The MgO-C samples (40mm x 40mm x 160mm) used in this study had graphite (Gr) content of up to 40%; a fired MgO brick was used as a Gr-free reference sample. The fracture behavior of these samples was evaluated in 3-point bending test with monitoring by acoustic emission under the following conditions; reference potential and amplitude threshold were set to 1 microvolt and 40dB, respectively, and the Hamming function was used for the window function. During the bending test, for the samples with high graphite content, acoustic emission was detected mainly in the low-frequency range (from 25 to 100 kHz), which indicates low-frequency AE is related to crack propagation in the matrix portion of MgO-C samples, where the graphite mainly exists. Furthermore, we analyzed how the amplitude distribution of these AE signals was related to the fracture behavior before the subsidiary fracture, in four frequency ranges, (a) 25 to 90 kHz, b) 90 to 100 kHz, c) 150 to 200 kHz and d) 200 to 300 kHz). The cracking or deformation behavior seemed to have an effect on the approximated linear gradient for these distributions only in the case of the b) and c) ranges. In these frequency ranges, in the case of samples with lower bending modulus, the gradient values were confirmed to be higher. Data will be presented and discussed for the various graphite contents, compared with the graphite-free MgO sample.

Abstract-Number: *144*

PHASE EVOLUTION, MICROSTRUCTURE AND THERMO-MECHANICAL CHARACTERISTICS OF TITANIA BEARING SPINEL-PERICLASE REFRACTORIES FOR RH DEGASSER

Mandal S.[1], Dileep Kumar C.J.[2], Adak S.[3], Kumar D.[1], Chattopadhyay A.K.[3]
[1]Indian Institute of Technology (BHU), Ceramic Engineering, Varanasi, India, [2]TRL Krosaki Refractories Limited, R&D, Belpahar, India, [3]TRL Krosaki Refractories Limited, Belpahar, India

RH Degasser refractories experience extreme operating conditions especially those used in lower vessel and snorkel. The major factors that contribute to the degradation are spalling and erosion. The refractories for this application should possess excellent thermal shock resistance along with good H-MOR to achieve the required erosion resistance. In addition to this, refractory is expected to have good corrosion resistance to the slag in Degasser. Direct bonded magnesia-chrome refractory is the standard for this application and the search for a successful alternative is on. Having an engineered microstructure with low porosity and very good sintering is a prerequisite to meet the requirements. This paper evaluates the characteristics of an in-situ spinel bonded Spinel-Periclase refractory with Titania addition to ascertain its suitability for this challenging application. The composition has been tailor made to have a spinel : periclase weight ratio of 1:1 with an in-situ spinel content above 10 wt%. The titania content has been varied from 0-15 wt% and it is expected to form magnesium titanate as well as aluminium titanate, in-situ. In contrary to a previous work from our laboratory, which used iron bearing rutile mineral, ultrafine pure titania (Anatase) has been used to ensure uniform distribution, high reactivity and purer matrix which is expected to have high erosion resistance. Open porosity < 14% is targeted through proper particle size distribution of the raw materials and in-situ spinel formation. The compositions fired at 1700°C were evaluated for their density, porosity, microstructure, thermo-mechanical properties and slag corrosion resistance. XRD and SEM with EDS have been used to understand the phase evolution and distribution in the microstructure. To evaluate the spalling resistance of the compositions C-MOR and MOE measurements were carried out before and after thermal shock experiments. In contrary to the normal observation, in case of in-situ spinel formation, the composition without titania addition exhibited minor shrinkage after sintering. At the same time titania containing compositions exhibited slight expansion. The thermo-mechanical characteristics and corrosion behavior of the new compositions were compared to that of a standard magnesia-chrome composition to understand its suitability for RH Degasser application.

Abstract-Number: *146*

DESIGNING OF MATRIX AND ITS INFLUENCE ON DIFFERENT PROPERTIES IN LOW CEMENT CASTABLES

Satpathy S., Samanta A.K., Ganguli S., Adak S., Panda P.B., Chattopadhyay A.K.
TRL Krosaki Refractories Limited, Technology, Belpahar, India

Monolithics are semi-finished products and therefore its proper installation is very important to get the best performance particularly for low cement castables. In case of low cement castables, good flowability, optimum water demand and setting time within the specified time are most important which control the installation of castable. Most of the monolithics refractories are applied either in high temperature or any chemical processing units. The performance of castables depend upon several properties out of which some of the key properties are very important like abrasion resistance, inertness towards chemical attack, mechanical strength and volume stability at application temperature, stability under thermal fluctuation, shock absorbing capability etc.
All the properties can be achieved by proper designing of matrix with best suitable raw materials and its fineness. In refractories

some of the base raw materials are synthesized through chemical process, others are either naturally occurring or made available through fusion. Since the source for different raw materials is different, its influence on castable properties is also remarkable while using them to design the matrix. In this present work, low cement castable is designed with Brown Fused Alumina as base raw material. Bauxite, Andalusite, Silliminite and WTA are used as matrix. Since the matrix raw materials are having different chemical property particularly for Al_2O_3 and Fe_2O_3, there is difference in chemical property in final product also. But the physical properties vary due to nature of matrix raw material and its conversion while firing the castables at different temperatures. Keeping good installation in mind, water demand, flowability, flow decay and setting time are measured initially followed by others properties like hot modulus of rupture, thermal spalling resistance, volume stability, strength development, different mineralogical phase formation and microstructure along with other relevant properties. Attempt has been made to explain the variation in different properties in final product on the basis of mineralogical phases formation, its orientation and microstructure of the castable.
Key Words: Low Cement Castable, Aggregates, Matrix, Brown Fused Alumina, Water Demand, Microstructure

Abstract-Number: *147*

TENSILE AND COMPRESSIVE CREEP TESTING OF REFRACTORIES AT SERVICE RELATED LOADS

Sidi Mammar A., Jin S., Harmuth H., Gruber D.
Montanuniversitaet, Department of Mineral resources and Petroleum Engineering - Chair of Ceramics, Leoben, Austria

Creep under compressive and tensile loads may significantly contribute to the behavior of refractories under service conditions. While standard testing methods for refractory creep under tensile loads are not available, those for compressive creep testing are applied for a rather low load levels only. Therefore two testing devices applying tensile and compressive loads at service related levels were developed for high temperature measurements, respectively. Special measures were taken to control the specimen and loading alignments. Norton-Bailey creep law was used to describe the creep behavior in three stages and inverse estimation procedure was employed to identify the creep parameters by means of Levenberg-Marquardt algorithm. Magnesia chromite bricks were selected as a case study at different temperatures and loads. The results show that significant creep of refractories can be detected in a reasonable time and the three stages can be revealed as well. Moreover, different creep behavior of magnesia chromite bricks in compression and tension was highlighted.

Abstract-Number: *148*

DEVELOPMENT OF MGO-CAO-ZRO_2 BASED REFRACTORIES (CHROME FREE) WITH ADDITION OF SPINEL

Murugesan S., Jana M., Adak S., Panda P.B., Chattopadhyay A.K.
TRL Krosaki Refractories Limited, Jharsuguda, India

MgO and $CaZrO_3$ have been suggested as chrome free refractories for non-ferrous industries to replace not only MgO-Cr_2O_3, but also MgO-$MgAl_2O_4$ spinel refractories currently in use. MgO spinel bricks are highly resistant to thermal shock, non-sensitive against reducing/oxidizing conditions and corrosion under severe thermal loads. Spinel also forms low-melting phases with the result of premature wear. In other hand, $CaZrO_3$ is one of the most promising refractory compounds used in steel and cement industry. Since, $CaZrO_3$ based magnesia refractories works effectively in improving the resistance against both alkali attack and clinker phase melting. $CaZrO_3$ possesses high melting point (~2340°C) and it is compatible with MgO and does not form any liquid phase below 2060°C. Moreover, solid state bonding between periclase and $CaZrO_3$ phases is highly resistant to the infiltration of fluxes from the clinker.
Many studies conducted by the refractory industry responds to the need for the development and implementation of new chrome-free basic bricks that meet the requirements presented in the kilns. Innovative chrome-free basic refractory bricks have been designed based on the use of MgO-$CaZrO_3$ technology using $MgAl_2O_4$ spinel as ceramic bonding in order to improve their properties. Industrial refractory bricks have been manufactured by solid state sintering of raw dolomite and zirconia to have MgO-based $CaZrO_3$ aggregates with $MgAl_2O_4$ spinel at 1650°C. Physical and microstructural characteristics of new refractory bricks have been characterized in terms of density, porosity, crystalline phases (using XRD), pore size distribution (using Mercury Porosimeter) and morphology (using Optical Microscopy). The mechanical behavior has been evaluated in terms of cold crushing strength (CCS) and three point bending strength (both cold and hot) modulus of rupture (MOR) at room temperature and 1260°C. Corrosion resistance (static and dynamic) test by chemical attack of clinker raw meal constituents have been carried out at 1450°C. Preliminary results have shown that thermo-mechanical properties of new refractory bricks significantly improved with increasing

the spinel content. Microstructural analysis revealed that spinel phases aided to develop a strong bond between the MgO and $CaZrO_3$ refractory aggregates. Finally, these refractory matrixes exhibit a good thermal stability and an excellent chemical resistance against clinker raw meal.

Abstract-Number: *149*

INFLUENCE OF HERCYNITE CONTENT ON THERMO-MECHANICAL AND CORROSION BEHAVIOUR OF SPINEL BONDED MAGNESIA REFRACTORIES

Jana M.[1], Dileep Kumar C.J.[2], Adak S.[1], Panda P.B.[1], Chattopadhyay A.K.[1]
[1]*TRL Krosaki Refractories Limited, Belpahar, India,* [2]*TRL Krosaki Refractories Limited, R&D, Belpahar, India*

Higher processing temperatures and concern regarding disposal of chromium bearing refractory waste is driving the quest for an alternative to chrome bearing refractories. Complex spinel as well as hercynite bonded Magnesia is a promising candidate. Hercynite bonded compositions has already replaced Mag-Chrome Refractories in Cement Kiln applications. These refractories possess excellent thermo-mechanical properties owing to high temperature characteristics of hercynite. Synthesis and stability of hercynite spinel is a major concern in the manufacturing and application of these refractories; and electro-fusion process is presently the major source for hercynite. Electro-fusion, though helpful in synthesizing the spinel, reduces its reactivity and hence sintering temperatures exceeding 1600°C is required to achieve properties. In-situ spinel formation is known to enhance sintering at lower temperatures. This paper reports the results of the study on synthesis of in-situ hercynite bonded magnesite refractories and the impact of hercynite content on the properties. Hematite powder as well as mill scale and calcined alumina were used as the starting materials for in-situ hercynite formation. Phase analysis of the stoichiometric hercynite batches using both mill scale and hematite, heat treated at 1500°C in reducing atmosphere, has shown near complete conversion to hercynite with very low residual corundum. Refractory compositions with targeted hercynite content of 1-10 wt% were prepared and heat treated at different temperatures in the range of 1300 - 1600°C. Microstructure development in the refractory compositions and distribution of hercynite phase has been evaluated using SEM and EDS. Quantitative estimation of hercynite content in compositions with > 5 wt% expected hercynite content has been carried out using X-ray diffractometry and Rietveld analysis. Density, porosity and cold crushing strength of the compositions revealed the effect of in-situ hercynite content on the sintering and strength development. The correlation amongst hercynite content and thermo-mechanical properties were evaluated through HMOR and spalling studies. The effect of hercynite content on the interaction of the refractory with cement clinker and non-ferrous slag was evaluated to understand the suitability for cement kiln and non-ferrous applications.

Abstract-Number: *150*

DESIGN OF HIGH PERFORMING CHEMICALLY BONDED SLIDE GATE PLATES FOR CASTING OF ALLOY STEEL AND MILD STEEL

Ganguli S., Samanta A.K., Satpathy S., Adak S., Chattopadhyay A.K., Panda P.B.
TRL Krosaki Refractories Limited, Technology, Belpahar, India

One of the most important refractory products used during casting of steel is slide gate plate. This material must have the balanced properties in the erosion resistance against molten steel and slag, anti-abrasion with sufficient strength against metal stream, thermal spalling resistance and anti-oxidation to free oxygen in metal or ambient air which can be sucked through the surface of the plates. To meet such requirements Al_2O_3-C material are being broadly applied. Moreover, life of slide plates mainly depends on the selection of refractory materials based on casting conditions and different steel grades to be cast. But now-a-days, for easy removal of non-ferrous inclusions and to control contaminants, addition of Ca, Mn and other alloys are being preferred by steel manufacturers. Fired Al_2O_3-C materials due to formation of low melting compounds, show high erosion and corrosion, resulting in poor life of the refractory, compared to that of the chemically bonded Al_2O_3-C materials. However, the only demerit with this chemically bonded materials is the poor oxidation resistance. To meet such requirements, scientists are working to develop a reliable chemically bonded slide plates suitable for different type of steel grades.
The present paper deals with the development of silica free Al_2O_3-C plates with the addition of preformed spinel in the range of 5% to 15%. The physical properties like AP, BD and CCS etc. were found to be superior in case of the optimized spinel containing plates than the normal Al_2O_3-C plates. X-ray diffraction and microscopic studies were also conducted to study the different phases and distribution of spinel in the matrix. The optimized product was heat treated at various temperatures in reducing condition followed

by measurement of CCS and oxidation strength to standardize the temperature at which it shows better oxidation resistance. Excellent resistance to corrosion with alloy steel, high resistance to abrasion at elevated temperature and high hot strength makes it superior in mild steel and alloy steel teeming. The life potential of these plates were found to be higher than the existing Al_2O_3-C and Al_2O_3-ZrO_2-C slide plates, which leads to higher confidence in operation, resulting in low cost of refractory per ton to liquid metal and make it user friendly.

Key Words: Slide Plates, Chemical Bond, Oxidation Resistance, Corrosion Resistance, Spinel, Casting.

Abstract-Number: *151*

NITRIDATION ENHANCING EFFECT OF FE, CO AND NI NANOPARTICLES ON SILICON POWDERS

Zhang H.
Wuhan University of Science and Technology, The state Key Laboratory of Refractories and Metallurgy, Wuhan, China

Silicon nitride was prepared by a catalytic nitridation method using Fe, Co or Ni nanoparticles as catalysts. The effects of catalyst's type and particle size on the nitridation of silicon were studied. The results showed that the presence of one of these transition metal catalysts in the starting material batches greatly enhanced the nitridation of silicon. A nanosized catalyst exhibited better catalytic effects on the nitridation of silicon than its micro-sized counterpart. The nitridation of silicon powder could be completed at 1300 ℃ when 1wt% nanosized Co catalyst was used but completed at 1400℃when no catalyst was present. Among the three types of metal catalysts, Co nanoparticles showed the best catalytic effect on the nitridation of silicon. SEM and TEM further revealed that significant amounts of Si_3N_4 whisker were formed in the final products via a process dominated by a vapour-liquid-solid (VLS) base-growth mechanism. Calculation of density functional theory showed that the enhanced nitridation of these nanoparticles as catalysts can be attributed two following factors, the increased bond length and weakened bond strength in N_2 caused by the electron donation from the Co atoms to the N atoms.

Abstract-Number: *152*

DEVELOPMENT OF IMPACT RESISTANT MGO-C BRICKS AT ROURKELA STEEL PLANT

Sarkar S.
SAIL , R & D Centre for Iron & Steel, Rourkela Centre, Rourkela, India

Rourkela Steel Plant has its brick plant for manufacturing pitch bonded MgO-C bricks of different qualities. These bricks are made for zoned application in Steel ladles and Converters of 150t capacity each. The performance of these MgO-C bricks is quite satisfactory (103 & 5529 heats respectively).
As per the design of taphole with converter, liquid steel having temperature of 1660-1680^{o}C from a height of 8.5 meter strikes on the steel ladle bottom and hence, erosion of refractory in the impact area is much more than that of other area. Presently alumina MgO-C (AMC) quality bricks are being used in this area, still a midterm repair is required after a life of 68 - 85 heats to match the full life.
RDCIS in association with RSP has taken a project and developed special quality MgO-C bricks for the striker area of ladle bottom so that the midterm repair is eliminated and enhance steel ladle availability in its full cycle life. A trial set of developed MgO-C bricks has been manufactured at RSP and industrial trial is in progress at SMS-II to evaluate its actual performance.
The paper will elaborate stepwise development of improved quality bricks, comparative properties of the different composition to optimise the final composition of developed MgO-C bricks.

Abstract-Number: *153*

INVESTIGATION ON THE FACTORS INFLUENCING PERMANENT LINEAR CHANGE TESTING FOR DENSE REFRACTORY CASTABLES

Campello-Garcia J.R., Castaño-Laviana D., Miranda-Martinez M.
Fundacion ITMA, Refractories, Llanera, Spain

Most standards currently used for the determination of physical, chemical and technological properties of refractory materials disclose little or no data on the used methods´ precision values. However, such data are typically the basis for communication between the refractory producer and the final user. Sometimes the differences between the technical information on the properties reported by testing laboratories and that provided by the refractory material supplier lead to subsequent discussion, even claims.
In this paper we report some results on Permanent Linear Change (PLC) testing of refractory materials, according to EN 993-10, EN 1094-6 and EN-ISO 1927-6 standards. These results were obtained within the frame of the European funded ReStaR research project. A factorial design of the experiments, followed by an ANOVA analysis, was carried out in order to identify the most influencing factors. Up to five testing factors were investigated by a multinational consortium of laboratories. As a result of these investigation, a set of recommendations and precision data for Permanent Linear Change (PLC) testing of refractory materials is provided.

Abstract-Number: *154*

AN EASY-TO-USE METHOD TO CARRY OUT QUANTITATIVE ANALYSIS OF MULLITE

Yin Y., Xu J., Xu J., Ge S.
The State Key Laboratory of Refractories and Metallurgy,Wuhan University of Science and Technology, Wuhan, China

Mullite is one of the most important raw materials for refractory industry, because of its excellent properties, such as high melt point, low thermal expansion, and good thermal shock resistance. However, mullite is a series of solid solutions with the same crystal structure but different chemical compositions, which results in there is still no mullite reference could be used for quantitative phase composition analysis by x ray diffraction (XRD) technique easily. Thereby, an easy-to-use method has been established for engineering use to control the quality of mullite. This easy-to-use method separates mullite and corundum phases from mullite sample through the dissolution of SiO_2 and glassy phases into the HF acid. Then the content of corundum in the separated mullite and corundum mix could be determined by XRD method using α-Al_2O_3 reference. Successively, the content of mullite could be calculated by subtracting the SiO_2, glass and corundum from the sample. In this way, the difficulty of mullite reference missing has been avoided. In fact, the slightly solution of mullite and corundum in HF acid has been also reasonable corrected when calculating the final result of mullite content.

Abstract-Number: *156*

TILTING RUNNERS: REFRACTORY SOLUTIONS FOR HIGH IRON IMPACT RESISTANCE

Duvauchelle N.[1], Dromain C.[1], Joly T.[2], Smekal N.[3], Soudier J.[1]
[1]*CALDERYS, Research department, Saint Quentin Fallavier, France,* [2]*CALDERYS, Technical support BU Europe, Sezanne, France,*
[3]*CALDERYS, Iron, Steel, Foundry Markets department, Issy les Moulineaux, France*

The role of the blast furnace trough system is to provide channels for the hot metal and slag flowing out of the BF to the transporter. The runner system is among the most important facilities of iron-making as their durability affects the production circulation. This is typically the case of iron tilting runner which is designed to variably change the direction of the molten iron stream to the hot-metal ladle cars. Each part of the tilter is exposed to different stress factors, which influence the selection of the right refractory products for maintaining a sufficient durability during operation. For instance, the spout area suffers frequent thermal shocking, leading to cracks formation, iron infiltration and consequently to strong erosion of the refractory lining. A material less sensitive to thermal cycling is highly recommended in this area. The impact zone is another critical area which sets stringent requirements on refractories for performance optimization of the tilter. Several recent field problems have also shown that the design of the tilter itself could modify the iron stream which becomes distorted, leading to an impact on sidewalls and not in the pool, and then sometime to a breakthrough. Calderys philosophy for iron tilter lining consists generally of high alumina, low cement castable fortified with SiC and carbon in order to guaranty a minimal corrosion resistance if slag pass through the skimmer. Based on Calderys experience from field, a new range of ULCC has been recently developed for improving the impact resistance in iron tilter. Optimization of the grain size distribution and the use of a new dispersing system have contributed to minimize the water demand in order to obtain materials of high density. The standard drying system usually based on reactive metallic powder has been changed to avoid inadequate combination between workability and hydrogen formation that may happen when the dispersing system is modified. The cement content has been lowered for improving the hot properties as well as the corrosion resistance while the SiC content was reduced to limit the effect of the dissolution by iron. Then, a first version developing high hot

mechanical strength has been specially designed for tilter presenting a severe wear at the impact. A second version containing spinel or forming spinel and presenting an excellent resistance to corrosion has been also designed for tilter suffering strong chemical attack.

Abstract-Number: *158*

INVESTIGATION ON THERMOLITH OLIVINE

Valalas T.[1], Surville A.[1], Trevlopoulos C.[1], Aneziris C.[2], Ulbricht J.[2], Fassauer C.[2]
[1]*THERMOLITH S.A., Kalyves, Greece,* [2]*Technische Universität Bergakademie Freiberg, IKGB, Freiberg, Germany*

Investigations on Greek Olivine combined with Greek Magnesia have been conducted with improved high temperature properties, such as high resistance to Thermochock, very high magnesioferrite precipitation and high Refractoriness under Load. Also very interesting is the Fosterite formation of Enstatite.

Abstract-Number: *159*

PROTECTING METALLIC ANCHORS AND VESSEL FROM ALKALI CORROSION : A SOLUTION WITH REFRACTORY PAINTS

Halapa V., Soudier J., Techer R.
Calderys France, Saint Quentin Fallavier, France

In thermal industries mainly, metallic parts of installation (anchors, tubes, shells…) are faced to many type of corrosion.
Two main corrosion mechanisms occur in these fields, often induced by alkali species:
- The *dry corrosion* which results from the corrosion of the metal by hot gases (O_2, H_2O, CO_2, CO, NaCl, HCl, Cl_2, SO_2…) with the main corrosion type is the oxidation.
- The *hot corrosion* induces by molten salts (NaCl, KCl, K_2SO_4, Na_2SO_4 coming from condensing vapors).
These two types of corrosion are linked. Indeed, molten salts are produced by reaction of hot gases and impurities (Na, K, S, Cl) present in the atmosphere
In these installations, metallic parts are protected by refractory linings retained by an anchoring system often in stainless steel. These metallic anchors are often the reason of refractory lining failure even if in many cases, the refractory is still in good working condition.
In order to avoid or limit these corrosion phenomena, refractory paints were designed to apply on different metallic parts of installations which are submitted to alkali corrosion attack.
This new technology can be use:
- As sublayer before refractory application (by casting, gunning…)
- As a protective layer of naked parts (no refractory applied over)
These refractory paints have for main property to form an impervious and glassy phase at low temperature which limit the penetration of alkali species.
This material, only mixed with water, is very easy to use and could be applied by different technics: brush, roller or with a gun-spray. Moreover, it has a strong adhesiveness on supports after application.
Tests at lab scale were carried out, simulating different type of corrosion (essentially corrosion by molten salts): corrosion by chloride salts, by sulfates salts in reducing or oxidizing atmospheres.
Results have shown that a metallic piece coated with the refractory paint technology presents a corrosion resistance twice higher compared to a naked metallic piece.
This new technology will be tested in real conditions (in incinerators) in order to have some feedbacks on corrosion resistance improvement on site.

Abstract-Number: *161*

FACTORS AFFECTING THE REPRODUCIBILITY AND REPETABILITY OF SPECIMEN PREPARATION OF MONOLITHIC REFRACTORIES IN THE ISO 1927 AND RELATED STANDARDS

Halapa V.[1], Marjerrison J.[2], Martin-Calle S.[1]
[1]*Calderys France, Saint Quentin Fallavier, France,* [2]*Calderys France, Issy-Les-Moulineaux, France*

At present, most standards published for the determination of physical, chemical and technological properties of refractory materials disclose little or no data on the precision of the determined values for those properties, which are nevertheless typically communicated between refractory producers and users. A mismatch of results provided by different laboratories can lead to discussion and claims against the refractory producers.
In order to define testing standards with higher precision, a multinational consortium of testing laboratories is currently engaged in the elaboration of improvements for several physical and technological testing methods of refractory materials.
This paper highlights the importance of the preparation methods of unshaped refractory samples dedicated to the characterization of their physical properties by EN ISO standard methods.
During the test piece preparation step, EN ISO 1927-5 the parameters which have a significant impact on unshaped test piece final properties are mixing time, vibration, water addition and the choice of equipment used.
The water content is the most crucial parameter to control. An excess of water leads to the reduction of mechanical strength, density and an increase in porosity. It is essential to follow the indications given by the manufacturer and use well defined detailed EN ISO procedures on test piece preparation and standardized equipment for the testing standards.
The samples of the medium cement castable (MCC B) were part of a homogeneous lot of material prepared for the ReStaR project. Complete and detailed tests were made to ensure homogeneity of the lot used in the project.

Abstract-Number: ***162***

DEVELOPMENT OF HIGH PERFORMANCE SPINEL BRICK FOR STEEL LADLE APPLICATIONS

Nayak J.P.[1], Ghosh B.[1], Panda P.[2], Tsuyuguchi K.[1], Chattopadhyay A.K.[2], Chatterjee S.[3]
[1]*TRL Krosaki Refractories Limited, Technology, Belpahar, India,* [2]*TRL Krosaki Refractories Limited, Belpahar, India,* [3]*Almatis India Private Limited, Kolkata, India*

Silica containing high alumina refractories such as andalusite or bauxite show high wear-rates with aggressive low melting calcium aluminate slag. Therefore a technical need requires in high performance alumina refractories for steel ladle linings. Additionally with the advancement of steel metallurgy for ultralow carbon and automobile grade of steels there is increasing restriction on carbon bearing refractory lining in steel ladle walls. The development of alumina-spinel fired brick made it suitable to meet these refractory demands where steel ladle side walls can withstand towards aggressive slag attack and thermodynamically stable in contact with steel.
All desired properties of alumina spinel brick can only be achieved by selecting suitable raw materials and appropriate granulometry. The present work describes the development of high performance alumina spinel brick where the recipe is designed with WTA, WFA and alumina rich sintered spinel as base raw material. Reactive alumina and spinel are used as matrix to increase the slag corrosion resistance and enhance the thermal shock resistance. Latest techniques of intense mixing, pressing and firing have been adopted for manufacturing the spinel bricks. Developed spinel bricks have been characterized for different physico-chemical properties like AP, BD and CCS. Thermo-mechanical properties have also been evaluated in terms of HMOR and RUL. Slag corrosion of the bricks at 1650^{0}C for 4hrs shows excellent chemical stability. Thermal shock resistance from 1350^{0}C to water of developed spinel brick has been carried out and shows good thermal stability. Microstructure evolution were studied using optical microscopy as well as SEM with EDS. Pore size distribution of spinel bricks were analyzed and showed the presence of micro-pores; which gives better resistance towards slag penetration. This specially designed product was put into the operation in Ladle Furnace (capacity 175 MT) in one of the leading integrated steel plant in India and the product is running successfully with the fullest satisfaction of the customer. For the end users, newly developed alumina-spinel brick not only helps for lining life enhancement but also avoids carbon pickup in steel from carbon containing bricks, reduces thermal conductivity of lining and controls temperature drop in the metal bath and prevents odour generation during preheating.
Keywords: Steel Ladle, Carbon, Spinel

Abstract-Number: ***163***

MAGNESIA - CARBON MONOLITHIC, NOVEL REFRACTORY SOLUTION

Chakraborty I.N., Sinha S., Bisen R.T.
Calderys India Refractories Limited, R & D, Nagpur, India

Magnesia - Carbon (MgO - C) is the most commonly used refractory for steel making vessels. Though repair of steel making vessels is carried out by Magnesia bearing monolithic products, the initial lining, however, always is with MgO - C bricks due to the non - availability of MgO - C monolithic materials. Development of MgO - C Monolithic material was undertaken to offer a true monolithic solution for steel making ladle - initial lining along with its hot as well as cold repairs.
During the initial stage of this work, conventional approach, i. e. water based system, was adopted for designing MgO - C monolithic formulations. During this work Magnesia - Silicate - Hydrate (MSH) and Calcium Aluminate Cement (CAC) bonded - microsilica containing MgO - C formulations were investigated. For both these systems good rheological as well strength properties could be achieved by using suitable dispersing agents for carbon. These formulations, however, developed crack during heating. The crack development in water based MgO - C castable has been attributed to Brucite formation, which is an expansive reaction as well as to weak bonding of the mass, owing to the presence of carbon. Weak bonding of water based system reduced the pressure withstanding capability of steam generated during drying process. Additionally, these formulations had very poor resistance to basic slag.
TGA data of MSH and CAC bonded Magnesia carbon formulations revealed that Brucite dehydration is over by 430 ^{0}C, i. e. Brucite is not thermodynamically stable beyond this temperature. If installation of water bonded MgO - C monolithic, thus, is carried out at a temperature > 450 ^{0}C, the MgO is unlikely to hydrate. This concept has been exploited for formulating the water based MgO - C hot gunning material discussed in second part of the paper.
Extensive work (rheological, thermo mechanical properties, slag corrosion study) was carried out with different non - aqueous liquid system, dispersants, Magnesites and carbonaceous materials to arrive at the final MgO - C castable formulation. The lab scale interaction study showed performance similar to MgO - C bricks and similar conclusion has also been drawn for field trial results. The details of the concept and the trial reports have been presented in this paper.

Abstract-Number: *166*

ADVANCES ON CERAMIC FILTERS FABRICATION PROCESS

Salvini V.R.[1,2], Savioli N.A.[2], Silva Jr A.C.M.[2], Pereira E.C.[2], Rojas F.A.R.[3], Bose Filho W.W.[1], Pandolfelli V.C.[2]
[1]University of São Paulo, Department of Materials Engineering, São Carlos, Brazil, [2]Universidade Federal de São Carlos, Department of Materials Engineering, São Carlos, Brazil, [3]Universidade Federal de São Carlos, Department of Statistics, São Carlos, Brazil

Ceramic filters have many technological uses such as liquid metal deep filtration, drinking water treatment, air purification, substrates for chemical reactions and others, based on their singular properties, which comprehend high permeability, low density and high specific surface area. The most usual manufacturing process, the organic sponge replication, provides the tridimensional network of struts and interconnected pores required for the applications highlighted above. However, a common drawback of all ceramic filters systems is their low mechanical strength associated to the hollow struts and microcraking, both generated at the thermal decomposition step of the polymeric sponge.
In this work the processing of ceramic filters was modified with the objective to filling up the hollow struts and sealing their microcracks. Samples of pre-heated Al_2O_3 filters were vacuum infiltrated for different times (1-5 min) with ceramic suspensions of different solids concentration (15-40 wt%), particle size distribution (nano to micrometric size) and sintered at 1150^{o}C per 1h.
The statistical analysis of data indicated that the best balance among mechanical strength, mass and strut´s thickness of filters was attained by infiltration with SiO_2 colloidal suspension (40 wt%). SEM analysis confirmed that the struts and microcracks were filled up with colloidal particles. Moreover, the results pointed out that the solid concentration of suspensions was more influential on the final properties of filters than the infiltration time.

Abstract-Number: *167*

PROPERTIES OF AL_2O_3-C REFRACTORIES BONDED WITH ORGANIC/INORGANIC COMPOSITE PHENOLIC RESIN

Wang F.C., Zhao L., Fang W., He X., Liang F., Chen H.
Wuhan University of Science & Technology, Wuhan, China

An organic/inorganic composite phenolic resin (CPR) was synthesized via silicon particles in situ composite with water-soluble lignin-phenolic resin. SEM, TEM and XRD were employed to characterize the microstructure and phase compositions of the CPR. It was observed that silicon particles were uniformly dispersed in the organic matrix. The thermal properties were investigated by TGA. The oxidation resistance and mechanical properties of the Al_2O_3-C refractories bonded with CPR were improved.

Abstract-Number: ***168***

THE MECHANICAL PROPERTIES AND SLAG RESISTANCE OF MGO-CAO BRICKS USING ONE-STEP CALCINED DOLOMA CLINKER AS RAW MATERIAL

Luo M.[1], Fang B.X.[1], Wu B.[1], Zhao Y.[2], Fang Y.N.[1], Cheng W.Y.[1]
[1]Zhejiang Zili Corporation Limited, R&D Department, Shaoxing, China, [2]Zhejiang Zili Corporation Limited, Marketing Department, Shaoxing, China

The doloma clinker with the bulk density higher than 3.30g/cm^3, CaO content from 55wt% to 60wt% as well as impurity content (Fe_2O_3+Al_2O_3+SiO_2) lower than 2wt% is prepared from natural dolomite ore with one-step sintering method in the rotary kiln. The MgO-CaO bricks with different CaO amounts of 20wt%, 25wt%, 30wt%, 35wt% and 40wt% are prepared using this kind of doloma clinker and fused magnesia as the raw materials. The bricks are burnt at the temperature from 1550 °C to 1650 °C for 3h. The results show that the firing temperature and CaO content play a very important role on the physical properties of burnt bricks. With the firing temperature increases, the apparent porosity decreases and the bulk density as well as HMoR increases accordingly. Meanwhile, the bulk density as well as the linear shrinkage of the burnt bricks increases with the CaO content in the bricks increasing. The slag resistance of the MgO-CaO bricks to VOD furnace slag improves as increasing the CaO content. The prepared MgO-CaO brick with 35wt% CaO shows much better slag resistance than the similar products obtained from the market, due to much lower impurity content and better physical properties.

Abstract-Number: ***169***

EFFECT OF FE_2O_3 AND/OR MNO_2 ADDITIVES ON MICROWAVE HEATING OF AL_2O_3-SIO_2 COMPOSITE

Ikuma Y., Senga K., Niwa K.
Kanagawa Institute of Technology, Department of Applied Chemistry, Atsugi, Japan

Microwave heating is an internal heating and is expected to be used extensively in the future. However, there are several problems that must be solved before it can be broadly applied. One of these problems is that there will be a temperature drop at the surface of the material because the temperature of whatever is holding the material in place will not be as high as that of the material itself. This can be a significant problem if there is a large difference in temperature between the material and whatever is holding the material in place because this creates an uneven temperature distribution in the material. Therefore, it is important to understand the behavior of refractories when they are exposed to microwaves, if refractories are to be used for the microwave heating of materials. In this work, we investigated the effect of additives on microwave heating of Al_2O_3-SiO_2 composite.
In the previous study, it was found that Al_2O_3-SiO_2 mixture was heated to 500°C by microwave exposure. But higher temperature could not be attained. It is known that Fe_2O_3 and MnO_2 absorb microwave and can be heated to higher temperatures. In this study we prepared the mixtures of Al_2O_3-SiO_2-Fe_2O_3 or Al_2O_3-SiO_2-MnO_2 and investigated the microwave heating characteristic of the mixtures.
In a first step, Al_2O_3 powder and SiO_2 powder were mixed at 1:1 mass ratio and then Fe_2O_3 was added to the mixture at 0.5-2.0 %. After pressing these mixtures into pellets, they were exposed to 2.45 GHz single mode microwave. Temperature of pellet was measured at the surface. The temperature was about 850°C at 0.5% and 1.0% Fe_2O_3. Thermal runaway was observed at 1.5% and 2.0% Fe_2O_3. Consequently Fe_2O_3 is not a good additive if we want to control the temperature of the mixture. When MnO_2 was added to Al_2O_3-SiO_2 composite at 0.5-2.0% and the mixture was exposed to microwave, the temperature was about 840°C and was stable. MnO_2 is a better additive to Al_2O_3-SiO_2 composite. Adding both MnO_2 and Fe_2O_3 at the same time to Al_2O_3-SiO_2 composite, temperature of 900°C was obtained during the exposure to microwave. Microwave characteristics of both MnO_2 and Fe_2O_3 appear in this mixture.

Abstract-Number: *170*

NEW CONCEPT OF REFRACTORY LININGS FOR ENTRAINED FLOW REACTORS: APPLICATION TO BIOMASS GASIFICATION

Poirier J.[1], Colombel L.[1], Seiler J.M.[2], Froment K.[2]
[1]*University of Orleans, CEMHTI /CNRS, Orleans, France,* [2]*CEA, LTB, Grenoble, France*

Entrained flow reactors are the most convenient way to to biomass gasification on a large scale. Once gasification has taken place, the ashes will soften, liquefy and deposit on the walls, hereby forming the slag. At high temperature (between 1300°C and 1500°C), this aggressive alkali-rich slag strongly corrodes the refractories, which also means that thick refractory lining should be avoided and the externally cooled wall technique (e.g. cold crucible technique) should be preferred.
The wall of the entrained flow reactor consists of an externally water cooled casing and a thermally conductive SiC refractory lining that supports on the hot side a solidified ash crust. The molten slag flows internally over the solidified crust.
In order to limit the wear of refractories, a deterministic approach is proposed that enables to determine the thickness of the solidified ash layer and the heat losses. The gas/slag interface temperature is the key parameter which determines the heat flux and the solidification of the slag layer. The heat losses and consequently the thickness of the solid ash layer are controlled by the liquidus temperature of the slag. The slag liquidus temperature is determined by thermodynamic calculations and lab experiments.
A relation, based on a thermal model, is established between the thickness of the solid ash layer, the slag composition, the optimal reactor operation temperature and the thermal properties of SiC refractories.
- An increase in the ash liquidus temperature, at constant gas temperature, will result in further solidification on the pre-existing solid ash layer.
- A decrease in the ash liquidus temperature, will result in a dissolution of the pre-existing solid ash layer.
Corrosion tests of SiC refractory materials by alkali-rich slag, under thermal gradient, validate this new approach.

Abstract-Number: *171*

NEW SLIDE GATE SYSTEM FOR HIGH REFRACTORIES LIFE

Galesi D.F.[1], Souza L.F.M.[2], Leão C.[2], Horiuchi T.[3], Morii H.[4], Takata A.[4], Carvalho V.[5], Correa W.[5], Pontes Junior J.C.[6]
[1]*Saint-Gobain High Performance Refractories, Product Engineering, Vinhedo, Brazil,* [2]*Saint-Gobain High Performance Refractories, Vinhedo, Brazil,* [3]*Shinagawa Refractories Co.,Ltd., Tokyo, Japan,* [4]*Shinagawa Refractories Co.,Ltd., Okayama, Japan,* [5]*Arcelormittal Tubarao, Serra, Brazil,* [6]*ArcelorMittal Tubarão, Steelmaking Technical Manager, Serra, Brazil*

Shinagawa has developed a new generation of slide gate system equipment for molten steel flow control at steelmaking plants. New slide gate system has many advantages as automatic face pressure loading, reduced refractories consumption, reduction of components part and improvement of refractory exchange work. Plate bricks are shaped to an optimum compact size based on thermal stress analysis and they are fixed by a unique fixation method. The new shape of the plates and the fixation method provides higher performance due to eliminate the stress concentration in the working region thereby avoiding crack formation in this critical region. Face pressure loading and load release of the newly developed SV equipment are very simple.
This paper describes the develop of the slide gate system and the good results in ArcelorMittal Tubarão in terms of refractories life and how it could provide greater availability of steel ladles for operation.

Abstract-Number: *173*

A COMPARATIVE STUDY ON SLAG RESISTANCE PROPERTIES OF RH REFINING FURNACE REFRACTORIES

Xilai C.
Zhejiang Jinlei Refractories Co., Ltd., Zhejiang, China

The slag resistance properties of 3 kinds of refractories including MgO-ZrO_2 based, MgO-MA based and MgO-Cr_2O_3 based on 3 kinds of slags including non-oriented silicon steel slag, oriented silicon steel slag and ordinary steel slag were comparatively studied in detail. The results indicated that, affected by the high slag resistance characteristics of components in matrixes, the order of priority of 3 kinds of refractories on slag resistance is MgO-Cr_2O_3 based, MgO-ZrO_2 based, MgO-MA based. Meanwhile, the matching relationship between steel kind smelting and refractories choosing are: magnesia chromite bricks for non-oriented silicon steel, MgO-ZrO_2 bricks for oriented silicon steel, MgO-spinel bricks for ordinary steel.

Abstract-Number: *174*

PROPERTIES EVALUATION AND MICROSTRUCTURE ANALYSIS OF MATERIALS WITH RECYCLING REFRACTORY AGGREGATES

Pan C.N., Shao C.H., Wong T.C., Lee Y.C., Tseng Y.H.
China steel corporation, Ceramic materials section, new materials R&D Dept., Kaohsiung, Taiwan, Republic of China

There were more than thirty thousand tons of spent refractories generated from China Steel Corporation (CSC) annually. For environmental protection and waste reduction, the recycling program of spent refractories was initiated since 2001 in CSC. In 2008, 28% of spent refractories were successfully recycled for refractory applications. For further raising the recycling ratio of spent refractories as well as making high value-added refractories, spent Al_2O_3-SiC-C (ASC) brick, roseki ASC brick and fire clay brick were reused as raw materials for developing new formula refractories in this study. Based on different conditions that refractories were used, we studied several properties of the refractories, including corrosion resistance, thermal shock resistance, hot modulus of rupture and microstructure analysis. The results showed that (1) the corrosion and thermal shock resistance of the refractory was improved by adding 10% of 10~30mm ASC brick coarse aggregate to blast furnace runner castable refractory. However, the hot modulus of rupture was decreased in this case; (2) the corrosion resistance of the refractory was improved by adding 10% of 0~3mm roseki ASC brick aggregate to tap hole clay, since a dense sintering layer was formed at the slag attacked interface. Meanwhile, hot modulus of rupture was still preserved; (3) When using 50% of 0~5mm fire clay brick aggregate to replace bauxite and chamotte of alumina-silica gunning material, it was found that the thermal shock resistance of new formula refractory and original material was comparable. Finally, these three new formula refractories were used in the field test, and the result showed that their performances were comparable or even better than the original materials'. Currently, the recycling ratio of spent refractories for refractory applications had already reached 35% in 2013 and the refractory consumption cost was also reduced.

Abstract-Number: *175*

A NOVEL DESIGN OF SUB ENTRY NOZZLE TO OPTIMIZE MOULD TURBULENCE FOR PRODUCING CLEANER STEEL & TO WITHSTAND LONGER SEQUENCE CASTING

Sen A.[1], Sahu J.K.[1], Tiwari J.N.[1], Prasad B.[2]
[1]OCL India Ltd, Rajgangpur, India, [2]OCL India Ltd, Refracrory Division, Rajgangpur, India

Sub-entry Nozzle (SEN) is used for shrouding the flow of molten steel from tundish to mould during continuous casting. SENs are generally made of Alumina-Carbon, Zirconia-Carbon and Magnesia-Carbon composites in different zones. The top/seat area of SEN constitutes of Magnesia-Carbon for Ca-treated steel and for other grades it is Alumina-Carbon. However, for slag band, Zirconia-Carbon is the most preferred material due to its excellent corrosion resistance towards lime and nascent fluorides of casting powder.
Production of cleaner steel at lower cost is the main focus of the steel makers. It is observed that defects in steel can come from mould powder entrapment which occurs mostly because of high mould surface turbulence. The flow profile of liquid steel, temperature distribution, turbulence intensity & meniscus velocity in the mould play an important role during casting. Authors of this paper have designed a novel SEN through innovation of a unique port configuration supported by simulation through CFD modelling to optimise the mould turbulence for casting cleaner steel.
The eroded material from refractory can also be a source of non-metallic inclusions (NMI) in steel. This paper also deals with different product mix suitable for seat area & slag band area of SEN to minimise erosion & withstand longer sequence casting. Additives in nano form are incorporated suitably to improve the oxidation, abrasion & corrosion resistance of SEN. Physico-mechanical tests, mineralogical studies, corrosion behaviour & oxidation tests have been carried out for this newly developed SEN along with actual field trials to compare with conventional SEN.

Abstract-Number: *176*

DEVELOPMENT OF LOW THERMAL EXPANSION SILICA BRICKS FOR HOT REPAIR OF COKE OVENS

Swain S.C., Panda B., Jha R.K., Tiwari J.N.
OCL India Ltd, Rajgangpur, India

Conventional silica bricks are extensively used for refractory lining of coke ovens. These bricks are made from quartzite & the fired brick contents mostly tridymite phase besides cristoballite which is so called stable at the operating temperature of coke oven.

During use, after few years of operations, silica bricks gets cracked near the coke oven doors due to severe thermal & structural spalling by frequent opening and closing of doors .During opening of a door, the temperature of the oven falls below 1000° C very quickly and due to sudden change in temperature, transformation from one phase to another takes place accompanies a large volume change which generates cracks. Generally, the extent of crack and other physical damages takes place from door side to several meters deep inside coke ovens. Till now, hot repair of coke ovens takes place by replacing silica bricks of same quality and same shapes. Due to this damage the life of coke ovens get shortened and after some years of operation, cold repair and subsequently rebuilding of coke ovens takes place. The recent technology hot repair of coke ovens have moved towards using very low thermal expansion & superior thermal shock resistant silica bricks for hot repair of coke ovens.
Based on indigenous and global requirement, Authors have developed a special type low expansion silica bricks suits to hot repair. The developed silica bricks will have high thermal shock resistance, high Alkali resistance, and ammonia liquor resistance. The developed bricks were used for hot repair (End flue walls) of coke ovens of an overseas steel plant and working satisfactorily.

Abstract-Number: *177*

INFLUENCE OF DIFFERENT RAW MATERIALS ON THE BEHAVIOUR OF LOW CEMENT CASTABLES

Möhmel S.[1], Weissenbacher M.[1], Kurz B.[1], Joubert O.[2]
[1]*CARRD, Villach, Austria,* [2]*IMERYS Refractory Minerals, Paris, France*

Different alumina (fused, sintered) as well as aluminium silicate raw materials (chamotte, mullite, bauxite, andalusite) were used as aggregates and partly as fillers for the preparation of low cement castables. Aim of our investigations was the effect of different compositions as well as impurity levels in the aggregates but especially in the matrix of the castables on the thermal-mechanical properties of the products.
The results obtained by characterising these materials especially with respect to refractoriness under load (RuL) but also to thermal shock behaviour and creep in compression (CiC) showed some interesting effects. Besides others the intermediate softening and re-stabilisation reactions observable within the course of the RuL were in focus of our investigations. In case of e.g. castables based on mullitic aggregates a slightly higher thermal stability was found for raw materials with only 47% alumina in comparison to aggregates on base of a 70% Al2O3 product. This was surprising since the higher alumina content was expected to lead to a better performance.
For alumina castables a higher RuL could be proved for a composition on base of a fused product in comparison to sintered alumina. Both effects are obviously related to the sodium present as an impurity in the raw materials. Nevertheless not only the absolute value is important but also the availability for the reactions occurring at high temperature.
Therefore especially attention was turned to the investigation of the reasons for the unexpected behaviour of the relevant castable compositions. For this, analytical techniques like scanning electron microscopy (SEM) and X-ray powder diffraction in combination with a heating chamber (HT-XRD) were used.
Interesting connections between matrix compositions and the behaviour of the castables could be detected, giving some insights on the course of high temperature reactions within the different investigated materials.

Abstract-Number: *179*

EFFECT OF SODIUM TRIPOLYPHOSPHATE ON HYDRATION BEHAVIOR OF DIFFERENT CALCIUM ALUMINATE CEMENTS

Shang X.[1], Zhang C.[1], Li H.[1], Li L.[1], Wang Q.[1,2], Ye G.[1]
[1]*Zhengzhou University, Zhengzhou, China,* [2]*Luoyang Institute of Science and Technology, Luoyang, China*

Different calcium aluminate cements (CAC) showed varied hydration rates at different curing temperatures. In order to acquire the appropriate workability of CAC bonded castables, sodium tripolyphosphate (STPP) was the customary dispersant. It was noticed that addition of STPP influenced the hydration rate of CAC. In this work, the effect of STPP addition on the hydration and setting behavior of different CAC at temperatures between 10°C and 40°C was studied through the hydration heat evolution and the phases of the cements after hydration at different temperatures for varied periods. The hydration heat evolution of the cements was monitored with the semi-adiabatic method. The vacuum freeze drying method was utilized to halt the cement hydration at the designated times, and X-ray Diffraction was conducted to analyze the phases of the hydrated products.

Abstract-Number: ***181***

SYNTHESIS OF MAGNESIUM ALUMINATE SPINEL AGGREGATES FROM NATURAL AND SYNTHETIC RAW MATERIALS

Ghosh A., Sinhamahapatra S., Tripathi H.S.
CSIR-Central Glass & Ceramic Research Institute, Refractory, Kolkata, India

Magnesia-rich magnesium aluminate spinel aggregates (MgO: Al_2O_3 molar ratio 2:1) was developed from (1) Indian natural magnesite (Salem region) and calcined Al_2O_3 and (2) Nedmag caustic magnesia and calcined Al_2O_3. The milled batches were pelletized and fired between 1450° to 1650°C. Aggregates were characterized in terms of bulk density, apparent porosity, Hot MOR, microstructure and crystalline phase analysis. In both the batches, spinel and periclase are the main crystalline phases. In case of spinel developed from Indian magnesite, forsterite is also present additionally as minor phase due to presence of silica as impurity. This is in agreement with alumina-magnesia-silica phase diagram in the magnesia-rich spinel region. Hot MOR of both the batches is comparable.

Abstract-Number: ***182***

EFFECT OF CITRIC ACID ON HYDRATION BEHAVIOR OF DIFFERENT CALCIUM ALUMINATE CEMENTS

Mu Y.[1], Zhou W.[1], Li L.[1], Shang X.[1], Wang Q.[1,2], Ye G.[1]
[1]Zhengzhou University, Zhengzhou, China, [2]Luoyang Institute of Science and Technology, Luoyang, China

Different calcium aluminate cements (CAC) showed varied hydration rates at different curing temperatures. In order to acquire the long-enough working time of CAC bonded castables, a retarder can be used to decelerate the hydration rates of some calcium aluminate cements. In this work, the effect of citric acid addition on the hydration and setting behavior of different CAC at temperatures between 10°C and 40°C was studied through the hydration heat evolution and the phases of the cements after hydration at different temperatures for varied periods. The hydration heat evolution of the cements was determined using the semi-adiabatic method. The vacuum freeze drying method was utilized to terminate the cement hydration at the designated times, and X-ray Diffraction was conducted to analyze the phases of the hydrated products.

Abstract-Number: ***183***

THE INFLUENCE OF SUBMERGED ENTRY NOZZLE AND TUNDISH NOZZLE DESIGN ON THE FLOW CHARACTER FOR THE SLAB QUALITY

Yanwen Y.[1], Yuxi Z.[2], Zhiming Z.[3]
[1]Baoshan iron & steel Co.Ltd, Baosteel making plant, Shanghai, China, [2]Bao steel group, Engineering and technology company, shanghai, China, [3]Baoshan Iron & Steel Co., Ltd., Baosteel making plant, shanghai, China

The present paper analyzes the current research status in regard to the mechanism of nozzle clogging and improving measures to solve the problem during CC (continuous casting) , and particularly introduces the improvement measures adopted at home and abroad for elimination of the trouble, and points out that the nozzle clogging is still a question that needs to be solved during continuously casting the Al killed steel. Effects of clogging, argon injection, and continuous casting conditions on flow and air aspiration in submerged entry nozzle as Metallurgical process such as Ca treatment process and composition of molten steel. Tundish nozzle clogging is a common problem and its harm is obvious. Firstly, it may result in termination casting in advance ,reducing casting machine productivity. Secondly, a frequent change of nozzle will increase the cost of Production of enterprises. The worst is that nozzle clogging causes bias current liquid level fluctuation at the mould and the clogging which is washed with peeling involved in the molten steel or floated to the protection slag, cause the change of protection slag composition and worsen the performance for protection slag and resulting in slab quality defects.

Abstract-Number: *185*

EFFECT OF PARTICLE SIZE CHANGE ON HYDRATION BEHAVIOR OF DIFFERENT CALCIUM ALUMINATE CEMENTS

Zhang C.[1], Wang Y.[1], Guo B.[1], Shang X.[1], Wang Q.[1,2], Ye G.[1]
[1]*Zhengzhou University, Zhengzhou, China,* [2]*Luoyang Institute of Science and Technology, Luoyang, China*

In order to acquire the desired curing time at different climate and/or for different castables, calcium aluminate cements (CAC) with different setting time are required. In this work, the effect of particle size distributions (PSD) on the hydration and setting behavior of different CAC was studied, with five commercial CAC ground for different times. The hydration heat evolution of the as-received and ground cements were tested at temperatures between 10°C and 40°C through the semi-adiabatic method, and the setting behavior was measured by Vicat needle. The vacuum freeze drying method was utilized to terminate the cement hydration at the designated times, and X-ray Diffraction was conducted to analyze the phases of the hydrated products.

Abstract-Number: *186*

ASSESSMENT OF THERMAL SHOCK RESISTANCE BY HMOR TEST WITH HIGH HEATING RATE

Sidi Mammar A.[1], Grasset-Bourdel R.[2], Gruber D.[1], Harmuth H.[1]
[1]*Montanuniversitaet, Department of Mineral resources and Petroleum Engineering - Chair of Ceramics, Leoben, Austria,* [2]*RHI AG, Technology centre, Leoben, Austria*

Many thermal shock tests have been proposed over the last decades to characterize the thermal shock resistance of refractories, some of them now being commonly used such as water and air quenching methods. Nevertheless most of them produce cold/downward thermal shocks although many products will especially suffer from hot thermal shocks in service (e.g. slide gate products in the steel industry). Moreover, thermal shock tests for carbon containing products are not numerous. This paper aims to present a test causing a hot thermal shock on the sample, which is not expensive and without any risk for the operator, with an easy way of damage assessment and also suitable for carbon-bonded refractories.
The combination of two high temperature bending tests performed at the same final temperature but with different heating procedures before applying the load is proposed. For the first bending test, where the hot modulus of rupture is determined ($HMOR_1$), a common heating up rate and reducing conditions is applied, while for the second ($HMOR_2$ or quick insertion test) a sudden and short heating step corresponding to an oxidizing hot thermal shock is chosen. HMOR values resulting from these two bending tests are compared for a significant number of products used as sliding gates; materials have not been impregnated. Only very small oxidation is observed on the surface of carbon-bonded products after the tests. In order to support the experimental results FEM simulations using the damaged plasticity model implemented in the software Abaqus have been performed for two products of different brittleness. They show high stresses due to the thermal shock of the method with the high heating rate, the less brittle product presenting a higher retained strength. The calculation of the ratio $HMOR_2/HMOR_1$ can provide first and quick information concerning the thermal shock resistance of products in service.

Abstract-Number: *187*

PROPERTIES OF CA900 CEMENT BONDED MULLITE CASTABLE FOR ROTARY KILN LINING

Han B.[1], Wang D.[2], Li N.[3]
[1]*Wuhan University of Science and Technology, The Key State Laboratory of Refractories and Metallurgy, Wuhan, China,* [2]*Zhengzhou Jianai Special Aluminates Co., Ltd, Zhengzhou, China,* [3]*Wuhan University of Science and Technology, Wuhan, China*

Using M70 mullite, super duty bauxite, andalusite, SiC, reactive alumina, micro silica as main raw materials, CA 900 high alumina cement as binder, sintering parameters (bulk density, apparent porosity), mechanical properties (modulus of rupture, cold crushing strength) and abrasion resistance as well as thermal shock resistance, corrosion resistance to vanadium containing slag of castables for rotary kiln based on the above materials were tested. Furthermore, effects of admixture NaCl and Na2SO4 on corrosion resistance of the prepared castables are discussed by static crucible method and simulated using Factsage thermodynamics software. The results show: Introduction of andalusite can compensates shrinkage and improves thermal shock resistance. However, andalusite can't improve the abrasion resistance, super duty bauxite has positive effects on abrasion resistance. NaCl and Na2SO4 are deleterious to slag resistance of the castable due to the high content low melting phases. Thermodynamic analysis confirms the formation of low melting compounds.

Abstract-Number: ***188***

INFLUENCE OF THE SURFACE CHEMISTRY ON THE FILTRATION OF ALUMINUM

Voigt C.[1], Fankhänel B.[2], Aneziris C.[1], Stelter M.[2]
[1]*TU Bergakademie Freiberg, Institute of Ceramic, Glass and Construction Materials, Freiberg, Germany,* [2]*TU Bergakademie Freiberg, Institute of Nonferrous Metallurgy and Purest Materials, Freiberg, Germany*

As is known, the molten metal filtration efficiency is affected by the macro pore size, the melt velocity and the inclusion size. However, limited information is available on the effect of the filter surface chemistry on the filtration.
In this work alumina filters with four different oxidic surface chemistries (alumina, spinel, mullite and titania) were tested with aluminum (AlSi7Mg). All prepared filters were casted successfully under industrial conditions. The casted aluminum samples showed no contamination caused by the filters measured with the help of a spark spectrometer.
The influence of the surface chemistry on the filtration effect was evaluated with the help of SEM investigations of the casted filters.
The best filtration effect determined by the quantity of the captured non-metallic inclusions in the filters after aluminum casting show alumina and spinel surface chemistries.
Additional wetting experiments were conducted with the four different tested materials (alumina, spinel, mullite and titania). The used sessile drop apparatus consists of a high-temperature furnace with a high vacuum combined with an inert gas system and a camera.
The wetting experiments yielded for all tested materials a non-wetting behavior whereupon alumina and spinel show higher wetting angle than mullite and titania.

Abstract-Number: ***189***

STUDIES ON DEVELOPMENT OF MAGNESIA REFRACTORY AGGREGATES FROM INDIAN MAGNESITE USING FE_2O_3 AS AN ADDITIVE

Haldar M.K.
CSIR-Central Glass & Ceramic Research Institute, Refractories Division, Kolkata, India

The phenomenal growth of Iron and Steel Industries in recent time increased the significance of basic refractories. The increase in production of Ferrous Metallurgical Industries is expected to increase the demand of magnesite for manufacturing of magnesia based refractories. India, has major deposits of natural magnesite in the Salem region of Tamilnadu which had been previously examined without using additive to assess their usefulness as refractory raw materials. In the present study, an attempt has been made to see the effect of Fe_2O_3 on the sintering behaviour of magnesite and the microstructure developed in the temperature range of 1550^{O}C-1650^{O}C.B.D and A.P are found in the range of 3.38-3.43g/cc and 2.9-2.4% respectively. The percentage densification is achieved up to the level of 99%. The micro structural characterization of sintered samples reveals the development of magnesioferrite phase in presence of Fe_2O_3.

Abstract-Number: ***191***

ELECTRON BACKSCATTER DIFFRACCION APPLICATION ON STEEL CONTINUOUS CASTING NOZZLES TO INCREASE THE KNOWLEDGE OF WEAR MECHANISMS

Brandaleze E.[1], Avalos M.[2]
[1]*Universidad Tecnológica Nacional - Facultad Regional San Nicolás, Metallurgy, San Nicolás, Argentina,* [2]*Instituto de Física de Rosario, Materiales, Rosario, Argentina*

The requirements for submerged nozzles are particularly harsh. They need to have good resistance respect to thermal shock and chemical attack during the nozzle immersion into molten steel and mould flux at 1530ºC, to prevent expensive production losses caused by break out during the service. One type of nozzle refractory material with optimum performance is the alumina-graphite (Al_2O_3-C) bonded with phenolic resin. The mould flux cause localized corrosion at the flux line and determines the life in service of

the submerged nozzle. For this reason, it is important to analyze the impact on the nozzle wear mechanism of new mould fluxes in which the Li_2O is used for the substitution of Ca_2F content. In this paper, the characterization of the nozzle include thermal analysis DTA TG, dilatometry, thermomechanical properties. By DTA TG and dilatometry, changes of the refractory nozzle material in relation with temperature, were studied. Also, physical properties such as viscosity and surface tension results measured by experimental tests were considered at industrial temperatures conditions and corroborated by mathematical models calculation. The corrosion study includes experimental cup test and a post mortem study. The structural evaluation was carried out applying light microscopy, scanning electron microscopy with EDS analysis and the application of Electron Backscatter Diffraction (EBSD). The EBSD technique provides quantitative microstructural information about crystallografic nature of the aggregates in the nozzle. It reveals grain size, boundary character, grain crystallografy, misoreintation angles associated with the suceptibility of chemical attack. The chemical reactions between flux and nozzle were stablished by SEM with EDS analisys and corroborated by thermochemical simulation applying Fact Sage. This software provides good results for complex equilibrium systems.
Through the results a deep understanding on the wear mechanisms of the Al_2O_3-C nozzles was achieved, new information obtained by EBSD allow to increase the knowledge on the chemical attack susceptibility of the refractory aggregates. Also the thermochemical simulations provide the possibility to corroborate the chemical reactions in the system between nozzle and mould flux.

Abstract-Number: *192*

IMPROVING THE CORROSION RESISTANCE OF AL_2O_3-SIC-C CASTABLE BY COMPOSITION DESIGN

Liang Y., Yin Y., Ge S., Nie J., Liu Z.
The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China

Al_2O_3-SiC-C castable is still widely used as refractory lining for blast furnace main trough until now. However, with the blast furnaces becoming bigger and bigger, Al_2O_3-SiC-C castable is facing much more challenges, in which, corrosion caused by slag is one of the most important factors affecting its service life. Thereby, super fine TiO_2 powder(SFTP) has been introduced into Al_2O_3-SiC-C castable, with the aim to synthesize Ti(C,N) through in-situ reactions, and thus to improve the corrosion resistance of Al_2O_3-SiC-C castables. Thermodynamic calculations suggest it is possible to synthesize Ti(C,N) through in-situ reactions in Al_2O_3-SiC-C castable. The X-ray diffraction(XRD) and Scanning electronic microscope equipped with energy dispersive X-ray analysis (SEM-EDAX) performed on Al_2O_3-SiC-C castable with 2wt% SFTP fired at 1450°C in a reducing atmosphere, confirmed the possibility to in-situ synthesize Ti(C,N) in Al_2O_3-SiC-C castable. The corrosion resistance of Al_2O_3-SiC-C castables without and with 2wt% SFTP were compared after static crucible corrosion test. Results indicate the corrosion resistance of Al_2O_3-SiC-C castable with 2wt% SFT is better than that without SFTP, this might associate with the location of in-situ formed Ti(C,N) solid particles in the liquid slag, which would prevent the penetration of molten slag into the structure through their effect on the viscosity increase.

Abstract-Number: *193*

A COMPARATIVE EVALUATION STUDY OF METHODS FOR THERMAL SHOCK ASSESSMENT

Schmitt V., Seifert G.
Fraunhofer Institute for Silicate Research, Center for High Temperature Materials and Design, Bayreuth, Germany

Lifetime assessment of refractories is a key issue to improve resource and cost efficiency of high temperature processes. A detrimental factor limiting the lifetime is thermal loading, which causes severe thermo-mechanical stresses. These can result in the degradation of the mechanical strength, stiffness and overall material properties and ultimately lead to component failure. To evaluate the lifetime of components under a certain load, the flaws in the initial state of the material as well as after thermal loading have to be investigated. There is extensive literature on various testing methods for the evaluation of thermal shock damage, the focus being on non-destructive testing using ultrasonic techniques. However, the need for advanced yet simple testing methods to reliably assess the thermal shock damage still persists.
This study aims to compare different evaluation techniques regarding their adequacy and accuracy to assess damage caused by thermal stresses as well as their potential for practical application. To this end, shaped refractory materials were subjected to static temperature gradients and conventional thermal shock experiments (quenching with air or in water). The materials were tested before and after thermal loading using both mapping/imaging and integrating techniques. The former techniques, i.e. X-ray computed tomography, ultrasonic, thermal and terahertz imaging, allow to locate flaws in the material and to visually track the growth of cracks after thermal loading cycles. Integrating techniques such as the ultrasonic velocity or resonance frequency testing

provide a quick insight on the total amount of defects. From the obtained results, the practical applicability and the use for damage and lifetime assessment of the various methods is evaluated.

Abstract-Number: *194*

THE INFLUENCE OF ALUMINA POWDER ON THE HYDRATION BEHAVIOR OF DIFFERENT CALCIUM ALUMINATE CEMENTS

Hou D.[1], Zhang C.[1], Li H.[1], Shang X.[1], Wang Q.[1,2], Ye G.[1]
[1]*Zhengzhou University, Zhengzhou, China,* [2]*Luoyang Institute of Science and Technology, Luoyang, China*

It is known that additions of alumina, especially with high specific surface areas, accelerate the hydration rate of calcium aluminate cements (CAC). As different CAC may have different hydration rates, this work is to investigate the effect of alumina powder on the hydration behavior of five commercial CACs at different temperatures.
The hydration heat evolution of the Al_2O_3/CAC mixtures was tested at temperatures between 10°C and 40°C through the semi-adiabatic method, and the setting time was measured by Vicat needle. The vacuum freeze drying method was utilized to arrest the cement hydration at the designated times, and X-ray diffraction was conducted to analyze the phases of the hydrated products.

Abstract-Number: *196*

SAFE USE OF ISOSTATICALLY PRODUCED REFRACTORY COMPONENTS AT CC DUISBURG-BRUCKHAUSEN (TKSE AG)

Karrasch S., Baaske A.
ThyssenKrupp Steel Europe AG, Duisburg, Germany

Several isostatically produced components are used at the tundish of the CC Duisburg-Bruckhausen. Because they have a very high influence on the safety situation during continuous casting, a lot of work have been done to improve them. To achieve resonable costs today different suppliers are used from all over the world. Furthermore the aim to reach no accidents at all comes first.
In this paper investigations on failures of isostatically produced components and there consequences to safety are presented. Some failures are based on the production of the supplier. Failures could also appear by the transportation to or inside the casting plant or even during preparing of the tundish.
Aditionally some reference analysis have been done. Chemical und physical properties are controlled, also mineralogy analysis are carried out. Weak conditions could be observed at a very early stage. These reference analysis are the keyfactor to avoid failures and to reach finally the aim of zero accidents on the casting platform of the CC Duisburg-Bruckhausen.

Abstract-Number: *197*

SEEKING SUITABLE REFRACTORIES TO LIMIT THE WEAR IN ROTARY KILNS FOR INDUSTRIAL WASTE INCINERATION

Villalba Weinberg A.[1,2,3], Poirier J.[1], Goeuriot D.[2], Varona C.[3], Chaucherie X.[4]
[1]*CEMHTI-CNRS, Université d'Orléans, Orléans, France,* [2]*SMS, Mines, Saint-Etienne, France,* [3]*BONY S.A. - Produits réfractaires, Saint-Etienne, France,* [4]*SARPI-VEOLIA, Limay, France*

A challenge for industrial countries is to allow industrial progress on the one hand and to accomplish increasingly stringent environmental standards on the other hand. In this respect, it is important to neutralize toxic waste produced by the industry. Their treatment by incineration offers the advantage that organic, toxic substances are decomposed and waste volume is highly reduced at the same time. One of the most efficient systems for such applications is the rotary kiln, since it is able to treat solid, pasty and liquid wastes all together. Currently, high alumina bricks and alumina chromia bricks are used for the linings of these rotary kilns. Often, after one or two years, some bricks should be replaced by new ones because their thickness is reduced to few centimetres. This work consists of two parts: In a first step, used refractory bricks from three different industrial waste incineration plants are examined and characterised by optical microscopy, scanning electron microscopy, x-ray diffraction and x-ray fluorescence. In order to get the whole picture of the degradation process, a look at the kiln conditions is also taken, regarding temperature, atmosphere,

and slag properties. After having understood the wear mechanisms, alternative refractory materials are tested at the laboratory scale and innovative solutions are discussed in a further step.

Abstract-Number: *198*

RESTAR - COLLABORATIVE INITIATIVE IN THE EUROPEAN REFRACTORY SECTOR TO REVIEW AND IMPROVE TESTING STANDARDS

Brochen E.[1], Quirmbach P.[1], Volckaert A.[2]
[1]*European Centre for Refractories (ECREF), Hoehr-Grenzhausen, Germany,* [2]*Cerame-Unie / European Refractories Producers Federation (PRE), Brussels, Belgium*

EN testing standards for refractory products are widely used throughout Europe, and even worldwide, for quality evaluation purposes and the establishment of technical data sheets of refractory products. European standards (EN) have helped with the harmonization of trade within Europe and globally. Although EN testing standards are well-established and accepted, their roots stretch back over 60 years and to this day their content has only been adjusted to modern processing technology. No global and in-depth investigations of the repeatability, precision and reproducibility of the EN testing standards for refractories have been carried out for decades.
Based on the common understanding that the fundament of EN testing standards for refractories needs to be consolidated and made future-proof, a research and innovation (R&I) consortium of refractory producers and refractory research institutes from throughout Europe has been formed to investigate, review and improve the current EN testing standards. This work is being carried out in the project ReStaR (Review and improvement of testing Standards for Refractory products) and is being funded by the European Commission in its Seventh Framework programme.

Abstract-Number: *199*

PRODUCTION PROCESS FOR NEW LIGHTWEIGHT KILN FURNITURE AND THEIR RELEVANCE FOR THE TEMPERATURE DISTRIBUTION WITHIN THE KILN

Scheithauer U.[1], Slawik T.[1], Schwarzer E.[1], Tscharntke F.[1], Schmidt T.[2], Jegust S.[2], Richter H.-J.[1], Moritz T.[1], Michaelis A.[1]
[1]*Fraunhofer IKTS Dresden, Dresden, Germany,* [2]*Inmatec GmbH, Rheinbach, Germany*

The main requirement on kiln furniture is the save support or transport of ceramic products during the thermal processing. Therefore a high compression and bending strength especially at high temperatures is needed. State of the art are thick dense or porous ceramic plates. But these structures have a high thermal mass which has to be heated and quenched during every heat treatment cycle. Furthermore a homogeneous temperature distribution in the kiln can only be realized at low heating or cooling rates. Higher rates could result in thermal induced mechanical stresses which could damage or destroy the kiln furniture and the supported ceramic products.
Due to these problems the Fraunhofer Institute for Ceramic Technologies and Systems has investigated the manufacturing of a novel generation of kiln furniture with advanced properties.
These novel kiln furniture are realized by the combination of different green ceramic pre-products made by ceramic tape casting or extrusion. The manufactured kiln furniture had a low density and heat capacity but still a high stiffness and a good thermal shock behaviour. Planar green tapes are laminated with a supporting structure, which has macroscopic cavities allowing passage of air or gas and additionally reduce the density of the structure.
The presentation will show the manufacturing and the advantages of the new kiln furniture. Beside the possibility of saving energy and time, which were investigated in different tests, results will be shown that a higher work load and a better homogeneity of the temperature distribution within the kiln can be achieved which could also be demonstrated by the simulation of the temperature distribution during heating and cooling processes.

Abstract-Number: *200*

AVALIATION OF THE BENEFITS OF DIFFERENT COLLOIDAL BINDERS IN THE DEVELOPMENT OF WORKING FACE MONOLITHIC INSULATING REFRACTORY WITH LOW WETTABILITY BY MOLTEN ALUMINUM ALLOYS

Valenzuela F.A.O., Ziegler F.L., Ziegler Sr F., Ziegler F.
ZTech Refractory Industry Ltd, Research & Development, Blumenau, Brazil

The use of microporous alumina grains associated with anti-wetting minerals allows to obtain castables to direct contact with molten aluminum with little heat loss, low adhesion of molten metal and lower tendency to generate corundum. But the traditional use of high doses of aluminous cement as a binder of insulating castables cause low refractoriness and reduce the speed of drying and sintering rate of the microstructure of the material. Also imposes low mechanical strength to the monolithic at the operating temperature of the furnace to aluminum foundrys (750 to 950°C). In this work the study and the selection of colloidal binders available in the market enabled to utilize the best colloidal consolidation agent associating adequate green strength, a heating rate 30% above the traditional cement concretes, compressive strength after 850°C up to 60% larger than conventional insulation castables, decreasing thermal conduction and greater repellency aluminum casting alloys with less tendency to oxide formation on the surface of the refractory. Following numerous laboratory tests, and industrial-scale application, the newer monolithic insulating with low wettability to furnace working face based in microporous alumina consolidated with colloidal additive performance scores superior to the linnings currently in use, comprising insulating and dense layers, revealing a trend of anti-wetting high mechanical strength insulating that will govern the future of monolithic refractories linnings to furnaces in the aluminum industry, not only by greater durability and less maintenance, but mostly by lower consumption of energy for their operation.

Abstract-Number: *201*

CFD SIMULATION OF A SINTER-FURNACE INCLUDING CONVECTIVE AND RADIATIVE HEAT TRANSPORT

Dannowski M., Beckert W., Scheithauer U., Michaelis A.
Fraunhofer IKTS Dresden, Dresden, Germany

The high thermal inertia of the sintering process in a furnace is to a significant degree caused by the high thermal mass of common sintering support plates. The use of novel ceramic lightweight sintering support structures therefore offers a high potential for cost saving due to reduction of energy usage and process times. The effect on thermal homogeneity in the furnace, especially in dynamic operation has yet to be analyzed. Negative influences may be expected from the strongly reduced thermal conductivity of the lightweight structures, a positive effect could be obtained from their permeability to gas flow by an increased potential for convective heat transport within the furnace. There are very few options for an experimental analysis of this topics due to the limited availability of the structures (allowing only small furniture geometries) and the high expense for a comprehensive thermal and fluidic instrumentation. The usage of a 'virtual' numerical model of the set-up offers an excellent and efficient way for thermal analysis.
A transient 3d model analysis of a sinter furnace with built-in structures (sintering support + example sintering bodies) is presented. It was implemented using the CFD-code Fluent which allows to include internal gas flow and convective heat transport into the analysis, additional to conductive and radiative heat transport as reported in work from the literature. First analysis results make clear, that convective heat transport is a significant mechanism for distribution of thermal heat in the furnace especially in the early heating up period up to 500°C. In this phase temperature gradients within and between the sintering bodies may result in a nonuniform debinding process with an increased risk of crack formation in the sintered parts and the support structures. After the temperature has raised to its stationary level for sintering, thermal radiation is dominating the process. This state is in better compliance with the assumptions of the common furnace model analyses known from the literature, neglecting gas flow effects. The current status of the model is presented in the work. Extensions are planned towards an efficient description for highly permeable lightweight structures.

Abstract-Number: *202*

BIO INSPIRED REFRACTORY DEVELOPMENT (B.I.R.D.): HIGH STRENGTH AND TOUGH MGO-C BRICKS FOR BOF

Pagliosa C.[1], Resende C.[2], Pandolfelli V.C.[3]
[1]Magnesita Refratarios S.A., R&D, Contagem, Brazil, [2]Magnesita Refratarios S.A., Contagem, Brazil, [3]Federal University of São Carlos (UFSCar), São Carlos, Brazil

Basic oxygen furnace (BOF) or LD converter process is a relatively cheap process for refining iron into steel. Vessel size depends on each customer and usually its maximum capacity is close to 320t. BOF is the most important steel making equipment in terms of refractory tonnage and the novel demands on low carbon metal have been increasing the oxygen volume flow applied. Also the combination of top and bottom blowing are often used to decrease operating costs via more efficient stirring action in the molten steel. Due to this, MgO-C bricks are been exposed to severe oxidation and corrosion by gases and slags, erosion due to higher emulsion agitation and thermal shock. This new pattern of wear mechanisms requires a new approach to the development of MgO-C, mainly for BOF critical areas.
Trunnions and impact pad require very special properties such as high mechanical strength and optimal thermal shock damage resistance. At first, these properties are generally mutually exclusive and for this reason the MgO-C improvements had to balance between strength and toughness. Although, some natural materials rely on both intrinsic and extrinsic toughening, seashells structure highlights how nature has been far more successful than us in making damage-tolerant (hard and tough) materials. This is associated to the hierarchical architecture of most biological and natural materials, which present characteristic structural features on multiple length scales from molecular to near-macroscopic dimensions. The origin of the intrinsic (plastic deformation) mechanisms tends to be at the smaller end, akin to the nanometric scale. Human cortical bones and mollusk shells are other inspiring examples.
A new development of MgO-C bricks was conducted in order to mimic some materials in the nature to attain both strength and toughness. Special phenolic resin binder was combined with nano graphite particles in several proportions. A comparative evaluation among classic MgO-C bricks and bio inspired compositions was carried out to show the potential of this new approach. Product properties, thermal shock evaluation and wedge splitting test at 1400ºC are presented in this paper.

Abstract-Number: *203*

MANUFACTURE AND CHARACTERISATION OF NOVEL REFRACTORIES BASED ON MULTI-LAYERED CERAMICS FOR STEEL CASTING APPLICATIONS

Jakobsen D., Götschel I., Roosen A.
University Erlangen-Nuremberg, Glass and Ceramics, Erlangen, Germany

In this work, the ceramic multilayer technique, which is based on tape cast green sheets, was applied to generate advanced refractory composite structures. High purity refractory oxides like alumina, magnesia, Mg-Al-spinell and zirconia were used for casting tapes with thicknesses of several mm. Tapes of different porosity and microstructure were obtained using multi-modal slurries of grain sizes up to 1 mm. The green tapes are transferred to multilayer structures by means of thermo-compression and cold low pressure lamination and subsequently fired at 1700 °C. Planar sliding gates as well as nozzles were manufactured for application in the steel casting industry. Due to the use of carbon-free raw materials, the inferior thermal shock behaviour of multi-layer composites has to be compensated, which will be conducted via generation of residual stresses and weak interfaces, respectively.
The presentation will describe the processing route for the manufacture of planar and rotationally symmetric ceramic multilayer structures. The fabricated structures are characterized concerning their microstructure, thermal shock and corrosion behaviour. The interrelation between processing, multilayer design, microstructure and properties of these advanced refractory structures will be discussed.

Abstract-Number: *204*

COLLOIDAL SILICA BONDED CASTABLES FOR HIGH END REFRACTORY APPLICATIONS

Klippel U.[1], Soudier J.[1], Wahyu A.[2]
[1]*Calderys France, R&D Center, Saint Quentin Fallavier, France,* [2]*Calderys Indoporlen, Bekasi, Indonesia*

The electric arc furnace delta section has to withstand high thermal loads, thermal cycling and as a result severe thermal stresses in the lining. This is even intensified in cases where the electric arc furnace roof is not cooled. A comparative investigation between a low cement bauxite castable, an ultra low cement alumina castable and a colloidal silica bonded non cement alumina castable is presented. Significant differences in properties are highlighted. Achievements of industrial trails in Indonesia are discussed in terms of service performance.

Abstract-Number: ***205***

IMPROVEMENT IN THE PERFORMANCE OF MGO-CAO-C REFRACTORIES BY NOVEL HEAT TREATMENT PROCESS

Wang X.[1], Wang Z.[1], Ma Y.[1], Liu H.[1], Xu Y.[2], Yao J.H.[2], Xu Y.[2]
[1]Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallurgy, Wuhan, China, [2]Zhejiang Jinlei Refractories Co., Ltd., Huzhou, China

MgO-CaO-C refractories have received great attentions in recent years due to the increasing demands for clean steel. In this work, MgO-CaO-C materials were prepared by using sintered MgO-CaO clinker, fused MgO and natural graphite as raw materials and anhydrous phenolic resin as binder. The effect of heat treatment process on the hydration process, phase transition and the physical properties of the MgO-CaO-C materials were investigated. In addition, MgO-CaO-C bricks were manufactured by a shaped refractory producing process. A trial application in slag line zone of stainless steel refining ladle was carried out. The results showed that the hydration of CaO detected in the present materials was caused by water from air and resin polycondensation during conventional heating treatment process. By increasing heating treatment temperature, the hydration could be restrained and the strength of the materials could be enhanced. The industrial application indicated that the developed MgO-CaO-C bricks were suitable and competitive for stainless steel refining ladle lining with high performance and reasonable cost.

Abstract-Number: ***206***

HIGH TEMPERATURE CHARACTERISTICS OF POTASIUM GEOPOLYMERS

Machino T.[1], Hashimoto S.[1], Hirano H.[2], Honda S.[1], Iwamoto Y.[1]
[1]Nagoya Institute of Technology, Nagoya-shi, Japan, [2]Towa Refractory Engineering,Co.Ltd., Kani-shi, Japan

Geopolymers are amorphous alkali-aluminosilicate hardened bodies fabricated from a mixed slurry of an amorphous aluminosilicate such as metakaoline (produced by heating kaolinitic clay at approximately 700ºC for several hours) or fly ash (exhaust from a coal-burning power plant) and alkali-solution (NaOH, KOH). Usually, water glass (sodium or potassium silicate hydroxide) is also added to the staring slurry as an active reactant. The hardening of geopolymers occurs via the formation of a silica(IV) network accompanied by the substitution of aluminum(III) ions with alkali ions such as sodium or potassium(I) in order to maintain the charge balance of the network. Generally, curing time requires several days to one week at 50~80ºC and 80~100% in relative humidity. The resultant geopolymers are anticipated to have applications as construction and building materials at room temperatures, since their mechanical properties are similar to those of cement and concrete materials. Recently, since geopolymers show excellent high temperature properties, geopolymers are also expected to be used as refractory materials. However, co-existence of alkali components decreased the physicochemical properties of refractories at high temperatures due to the formation of compounds with lower melting points. On contrary, alkali-containing refractories are required to be used as municipal waste melting furnace or acid corrosion furnace. Hence, in this study, in order to expand the use opportunity of alkali-containing refractories, three kinds of geopolymers were prepared and their properties were evaluated. One was conventional geopolymer which is a standard use at room temperature as construction and building materials. Second was potassium geopolymer paste which is tuned in chemical composition with a high melting point. Third was a mixture consisting of the previous second tuned geopolymer and alumina clinkers. Compressive strength of the three kinds of geopolymers was examined after heating at various temperatures. When the crystal phases in potassium geopolymers after heating were leucite and kalsilite with high melting points of approximately 1700ºC. Furthermore, addition of alumina clinkers into the potassium geopolymers improved the compressive strength. As a result, potassium geopolymers with alumina clinkers, which were controlled in chemical composition with a high melting point, can be used as refractories at more than 1500ºC.

Abstract-Number: ***207***

APPLICATION OF DRY COATING TECHNIQUE FOR CC TUNDISH

Takashima S.[1], Kubo Y.[1], Ootsuka M.[2], Yamazoe H.[3]
[1]*Nippon Steel & Sumikin Koutetsu Wakayama Corporation, Refractories Technical Dept. Steel Making Div., Wakayama City, Japan,* [2]*Nippon Steel & Sumikin Koutetsu Wakayama Corporation, Steel-making Technical Section Steel Making Div., Wakayama City, Japan,* [3]*Nippon Steel & Sumikin Koutetsu Wakayama Corporation, Steel Making Div., Wakayama City, Japan*

At Wakayama steel works of NSSMC, low hydrogen steel production occupies 75% of wide size slab steel. Dehydrogenating treatment has been operated on RH, so it is difficult to remove hydrogen from steel after secondary steel refining process. If CC tundish is coated with spraying refractory, which needs a little water addition, it has possibility to increase hydrogen. In order to prevent the increase of hydrogen, dry coating technique was applied for CC tundish. It is a character of dry coating refractory that it uses polysaccharide binder. Refractory of dry coat tundish does not contain any fluid as compared with spraying refractory which uses water. Major advantages of dry coating technique are low risk of hydrogen pickup in tundish, and easy to demolish tundish after casting because of no bond with back wear refractory, and elevating temperature time is shorter than spraying refractory because of no explosive fracture caused by water vaporization. Due to advantages of dry coating technique, it become possible to accommodate limitation of casting schedule. And it become possible to heat tundish refractory rapidly. Dry coating technique has a disadvantage on the other. It takes long time to fill the dry material between the mold flame and tundish side wall including setting the flame on tundish and removing it. Also, curing time is required to harden the organic binder. At the early times of applying dry coat method, cycle time of maintaining is 3.5 hours longer than using spraying refractory. In order to compress time of maintenance of dry coat method, we improved 3 points, which were to fix a core into tundish and to throw the powder of dry coating refractory into an opening between a core and surface of wear refractory of tundish, and the method of heating tundish. After these improvements, cycle time of maintenance CC tundish became about 3 hours shorter compared with spraying method. By dry coat technique, the amount of hydrogen picking up decreased compared with spraying refractory method. Hydrogen pick-up could dropped within 0.3ppm after applying dry coating tundish, while it was within 1.0ppm formerly. Thanks to low hydrogen picking up, dehydrogenating treatment time can be reduced, and low hydrogen steel can be casted any time with dry coat tundish. In conclusion, it became possible to reduce maintenance time by some improvements. By applying dry coating method, hydrogen pick-up could be less, the time to temperature rising could be short.

Abstract-Number: *212*

EFFECT OF SULFUR ON THE PROPERTIES OF CALCIUM ALUMINATE CEMENT IN A CONVENTIONAL REFRACTORY CONCRETE

Zhang Y.[1,2], Li N.[1]
[1]*Wuhan University of Science and Technology, The state Key Laboratory of Refractories and Metallurgy, Wuhan, Hubei, China,* [2]*Zhengzhou Jianai Special Aluminates Co., Ltd, Zhengzhou, Henan, China*

An investigation was carried out to study the effect of sulfur content contained in Calcium Aluminate Cement (CAC) on the bonding strength of a conventional refractory concrete. Compressive strength (CCS) of bauxite based castable was compared between curing 6 hour, 24 hour at 20℃ and then dry out at 110℃ for 24 hours. Inserting thermocouple, X-ray diffraction and scanning electron microscopy methods were used to monitor the internal temperature evolution and microstructural changes of these specimens. It is apparent that sulfur postpones hydration process and influences hydrates of CAC. For high sulfur content CAC, CCS of catable specimen curing at 20℃ for 24h was higher than that after dried out. However, for low sulfur content CAC, it was inverse.

Abstract-Number: *214*

THE ROLE OF LA_2O_3 ON THE PERFORMANCES OF CAO-MGO-SIO_2 CERAMIC FIBER

Liu H., Wang X.T., Wang Z.F., Ma Y.
Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallurgy, Wuhan, China

The CaO-MgO-SiO_2 ceramic fibers containing La_2O_3 were prepared by melt-blowing technique. The fiberization, crystallization and dissolution behavior of fibers were investigated by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive Spectrometer (EDS), Differential Thermal Analysis (DTA) and viscosity test. It was indicated that the introduction of La_2O_3 effectively decreased the viscosity of the studied melt and enhanced the fiber-forming ability of the investigated compositions. The fibers were prone to surface crystallization, and the inhibited crystallization was caused by the intensified silicate structure from the addition of La_2O_3. Though the initial dissolution rate of fibers in Gamble solution was decreased for the strengthened silicate structure, La^{3+}

participated in the construction of calcium-magnesium silicate hydrate layer on the fiber surface at the subsequent dissolution stages.

Abstract-Number: *215*

OXIDATION RESISTANCE TO HIGH TEMPERATURE VAPOR OF NITRIDE BONDED SILICON CARBIDE REFRACTORIES FOR CALCINER

Wang W.W.[1,2], Huang Z.G.[1,2], Wang J.P.[1,2], Li J.[1,2], Wu J.G.[1,2]
[1]*Sinosteel Luoyang Institute of Refractories Research Co., Ltd., Luoyang, China,* [2]*State Key Laboratory of Advanced Refractories, Luoyang, China*

Oxidation resistance to vapor at 900℃ of silicon nitride/silicon oxynitride and SiAlON bonded silicon carbide refractories using ASTM-C863 method was tested. Phase composition and microstructure before and after oxidation were analyzed by XRD and SEM. The results show that silicon nitride/silicon oxynitride bonded silicon carbide refractories have better oxidation resistance to vapor than SiAlON bonded silicon carbide refractories. For the former, the oxidation speed is high and the volume expansion is obvious in the early 100h; with the oxidation time prolonging, the volume expansion gets slowly; after 300h, the oxidation saturates; during the oxidation, the formed high silicon glass phase covers silicon nitride, silicon oxynitride, and silicon carbide forming the protection layer and filling the pores, which is the protective oxidation mechanism. For the latter, with the oxidation time prolonging, the volume expands gradually, even the oxidation doesn't saturate after 500h. The main reason is SiAlON is oxidized into mullite continuously.

Abstract-Number: *216*

STUDY ON MECHANISM OF EXPLOSIVE SPALLING OF ULC CASTABLES DURING RAPID DRYING

Wang Z.[1,2], Zhao J.[1,2], Cao X.[1,2], Yu L.[1], Zhang S.[1], Shi G.[1], Huang Y.[3], Zhu Z.[1]
[1]*Sinosteel Luoyang Institute of Refractories Research Co., Ltd., Luoyang, China,* [2]*State Key Laboratory of Advanced Refractories, Luoyang, China,* [3]*Hechi University, Yizhou, China*

Dense refractory castable lining is usually destroyed by the explosion or spalling due to rapid drying. Research on mechanism of explosion or spalling of castables during heating is helpful for the improvements on explosion resistance and the further development of castables. Inner vapor pressure and temperature of refractory castables during heating are measured by embedding pressure transmitting pipes and thermocouples during casting. The measured vapor pressure variation combined with temperature, tensile strength, porosity and dehydration behavior of refractory castables are analyzed and discussed. The results show that the maximum vapor pressure 1.85 MPa of the casting shapes with multidirectional heating system takes place at 225 °C and at the center of the specimen, and counterpart of unidirectional heating system is 5.88 MPa at 286 °C and at 100 mm from the heating surface. The vulnerable place to explosion or spalling and the corresponding temperature and vapor pressure can be forecasted by values of inner temperature and vapor pressure of castables during drying. Explosion mechanism of dense refractory castables during rapid drying are discussed by analysis and comparison of the inner vapor pressure, temperature, tensile strength and porosity as well as dehydration behavior of castables during heating.

Abstract-Number: *219*

INNOVATIVE SEPARATION TECHNOLOGIES FOR REFRACTORY WASTE

Ducastel A.[1], Guéguen E.[1], Horckmans L.[2], Bouillot F.[3], Fricke-Begemann C.[4], Knapp H.[5], Makowe J.[6], Stark A.[7]
[1]*Magnesita Refractories GmbH, Hilden, Germany,* [2]*VITO, Mol, Belgium,* [3]*RECMIX, Sint Truiden, Belgium,* [4]*ILT Fraunhofer, Aachen, Germany,* [5]*AMR - RWTH, Aachen, Germany,* [6]*LSA-systems, Aachen, Germany,* [7]*Tritec Metal, Kecskemet, Hungary*

A good raw material source is the key to manufacturing high quality refractories. Prices of refractory raw materials have increased drastically during the last years, however, the prices of finished refractory products didn't follow this trend. This is the reason why usage of refractory wastes appeared necessary and increased during the same period of time.
The use of recycled spent refractory materials has in two aspects a positive impact: one is the environmental part by reducing pollution and protecting of natural raw material resources; the other is the cost stabilisation or even reduction in manufacturing new refractories.

The recycling of refractories needs sophisticated processes to separate the used refractory itself from adhering metal, slags and altered parts; further a clear material detection which allows a separation into different material classes is needed. The first step is currently well practised in several industries, but for the second step no industrial applications are currently available. The European FP7-project REFRASORT aims to develop an automated sorting equipment able to separate initially 3 main types of refractories with progression to at least 8 types of refractories used in the steel industry.
The main challenges of the REFRASORT project are to develop 1) a reliable sensor for inline identification of refractory material in an industrial environment and 2) an automated sorting equipment suitable for large size, heavy particles able to sort up to 8 material types.
For the identification step the emerging and promising LIBS (Laser-induced breakdown spectroscopy) technology is investigated, in combination with other identification and material pre-treatment techniques such as surface cleaning and metal removal. First practical tests have shown the ability of such a system to distinguish different refractory material classes based on the analyses of three major elements. For the sorting step, a mechanical sorting concept has been developed and practical tests are ongoing.
Preliminary results of the project show that the introduction of a non-destructive laser based identification and sorting system seems an encouraging route to convert undefined refractories into homogeneous re-usable refractories, indeed, out of 8 different refractory sources, the system showed to be promising to distinguish each of them.

Abstract-Number: *221*

THE BINARY ZRO_2-SIO_2 AS EXPLORED BY CONTAINERLESS AERO-ACOUSTIC LEVITATION

Telle R.
RWTH Aachen University, Mineral Engineering (Gesteinshuettenkunde), Aachen, Germany

The binary ZrO_2-SiO_2 system forms the basement of many technically important ceramic and refractory products as well as provides thermodynamic information for the understanding of slag-ZrO_2 corrosion or melt-casting of zirconia bricks for glass making tanks. Abundant literature data contain, however, still many contradictions and uncertainties regarding the liquid phase, the miscibility gap in the liquid as well as their metastable continuation into low-temperature regions as well as on the formation of zircon, $ZrSiO_4$. In this study, the liquidus surface of the system was re-treated first time after the publication by Toropov & Galakhov in 1956 by means of a fully automated containerless aero-acoustic levitation melter. This device allows for levitating and heating a spherical sample by laser irradiation to more than 3000°C and recording liquefaction, convection, deformation, evaporation, and solidification with a high-speed camera. Release of the Energy of Solidification can be directly measured upon cooling by a high-speed pyrometer.
The liquidus surface of the ZrO_2-SiO_2 could be characterized well in spite of the strong SiO_2-evaporation. The miscibility gap has been experimentally proven by direct observation of demixing and SEM/EDX analyses of polished sections. In the liquid state the system exhibits a turbulent Marangoni-convection with velocities of 1-2 m/s. Polished sections accordingly show reams of individual solidified droplets of ZrO_2- and SiO_2-rich liquids which allow for the construction of the metastable continuation of the miscibility gap. Videos of demixing and consolidation will be shown. A conclusive phase diagram will be presented. Shape and internal compositions of these emulsions will be discussed in respect to the features of the well-known demixing in sodium-potassium borosilicate glasses.

Abstract-Number: *223*

EFFECT OF MAGNESIUM FLUORIDE ON THE HYDRATION OF MAGNESIA CASTABLES

Moulin Silva W.[1], Aneziris C.[2]
[1]*Magnesita Refratarios S.A., Vienna, Austria,* [2]*Technische Universität Bergakademie Freiberg, Institut für Keramik Glas und Baustofftechnik, Freiberg, Germany*

Hydration control is key for the improvement of magnesia castables. If hydration is totally avoided by the use of some additives like citric or boric acid, the properties of the castable will be impaired and the resulting material will be of very limited commercial interest. On the other hand, if hydration is allowed to occur without any sort controlling mechanism, cracking and mechanical destruction of casted pieces are inevitable. Hence, hydration of magnesia and materials made thereof is subject of research for more than 100 years, and questions about its control still abound.
One of the most effective additives used to prevent the hydration of magnesia-based castables is the addition of microsilica, which effectively captures magnesium ions to form gel-like structures that avoid the build-up of brucite during cure and heat-up.

Nonetheless silica is detrimental to the properties of magnesia-rich materials and the reduction of its content is desirable. The present research studies the effect of the addition of magnesium fluoride to reduce the total content of microsilica in a magnesia-based refractory concrete on the formation of hydration cracks and mechanical properties of cured materials. The total content of microsilica could be halved, without major prejudices to the properties of the resultant material. A comparison between magnesium fluoride and other additives is presented, and it was observed that the fluoride performed best in comparison to other additives reported on the literature.

Abstract-Number: *224*

INFLUENCE OF APPLICATION METHOD AND SINTERING TEMPERATURE ON POROSITY AND THERMAL CONDUCTIVITY OF TWO COMMERCIAL SILICON CARBIDE BASED CASTABLES

Silvonen J.[1], Ruusila V.[1], Levänen E.[1], Uusitalo M.[2]
[1]*Tampere University of Technology, Department of Materials Science, Tampere, Finland,* [2]*Valmet Technologies, Tampere, Finland*

Information about thermal conductivity of refractory castables is crucial in heat conducting structures. Two commercial castables were studied to find out the effect of silicon carbide content (58-67 %) and installation method on thermal conductivity. One castable was designed to be installed by casting and the other one was shotcreting castable. The castables were cast and shotcreted in to metal mold sized 200x200x50 mm. Porosities and thermal conductivities were measured from samples after heat treatment at 400, 600, 800 and 1000 ˚C. Thermal conductivities were measured by transient plane source method, porosities were measured by Arkhimedes' method and microstructures were characterized by scanning electron microscopy. Thermal conductivities varied from 6.8-16.3 W/mK and porosities 12.74-21.92 %.
The thermal conductivities in casted samples were slightly higher than in shotcreted respectively and increasing SiC content increased thermal conductivity as expected. However, porosities in vibrated castables containing 60 % SiC were slightly higher than in shotcreted samples but in castable containing 70 % SiC porosities were lower in shotcreted samples. So the interconnection between low porosity and high thermal conductivity was not as clear as expected.

Abstract-Number: *225*

PROCESSING OF SPENT MGO-C REFRACTORIES: A COMPARATIVE STUDY BETWEEN CONVENTIONAL COMMINUTION AND ALTERNATIVE METHODS FOR THE LIBERATION OF MAGNESIA AND CARBON

Strubel S.[1], Flachberger H.[1], Nilica R.[2]
[1]*Montanuniversitaet Leoben, Chair of Mineral Processing, Leoben, Austria,* [2]*RHI AG, Leoben, Austria*

Magnesia-carbon (MgO-C) bricks are refractory products classified also as unfired basic bricks. They consist mainly of magnesia (dead burned magnesia and fused magnesia) and carbon. Their main application is in the steel industry, which consumes more than 60 % of all manufactured refractories. Depending on the specific application refractories have to be replaced after several minutes or some months. Therefore, a large amount of scrap is produced worldwide. Consequently, there exists a high demand for new recycling concepts. Presently, most of the spent MgO-C bricks are reused by the steel industry as slag conditioner. To some extent, MgO-C scrap is used as secondary raw material for the production of refractories by blending with primary raw materials. After manual sorting a typical recycling process contains separation of adhesive contaminations, magnetic separation of metals, crushing and screening.
The aim of this research project is to separate graphite and to recover magnesia as pure as possible.
In order to evaluate the processability of this type of material an extensive raw material characterisation is necessary, which includes chemical and mineralogical examinations, intergrowth analysis and the analysis of specific separability characteristics. Special interest is given to intergrowth analysis. The examinations point out that there is an intensive intergrowth between magnesia and carbon in all particle size classes. Moreover, no sufficient degree of liberation can be achieved by conventional comminution. Consequently, processing poses a challenge due to the fine intergrowth characteristics. For this purpose it is necessary to find alternative liberation/comminution methods like for example high voltage pulse power fragmentation. The lecture aims to introduce alternative liberation methods for the processing of spent MgO-C bricks and to provide an overview of the conducted experiments. The focus is on comparing samples prepared by conventional comminution with samples obtained by alternative methods using systematic and comprehensive investigations on material characterisation. Furthermore, the results of exploratory separation tests (e.g. flotation) are compared with each other in detail in order to draw conclusions about the separation of carbon and magnesia from spent MgO-C bricks.

Abstract-Number: ***226***

REFRACTORY CASTABLES FOR MAIN RUNNERS - DEVELOPMENTS FOR NEW CHALLENGES IN BLAST FURNACE CASTHOUSE OPERATION

Domiciano V.G.[1], Ollmann A.R.[2], Ribeiro A.S.[2], Brito M.A.M.[1]
[1]Magnesita Refratarios S.A., Research & Development Center, Contagem, Brazil, [2]Magnesita Refratarios S.A., Technical Assistance Dept., Contagem, Brazil

In recent years, the huge competition in the global steel market has promoted major changes in the Brazilian Ironmaking scenario. In Blast Furnace, the use of economically competitive raw materials (*iron ore, coke, alternative fuels, etc*) has allowed a reduction of production costs of hot metal. At the same time, frequent oscillations in the Blast Furnaces operating conditions (*production, casting temperature, slag-rate, slag composition, etc*) has been noticed, which has shown a direct impact on the refractories' performance (*castables, ramming mixes, taphole clays, etc*) used in the casthouse. The need to adjust the products to increasingly severe and unstable operating conditions has been a major challenge for refractory suppliers in order to guarantee the runner's safety and its availability for operation. This paper presents the main properties of new design refractory castables (*installed by vibration or shotcrete*) developed to endure the severe operating conditions that main runners are facing in today´s Blast Furnace casthouse operation. Emphasis was given to improve the castables' corrosion resistance at the metal line (slag-metal interface) without harming slag line performance. Practical results revealed lower wear speeds of the refractory linings using the new design refractory castables when compared to standard products.

Abstract-Number: ***227***

DESIGN OF MAGNESIA-CARBON LADLE PRODUCTS IN ORDER TO MAXIMISE PERFORMANCE WHEN PRODUCING A RANGE OF STEEL QUALITIES

Hill K.J.[1], Silva S.C.[2], Bellandi N.E.[3]
[1]Magnesita Refractories, Research and Development, Dinnington, United Kingdom, [2]Magnesita Refratarios S.A., Research and Development, Contagem, Brazil, [3]Magnesita Refractarios Argentinos, Research and Development, San Nicolas, Argentina

Magnesia-carbon bricks are widely used as the working lining in steel ladles. These products can vary in terms of magnesia raw material quality, type and amount of carbon addition, binder system and use of antioxidant additions. Changes in the use of the aforementioned materials can affect various characteristics of the brick such as chemical corrosion resistance, strength, oxidation resistance and thermo-mechanical behaviour. In this paper we outline the modification in brick characteristics which can be achieve by changes in the raw materials used and the subsequent use of this as a method to maximise the service performance of the bricks in a range of steelmaking conditions.

Abstract-Number: ***228***

COUPLING BETWEEN HOMOGENIZATION TECHNIQUES AND BRITTLE MECHANICS FOR MODELLING THE VISCOPLASTIC BEHAVIOUR OF MICRO-CRACKED REFRACTORY LININGS

Rekik A., Nguyen T.T.N., Gasser A.
Polytech Orléans, Laboratoire PRISME, Orléans Cedex, France

During service, refractory linings are often subjected to severe thermo-mechanical loadings. Accordingly, these masonries may behave linearly or nonlinearly in a viscoelastic and/or viscoplastic manner. It is then interesting to investigate the creep behaviour and cracking of refractory linings. In the last decades, multi-level techniques have demonstrated their efficiency for predicting the global and local behaviour of masonry structures with low numerical cost. In this context and as a first step, we propose in this work to model masonries with safe bricks and a mortar following the Burgers or modified Maxwell rheological models at its safe and microcracked states. The proposed model is based on the coupling between linear homogenization technique and the Griffith theory. This allows the determination of the effective creep function of the microcracked mortar. The time-dependent macroscopic behaviour of the masonry is determined thanks to analytical periodic homogenization technique. The relevance of the proposed model is evaluated by reference to a numerical solution computed by finite element method based on an incremental scheme. A

similar methodology is then adapted to viscoplastic masonries at safe and micro-cracked states using one of the available linearization schemes.

Abstract-Number: *230*

DETERMINATION OF THE RHEOLOGICAL BEHAVIOR OF REFRACTORY CASTABLES BY USING THE BALL MEASUREMENT SYSTEM (BMS)

Stein T., Tischer D., Krause O.
Hochschule Koblenz, Höhr-Grenzhausen, Germany

At present there exists no reliable method for the determination of the dynamic viscosity of refractory castables. Especially for pumpable mixes that are used as e. g. shotcrete materials the lack of data remains as an outstanding issue. Reliable data for coarse grain containing mixes may lead to a more systematic development of the said materials.
In this presentation an attempt is undertaken to generate this data by using a ball measuring system (BMS). Previous publications showed that this device is able to determine differences in the viscosity with a high resolution. However, only relative values are available at present.
TYRACH and SCHATZMANN developed an approach to determine the absolute dynamic viscosity by using the ball measurement system. They took the specific geometry of the apparatus in account. In their theory only two coefficients are necessary to determine the absolute dynamic viscosity out of the relative viscosity.
The presentation will show if the existing approach is suitable for ball measurement systems with different geometrical properties and if the theory is likewise suitable for refractory materials. The limits and possibilities of the ball measurement systems for materials with a larger grain size will be envisaged.

Abstract-Number: *231*

TOWARDS ROBUST SINTERING OF DRY VIBRATED LININGS IN INDUCTION FURNACES IN VERSATILE CONDITIONS: A SOLUTION WITH REFRACTORY PAINTS

Techer R., Soudier J., Halapa V.
CALDERYS, Saint Quentin Fallavier, France

The coreless induction furnace is the most flexible iron and steel melting unit and is widely used in ferrous foundries. Scrap can be melted from cold and the furnace can be used for successive melts of widely differing analyses. These applications required suitable dry vibrated mixes, showing in particular a high resistance to wear and infiltration. The lifetime of the standard lining is related to early surface sintering; nevertheless this important step suffers from many potential failure may come from low metal temperature, low burner heat, unsuitable metal quality for first batches and so on.
Iron foundries using zinc-scrap undergo zinc migration/condensation on coil leading to electrical arc which damages the furnace. Besides, zinc deposit in unsintered refractory hinders the sintering and then metal and/or slag penetration cannot be prevented. In steel foundries, damages at early stages due to the high wear of lining refractory are linked to low spinel forming rate.
Refractory paints dedicated to be applied on formwork used for dry vibrated mixes placement have been investigated - modifying surface properties of monolithics by local modification of their sintering behavior towards higher performance at young ages, therefore mitigating melting's side effects. In iron foundries, the refractory paint which forms an impervious and glassy phase at low temperature will lower the temperature needed to reach sintering. In steel foundry, the refractory paint will promote spinel formation at lower temperature thanks to mineralizers.
Innovation in paint coating technology for coreless induction furnace has given the following benefits: higher robustness of vibrated lining in young ages, to prevent zinc migration (iron foundry) and to improve corrosion resistance during first batches (steel foundry).

Abstract-Number: *232*

THE VALUE OF ADDITIVES IN REFRACTORY CASTABLES - CASTABLES WITHOUT SILICA FUME

Kockegey-Lorenz R.[1], Buhr A.[2], Schmidtmeier D.[1], Tian Z.[3], Zacherl D.[4], Chatterjee S.[5], Dutton J.[6]
[1]Almatis GmbH, Ludwigshafen, Germany, [2]Almatis GmbH, Frankfurt, Germany, [3]Qingdao Almatis Co. Ltd., Huangdao, China, [4]Almatis Inc., Leetsdale, United States, [5]Almatis India Private Limited, Kolkata, India, [6]-----, Stourbridge, United Kingdom

Since the use of low cement castable technology became extensive in the early 1990's, the application of additives for the efficient dispersion of fine and ultra-fine matrix components has become essential.
This paper discusses the value of additives in general, and compares the differences in various traditional and modern additive concepts covering flow properties, working time, setting behaviour, and their impact on physical properties incl. hot properties in silica fume-free low cement castables.

Abstract-Number: *233*

THE EFFECT OF STOICHIOMETRY ON THE MGAL2O3 SPINEL EXPANSION

Vidal de Almeida B., Duncan F., Bradt R.C.
The University of Alabama, Tuscaloosa, United States

Whenever both alumina and magnesia are present in a refractory, when they react to form the spinel there are two expansions. One is the normal spinel formation expansion and the second is over and above the simple volume increase of the spinel formation. This paper address the amounts of regular and extraordinary expansions for different spinel stoichiometries from high purity powders of different particle sizes for different reaction times and temperatures.

Abstract-Number: *234*

THE DISSOLUTION BEHAVIOR OF AL_2O_3 IN LOW-MELTING PHASE CONTAINING TIO_2 FOR ALUMINA-MAGNESIA CEMENT-BONDED CASTABLES

Yuan W., Shang H., Zhu Q., Deng C., Zhu H.
The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China

Spinel forming castables present a good corrosion resistance and provide stress relaxation features in ladle side walls. Silica fume was considered as a key component when designing in situ spinel-forming castables and played the role by the formation of liquid. In order to attain enhanced properties, mineralizer compound TiO_2 was added in alumina-magnesia castables. The TiO_2 addition resulted in the significant variation in properties of castables. The subsequent reactions and microstructural evolution depended on the low-melting phase (previous liquid) derived from raw-materials (Al_2O_3, MgO, SiO_2 and aluminate cement) in castables at a relatively low temperature because the liquid phase favored the mass transfer. The dissolution behavior of Al_2O_3 in CaO-Al_2O_3-MgO-SiO_2-Na_2O low-melting phase containing various TiO_2 contents was investigated for evaluating the effect of TiO_2 addition. The dissolution of Al_2O_3 into the liquid at different temperatures was characterized by scanning electron microscopy. The thermodynamic simulations of equilibrium compositions at the interface between oxides and low-melting phase were carried out by using FactSage software. The results showed that TiO_2 could promote the interactions among the components as a consequence of more liquid phase formation at the high temperature.

Abstract-Number: *235*

THE OPTIMISATION OF THE CARBON FOOTPRINT OF CALCIUM ALUMINATE CEMENT CONTAINING CASTABLES

Henry-Lanier E., Szepizdyn M., Parr C., Wöhrmeyer C., Zetterstrom C.
Kerneos SA, Paris - La Défense, France

This paper presents the environmental footprint assessed for Calcium Aluminate Cements (CAC) according to the guidelines defined in the ISO standards 14040 and 14044 for Life Cycle Analysis (LCA). After a focus on the methodology and data used, the paper presents some results on the intrinsic environmental footprint of CAC production from cradle to factory gate with an emphasis on

the key parameters that influence the footprint.
A second part of the paper investigates the environmental impact of CAC in different model castable systems and comparisons will be made with other types of refractories along with corresponding life cycle analysis for some model applications. These results show the intrinsic opportunity to reduce the carbon footprint of specific refractory applications through the application of calcium aluminate containing monolithic refractories.
The results demonstrate the key value of CAC as a catalyst that can significantly reduce the consumption of various formulation ingredients with a higher environmental footprint. The analysis also shows the opportunities for energy saving and reduction of the carbon foot print during the dry out phase. Significant environmental benefits can be achieved with CAC-based formulations, in comparison with alternative refractory systems. In order to safely increase the drying rate a number of material characteristics need to be considered.
The permeability of refractory concretes is an important parameter but experimental data has also shown that permeability alone is insufficient to predict the ability to successfully dry out dense deflocculated castables. Other techniques have been developed to give a more complete picture of the parameters that govern castable dry out.
This paper will discuss experimental simulations of explosions during dry-out under safe conditions with one-sided heating as well as the more traditional furnace based approach. The results reveal significant differences in dry out ability as a function of formulation parameters as well as external conditions such as the water addition. Based on this data different dry out rates can be estimated and the energy input that is required for heat up to a given temperature calculated from a theoretical perspective. Comparisons are made with differing formulation parameters as to the most efficient system in terms of energy consumption. Conclusions suggest possible routes to yield significant energy savings and a reduced carbon footprint.

Abstract-Number: *236*

EFFECT OF SINTERING AIDS ON THE THERMO-MECHANICAL PROPERTIES OF A LCC DETERMINED BY WEDGE SPLITTING TESTS AT CRITICAL TEMPERATURES IDENTIFIED BY THE METHOD OF MONOTONIC HEATING (MMH)

Brochen E.[1], Simmat R.[1], Dannert C.[1], Krause O.[2], Rathaj M.[2]
[1]*Forschungsgemeinschaft Feuerfest e.V., Hoehr-Grenzhausen, Germany,* [2]*Hochschule Koblenz, Hoehr-Grenzhausen, Germany*

Thermal stress induced damaging is a well-known problem for refractory linings of high temperature process vessels and industrial furnaces. In service, refractories endure steady and/or transient thermal loading, which induces thermal stresses able to damage refractory components, even to lead to the failure of the refractory structure. Materials that display relatively low degradation under thermal stresses are usually called “flexible”.
Under operating conditions and at the hot face of the refractory linings, the occurrence of melt phases is supposed to enable a relaxation of the thermal stresses as well as to improve the refractory flexibility. However, an excessive formation of melt phases causes a dramatic loss of the refractory mechanical properties.
An extensive investigation of the formation of viscous phases and their impact on the thermomechanical properties at high temperature was carried out on LCCs with different sintering aids additions. The Method of Monotonic Heating (MMH) was used to identify the temperatures at which the melt phases are first formed within the refractory microstructure. With a high temperature testing system, wedge splitting tests according to Tschegg were then carried out. The nominal tensile strength and the specific fracture energy of the LCCs were measured just before and after the formation of melt phases. The impact of the sintering aids content on the thermo-mechanical properties at high temperature could be quantified.

Abstract-Number: *239*

FIRING RESEARCH FOR REFRACTORIES IN STEEL LADLE APPLICATIONS

Parr C.[1], Harmuth H.[2], Pandolfelli V.[3], Poirier J.[4], Rigaud M.[5], Sinnema S.[6]
[1]*FIRE, Neuilly sur Seine, France,* [2]*Montanuniversitaet Leoben, Chair of Ceramics, Leoben, Austria,* [3]*Universidade Federal de São Carlos, Departamento de Engenharia de Materiais, Sao Carlos, Brazil,* [4]*Polytech'Orléans, Conditions Extrêmes Matériaux Hautes Températures et Irradiation, Orléans, France,* [5]*University of Montréal, École Polytechnique, Montréal, Canada,* [6]*Materials Engineering & Mathematical Modelling Tata Steel Europe, Ceramics Research Centre, Ijmuiden, Netherlands*

The Federation for International Refractory Research and Education (FIRE) is a non-profit organisation established to promote refractory related research and education on a global basis. FIRE is committed to a series of research programmes which are by definition pre-competitive and are aimed at leveraging the research network capability of FIRE with contributions from both industrial and academic partners. This paper details one of the basic research programmes that FIRE has coordinated within the field of ladle refractories to provide elements to understand the complex thermo-mechanical, thermo-chemical interactions along with a greater understanding of the impact of material properties and their combination on performance in use.
The paper discusses recent research into three areas of fundamental importance for ladle refractories where value can be brought through reduced downtime and increased durability/ in service life. The presented results rely on a combination of modeling, simulation and measurement to demonstrate how research can bring value to the usage chain of steel ladle refractories. Three aspects of the thermo mechanical behavior of refractories, modeling and testing, the design of microstructurally engineered corrosion resistant castables, and an approach to determine the thermochemical behavior of refractories from the perspective of modeling and corrosion testing will be discussed and results presented. Conclusions will be drawn from the key learnings of these three multi-partner research programmes and how this can be applied to create further value through the usage chain of refractories in steel ladle applications.

Abstract-Number: *240*

RHI'S INTERACTION WITHIN ITS NONFERROUS MAGNESIA-CHROMITE-BASED REFRACTORY ENVIRONMENT

Franzkowiak A.[1], Ofner-Ressler A.[2]
[1]*RHI AG, Technical Marketing & Product Management NFM, Vienna, Austria,* [2]*RHI AG, Leoben, Austria*

An inherent part of RHI's product portfolio for decades have been magnesia-chromite refractory bricks. They are widely applied in the nonferrous metal industries, especially copper producing applications. However, the multiple pyrometallurgical production routes and high specification diversity require appropriate refractory material use in the different furnaces and reactors. This necessitates a strong interaction between several departments within a refractory producing company.
This paper highlights the complexity of services and tasks performed by both technical marketing and research & development and the interconnection between the two areas with the example of magnesia-chromite-based refractory brick characterization. It provides information concerning the investigated properties, which have a high impact on the lining performance, like thermo-chemical and mechanical stresses, that are always correlated to technical product management.
In addition, the results of laboratory scale analyses are established for diverse slag testing of specific magnesia-chromite brick grades and their interaction with specific customer slag samples. The interrelationship between all tested properties at room temperature and different process temperatures enhances the lining concept decisions for different customer applications in the nonferrous metals industry.

Abstract-Number: *241*

THE VALUE OF ADDITIVES IN REFRACTORY CASTABLES - SILICA FUME CONTAINING CASTABLES

Schnabel M.[1], Buhr A.[1], Schmidtmeier D.[2], Tian Z.[3], Zacherl D.[4], Chatterjee S.[5], Dutton J.[6]
[1]*Almatis GmbH, Frankfurt, Germany,* [2]*Almatis GmbH, Ludwigshafen, Germany,* [3]*Qingdao Almatis Co. Ltd., Huangdao, China,* [4]*Almatis Inc., Leetsdale, United States,* [5]*Almatis Alumina Pvt. Ltd., Kolkata, India,* [6]*-----, Stourbridge, United Kingdom*

The use of fine matrix fillers such as silica fume and reactive alumina in LC- and ULC-castables requires the addition of additives for dispersion and for adjustment of working time during installation. The choice of the additive has a significant influence on the flow properties, working and setting time and also the strength development of the castable.
This paper discusses extended test series performed with different additive systems in silica fume containing castables and highlights their influence on workability and setting behaviour. The results of short term aging tests of dry mixed castables with different additive systems are also discussed.

Abstract-Number: *242*

MICROSTRUCTURAL CHARACTERIZATION OF ARC-MELTED REFRACTORY PRODUCTS

Szczerba J., Madej D.
AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Krakow, Poland

Magnesium oxide (MgO) and calcium zirconate ($CaZrO_3$) are compounds with relatively high melting points of 2825°C and 2345°C, respectively, and are the most important group of materials used in the production of ceramics having the ability to withstand high temperatures. Most refractory materials are prepared through the conventional solid-state reaction route. The ceramic method consists heating together two solids which react to form the required product or heating pure powder to obtain dense mono-phase material.
Pure MgO powders are hard to be densified into compacted ceramic sinters through the standard processing route via pressureless sintering due to their high melting point. Intermediate grinding is also necessary step during the synthesis of the $CaZrO_3$ phase via reactive sintering process of mixture of chemically pure reagents ($CaCO_3$ and ZrO_2).
In order to overcome these disadvantages, arc-melting technique has successfully been used to prepare homogeneous dense refractory products. This paper investigates dense $CaZrO_3$, MgO and MgO-$CaZrO_3$ materials produced by electric arc melting and compares them to solid state synthesized $CaZrO_3$, MgO and MgO-$CaZrO_3$. In this paper the experimental results of microstructural characterization of arc-melted refractory products using scanning electron microscopy (SEM) are mainly reported. Scanning electron microscopy (SEM) has been carried out on an electron microscope system (NovaNanoSem 200) with the energy dispersive spectrometer (EDS). The phase composition of the samples was also analyzed by XRD (Panalytical X'Pert-Pro diffractometer).

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Abstract-Number: *243*

HIGH DURABILITY CARBON-FREE LINER SUBMERGED ENTRY NOZZLE

Galesi D.F.[1], Souza L.[2], Leão C.[2], Nascimento A.D.D.[3], Pontes J.[3], Correa W.[3], Horiuchi T.[4], Wakae T.[4], Pigatti G.M.[5]
[1]Saint-Gobain, Vinhedo, Brazil, [2]Saint-Gobain High Performance Refractories, Vinhedo, Brazil, [3]Arcelormittal Tubarao, Serra, Brazil, [4]Shinagawa Refractories Co. Ltd., Tokyo, Japan, [5]ARCELORMITTAL TUBARÃO, Steel Making and Continuous Casting Tecnical Division, Serra, Brazil

Preventing the alumina adhesion of submerged entry nozzles (SENs) is of great importance not only for prolonging SEN service life but for improving steel quality. Carbon-free layer in inner lining of SENs has been adopted for this purpose with good results, nevertheless the corrosion of carbon-free liner is an important element to improve the SEN life and extend its benefits. This paper describes the develop of high durability carbon-free liner SEN and the good results in ArcelorMittal Tubarão in terms of clogging and how it could extend SEN life and improve steel quality even when the alumina clogging is not an issue.

Abstract-Number: *244*

THERMAL SHOCK RESISTANCE OF LOW CARBON MGO-C REFRACTORIES BONDED BY AN FE NANOSHEET-MODIFIED PHENOL RESIN

Wei G.[1], Fang B.[1], Zhu B.[2], Ma Z.[1], Zhao Y.[1], Wu B.[1], Shen M.[1]
[1]Zhejiang Zili Company Limited, Shaoxing, China, [2]Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallurgy, Wuhan, China

With the development of low carbon or ultra low carbon steelmaking technologies and energy saving regulations, carbon content reduction is required for the production of conventional MgO-C refractories. However, the reduction of the carbon content usually leads to a dramatic reduction of their thermal shock resistance of MgO-C refractories. It is realized that in order to overcome the problem mentioned above, a possible way is to optimize the pyrolytic carbon structure derived from the binder. In this paper, the effects of the particle size and content of the Fe nanosheets catalyst, coked temperature, and heating rate on the microstructure and thermal shock resistance of low carbon MgO-C refractories bonded by an Fe nanosheet-modified phenol resin. The results show that well-crystallised carbon nanotubes (CNTs) of 50-100 nm in diameter and of micrometre scale in length could be generated at 1000 ℃ in the matrix of low carbon MgO-C refractories. The mechanical properties and thermal shock resistance at 1000-1400 ℃ of the specimens with 0.5 wt% Fe nanosheets catalyst are greatly improved compared with specimens without Fe

catalyst. The results are attributed to in situ formation of CNTs and the subsequent generation of bridging and crack deflection mechanisms in the matrix.

Abstract-Number: *246*

EFFECTS OF DOPING RARE EARTH OXIDES ON PROPERTIES OF MGO-CAO REFRACTORIES

Wang Z.F., Wang X., Liu H.
Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallurgy, Wuhan, China

The effects of Y2O3, La2O3, Sm2O3, CeO2 and Nd2O3 on the sintering and mechanical properties of MgO-CaO refractories were investigated. Addition of different rare earth oxide (ReO) to MgO-CaO refractories increases the bulk density, decreases the porosity and improves the mechanical strength of the refractories. The improved sinterability was attributable to the promotion of doping rare earth oxides to MgO and CaO Grain Growth and the solid-solution between MgO and CaO. In the samples with ReO, new phases containing rare earth form at MgO and CaO grain boundaries, providing additional bonding between MgO and CaO grains. Consequently, the samples with ReO showed higher high temperature strengths than those without ReO, especially in the case of 1%Nd2O3 addition.

Abstract-Number: *249*

INFLUENCE OF ZINC ADDITION ON IN-SITU REACTION OF METAL COMPOSITE MGO-C REFRACTORIES

Ma C.[1], Meng D.[1], Ren Z.[1], Ma X.[2], Ge T.[1]
[1]*High Temperature Ceramics Institute, Zhengzhou University, Zhengzhou, China,* [2]*Sichuan University, College of Chemistry, Chengdu, China*

With clean steel production increased year by year, low carbon MgO-C refractories become the new hot spot. The preliminary study of applicant found that Zinc have unique effect on properties of MgO-C refractories, study Object of the work focus on metal Al / Zn composite low carbon MgO-C materials. The physical and chemical changes of Zn, Al, MgO, C and other in heating process of MgO-C materials, activation energy of in-situ MA spinel formation, and its microstructure after and before treatment have been investigated. The results show that
(I) For the specimens which do not contain Zinc, the in-situ spinel tends to be produced in these samples only over 900℃ or holding a long time at 900℃, which totally differs with the specimens containing Zn;
(II) From the aspect of activation calculation, the amount of in-situ spinel rises with the holding time and the temperature increasing as well as Aluminum and Zinc ratio growing by means of XRD analysis; meanwhile it reaches the maximum when the ratio of Aluminum and Zinc is equal to 4:1. Compare activation energy, the activation energy of in-situ MA formation for the specimens containing Zinc is lower than that of the samples which have no Zinc ;
(III) From microstructure perspective, after the same treatments to the specimens containing Zinc and the samples that have no the metal, the former has more spinel than the latter. And the spinel in the former specimens is distributed widely and homogeneously, while the spinel produced in the latter samples does not follow the same pattern: it is only distributed sporadically and heterogeneously. At the same time, the condition of in-situ MA development for the former is better than that for the latter.

Abstract-Number: *251*

INFLUENCE OF MICROSTRUCTURE ON FRACTURE BEHAVIOR OF MAGNESIA-SPINEL REFRACTORY BRICKS

Sakaida Y.[1], Suzuki K.[2], Yanagisawa Y.[2], Yashiro S.[1]
[1]*Shizuoka University, Department of Mechanical Engineering, Hamamatsu, Japan,* [2]*Shizuoka University, Grad school of Eng, Hamamatsu, Japan*

The fracture behavior of sintered refractory bricks depends on both porous microstructures and elastic properties. In this study, the two kinds of magnesia-spinel refractory bricks manufactured for a cement rotary kiln were used. An initial elastic modulus of each bend bar specimen was measured by the ultrasonic pulse method. After measuring the initial elastic modulus, the single edge U-notch with a width of 0.7mm was machined using a diamond wheel. The fracture resistance curves were derived from the

relationship between the applied load and the back-face strain of the notched specimen. The back-face strain was monitored using a strain gage cemented on the back-face of the notch. The crack extension was estimated from the compliance change. The fracture resistance was calculated based on fracture mechanics. The back-face strain of these bricks was found to increase nonlinearly with an increase in the applied load. The elastic region was so small that an initial compliance without crack extension was determined from the slope of the tangent at the origin of the applied load vs. the back-face strain curve. In this study, the compliance change was derived from the change in the slope of the tangent at the origin during loading the gradual increased applied-load. As a result, the initial compliance, the nonlinearity of the applied load vs. back-face strain curve and the crack propagation behavior were found to depend on the microstructures composed of coarse aggregate, matrix and pore of the bricks. After the crack initiation from the initial notch, the fracture resistance increased with an increase in the crack extension. The fracture resistance curves were found to show the “rising R-curve behavior”, like the fracture resistance curve of porous ceramics used for the dust removal filters.
Acknowledgment: This study was supported by Research Grant in 2013 from the Technical Association of Refractories, Japan.

Abstract-Number: *252*

INFLUENCE OF TIO_2 AND ZRO_2 COMPOSITE ADDITIVE ON THE STRUCTURE AND PROPERTIES OF MGO-$MGAL_2O_4$ REFRACTORIES

Zhao H.Z.[1,2], Cui J.T.[2], Jingjie L.[1]
[1]*Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallurgy, Wuhan, China,* [2]*Zhengzhou hunter refractories Co. Ltd., Zhengzhou, China*

In order to reduce the harm to the environment of MgO-Cr_2O_3 refractory used in burning zone of cement rotary kiln, the periclase-magnesia alumina spinel bricks samples were prepared in the laboratory using fused magnesia, high purity sintered magnesia, magnesium rich sintered spinel and α-Al_2O_3 powder, by mean of analysis instrument of X-ray diffraction, scanning electron microscope and energy dispersive spectrometer, etc. The influence of a small amount of composite additive of amorphous TiO_2 and monoclinic ZrO_2 on the structure and properties of MgO - $MgAl_2O_4$ refractories were investigated. The results showed that the mixing of samll amount of composite additive can increase the bulk density and decrease the apparent porosity obviously. The experiment of kiln coating adherence performance of the MgO - $MgAl_2O_4$ samples demonstrated that the composite additive can react with cement clinker to form CaTiO4 in the surface of MgO-$MgAl_2O_4$ refractories samples, or form $Mg_2Zr_5O_{12}$ solid solution phase between the grain boundary of periclase and magnesium aluminate spinel on the conditions of operating temperature, which all are benefit to the kiln coating adherence performance.

Abstract-Number: *253*

DETERMINATION OF FRACTURE ENERGY OF REFRACTORY MATERIALS BY WEDGE SPLITTING TEST

Li H., Qin H., Liu G., Yang B.
Luoyang Institute of Refractory Research, Luoyang, China

Fracture energy has great effect on thermal shock resistance of refractory materials, the wedge splitting method was researched for determining fracture energy of different refractories from room temperature to 1400℃. Experimental parameters such as the ratio of notch depth to height of tested specimen, loading rate and support forms on the experimental results were investigated. It was found that reasonable testing results could be obtained with loading rate at 0.5mm/min and full-scale support form when the ratio of notch depth to height of tested specimen is 15%. In addition, fracture energy of different kinds of refractory materials was investigated by wedge splitting test.

Abstract-Number: *255*

INFLUENCE OF MICROSTRUCTURAL DEVELOPMENT ON SLAG CORROSION RESISTANCE OF UNBURNED AL2O3-MGO BRICK

Doi N., Tomiya H., Iida A., Iida M.
SHINAGAWA REFRACTORIES CO.,LTD., Research Center, Bizen, Japan

Recently, application of unburned Al_2O_3-MgO bricks to metal line of steel ladle have been gradually increasing as alternatives of high alumina bricks or graphite containing unburned bricks such as MgO-C bricks. Advantages in features of unburned Al_2O_3-MgO bricks are listed as; (1) better corrosion resistance than high alumina bricks, (2) larger permanent linear change, (3) suitable creep deformation behavior, (4) graphite-free composition and (5) lower thermal conductivity. These features are attributed to the technology utilizing in-situ spinel forming reaction which has been developed for Al_2O_3-MgO monolithic refractories.
While inorganic binders have been used for unburned Al_2O_3-MgO bricks, application of organic binder was examined since improvement of corrosion resistance had been expected under assumptions that (i) density would be increased due to lubricating effect of organic binder in pressing and (ii) carbon bonded firm structure similar to MgO-C bricks would be achieved. Therefore, slag corrosion test was performed for organic binder specimen and inorganic binder specimen.
As a result, however, organic binder specimen exhibited considerable amount of corrosion while only a small corrosion was observed for inorganic binder specimen. In addition, carbon deposit in inner part of organic binder specimen was recognized. Thus, it is considered that negative effect of organic binder is induced by carbon deposit.
In order to clarify the influence of carbon, microstructures of organic binder specimens after heated in air and in coke breeze were compared. In the specimen heated in air which reproduces the carbon free status, Mg diffusion and spinel formation were observed in liquid phase of well sintered structure characterized by sufficient growths of grain and neck. On the contrary, no interparticle bridging structure was recognized in the specimen heated in coke breeze which corresponds to the carbon coexisting condition. In this case, Mg diffused as gas phase to form cavity along the rim of MgO grain followed by dust-like spinel formation on surface of alumina particle. Assuming that molten slag penetrates into the structure without interparticle bridging, particle will flow out to molten slag immediately. Hence, it is concluded that suppression of matrix sintering induced by yielded carbon causes the considerable deterioration in corrosion resistance of organic binder bonded unburned Al_2O_3-MgO bricks.

Abstract-Number: *257*

DENSIFICATION AND CHARACTERIZATION OF MULLITE-BASED COMPOSITES

Lee K.S.[1], Feng F.J.[1], Jang B.-K.[2]
[1]*Kookmin University, School of Mechanical Systems Engineering, Seoul, Korea, Republic of,* [2]*National Institute for Materials Science, High Temperature Materials Unit, Tsukuba, Japan*

Mullite refractory has been studied for excellent high temperature strength, low thermal expansion coefficient and good thermal stability. Mullite is also a promising material for protecting sub-materials from oxidation and steam corrosion. Powder preparation and densification process are normal procedure for the fabrication of mullite refractory, while mullite coatings by air plasma spray are also studying for introducing the protection layer. As the dense body is desirable in any case, densification study is required for improving stability.
In this study we fabricated mullite composites by addition of Y_2SiO_5 or Yb_2SiO_5 for densification. Sintered bulk and coating layers of mullite ceramics are fabricated by common powder processing method and air plasma spray, respectively.
Characterizations on the mullite bulk and coatings are conducted by density measurement, SEM observation and XRD analysis. Densification behaviors by addition of Y_2SiO_5 or Yb_2SiO_5, microstructure change by the addition and the analysis on the crystalline phases are investigated.
Spherical indentation tests as a new evaluation method are used to evaluate mechanical damage tolerance of mullite composites. The tungsten carbide balls are used to evaluate the damages by contact test. Thermal shock tests from 1200°C to room temperature for 1000 cycles in air are conducted for evaluating the stability of coating layer.
The densification behavior and thermal/mechanical stability of the mullite bulk and coatings will be discussed at the presentation.

Abstract-Number: *258*

MICROSTRUCTURAL DETERIORATION OF ALUMINA-CARBON REFRACTORIES FOR SLIDING GATE PLATES DUE TO REACTION WITH MOLTEN STEEL

Mizobuchi F., Lin W.
Shinagawa Refractories Co.,Ltd., Bizen, Japan

Alumina used in sliding gate plate had been regarded as stable at continuous casting temperature, however, its decomposition has been revealed experimentally. Reaction tests were carried out immersing alumina-carbon specimens into three types of molten steel; ultralow carbon aluminum-killed steel, low carbon aluminum-killed steel and ultralow carbon silicon-killed steel, for thirty

minutes at 1560°C.
In all cases of steel grades, alumina layer was formed at the refractory surface of immersed part, and deteriorated zone in which the pre-existing carbon and alumina disappeared at the inside of the alumina surface layer. The alumina layer which was formed in test using ultralow carbon silicon-killed steel was the densest, and thin and porous alumina layer was formed in the case of the other steels. The thickness of the deteriorated zone varied, which was the thickest in the case of ultralow aluminum-killed steel and the thinnest in the case of ultralow carbon silicon-killed steel.
The mechanism was considered to be a reduction of alumina by carbon; 1/3Al2O3 + C(s) = 2/3Al(g) + CO(g), driven by the gradient of partial pressure of Al(g) and CO(g) between the refractory inside and the interface of molten steel, and then these gases formed alumina at the interface of refractory and molten steel. The partial pressure gradient depends on carbon activity of molten steel, therefore, the thickness of deteriorated zone in the case of ultralow carbon aluminum-killed steel which has lower carbon activity increased comparing to the case of low carbon aluminum-killed steel. On the other hand, it did not increased in the case of ultralow carbon silicon-killed steel due to the dense alumina surface layer which prevent diffusion of gases from refractory inside to molten steel.

Abstract-Number: *259*

EFFECT OF THE REACTIONS AMONG SPINEL,MGO AND AL_2O_3 ON THE MICROSTRUCTURES AND PROPERTIES OF THE MATRICES OF AL_2O_3- MGO CASTABLES

Tan X.[1,2], Li N.[1], Yan W.[1]
[1]*Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallurgy, Wuhan, China,* [2]*Beijing Lier High Temperature Materials Co., Ltd., Beijing, China*

Al_2O_3-MgO castables have been widely used in secondary refining steel ladle due to their excellent performance. Usually, the pre-formed spinel and magnesia (in situ spinel) were added into the matrices of the castables to enhance the slag resistance. The pre-formed spinels includes alumina-rich spinel, spinel and magnesia-rich spinel. While, when the pre-formed spinels and MgO were introduced into the matrices simultaneously, the reactions among the spinel, MgO and Al_2O_3 at high temperature would affect the microstructures of the matrices and the crystal characteristics of the spinel, which would further strongly affect the slag resistance of the castables.
In order to improve the slag resistance of the castables, the matrices are selected as the research object in the present work. Firstly, three matrices are prepared through using magnesia, corundum, alumina-rich spinel, spinel and magnesia-rich spinel as the main raw materials, and fixing the contents of corundum and magnesia and changing the kinds of spinel; and the microstructures and the spinel crystal characteristics are analyzed through XRD, SEM and EDS, and the reactions among the spinel, MgO and Al_2O_3 are investigated. Secondly, the reactions between the matrices and the slag were simulated through FactSage® software, and the corrosion of the matrices by the secondary refining slag are conducted. Lastly, the corrosion mechanism are investigated based on the simulation and experimental corrosion results, the microstructure of the matrices and the crystal characteristics of the spinels.

Abstract-Number: *260*

EFFECT OF NANO- TIO_2 ADDITION ON SINTERING CHARACTERISTIC OF CORUNDUM BRICK

Li S., Zhong X.
High Temperature Ceramics Institute, Zhengzhou University, Zhengzhou, China

The effects of 0.2%-1.5% nano-TiO_2 addition on sintering characteristic and thermo-mechanical properties of corundum brick have been studied.
The results indicate:
1) Addition of nano-TiO_2 to corundum brick would lead to noticeable lowering of sintering temperature from 1650 degree C to 1400 degree C with 0.2% addition and to 1350 degree C with 0.6% TiO_2 addition. The sintering mechanism is discussed.
2) The thermo-mechanical properties of specimens with nano-TiO_2 addition sintered at lower temperature (1350-1400 degree C) are at the same level as those of corundum brick sintered at 1650 degree C; the hot modulus of rupture at 1400 degree C is 6-8MPa, the residual strength ratio after thermo-shock (1100 degree C, water cooling) is 20-30%.
Key words: TiO_2 nano-powder; Corundum brick; Sintering Characteristic; thermo-mechanical properties.

Abstract-Number: *261*

EFFECT OF DIFFERENT ALUMINA ON THE PERFORMANCE OF TABULAR ALUMINA

Huang K., Zhao Y., Ma Z., Song Y.N., Ye L.
Zhejiang Zili Alumina Material Technology Co.,Ltd, Shaoxing, China

To reduce the production cost of tabular alumina, Zili researched that different alumina powder as raw material impact on crystal transfer, sintered process under high temperature when producing tabular alumina, and the performance of tabular alumina as well. The research is combining different ratio of industrial alumina and calcined alumina as raw material, then analyzing the change of volume, phase and the microstructure after sintered in the shaft kiln, thus finding out that the impact on the performance of tabular alumina. The research indicated as below when applying industrial alumina to produce tabular alumina,
1: the water demand in Pelletizing system is 5% higher than when applying calcined alumina.
2: the volume shrinkage is much higher than when applying calcined alumina.
3: the calcinations temperature is higher than when applying calcined alumina.
4: There is not much difference of microstructure in tabular alumina between that when applying calcined alumina.
Therefore, to reduce the production cost, it is workable that applying moderate industrial alumina instead of calcined alumina to produce tabular alumina.

Abstract-Number: *262*

INTERFACIAL REACTION BETWEEN MAGNESIA-CHROME REFRACTORY AND IRON SILICATE SLAG MELT

Takebe H., Shimada G., Fukui T.
Ehime University, Matsuyama, Japan

Corrosion tests of magnesia-chrome refractories by molten copper smelting slag have been studied. XRD results showed that the refractory sample consisted of magnesia (MgO) and pichromite ($MgCr_2O_4$) phases. The $MgCr_2O_4$ phase may contains other impurities such as Fe and Al, detected by XRF analysis. SEM-EDX analysis revealed that the magnesia-chrome refractory sample had a microstructure of coarse pichromite grains and relatively-small mixed area consisting of fine magnesia and pichromite grains. A piece of the refractories was reacted with FeO_X-SiO_2 molten slag at 1250 ºC up to 120 minutes in Ar atmosphere with an oxygen partial pressure of 10^{-3} atm. Molten slag penetrated into pore regions existing between grains. The region of coarse/fine pichromite grains had good corrosion resistances with the formation of Fe-O rich thin layer (< 10 µm in thick) on the surface. On the other hand, magnesia grains dissolved into the molten slag and the Fe-O rich slag component entered deeper regions of the refractory. The reaction process are discussed based on experimental data and thermodynamic analysis.

Abstract-Number: *265*

DEVELIOPMENT OF ALUMINA-MAGNESIA CASTABLE WHICH CONTAINS RECYCLED MAGNESIA-CARBON BRICKS AND ALUMINA-MAGNESIA CASTABLE

Sawada H.[1], Nakanishi K.[1], Kobayashi K.[1], Miyake K.[2], Shibata T.[2], Takakura Y.[3]
[1]KOBE STEEL, Ltd., Steel Making Department, Kakogawa, Japan, [2]CERA TECHNO Co.,Ltd., Bizen, Japan, [3]CERA TECHNO Co.,Ltd., Akashi, Japan

Alumina-magnesia castable which contains recycled magnesia-carbon bricks and alumina-magnesia castable, used in Kakogawa Works was developed.
This castable was composed 25 mass % of magnesia-carbon bricks used in Converters, and 30 mass % of alumina-magnesia castable used on side wall of molten steel ladle.
When this castable was used in spout of torpedo cars, its durability was comparable to the conventional ones.

Abstract-Number: *266*

MAGNESIA BRICKS CONTAINING IRON SPINEL - TROUBLESHOOTERS FOR THERMOMECHANICALLY STRESSED KILNS

Wirsing H., Klischat H.-J., Vellmer C.
Refratechnik Cement GmbH, Research & Development, Göttingen, Germany

The increasing average age of the rotary kiln shell enforces the refractory producers to develop new brick types with higher thermomechanical resistance. It goes without saying that the other brick properties, mainly coating friendliness, thermochemical and thermal resistance have to be kept at the required high level. A reduction of the thermomechanical stresses caused by thermal shocks and kiln shell ovalities can be achieved by a low modulus of elasticity adjusted with a high strength, and/or by a high amount of thermoplasticity while maintaining a sufficient refractoriness. One parameter which can be used to adjust the thermoplasticity is the used magnesia. A very pure material, e. g. a magnesia with > 98 % MgO and a CaO/SiO2 ratio > 2 will result in a brick with high refractoriness and high elasticity, while a magnesia with a high iron oxide content, e. g. > 6 %, and a corresponding MgO content of 88-92 % will result additionally in a high thermoplasticity, which can additionally release the mechanical stresses by crack-free plastic/ductile deformation. Furthermore, the elastifier enhances the stress relieving ability. In the past, magnesium alumina spinel was the material of choice, but latest developments have shown the superiority of iron containing spinel minerals when mechanical stresses are present in the refractory lining. Hercynite and pleonastic spinel (the latter from the ternary system MgO-Al2O3-iron oxide) offer top values of stress relaxation, e. g. measured by the creep-under-compression test, while pleonastic spinel alone provides high resistance to attack by calcium containing melts and also is stable under oxidizing conditions when attacked by alkali compounds. When pleonastic spinel is used, the structure of the bricks can even be kept close thanks to its inert behaviour in a magnesia environment, while hercynite supplies some porosity due to in-situ reaction with the surrounding magnesia which may support thermochemical corrosion by cement clinker. In praxis, the conditions in the cement or lime kiln have to be evaluated to select the most advantageous brick grade. Especially in the presence of mechanical tensions, iron-containing spinels in combination with iron-containing magnesia give superior performance.

Abstract-Number: *267*

AL2O3-C REFRACTORIES WITH INCREASED THERMAL SHOCK RESISTANCE BY THE ADDITION OF FIBRES AND NANOPARTICLES

Echeberria J.[1,2], Hernandez A.[1], Ariztimuño J.[3]
[1]*Ceit, San Sebastian, Spain,* [2]*Tecnun (University of Navarra), San Sebastian, Spain,* [3]*Deguisa, Amurrio, Spain*

Thermal shock resistance of refractory materials is one of the most important parameters since it determines their performance in many applications, such as sliding gate plates (in the continuous cast secondary steel industry). It is known that the crack nucleation and propagation takes place when the refractory material is subjected to thermal cycles, resulting in loss of stiffness, mechanical strength and overall material degradation. Therefore, its characterisation and studies for increasing the thermal shock resistance is very important to enhance the performance of refractories in industrial applications. This is why the aims of this study are the improvement of the thermal shock resistance of carbon bonded high alumina refractories by the additions of different additives, such as fibres and nanoparticles. The evaluation of the thermal shock resistance was carried out by water quench tests. The samples were heated at 1000°C under inert atmosphere and after holding for 15 min they were then moved into water and left for 5 min before returning to the furnace. This procedure was repeated five times. MOR was measured before and after the five subsequent quenches by three point bending tests. The influence of these additives, dispersed in the matrix of the refractory, was investigated by the measurement of the MOR resistance reduction caused by the thermal cycles and by field emission scanning electron microscopy (FESEM)/ energy dispersive spectroscopy (EDS). It is important to emphasize that, specially fibres, produce a significant increase of the thermal shock resistance.

Abstract-Number: *268*

ASSESSMENT OF SUITABILITY OF DOLOMITES FROM “NEW DEPOSIT” OF SILESIA REGION FOR PRODUCTION OF REFRACTORY MATERIALS

Onyszkiewicz A.B.[1], Kielski A.[2], Goławski C.[3], Sułkowski M.[1], Obszyńska L.[4]
[1]*Arcelormittal Refractories, Technologist, Cracow, Poland,* [2]*AGH University of Science and Technology, Department of Ceramics and*

Refractories, Cracow, Poland, [3]Arcelormittal Refractories, Director of Technology, Process and Quality Control, Cracow, Poland, [4]Arcelormittal Refractories, Chief Technologist for Basic Products, Cracow, Poland

Properties of dolomite from the Silesia province were analyzed (Poland, Silesia region) with a special focus on the dolomites occurring in the vicinity of the metallurgical waste landfill 'new deposit´ of Silesia region. It has been found that the dolomites are average quality raw materials that are suitable for the production of refractory materials provided a multistage method is used along with additional technological operations that involve thorough grinding and homogenizing the decarburized material.Samples of the dolomite clinker obtained this way were characterized by a high degree of sintering despite a low content of iron compounds. It was caused by a fine-crystalline structure of the very dolomite and its impregnation or cementation by iron hydroxides.It was also found that the silica content in the clinker can be reduced by an appropriate decarburization process and screening off the coarse-grain fractions.

Abstract-Number: *269*

MOLTEN SALT SYNTHESIS OF $MGAL_2O_4$ SPINEL IN ALKALI-CHLORIDES-KF SYSTEM

Ke C., Gan L., Zhang J., Wang J.
Wuhan University of Science & Technology, The State Key Laboratory of Refractories and Metallurgy, Wuhan, China

Molten salt synthesis of $MgAl_2O_4$ spinel from industrial alumina and light calcined MgO in alkali-chrorides (NaCl, KCl, KCl-NaCl, KCl-LiCl) and the influence of KF were investigated at the temperature of 500-1000℃. Product powders were characterized by means of XRD, Laser particle Analyzer and SEM, and the reaction mechanism were discussed as well. The results show that apart from KCl-LiCl, KCl and KCl-NaCl are good reaction media for molten salt synthesis of $MgAl_2O_4$, although less effective than KCl-LiCl. KF showed great accelerating effects on the formation of $MgAl_2O_4$. Synthesis of $MgAl_2O_4$ spinel in the molten salts without KF were controlled by “template-growth” mechanism, but in the molten salts with KF, the “template-growth” mechanism played an important role in molten salt synthesis of $MgAl_2O_4$ and the “dissolution-precipitation ” mechanism was also to some extents involved.

Abstract-Number: *270*

THERMOMECHANICAL NUMERICAL SIMULATION OF THE COOLING-DOWN OF HIGH ZIRCONIA FUSED-CAST REFRACTORY BLOCKS

Zhang Y., Boussuge M., Ryckelynck D.
Centre des Matériaux/MINES-ParisTech, Evry cedex, France

This PhD work is part of the national program ASZTech which is an extension of the NOREV project. These programs aim to provide to Saint Gobain Company numerical tools for improving the process and particularly the cooling-down conditions. The bi-dimensional model developed in the framework of NOREV program [1] is currently used by Saint Gobain to optimize the processing of blocks. However, this model does not consider the thermal and mechanical effects induced by the zirconia transformation from tetragonal to monoclinic (T-M). Previous studies revealed the major importance of the phase transformation in the processing of new products and the improvement of quality. The target of the present work consists in improving the existing model and in implementing, from specific mechanical tests results, a realistic description of the zirconia transformation thermal and mechanical effects.
HZ blocks were molded at Saint Gobain CREE and instrumented with thermocouples and acoustic emission sensors. Blocks are casted into a graphite mold isolated by an annealing agent (alumina powder), canned in a metallic case. Thermocouples are positioned within HZ block, graphite mold and annealing agent.
A tri-dimensional mesh of the whole molding box has been built. The thermocouples recordings revealed a change in the cooling-down rate during the T-M transformation. The shrinkage of the block and the thermal expansion mismatch between the block and the mold induce an interfacial thermal resistance. This phenomenon has been modeled by introducing an interfacial thermal conductivity coefficient h ($Wm^{-2}K^{-1}$) varying with temperature. Its value was quantified by an inverse method from the result of the temperature recordings. A reduction model method was developed to reduce the calculation time.
Compression, tension and flexion experiments have been carried out to identify the mechanical effects of the T-M transformation.

Reference:

[1] Laetitia PETRONI, Étude du refroidissement post-coulée de réfractaires électrofondus à Très Haute Teneur en Zircone (THTZ), thèse de doctorat en Sciences et Génie des Matériaux, MINES-ParisTech, 09 Septembre 2011

Abstract-Number: *271*

DEVELOPMENT OF A NOVEL HYBRID METHOD FOR THE PRODUCTION OF MACROPOROUS FOAM CERAMICS

Rath M.[1], Lebeda C.[2], Bruckner H.[2]
[1]*spumix Dämmstoffe GmbH, Vienna, Austria,* [2]*Vienna University of Technology, Institute of Building Construction and Technology, Vienna, Austria*

Macroporous ceramics with a porosity in the range of 10% to 90% have been produced for a number of applications, such as molten metal filtration, catalysis, refractory insulation, and hot gas filtration. With macroporous foam ceramics it was possible to achieve a porosity of more than 90%. The main processing routes that can be used for the fabrication of macroporous foam ceramics with tailored microstructure and chemical composition are replica, sacrificial template, and direct foaming techniques. These technologies are well described in the literature and did not lead to a large technically feasible, cost-effective production process. To accomplish a simple and inexpensive manufacturing process, a novel hybrid method of direct foaming and replica technique was developed. In this new process, a suspension is made of a first ceramic raw material, which is primarily foamed with air, and then mixed with a second suspension or a ceramic powder. Consequently it is a staged mixing process. The foam of the first raw material serves as a template for the second suspension or the ceramic powder. To meet different requirements the ceramic foam can be adjusted concerning pore size and porosity over a wide range by varying the raw materials, the foaming process, the foaming agent and the binder. The ceramic foam produced has a low density and low thermal conductivity and is suitable as thermal insulation in high temperature applications up to 1800°C.

Abstract-Number: *272*

DEVELOPMENT OF RH-DEGASSER LINING CONCEPTS AT VOESTALPINE STAHL GMBH - AN OVERVIEW

Winkler W., Exenberger R., Grimm G., Gantner A.
voestalpine Stahl GmbH, Linz, Austria

The steel plant LD3 of voestalpine Stahl GmbH presently operates with 3 RH-degassers and will expand its capacity with a fourth degasser in fall 2015, which is currently under construction. About 60% of the total steel production is vacuum treated with an increasing tendency. Steel qualities with special requirements need RH-treatment by alloying with certain elements (e.g. Nb, Ti, B), for reaching strict ranges of chemical analyses, for improvement of steel cleanliness, for the correction of oxygen content, removal of Nitrogen and Hydrogen, etc…..As the lower vessels are the most critical part of the RH-degasser with their main vessels and their two legs respectively snorkels each, the condition of the lower vessels is most important regarding their lining concept and the wear of the lining. The lining, therefore, needs to fulfill specific requirements: 1)Thermal: high temperatures (gas-oxygen burner, oxygen lance, chemical “heating”), thus the material must be thermally resistant; besides, the wear lining needs to withstand thermo-shock due to discontinuities during operation; 2) Chemical: wear based on slag, changing redox conditions (oxidizing and reducing); 3) Mechanical: erosion by the circulation of steel, movements of the steel bath caused by the oxygen lance. In order to meet these needs, originally only magenesia-chromite bricks were used in the lower vessels. Different qualities, such as direct-bonded bricks or prefused bricks were used in the safety and wear lining of wall, bottom, legs and snorkels. The original lining concept included MgCr prefused bricks in the wall, but were then replaced by MgO-C bricks in order to use the possibilities of the brick plant situated at voestalpine Stahl GmbH. Then the brick quality of the inlet and outlet leg were optimized due to changes in the product mix and therefore changes in wear behavior. The most recent changes were introduced in the inlet leg, as the joints are exposed to extreme stress there and these joints opened from time to time and finally caused a breakout. Simply the position of the joints - not the quality of the bricks -in relation to the safety lining and the steel shell was changed and thereby the problems given above could be reduced. Further trials are planned with other qualities in order to balance the wear over the whole vessel.

Abstract-Number: *273*

EXPERIMENTAL STUDY TO DETERMINE THE REOXIDATION STABILITY OF REFRACTORY MATERIALS

Clasen S.[1], Dannert C.[1], Redecker L.[2], Sax A.[2], Quirmbach P.[2]
[1]*Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany,* [2]*Universität Koblenz-Landau, Koblenz, Germany*

A major aim in steel production is to ensure a high degree of cleanness of the molten steel ("clean steel" technology), so that superior properties of the steel products can be guaranteed. With state-of-the-art ladle refining methods, a very high cleanness of molten steel can be achieved, but liquid steel reoxidises easily after this process e.g. during casting. Potential sources of oxygen for the formation of oxidic inclusions in liquid steel are refractory materials. They consist of oxides that can be reduced by chemical elements with high oxygen affinity, which are present in the liquid steel, and oxidic inclusions are formed. These chemical elements, especially aluminium, are introduced as alloying or desoxidation elements into the steel melt. Until now, the determination of the reoxidation stability of refractory materials was only possible with high experimental effort. In the same way in that it is used for the determination of oxygen in steel melts, the Carrier Gas Hot Extraction method (CGHE) could be used for the measurement of oxygen in refractory materials. The advantage of this method is that the reducible oxygen content of the refractory material is transformed into the gaseous reaction products CO and CO_2, which can be used for quantitative oxygen analysis very easily by conventional gas analysis systems. Therefore, a test method based on the Carrier Gas Hot Extraction method is being developed to determine the reoxidation stability of refractory materials at steelmaking temperature by using carbon instead of aluminium as reducing agent. Several open questions are to be answered with regard to the measured oxygen quantity as a stability criterion of refractory materials and to the comparability of the CGHE setup with a Fe-Al melt as reducing agent under steelmaking conditions. In this study the reaction mechanisms during reduction of refractory oxides by carbon were investigated using thermodynamic calculations and experimental investigations with the CGHE method. The results were evaluated by comparing them to the results of conventional crucible tests with Fe-Al-melt under controlled atmosphere. The theoretical predictions of carbon - oxide - reactions by thermodynamic calculation and the experimental measured oxygen release by CGHE experiments were found to be in good agreement. The crucible tests with simulation of steelmaking conditions confirmed the reoxidation stability measured with the CGHE method.

Abstract-Number: *274*

INVESTIGATION OF THE PARAMETERS INFLUENCING THE REFRACTORINESS UNDER LOAD (RUL) TESTING RESULTS FOR REFRACTORY MATERIALS

Stuppfler A.
ICAR, Research, Moncel Les Lunéville, France

The project ReStaR includes a complete investigation on R.U.L. (refractoriness under load) testing method, in order to suggest upgrading of related standards (EN ISO 1893 and ISO 1927-6 /9), in focusing on quality improvement, cost reduction, convenience in use and time saving.
The R.U.L. EN standard specifies a method for determining the deformation of dense and insulating shaped/unshaped refractory products, when subjected to a constant load under conditions of progressively rising temperature, by a differential method. Such a measurement is very useful to determine the temperature from which the plastic behavior of a product occurs: so a temperature limit for use can be determined in considering RUL Temperature T0 - 200°C.
The first step of the present investigations consisted in carrying out multi-factorial design plans on different kinds of materials: dense shaped, insulating shaped and dense unshaped materials, in order to determine the relevant influencing factors on test results. Among the parameter tested, level of loading, use of platinum sheet between test-piece and column, level of surface finish, height of the test-piece, position of measuring thermocouple and casting direction of test-piece (only for unshaped products) have been identified as significant factors. The campaign has involved one laboratory (ICAR), which is identified as “test method leader” for the following steps of the project.
The second step of the project has for goal to find/check the combination of values of the factors previously mentioned, which conducts to the best reproducibility, keeping in mind the compromise quality/practice of the test. For that, collaborative tests between 4 laboratories have been achieved, in order to gather consistent values enabling pertinent assessment of repeatability and reproducibility values.

Abstract-Number: *275*

SINTERING BEHAVIOUR OF REFRACTORY CASTABLES DETECTED BY CHANGES OF THEIR THERMAL DIFFUSIVITY

Kasper J., Simmat R., Dannert C.
Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany

The sintering and solidification of refractory castables can be monitored by the means of their thermal diffusivity. Directly after the setting and curing, refractory castables show a weak interparticle connection and resulting low thermal conductivity. During sintering and solidification, the interparticle connections change in size and number due to dehydration of hydrates, solid phase sintering of the fines, melting of microsilica and other melt-forming raw materials, formation of new minerals and grain growth due to solid and liquid phase sintering. Generally speaking, every enhancement of the interparticle connection increases the thermal diffusivity. The kind of sintering reaction(s) and the amount of new secondary phases are key parameters for the magnitude of the thermal diffusivity change. Temperature dependent thermal diffusivity values can thus be used to optimise respectively shorten the heating up and sintering schedules of industrial prefabricated shapes or linings made from refractory castables.
The proposed paper will outline the temperature-dependent influence of the composition of refractory castables on their thermal diffusivity. The thermal diffusivity measurements are being conducted by a laser-flash device for refractory samples. The obtained temperature-dependent thermal diffusivity values are accompanied by studies of the microstructural evolution of refractory castables.

Abstract-Number: *276*

ALKALI SALT CORROSION OF CALCIUM SILICATES

Hölscher T.[1], Schneider H.-J.[1], Schlegel E.[2], Aneziris C.[2]
[1]*Calsitherm Silikatbaustoffe GmbH, Bad Lippspringe, Germany,* [2]*Institut für Keramik, Glas- und Baustofftechnik, Freiberg, Germany*

There have been considerations not to use calcium silicate thermal insulation materials in high temperature furnaces where there is a huge content of alkaline in the combustion atmosphere. Its reason is linked to the increasing usage of secondary fuels started 15 years ago.
Systematic researches of alkali corrosion of calcium silicates are unknown. Therefore the corrosion has been researches according to V DIN 51069 as a crucible test method. The tests started at 600 °C - just a bit lower of formation of salts of the salt mixtures - and ended at 1100 °C which is the maximum service temperature of calcium silicates. KCl, K_2SO_4 and K_2CO_3 have been tested separatly and in combination. The crucibles have been analyzed according V DIN 51069 in regard to infiltration. X-ray of crystal phases were used to support the results.
As soon as the melting point of the salts itself is reached the crucibles will be infiltrated. It happens for the salt mixtures above their eutectic temperature also. The salt melt causes infiltration, a bit sintering and shrinkage of the highly porous crucibles. In some cases little cracks at the bottom occur.
Only K_2CO_3 alone leads to a catastrophic dissolution and destruction of the crucibles at temperatures starting at 1000 °C whereas the other salts infiltrate only. X-rays prove that KCl and K_2SO_4 - separately and in combination as well - do not react with the calcium silicate phases. However K_2CO_3 already reacts with the calcium silicate phases at 650 °C in a combination of all 3 salts. New silicates will form, K_2CaSiO_4 especially.
K_2CO_3 has never been found in many post-mortem-analyses of calcium silicates in cement kilns though. In conclusion it has no or hardly any relevance for the industrial practice and cannot cause corrosion of calcium silicate materials therefore.
To support this theory crucibles have been filled with alkaline dusts out of the bypass of a typically cement kiln instead of salts: One chloride rich dust containing 23 M-% chlorides, 11 M-% sulfates and 4 M-% $K_2Ca(CO_3)_2$ and the other sulfate rich dust containing among others 13 % KCl and 24 % sulfates. With these 37 or 38 % respectively extremely high concentration of corrosive substances the crucibles didn't corrode particularly. Only a small infiltration of 2 % can be measured at the test temperature of 1100 °C. No resolutions are visible at all.

Abstract-Number: *277*

DEVEOPMENT OF CEMENT-FREE MGO CASTABLE BY CONTROLLING ITS HYDRATION BEHAVIOUR

Peng H.[1], Ning L.[2], Myhre B.[1]
[1]*Elkem Silicon Materials, R&D, Kristiansand, Norway,* [2]*Wuhan University of Science and Technology, Wuhan, China*

Magnesia castables are still not widely used in state-of-art steel-making. The major challenges are volume expansion and cracking when brucite is formed ($Mg(OH)_2$) during MgO hydration - a phenomenon commonly called “slaking”. Previous studies are mostly based on “MgO- containing” castables such as cement containing spinel-magnesia castables. Little work has been reported on MgO-rich cement-free castables. Moreover, most of the results are based on small-scale laboratory specimens rather than on real-size MgO castables.

In this paper the focus is on understanding the hydration behaviour of MgO in both lab-scale and industrial-scale specimens. Samples taken from the specimen interior during the drying-out process are studied using SEM and XRD techniques The results demonstrate that microsilica, dispersants, specimen size and curing time all have a significant impact on the hydration of the MgO. To produce crack-free MgO castables, a minimum of 3 wt% microsilica is necessary for lab-scale specimens, while more microsilica is needed for industrial-scale samples. Microsilica in combination with a specifically designed dispersant makes an effective anti-hydration additive package for MgO castables. By controlling the MgO hydration behaviour, cement-free castables based on the $MgO\text{-}SiO_2\text{-}H_2O$ bond system have been developed. They exhibit good placing properties and high hot-strength. Since $MgO\text{-}SiO_2\text{-}H_2O$ contains only small amounts of bound water, the castables can be fired at very high heating rates once the free water is removed.

Abstract-Number: *278*

THERMAL CHANGES OF CORUNDUM-BASED AND MULLITE-BASED WOOL HEATED IN HYDROGEN ATMOSPHERE

Sugiyama M.[1], Terada H.[1], Fujii M.[1], Takeuchi N.[2]
[1]*ITM Co., Ltd., Katori-gun, Chiba, Japan,* [2]*Kyoto Institute of Technology, Department of Chemistry and Materials Technology, Kyoto, Japan*

Thermal changes of corundum-based and mullite-based wool heated in hydrogen atmosphere were investigated. The samples were set in the tube electric furnace. Hydrogen gas introduced from inlet of the tube furnace at the rate of 200 ml/min. The temperature was raised at the rate of 5 ˚C/min up to 1600 ˚C. The samples were soaked for 5 h at 1600 ˚C and then cooled down at the rate of 5 ˚C/min. Phase transition, weight change and chemical composition change were investigated for the samples before and after heat treatment. XRD results revealed that disappearance of cristobalite phase and decrease in the peak intensity of mullite phase during heat treatment in hydrogen atmosphere. The results of weight changes and XRD results indicated that reduction reaction of the phases containing silica by hydrogen was occurred during heat treatment.

Abstract-Number: *279*

HEAT CONDUCTIVITY MEASUREMENT OF REFRACTORIES - COMPARISON OF METHODS AND CRITICAL REVIEW OF APPLYING RESULTS

Lorenzoni B.[1], Neuböck R.[2], Klikovich M.[3]
[1]*RHI-AG, DRP - R&D Physics, Leoben, Austria,* [2]*RHI-AG, DRB - R&D Basic Bricks, Leoben, Austria,* [3]*RHI-AG, STD - Technical Drawings Steel, Vienna, Austria*

Thermal conductivity is one of the key properties of refractory products. It is used to determine the design of the overall refractory lining and the steel construction, but also the dimensions of potential cooling equipment of all industrial high-temperature applications. It is even a knock-out criterion for the decision to install a certain refractory material or not.
This paper describes the most used measurement methods for heat conductivity. These are the Hot Wire Test (ASTM C 1113, DIN EN 993-14 and 15), Laser Flash, ASTM C 201 and Dr. Klasse. The methods expose differences in the values generated on the same material and have different levels of uncertainty. Not only the measurement type but also the sampling can have significant influence on the results. Furthermore the influences on the heat transfer calculation have to be taken carefully into account when designing a lining concept.

Abstract-Number: *280*

TAILORING THE MORPHOLOGIES OF CALCIUM HEXALUMINATE IN THE PRESENCE OF DIFFERENT TYPES OF AL_2O_3 SOURCE

Li W.[1], Wu R.[2], Ge T.[1], Jia Q.[1]
[1]*Zhengzhou University, High Temperature Ceramics Institute, Zhengzhou, China,* [2]*Jiangsu Sunpower Technology Co. Ltd, Nanjing, China*

Calcium hexaluminate (CA_6), as a promising high temperature materials, possesses many excellent high temperature performances, such as chemical resistance in alkaline, high stability in a CO reducing atmosphere. It also can form solid solution with iron oxide in a large range. Calcium hexaluminate has been synthesized by using $CaCO_3$ and different types Al_2O_3 ($Al(OH)_3$, industrial alumina, ultrafine alumina and $AlCl_3{\cdot}6H_2O$) as raw materials. The effects of different Al_2O_3 raw materials, firing temperatures on the phase composition and microstructure of resultant products have been studied. The results show that the different source of alumina has a significant impact on the initial temperature of formation of CA_6, which is 1200°C, 1300°C, 1300°C, 1400°C, respectively for using $Al(OH)_3$, industrial alumina, ultrafine alumina and $AlCl_3{\cdot}6H_2O$. With temperature rising, apparent porosity of samples with $Al(OH)_3$ or industrial alumina addition changes slightly. The morphologies of CA_6 grains are well developed platelike shape with using $AlCl_3{\cdot}6H_2O$ as raw materials, which are granular as for to industrial alumina, ultrafine alumina as raw materials.

Abstract-Number: *281*

DEVELOPMENT OF TAPHOLE CLAY USING GLYCOL-BASED ADDITIVE FOR IMPROVEMENT OF PLUGGING PROPERTIES

Kim T.W., Kim W.H., Han J.H., Go J.S., Lee S.K.
Korea Refractories Co., Ltd., R&D Center, Dangjin, Korea, Republic of

Both easiness of plugging, tapping and formation of stable structures in a blast furnace are highly important to taphole clay. To satisfy these requirements, taphole clay must exhibit excellent plugging properties. In this study, to improve the plugging properties, various experiments were conducted by applying a glycol-based additive which typically used for lubricants due to coating properties for particle surface and stability by low reactivity with other materials[1)]. Through these tests, it was confirmed that improvement of workability, liquidity and structural defect.
The workability in relation to the amount of glycol-based additive was measured by a marshall stability tester. The extrusion pressure decreased when the glycol-based additive increased. However, packing fraction decreased critically because the extrusion pressure decreased to disallowed range when content of glycol-based additive was over the appropriate amount.
The liquidity was evaluated by a specially designed tester[2)]. The test results were revealed that penetration behaviors of taphole clay applying glycol-based additive were stable. It is considered that these results of workability and liquidity are caused by increment of lubrication force between taphole mix due to glycol-based additive.
The relation between the number of cracks and the volatilization rate was confirmed by measuring the amount of tar volatilized over time under rapid heating. Tar was volatilized favorably in the tahole clay applying glycol-based additive because the micro pores were formed by volatilization of glycol-based additive at the low temperature(200~240°C). And this inhibited cracking of sample.
According to the results, taphole clay with a glycol-based additive was applied to a blast furnace. Such a taphole clay reduced problems during the tapping process and extended the taphole length. Also, improvement of plugging properties was confirmed.

References:

1) Leslie R. Rudnick : Lubricant Additives(Chemistry and Applications) 209-203 (2003).
2) Tatsuya Kageyama, Kazushi Maruyama, Masatsugu Kitamura, Daisuke Tanaka : TAIKABUTSU 56[3] 108 (2004).

Abstract-Number: *283*

EFFECT OF MICROWAVE CURING AND DRYING ON PROPERTIES OF ALUMINA LOW-CEMENT CASTABLES

Majchrowicz I.K., Czechowski J.
Institute of Ceramics and Building Materials, Division of Refractory Materials, Gliwice, Poland

Effect of microwaves on curing and drying of alumina castables was investigated. The castable on the basis of tabular alumina with 3% of microsilica was prepared. One part of samples were cured in climatic chamber at 20°C 95% r.h. for 48 hours and dried in electric dryer for 24 hours. The other part of samples were cured in climatic chamber at 20°C 95% r.h. for 24 hours and then the curing process was continued in microwave dryer in a plastic container for different time up to 24 hours. Then the samples were removed from the container and dried in microwave dryer. Properties such as cold crushing strength, open porosity and bulk

density of samples cured and dried in different manner were compared. The microstructure and phase composition of samples were characterized.

Abstract-Number: *284*

SOL-BONDED ALUMINA-SILICA MONOLITHICS - FUNDAMENTALS, PROPERTIES AND APPLICATIONS

Blajs M.[1], von der Heyde R.[2], Krischanitz R.[3]
[1]*RHI AG, Leoben, Austria,* [2]*RHI AG, Mühlheim-Kährlich, Germany,* [3]*RHI AG, Vienna, Austria*

A few years ago a new cement-free castable generation was introduced to the market of non-basic monolithics. Since that the product portfolio of these “sol-bonded mixes” was expanded constantly throughout the years. Today these special monolithic products are available in a wide range of raw material bases and all commonly used installation methods. They were successfully introduced in many different industries like cement, steel, non-ferrous, energy, environmental, chemistry and glass applications. Especially within a cement line generally monolithic linings are gaining more and more importance for stationary units, including cyclones, calciner, inlet chamber, kiln hood and cooler. However, the advantages in terms of installation time and complexity of installation in geometrically complicated areas are often counterbalanced by the more complicated drying and heat-up requirements.
Contrary to common conventional and low cement castables, solbonded mixes counteract this disadvantage by providing the possibility for faster, easier and safer drying.
Additional to that the binder dosing is easier and setting is less sensitive to different ambient temperatures.
Furthermore the sol-bonded monolithics feature a lot of improvements in terms of performance and durability, compared to the widely used hydraulically bonded products. Superior thermal shock resistance, reduced brittleness, improved refractoriness and abrasion resistance at elevated temperatures, as well as high resistance against alkali attack, are some of the advantages which lead to the outstanding performances of solbonded mixes in highly loaded application areas.
The paper provides the fundamentals of sol-bonding system and the application in Alumina-Silica mixes. The advantageous properties of the sol-bonded monolithics are illustrated by presenting the results of extensive research work. Furthermore some outstanding and comparative results from different application areas in the field are presented.

Abstract-Number: *286*

COMPARISON OF TWO DIFFERENT TUNDISH LININGS AT VOESTALPINE STAHL GMBH IN LINZ, AUSTRIA - A CHEMICAL AND MINERALOGICAL APPROACH

Winkler W., Stallberger J., Exenberger R.
voestalpine Stahl GmbH, Linz, Austria

At voestalpine Stahl GmbH in Linz, Austria four different continuous casting facilities (3 single strand, 1 double strand) are in operation at the steel plant LD3. The tundishes have been under observation and investigation concerning their characteristics during and after operation. In a number of tundishes a certain effect showed: the safety lining - consisting of andalusite castable - curved to the inside of the tundish and therefore the stability between safety and wear lining decreased, spalling and increased repair work was the consequence. For this reason two different tundishes with different lining concepts were investigated. The first lining concept consists of insulation material in the form of fiber mats and the andalusite castable as safety lining (tundish 1), the second concept consists of fiber mats, insulating boards and the same andalusite castable as safety lining (tundish 2). The samples from the two tundishes were taken from the inner (hot face) part, the middle and the outer (cold face) part of the safety lining. These 3 respectively totally 6 samples from both tundishes were ground for chemical analyses and X-ray diffraction analyses. The results from X-ray diffraction were different for the two tundishes. Beside the expected mineral phases like e.g. andalusite, mullite and aluminum oxide several newly formed minerals could be observed. In tundish 1 the samples from the hot face and the middle included the mineral nepheline. In tundish 2 nepheline could be detected in all 3 samples across the section of the safety lining from the hot to the cold face. In the sample of the hot face and the sample from the middle futher feldspar minerals, such as andesine and sanidine could be detected. All three feldspar minerals include sodium and are, from the chemical point of view, sodium-aluminum-silicates. As the degree of recrystallization from andalusite to mullite can be regarded as a “thermometer” for the refractory material, the cold face in tundish 2 shows more mullite than the cold face of tundish 1. As the crystallization of nepheline is dependent on the amount of mullite available, the nepheline content is also higher in tundish 2 than in tundish 1. The

origin of sodium could be detected in the gunning material which includes sodium silicates as binder. As a consequence the insulation was reduced and therefore also the mullite content. The curving and spalling of the lining could thus be eliminated.

Abstract-Number: *287*

FIRED DOLOMITE REFRACTORIES BASED ON VARIOUS KINDS OF DOLOMA AND DOLOMA-MAGNESIA CLINKERS

Niesyt M.
Institute of Ceramics and Building Materials, Refractory Materials Division, Gliwice, Poland

Refractory products based on burnt doloma are mainly used in the steel industry. There are two types of dolomite refractory bricks: fired (ceramically-bonded) bricks sintered at the temperature not lower than 1500^{o}C and carbon-bonded bricks treated at approximately 300^{o}C. In the case of fired bricks, for potential use in the production of clean steel, very good quality of dolomite is needed with an emphasis on low accompanying oxides level. Poland is a country rich in dolomite's deposits, although most of them are medium or second-rate quality. There are however a few domestic deposits of coarse-grained and quite pure dolomite that can be used to obtain applicable clinker by two-stage sintering. One of them was chosen for the further investigation.
The main aim of this study is to obtain fired dolomite samples with reduced content of impurities using appropriate anhydrous binder. To lower the amount of fluxes and improve some properties such as hydration resistance, additional MgO input was introduced. Good results were achieve for fired samples prepared on the base of fused doloma-magnesia co-clinker compared with samples obtained from the mixture of two kinds of clinkers: doloma and magnesia. The samples were sintered using anhydrous binders such us coal tar pitch or tall oil which is secondary product derived from a wood pulp manufacture. The ones prepared with tall oil revealed better properties compared with samples obtained with coal tar pitch. An addition of polar substance to the oil improved cold crushing strength before samples' sintering.

Abstract-Number: *288*

IMPROVEMENT OF HOT METAL LADLE LIFE WITH LINING TEMPERATURE CONTROL

Takeuchi H.
Nippon Steel & Sumitomo Metal Corporation, Kimitsu Works, Kimitsu City, Japan

In hot metal ladles of No.2 steel plant in Kimitsu Steel Works, the service life of bottom refractories was short and it determined repairing interval of the hot metal ladles. Pylophylite - alumina - SiC - C bricks was used as bottom refractories in consideration of KR treatment influence. On that bricks surface peeling were observed due to thermal shock.
In this study, the thermal shock to the bricks was eased by improvement of temperature control. Action based on mineral transformation in pylophylite - alumina - SiC - C brick led to success. We found the refractory lining should be kept at higher than 850K, and realized it with coke combustion in the ladle and quick cleaning of the ladle. Thereby surface peeling was reduced, and life of bottom refractories was prolonged.

Abstract-Number: *290*

NO-CEMENT ALUMINA-MAGNESIA CASTABLES FOR STEEL LADLE

Wang Y.C., Chang K.M.
Sunward Refractories Co., Ltd., Kaohsiung, Taiwan, Republic of China

No-cement alumina-magnesia castable for steel ladle lining was developed in this study. Hydratable alumina powder was introduced as binder, and well workability was achieved by using a polymeric dispersant and combined with size-adjustment of recipe. The result shows that the water addition for no-cement castable can be lower about 1% and possessed highly self-flow ability then present cement-bonded castable by using polymeric dispersant and partially replaced tabular alumina aggregate by white fused alumina. Dried green body strength has much improved by increase an appropriate amount of microsilica, and result in higher mechanical strength after sintering. No-cement castable also shows better corrosion resistance then present cement-bonded castable on slag corrosion test.

Abstract-Number: *291*

IMPROVING CASTABLES WITH RECYCLED AGGREGATES THROUGH AN OPTIMIZED MONO-CALCIUM BINDER

Kreuels N.[1], Ostrander D.[2], Schaffhauser H.[3]
[1]*Calucem GmbH, Höhr-Grenzhausen, Germany,* [2]*Calucem Inc., Allentown, United States,* [3]*Calucem GmbH, Mannheim, Germany*

Using recycled raw materials in refractory products is a state of the art technology which contributes to the need of sustainability in the industry.
However, this technology requires a different approach compared to the use of virgin raw materials. Even if a proper selection and processing of the recycled raw materials is ensured, they contain a higher amount of accompanying elements than virgin ones. In order to keep an eventual negative input as low as possible, it is necessary to limit oxides, which are introduced into the castables through cement or other binders to a minimum.
The paper describes the use of a new type of Mono Calcium Aluminate binder, which consist mainly out of the hydraulic active phase CA. Thus it is possible to limit the addition to a minimum and keep the CaO content as low as possible and reducing thus a feldspar formation, which leads to lower melting temperatures.
The paper describes this approach, where first different castable types, based on Fireclay, with varying cement content are tested according to standard test methods and also with high temperature tests. The first results indicate already an improvement in flow, i.e. lower water requirement and higher physical strengths after firing, which amount up to + 20%. Refractoriness under load confirms these results.
In a second step, the aggregates are replaced by recycled bauxite/fireclay reclaimed material and the same tests are carried out. According to first previous test results, the physical strength remains with the use of this new binder type on the same level. The paper will describe the appropriate results and can give recommendations for designing efficient castables containing recycled aggregates.

Abstract-Number: *292*

DETECTION OF MELT FORMATION IN A LCC SPIKED WITH SINTERING AIDS BY THE METHOD OF MONOTONIC HEATING (MMH)

Krause O.[1], Rathaj M.[1], Brochen E.[2], Simmat R.[2], Dannert C.[2]
[1]*Koblenz University of Applied Science, Materials Glass and Ceramics, Höhr-Grenzhausen, Germany,* [2]*Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany*

This presentation will contribute to a deeper understanding of the sintering behaviour and melt formation in refractory LC castables during the first heat up and under discontinuous operation.
By means of the Method of Monotonic Heating (MMH) one can understand the physical and mineralogical changes within refractories in situ and under thermal load. The presentation will demonstrate the application of this method to investigate the sintering behaviour of a tabular alumina based LC castable that is spiked with distinct amount of a sintering aid (0-5 wt.-%) that itself melts at temperatures of 1000 °C.
The change of the apparent thermal diffusivity (a) as a function of temperature (T) between 350 and 1550 °C and peaks in the course of a(T) caused by the enthalpy of fusion and recrystallization depict the sintering behaviour.
In this presentation the results of MMH are correlated with mineralogical investigations that help to understand the evolution of the thermal diffusivity during heating and cooling of a LC castable spiked with sintering aids. It can be shown that the amount of sintering aid impacts the curve progressions of MMH systematically. The temperature at which a liquid phase is generated can be determined within ± 10 °C. In further an attempt can be undertaken to determine the amount of melt at a distinct temperature.

Abstract-Number: *293*

SPINEL FORMATION AND TECHNICAL PROPERTIES OF ALUMAGCARBON BRICKS WITH DIFFERENT ALUMINA AGGREGATES

Klewski M.[1], Maracha G.[2], Buhr A.[3], Schnabel M.[3], Dutton J.[4]
[1]ARCELORMITTAL REFRACTORIES, Krakow, Poland, [2]ARCELORMITTAL STEEL, Krakow, Poland, [3]Almatis GmbH, Product and Market Development, Frankfurt, Germany, [4]private, Kingsbridge, United Kingdom

AluMagCarbon (AMC) bricks have become a common material for steel ladle lining. They are applied in demanding places such as the impact area in bottom and side wall but they are also used for complete ladle lining in bottoms and sides walls, except slag lines. The spinel formation during use is a key feature of AluMagCarbon bricks, which is essential for their high wear resistance. It continuously creates a slight expansion at the hot face of the bricks, which helps in overcoming a joint opening in the brickwork due to thermal cycling of the steel ladles. In addition, the spinel formed has high refractoriness and slag resistance and therefore helps to protect the thin de-carburised layer from chemical wear.
Different alumina aggregates can be used as basis for AMC bricks, ranging from bauxite and brown fused alumina to synthetic alumina based aggregates such as tabular alumina or white fused alumina. The chemical purity of the aggregate has a significant influence on the wear resistance and therefore higher purity aggregates are used in the most demanding areas, e.g. the bottom impact. The nature of the alumina also has a big influence on the spinel formation during use, and besides the chemical purity also the microstructure of the aggregate plays a role.
This paper investigates the spinel formation and technical properties of AMC bricks based on fused and sintered alumina aggregates. A special focus is given on a new European based sintered aggregate with 96% Al_2O_3 (BSA 96). Learning from mineralogical investigation of bricks after firing was used for the development of bricks with the new aggregate. The microstructural changes are related to the macroscopic brick properties, and field results with newly developed brick formulations are included in the investigation.

Abstract-Number: *294*

LASER-INDUCED BREAKDOWN SPECTROSCOPY AS A POWERFUL TOOL FOR ON-LINE QUALITY CONTROL IN THE REFRACTORY INDUSTRY

Baryshnikov A.[1], Gaft M.[1], Groisman Y.[1], Akselrod L.[2], Savchenko A.[2]
[1]Laser Distance Spectrometry Ltd, Petah Tikva, Israel, [2]Magnezit Group, Moscow, Russian Federation

Raw materials have a significant influence on the quality of the final refractory products and make up a considerable part of their cost. Therefore, one of the main problems in the refractory industry is a variable chemical composition of raw materials, arriving for crushing and benefication, as it leads to irregular product quality, customer's claims, and increased consumption of energy and fuel materials.
This paper introduces an effective solution for real-time elemental analysis of the chemical composition of raw materials on a conveyor, using the cutting-edge Laser-Induced Breakdown Spectroscopy (LIBS) technology. The automatic quality control system, based on precise information provided in real time by the elemental laser analyser, allows to perform batch sorting of ore, provide corrective additions for raw mix chemistry stabilization before it is too late for a process.
The LIBS technology involves no sampling and can operate under heavy, dusty, humidity, corrosive conditions in the refractory industry without any hazardous neutron, gamma or X-ray radiation. As a result, it provides safe working conditions for the personnel and meets the growing requirements for environment sustainability. No human mistake is possible, which is common in sampling and sample preparation.
Case studies demonstrate benefits provided by the LIBS analysers in refractory plants. The results obtained show that it is a low cost and effective way to increase the production of high grade refractories by automatic rejection of contaminations and grade sorting of raw magnesite in real-time mode (both at the benefication plant and built into the mobile crushing and screening unit). LIBS can be successfully used for optimal charge of different types of kilns. The results do not depend on the quality of the surface of the analyzed material, size of the pieces and thickness of the layer. Even a small amount of mineral material can be analysed (20-30m segment of the belt). Besides, the laser analysers based on the LIBS technology involve low operation and maintenance cost.

Abstract-Number: *296*

PRODUCTION PROCESS FOR NEW LIGHTWEIGHT KILN FURNITURE AND THEIR RELEVANCE FOR THE TEMPERATURE DISTRIBUTION WITHIN THE KILN

Schnieder J., Sannikow V., Traon N., Tonnesen T., Telle R.
Institute of Mineral Engineering, Department of Ceramics and Refractory Materials, Aachen, Germany

To understand the mechanical fracture and microstructural changes in refractory materials occurring during thermal shock treatment, the process zone during damaging has to be divided into two different zones. The crack tip where toughening mechanisms like crack branching, crack deflection and interaction with microcracks can occur and the region behind the frontal zone of the crack well known as the wake region. In this wake region, the strengthening effects due to crack bridging, liquid phase bridging and friction between aggregates and the matrix are essential. The aggregates size, their own properties and their shape play a major role for these effects.
Different kinds of fused eutectic aggregates (Al_2O_3-ZrO_2-SiO_2, Al_2O_3-ZrO_2) and andalusite with a grain fraction of 2,24 - 3,00 mm were incorporated in a model tabular alumina castable formulation. The impact of these aggregates on the elastic and thermo-mechanical properties as well as on the crack path is examined.
Thermal shock experiments with progressive ΔT, between ΔT= 200 K and ΔT= 1200 K, could reveal for each material a specific critical temperature difference for crack initiation and crack propagation. At the wake region, crack bridging and liquid phase bridging could be observed.

Abstract-Number: *298*

CATION DISTRIBUTION AND PHASE STABILITY OF PSUEDOBROOKITE-TYPE OXIDES

Ohya Y., Kawauchi Y., Ban T.
Gifu University, Chemistry and Biomolecular Science, Gifu, Japan

Psuedobrookite type oxide ceramics such as Al_2TiO_5 (AT), Fe_2TiO_5 (FT) and $MgTi_2O_5$ (MT) are well known for their very low thermal expansion coefficient. The low thermal expansion is due to grain boundary microcracking caused by their large thermal expansion anisotropy. A study interest of the ceramics, therefore, is strengthening of the ceramics maintaining their low thermal expansion. Another interest concerns stability of the AT ceramics. AT tends to decompose into rutile and corundum around 1100°C, whereas FT and MT do not. Since the formation of AT from corundum and rutile is an endothermic reaction, AT should be stabilized by entropy term, *TΔS*. Psuedobrookite type structure has two different octahedral and electrostatically equivalent cation sites of 4c and 8f. The distribution of cations into the two different sites introduces the configuration entropy to stabilize AT.
We studied the cation distribution of the tree psuedobrookite-type oxides by Rietveld analysis. The samples were synthesized by a conventional powder processing and the moldings were water-quenched from various temperatures to confirm their high temperature cation distributions. Measure of the cation distribution is defined as an occupation of Ti^{4+} ion in 4c site and the random distribution leads the value to 0.333, 0.333 and 0.667 for AT, FT and MT, respectively. Rietveld analysis revealed that the occupancy in AT and FT is about 0.4 and 0.2-0.25, respectively. The value seems not close to the random distribution, but results of a calculation of configuration entropy were almost the same as that of the random distribution. The occupancy of the two oxides was independent of the temperature; this means constant configuration entropy *ΔS*. The occupancy of MT is about 0.4 at 1500°C and decreased with lowering temperature. In MT structure, Ti^{4+} ion favored 8f site and this tendency increased at lower temperature decreasing the configuration entropy. Since the cation distribution in AT did not depend on the temperature, temperature itself governs the entropy term of *TΔS*. Thermodynamically the decomposition of AT is due to the very stable corundum phase.
Maximum entropy method revealed considerable electron density between oxide ion and metal ion in AT and FT. Bond valence sum also suggest some degree of covalent bond in AT and FT. These results explain the independent cation occupancy in AT and FT of temperature.

Abstract-Number: *299*

EFFECT OF PYROPHYLLITE ON DURABILITY OF AL_2O_3-SIC-C BRICKS

Yoshida K.[1], Hino Y.[1], Matsunaga H.[1], Watanabe K.[1], Tomiya H.[2], Iida A.[2], Ogata M.[2]
[1]JFE Steel Corporation, Chiba, Japan, [2]Shinagawa Refractories Co.,Ltd., Okayama, Japan

The hot metal ladle, which is used as a vessel for hot metal transportation, has the disadvantage of large cyclical heat inputs and discharges due to repeated charging and discharging of hot metal. Therefore, Al_2O_3-SiC-C bricks, which contain pyrophyllite, have generally been used as wear lining bricks due to their excellent thermal spalling resistance and lower deterioration under repeated heating and cooling. In this study, the effect of pyrophyllite on the durability of Al_2O_3-SiC-C bricks was investigated.
Two kinds of samples, one containing no pyrophyllite and the other containing 20 mass% pyrophyllite, were prepared. All samples

were heat-treated in a reducing atmosphere for 3 hours at 1273K or 1773K, after which their physical properties and mechanical properties were evaluated. Subsequently, thermal expansion under no load and loading of 1MPa was evaluated. Furthermore, thermal stress in the brick was evaluated by an examination in which the bricks were heated under a restricted condition, and microstructure observation was conducted using a microscope to clarify the correlation between thermal expansion behavior and phase transformation.
As a result, it was found that addition of pyrophyllite resulted in improved thermal shock resistance after heat-treatment and a lower modulus of elasticity at high temperature, and these properties reduced thermal stress.
It was predicted that this decrease of the modulus of elasticity would be caused by micro cracks, pore formation and suppression of sinter due to transformation of silica and formation of mullite.

Abstract-Number: *301*

PREPARATION OF AL_2O_3-SIO_2 SOL AND APPLICATION IN CORUNDUM-MULLITE CASTABLE

Yu J., Zhao H., Zhang H.
Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallurgy, Wuhan, China

High purity and stability Al_2O_3-SiO_2 sol was synthesized by sol-gel method using ethyl orthosilicate and aluminium chloride as raw material. The influence of PH value on the Zeta potential and dynamic mobility of Al_2O_3-SiO_2 sol was investigated. It was found that the mobility of Al_2O_3-SiO_2 sol increased with pH value decreasing, which was mainly attributed to the promotion of H^+ to the disintegration of aluminum-based colloidal particles. However, aluminum content in Al_2O_3-SiO_2 sol may reduce in the acidic environment, which can lead to the formation of mullite and quartz phase after high temperature sintering of sol and impact the product purity. Therefore, from the practical application, considering the sol liquidity and stability, 6~8 PH value was chose in this experiment. According to the XRD analysis, activation energy and chemical reaction order calculation, it was shown Al_2O_3-SiO_2 sol can completely react mullite at 1200℃.
In addition, the application of Al_2O_3-SiO_2 sol instead of water in mullite-corundum castable was studied. The results showed that Al_2O_3-SiO_2 sol bonded mullite-corundum castables had similar drying strength to common low cement mullite-corundum castables. The strengths after heat treating at 815℃ and1100℃ were higher than the drying strength. After 100 times cycles of thermal shock (1100℃, water quenching), there was almost no crack on the shaped Al_2O_3-SiO_2 sol bonded mullite-corundum castables, and the crushing strength only declined by 17.2%. In simulated hot repair condition, the shaped Al_2O_3-SiO_2 sol bonded mullite-corundum castables had equal properties with that cast at room temperature. The on-site application showed that the remolding time and drying time of Al_2O_3-SiO_2 sol bonded mullite-corundum castables were greatly decreased, and the castables can be hot cast and serve well.

Abstract-Number: *303*

THE STUDIES ON THE REFRACTORY LINING OF THE CS_2 PRODUCING FURNACE

Sengupta P., Agarwal A., Gupta N., Mondal S.
SKG Refractories Ltd, R&D, Nagpur, India

Synthetic rayon manufacturer produces Carbon di sulphide as a solvent for their self consumption. The viscose rayon is allowed to hard in Carbon di sulphide bath.
Carbon di sulphide is produced in a vertical furnace in which molten Sulphur & charcoal, as a source of carbon, reacts at a temperature of around 1100 °C to produce Carbon di sulphide in vapour phase. Electric arc, passed between two vertical electrods, is used as the source of heat.
Traditionally, the working face of the reaction zone in this furnace is lined with high purity (92 % MgO) Magnesite radial bricks, followed by Alumino-Silicate refractories and the campaign life of the working lining is not good. The used Magnesite refractory collected from the furnace was analysed and studied.
This paper discusses the results of the analyses conducted and the thermodynamic stability of the Magnesite refractory in the furnace prevailing condition and has suggested 90 Al_2O_3 refractory with a side arch shape as a beter alternative, which isalready put into use in the same furnace and the performance looks to be very encouraging.

Abstract-Number: ***304***

A NOVEL METHOD FOR SYNTHESIS OF PARTIALLY STABILIZED NANO ZIRCONIA

Sahoo N.[1], Rauta P.R.[1], Sethy M.[1], Tiwari J.N.[2]
[1]*Dalmia Institute of Scientific & Industrial Research, Rajgangpur, India,* [2]*OCL India Ltd, Rajgangpur, Sudargarh, India*

Normally nano oxide powders such as $Al2O_3$, ZrO_2, TiO_2, Fe_2O_3, and MgO are added to refractory compositions to enhance their thermo mechanical and corrosion resistance properties. The present research work is aimed on production of MgO partially stabilized nano zirconia in a single stage of operation through spray pyrolyser route.
Calculated amount of zirconyl nitrate and magnesium nitrate were mixed and sprayed in spray pyrolyser at a temperature of 700°C and pressure of 4kg/cm^2. The nano particles produced were then calcined at a temperature of about 1100°C to produce MgO-partially stabilized nano zirconia. The prepared powder was characterized for its particle size and phases. The particle size of the developed product is in the range of 50 to 90 nm and the XRD graph shows the monoclinic and tetragonal phases. This partially stabilized nano zirconia has potentiality to be used in manufacture of refractories such as slide gate, sub entry nozzle, mono block stopper and metering nozzle etc. for application at high temperature.
Key words: Partially stabilized, nano zirconia, refractories, spray pyrolyser, MgO.

Abstract-Number: ***308***

PRECAST COKE OVEN DOOR: A FUTURISTIC PRODUCT

Mohammed B., Das S.P., Tiwari J.N.
OCL India Ltd, Rajgangpur, India

Environmental protection is a task of highest priority and the focus is more and more on tight coke oven doors. The use of precast coke oven door is emerging as an effective alternative in prolonging the life the coke oven door. It has not only enhanced the life of the door by minimizing the damage due to operational abuses, mechanical handling and pitting but also led to reduction in repetitive and often hazardous maintenance by bring down the frequency of door repairs and removal of doors from the oven. It has had a very positive impact on the environment by minimizing and eliminating emissions. This paper deals with the properties and advantages of such practice adopted in one of the leading integrated steel plant and the various development steps involved in design and application of precast doors.

Abstract-Number: ***311***

CASE STUDIES - STEAM EXPLOSION ON LOW CEMENT CASTABLE DURING INDUSTRIAL APPLICATION

Lee Y.M.[1], Kumar S.[2], Johnson K.[1]
[1]*ArcelorMittal Steel, Global R&D, East Chicago, United States,* [2]*ArcelorMittal Steel, Burns Harbor, United States*

Steam explosion could occur in large scale industrial application even with careful dry-out practice. Incidents of steam explosion during industrial application were investigated to find out key variables and countermeasures. Cases on steam explosion will be presented. Important aspects will be presented to establish the relationship between laboratory testing and large scale of industrial application.

Abstract-Number: ***312***

IMPROVEMENT OF THE OXIDATION RESISTANCE BY MGO ADDITION TO AL_2O_3-SIC-C BRICKS

Matsuo Y., Tanaka M., Yoshitomi J.
KROSAKI HARIMA CORPORATION, Technical Research Laboratories, Kitakyushu, Japan

The oxidation resistance of Al_2O_3-SiC-C bricks is remarkably improved by addition of MgO and it is more effective using by the smaller MgO. The composition of glassy phase in oxidation layer of
Al_2O_3-SiC-C bricks without MgO after oxidation test is binary system of SiO_2-Al_2O_3. Meanwhile, the composition of it with MgO is ternary system of SiO_2-Al_2O_3-MgO.
It is considered that the oxidation from lower temperature is inhibited caused by lowering of the melting point of glassy phase by addition of MgO.

Abstract-Number: *313*

THE ACTUAL TEST RESULTS OF A SLIDE GATE PLATE USING LOW THERMAL EXPANSION ZRO_2 SYSTEM RAW MATERIALS

Ohmaru Z., Makino T., Morikawa K., Yoshitomi J.
KROSAKI HARIMA CORPORATION, Fukuoka, Japan

In the previous study, we reported a new dense ZrO_2-mullite (ZM) raw material. This new ZM raw material showed lower coefficient of thermal expansion than conventional ZM. And furthermore, the ZM kept the original dense microstructure after heat treatment under reductive atmosphere in spite of containing SiO_2 as mullite. And using this raw material, the spalling resistance and corrosion resistance were improved.
In this study, a slide gate (SG) plate containing the new ZM raw material was used practically for several grades of steel and operating conditions. Consequently, the SG plate showed the excellent performance associated with the decrease of damage at sliding surface such as loss of bore edge, penetration of steel and abrasion. We could confirm the improvement for many customers and the test results were mainly reported.

Abstract-Number: *315*

EFFECT OF HOMOGENIZED BAUXITE AGGREGATE ON PROPERTIES OF AL_2O_3-SIC-C CASTABLE

Luo Q.[1], Chen Q.[2], Yan W.[2], Li N.[2], Hong Y.[1], Chen Y.[3]
[1]Henan Bauxitechina Co.,Ltd, Jiyuan, China, [2]The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China, [3]Kerneos (China) Aluminate Technology Co., Ltd, Tianjing, China

Homogenized bauxite is a high alumina sintered aggregate (sintered corundum), which have the characteristic of stable composition, stable performance, high bulk density, low water absorption, and excellent high temperature corrosion resistance. Homogenized bauxite is the best alternative product of brown corundum.
In this work, homogenized bauxite grade 90(HB-90) and brown corundum (BFA) in iron trough castable on physical properties at room temperature, high temperature bending strength and slag resistance were compared, and corrosion and penetration behavior of slag and samples for microscopic analysis by scanning electron microscopy and spectrum analyzer.
The study found: After 110℃, 1100℃ and 1500℃ heat treatment, bulk density of the sample with BFA as aggregate was slightly greater than the sample with HB-90 as aggregate, but higher apparent porosity and lower strength. HB-90 glass phase content was low, which had few effects on high temperature bending strength. Compared with BFA, the sample with HB-90 as aggregate had slightly worse slag corrosion resistance, but better slag penetration resistance. Aggregate on the effects of corrosion and penetration resistance needs into account, HB-90 can partially replace BFA in iron trough castable.
Keywords: homogenized bauxite; brown corundum; iron trough castable; slag resistance

Abstract-Number: *319*

EFFECT OF BINDING TYPES ON MICROSTURCTURE OF HIGH ALUMINA CASTABLES CONTAINING SI POWDERS AFTER NITRIDATION

Bi Z.[1], Li J.[1], Zhou N.[2]
[1]*Henan Haiger High Temperature Materials Co., Ltd., Luoyang, China,* [2]*High Temperature Materials Institute of Henan University of Science & Technology, Luoyang, China*

In this work, phase composition and microstructure of high alumina castables containing 7% Si powders, using different binding types after nitridation, have been investigated by XRD, SEM and FSEM. Four binding types including traditional cement binding with 8% CA cement, low cement binding with 4% CA cement, ultra low cement binding with 1.5% CA cement combined with 2.5% hydratable alumina and no cement binding by SiO_2 sol were adopted and compared. Results indicate that hot strength of high alumina castables can be remarkably improved by the formation of Si_2N_2O from in-situ reaction of Si powders during nitridation which mainly distribute in their normal position of Si powders and the pores and body of the matrix. Binding types can significantly affect the actual reaction condition of Si powders. Too much liquid phase at high temperature lead by higher CaO content may wrap the Si powders and clog the pores in the matrix more easily, and then restrain the reaction between Si powders and the atmosphere. Binders with lower and even no cement content are more conducive to the non-oxides reinforcement phase formation by in-situ reaction of Si.

Abstract-Number: *321*

THE DISTRIBUTION CHARACTER OF GLASS PHASE IN THE BAUXITE-BASED HOMOGENIZED GROG

Ge T., Yang S., Zhao F., Miao M.
Zhengzhou University, Zhengzhou, China

The Bauxite-based Homogenized Grog (BHG) has been rapidly developed in China in recent years. BHG will be the ideal refractory materials with homogeneous phases, stable components and excellent performance.The glass phase in BHG has important influence to its application performance. This paper discussed the distribution character and the content of glass phase in BHG (Al_2O_3,70%) with changing of sintering temperature and the particle size of raw materials. BHGs with different structure can be prepared through controlling different processing condition to meet different needs.

Abstract-Number: *323*

IMPROVEMENT OF MGO-C BRICKS FOR TUYERE OF CONVERTER BOTTOM

Shiohama M.[1], Tanaka M.[1], Yoshitomi J.[1], Tamura Y.[2], Taki N.[3], Saito Y.[4]
[1]*KROSAKI HARIMA CORPORATION, Kitakyushu, Japan,* [2]*Nippon Steel & Sumitomo Metal, Shintomi, Futtsu, Japan,* [3]*Nippon Steel & Sumitomo Metal, Tokaimachi, Tokai-City, Japan,* [4]*Nippon Steel & Sumitomo Metal, Oaza-Nishinosu, Oita City, Japan*

MgO-C bricks of converter's bottom tuyereis used under severe environments by cooling of gas bottom-blowing and back attack.Therefore high spalling resistance and high abrasion resistanceare required.
In this report, it is tried to apply the newly developed binder that has high fixed carbon content and forms high crystalline carbon after fired at 1400℃ in reducing atmosphere.
Compared with conventional type, this MgO-C bricks with newly developed binder showed lower porosity, higher thermal shock resistance and smaller change of porosity after long term firing.
Improved MgO-C was confirmed that the durability is higher than that of conventional type at operation in converter. From the analysis results of used bricks, it was judged that microstructure degradation was minimized, this would be lead to good performance in actual operation.

Abstract-Number: *324*

INFLUENCE OF MOLTEN STEEL ON EROSION RESISTANCE OF MGO-GRAPHITE MATERIAL FOR CONTINUOUS CASTING

Sasaki A., Matsumoto S., Morikawa K., Yoshitomi J.
KROSAKI HARIMA CORPORATION, Kitakyuushu, Japan

Continuous casting nozzles directly influence the quality of steel and therefore high reliability and high functionality are required. In continuous casting process, a wide range of steel grade are casted such as Al-killed steel, Si-killed steel and Al-Si-killed steel.

Recently, in addition, increasing amount of high-Mn steel, porcelain enamel steel and Ca-treated steel are casted. Generally, basic materials such as spinel and magnesia are chosen as the ingredient of inner bore side against these corrosive steel grades. However, the detailed mechanism of corrosion phenomenon under the casting process is not revealed. In this study, magnesia-graphite (MG) system is focused as the ingredient of continuous casting nozzles and we investigated the effect of molten steel on erosion/corrosion behavior of MG ingredient. Consequently, MG ingredient showed high erosion/corrosion resistance against Manganese steel, Al-killed steel and High oxigen steel and dense, uniform reaction layers were observed at hot surfaces. These dense reaction layers considered to form by the reaction between the inclusions in molten steel and Mg gas decomposed from MgO in refractories, which could result in the high erosion/corrosion resistance. It can be concluded that MG ingredient is promising as a universal material for casting nozzles against high-corrosive molten steels.

Abstract-Number: *328*

THE EFFECTS OF IRANIAN NANO DOLOMITE IN THE FORMATION OF SPINEL- HIGH ALUMINA CEMENTS REFRACTORIES

Nemati A.[1], Pouyamehr M.R.[2], Naghizadeh R.[3]
[1]*Sharif University of Technology, Department of Materials Science and Engineering, Tehran, Iran, Islamic Republic of,* [2]*Science and Research Branch, Islamic Azad University, Department of Materials Engendering, Tehran, Iran, Islamic Republic of,* [3]*Iran University of Science & Technology, Department of Metallurgy and Materials Engineering, Tehran, Iran, Islamic Republic of*

In this study, the effects of Iranian Nano dolomite was evaluated in the formulation of spinel- high alumina cements along with nano alumina and then, the physical and mechanical properties of the obtained refractories were analyzed. The samples were prepared, using sintered magnesia, tabular, calcined and nano alumina (for formation of in-situe spinel) along with Iranian calcined dolomite. The surface area of the Iranian dolomite was monitored in N_2 gas. Andreessen equation was applied to adjust grain size distribution of the raw materials. Samples were sintered from °1450C up to 1700 °C and their physical and mechanical properties were evaluated at room and high temperatures. The formed phases and resultant microstructure were also, analyzed by XRD and SEM.
The XRD results of the samples sintered at 1450 °C showed the formation of $MgAl_2O_4$ and $CaAl_2O_4$ as major phases and $Ca_{12}Al_{14}O_{33}$, $CaAl_{12}O_{19}$, MgO and Al_2O_3 as minor phases in the system. The relative amounts of MgO and Al_2O_3 phases in the system were reduced at higher temperature, along with increase of the major phases and as expected, the density of the samples was increased. SEM micrograph indicated the growth of grain size of spinel with temperature increase.
A comparison was made in the sample's properties with and without Iranian dolomite.

Abstract-Number: *329*

IMPROVEMENT OF CORROSION RESISTANCE BY THE FORMATION OF DENSE LAYER IN SLIDE GATE PLATE

Makino T., Ohmaru Z., Akamine K., Morikawa K., Yoshitomi J.
KROSAKI HARIMA CORPORATION, Fukuoka, Japan

When general-type SN plate (Al_2O_3-C) is used in the casting of high-oxygen steel, it is known that there is major damage due to oxidation and erosion, so an Al_2O_3-C SN plate with a lot of added Al metal is often used. In the case that a SN plate with a lot of Al metal added is used, it is known that corrosion resistance improves significantly. But it has a problem that excessive densification incurred remarkably high modulus of elasticity (MOE), this phenomena produce the damage like edge defect. In past times, we developed SN plate with high corrosion resistance and high thermal shock resistance by the adequacy of carbon content and material microstructure. The damage of running surface of this SN plate after used was less and dense layer was formed at running surface. It was considered that the damage of running surface was suppressed by the dense layer. In this report, we estimated the forming mechanism of surface dense layer and investigated the influence of amount of Al added and the influence of atmosphere of heating for forming surface dense layer. The microstructure around surface of specimen heated in coak breeze was like the microstructure around running surface of SN plate after used. In this case, it was found that surface dense layer was able to be formed in more 6 mass% Al added.

Abstract-Number: *330*

MAGNESIA CARBON REPLACEMENT OF DOLOMITE IN LADLE LININGS BY PROCESS AND LADLE SLAG PROCESS MANIPULATION IN AN ALUMINIUM KILLED EAF MELT SHOP

Pywell N.
Mayerton Refractories Ltd, Area Sales Manager, Solihull, United Kingdom

Is there a future for Dolomite in Aluminium killed steel plants? Recent work suggests it can be easily replaced with Magnesia Carbon (MgO-C) and in the process see a doubling of life; reduction in raw material consumption and enable use of recycled EAF/BOF brick as slag conditioner.
The steel industry generally finds it difficult to adapt to change with the primary concern being Health an Safety, integrity of the ladles and the continuity of steel production, with this in mind we set out to prove that MgO-C is the secure and cost effective option.
A customer with a ladle life of 40-50 heats using dolomite linings came to us with plans to introduce a VD unit and move to Al killed steel production, as well as increase ladle life by 50% and adjust operational parameters.
Our proposal; to use a MgO-C lining by adjusting the slag additions, reduce raw material consumption and improve the environmental impact of the customer by utilising waste brick.
The customer saturated the slags with lime as well as adding 10-20% fluorspar at LF to produce the slag they needed. There was also an unrecorded SL repair taking place.
For a MgO-C lining we advised a reduction in lime by 200Kg per heat and for it to be replaced with 200Kg of MgO. This would produce an MgO saturated slag, rather than a CaO saturated one and make a MgO-C lining viable.
To offset the cost of the MgO-C (compared to dolomite) we suggested the use of recycled EAF brick, from their own furnace to use as the MgO addition to the slag.
The customer was using >100Kg of flurospar with every heat at LF, we planned to better utilise standing time after LF.
Original lime addition reduced 150kg replaced with 150kg of MgO. Flurospar additions reduced to 8% from 10%-20%.
The first trial achieved 84 heats, via further trials we removed fluorspar and achieved average 97 heats.
The increase in average ladle life from around 45 to 97 heats has seen a reduction in ladle usage from 14 down to 6 with resultant savings on manpower costs and general maintenance costs.

Old Process
Lining Type - Dolomite
Killed Type - Silicon
Flurospar Additions - >150kg
Lime Addition - 800-1000kg
MgO Addition (Crushed waste brick) - None
Average Ladle Life = 45-50

New Process
Lining Type - Mg-O-C
Killed Type - Aluminium / Silicon
Flurospar Additions - None
Lime Addition - 650-850 kg
MgO Addition (Crushed waste brick) - 150 kg
Average Ladle Life = 97

Phase 2 is to optimise the new MgO-C design.

Abstract-Number: *332*

INVESTIGATION ON HOT STRENGTH DECLINE OF IN-SITU NONOXIDE COMPOSITED ALUMINA BASED CASTABLES BY HOT STRESS-STRAIN APPROACH

Yu R.[1,2], Zhou N.[1], Meng Q.[1]
[1]Henan University of Science and Technology, High Temperature Materials Institute, Luoyang, China, [2]Collaborative Innovation Center of Nonferrous Metal,Henan Province, Luoyang, China

In the *in-situ* nonoxide composited castables by Si powder addition and nitridation, a sharp decline of hot modulus of rupture (HMOR) occurs after reaching 1400°C in the case of CA cement (CAC) addition. The present work investigated hot stress-strain behavior of the castable specimens to help reveal the mechanism of HMOR drop. The binding system of the alumina based castables, using tabular alumina as a dominant raw material, was designed to vary from CAC containing to cement free by using

hydratable alumina to replace CAC, and the relationship of HMOR and stress-strain behavior with the binding system composition was investigated. The addition of CAC leads to a remarkable drop of HMOR at 1400℃, 26.5 MPa in the case of non-CAC addition vs. 4.72 MPa with 3% CAC addition. Plastic deformation occurs from 1200℃ up in the CAC containing system, and viscous flow appears from 1400℃ up in the specimen with 3% CAC addition. In the cement free system, however, little plastic deformation takes place at 1400℃. The *in situ* formed nonoxide bonding phases in the Si powder incorporated and nitridated castable specimens include β-Sialon and O'-Sialon. Glassy phase and anorthite are formed in the cement containing system, and the morphology of Sialon is featured by granular shape. While in the cement free system, no glassy phase is observed and the Sialon crystals are needle- or prism-like, favorable to the hot strength maintenance.

Abstract-Number: *333*

HYDRATION OF CALCIUM ALUMINATE CEMENT PHASES CA AND CA_2 IN REFRACTORY APPLICATIONS

Klaus S.[1], Buhr A.[1], Schmidtmeier D.[2], Kuiper S.[3], Götz-Neunhoeffer F.[4]
[1]Almatis GmbH, Product and Market Development, Frankfurt, Germany, [2]Almatis GmbH, Product and Market Development, Ludwigshafen, Germany, [3]Almatis BV, Rotterdam, Netherlands, [4]University of Erlangen-Nürnberg (FAU), GeoZentrum Nordbayern, Mineralogy, Erlangen, Germany

Calcium-mono-aluminate (CA) and calcium-di-aluminate (CA_2) are the main phases in iron free high alumina cements (CAC) used for demanding refractory applications. It is well known that the hydraulic reactivity of calcium aluminate phases increases with the calcium content of the phase, and therefore CA shows higher reactivity than CA_2. Some literature even claims that CA_2 would be an almost inert phase with regard to hydraulic reactivity. This study investigates the hydration of pure CA and blends of CA and CA_2 using heat flow calorimetry and quantitative in-situ X-ray diffraction (QXRD) during hydration.
The pure phases have been produced on laboratory scale from solid state synthesis. Mixes of CA and CA_2 together with $ZrSiO_4$ as inert filler were tested to be near to the practical mix-design for refractory binder systems and to ensure reproducible results. It is shown that the main reaction is predominantly influenced by the hydration of CA. However, the hydration of CA_2 begins as soon as the hydration of CA has reached its maximum speed and continues afterwards for an extended period of time, contributing a significant amount of heat of hydration to the reaction. Hydrate phases formed during hydration are C_2AH_8 / $C_2AH_{7.5}$ together with amorphous AH_3.
Heat flow was calculated by combining the QXRD data obtained during hydration of the mixes together with the standard enthalpies of formation of the participating phases. Comparing the observed heat flow from calorimetry with the heat flow calculated from QXRD data, good conformance could be obtained. The results show a very clearly pronounced influence of CA_2 on hydration of CAC and its heat of hydration during the first 22 hours. After more than 10 hours the hydration of CA_2 gives the major contribution to the heat flow.

Abstract-Number: *334*

ALUMINA-GRAPHITE BASED FUNCTIONAL COMPONENTS FOR APPLICATION UNDER INDUSTRIAL CONDITIONS

Roungos V., Ludwig S., Aneziris C.G.
TU Bergakademie Freiberg, Ceramic, Glass and Construction Materials, Freiberg, Germany

In continuous casting functional components are necessary to guarantee quality, performance and safety aspects. Especially, monoblock stoppers ensure the steel flow in the casting mold and have to fulfill great demands. So it is state of the art that these components consist of carbon bonded alumina material based on their excellent mechanical, thermomechanical properties and corrosion/erosion resistance. However, the use of carbon bonded refractories involves a major drawback: carbon burn out take place and may lead to a premature component failure during casting. In this work, monoblock stoppers with additives for a self-glaze formation were produced by isostatical pressing. Their (thermo-) mechanical properties, wetting behavior, as well as the corrosion resistance were investigated with regard to the development of pilot components. Such components were tested under industrial condition and characterized afterwards. It became clear that our developed components show similiar or better properties in comparison with industrial, commercially available products. Additionally, the corrosion/erosion resistance by molten steel and molten steel/slag was promising due to a poor wetting behavior of the self-glazed components which was investigated by

sessile drop measurements and finger tests. In the near future, it may be possible to substitute currently used functional components.

Abstract-Number: *335*

IMPROVEMENT OF THE REFRACTORY LINING IN THE LD- VESSEL AT VOESTALPINE STAHL GMBH LINZ

Exenberger R.
voestalpine Stahl GmbH, Linz, Austria

The LD-vessel is the essential furnace in the oxygen steel making process in Linz. In order to ensure the production of the required amount of steel an average life time of 4000 heats had to be maintained.
By optimizing the geometry of the converter mouth, the amount of sticking skulls and the outcoming time-consuming gunning repairs were reduced. Beside improving the refractory maintenance efforts were made to improve the refractory lining. Due to low refractory costs a maximum amount of brick shapes and qualities from our inhouse brick plant should be applied. Due to a short lining time the amount of different bricks had to be kept as small as possible.
Usually you can work on brick dimensions, brick qualities, and the geometrical design.
Since bricking was done manually a maximum brick length with a small weight had to be used. The wall, slag line and tapping side bricks are 1.000 mm long with a weight of 36 kg. The length of the bottom bricks are 1.200 mm with a brick weight less than 40 kg. The slagline is in the area where the diverting bricks from the bottom to the wall are installed. From the geometrical point of view, there was no chance for improvements, since we were using a poor stress dome concept. The brick length was with 1000 mm at its limit, too. So we had to focus on the brick quality. Trials showed, that magnesiacarbon bricks based on 98% magnesia raw material and 14 % residual carbon show a better performance than magnesiacarbon bricks based on 97% Magnesia raw material and 10 % residual carbon.
The critical prewear in the bottom was intensified by the impact of the scrap during charging. Since the brick dimensions are optimized in that area too, and the dome is a low stress concept , the only adjustable screw was the brick quality again. The reduction of residual Carbon from 14% to 10% and densifying the brick by pitch impregnation was successful in reducing wear.
As a result of the improvements the average life time of the converter has been increased to 4.170 heats.
Special attention had to be given to the converter mouth. When slopping occurs, skulls remain sticking. Cleaning with a heavy digger often causes damages. In the worst case bricks may fall out. In order to continue the vessel operation, an extensive gunning repair is indispensable. By widening the mouth diameter from 3.100 mm to 3.300 mm by using shorter bricks slopping was reduced. The result was less cleaning and further less damages.

Abstract-Number: *336*

PROPERTIES OF NATURAL AND SYNTHETIC ITACOLUMITIC MICROSTRUCTURES - RULES FOR GENERATING GEOMIMETIC FLEXIBLE REFRACTORIES

Telle R.[1], Ota T.[2]
[1]*RWTH Aachen University, Mineral Engineering (Gesteinshuettenkunde), Aachen, Germany,* [2]*Nagoya Institute of Technology, Advanced Ceramics Research Center, Tajimi, Japan*

Itacolumites are natural sandstones with surprising flexibility due to interlocking grain boundaries and circumferential micro cracks. For mimicking these unique kind of mechanical behavior, Brazilian and Indian itacolumites as well as granulitic metamorphic rocks have been examined by SEM and polarization microscopy in transmitted light in order to establish rules for creating a suitable grain shape and introducing micro cracks or weak grain boundary phases. It was found that the natural itacolumitic rocks exhibit puzzle-stone shape due to subgrain formation under dissolution/reprecipitation under high-pressure/high temperature conditions and interlocking subgrain structures as well as mica interlayers allowing elastic back stresses. Load-displacement curves display a pronounced hysteresis and a large strain prior to rupture. This behavior will be discussed in respect to Dyskin-Estrin-experiments with 2D-settings of elements with an alternatively convex and concave surface curvature.
Extracting rules from these observations, one of the authors, T.O., successfully designed aluminium titanate-based ceramics with interlocking grain shape and circumferential micro cracks and, together with some dopants, interlocking subgrain structures of a spinel phase. Load-displacement curves and micrographs of in-situ arrested cracks will be discussed. The other author (R.T.)

proposed a 3D microstructure by means of FEM and DEM modeling which can be generated by means of additive manufacturing techniques such as powder-bed printing and direct inkjet-printing.

Abstract-Number: *337*

CHARACTERISTICS OF MICROPORED SINTERED ALUMINA AND ITS USE AS AGGREGATES IN AL_2O_3-MGO CASTABLE

Li Z.[1], Zhang J.[1], Lv M.[1], Li Y.[1], Zhang J.[1], Zhou N.[2], Hu S.[2], Gu H.[3]
[1]*Jiangsu Jingxin High Temperature Materials Co. Ltd., Yangzhou, China,* [2]*Henan University of Science and Technology, High Temperature Materials Institute, Luoyang, China,* [3]*State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China*

For energy saving purpose, efforts of reducing heat loss through working lining refractories without deteriorating their service performances are receiving increased importance and attention. Lightening refractory linings by using appropriately micropored raw material is meaningful in reducing thermal conductivity, releasing structural stress and improving thermal shock resistance, while maintaining other key properties, which is contributive to higher durability while lower heat loss. By special technical approach and through modeling and simulation, micropored sintered alumina has been designed and produced, featured by reduced bulk density, about 3.4g/cm^3, and significantly increased closed pores with diameters around 0.5µm, leading to reduced thermal conductivity, while other properties remain equivalent to those of conventional sintered alumina. In a typical Al_2O_3-MgO castable, such micropored sintered alumina was used as aggregates with top size of 8mm to replace commercial sintered alumina up to 60%. Comprehensive properties, in particular cold and hot strengths and static slag resistance, of the castables were compared and found equivalent or even better with the increased replacement, while thermal shock resistance gets significantly improved.

Abstract-Number: *338*

CORROSION KINETICS OF HIGH ALUMINA REFRACTORIES BY LIME-ALUMINA-SILICA SLAG

Dombrowski M.[1], de Bilbao E.[1], Veron E.[1], Pilliere H.[2], Poirier J.[1]
[1]*CEMHTI CNRS UPR3079, Université d'Orléans, Orleans, France,* [2]*Inel France, Artenay, France*

This work aimed at studying the corrosion kinetics of high alumina refractories by lime-alumina-silica slag. Two slags were used:
1) 50 wt% CaO - 50 wt% Al_2O_3;
2) 45 wt% CaO - 45 wt% Al_2O_3 - 10 wt% SiO_2.
The tests were carried out with two alumina refractory/slag ratios:
1) 85 wt% of Al_2O_3 mixed with 15 wt% of slag;
2) 60 wt% Al_2O_3 mixed with 40 wt% of slag.
Every sample was treated at temperature ranging from 1380 up to 1600°C and for times holding between 10 minutes up to 100 hours. After being quenched, the corroded samples were analysed by X-ray powder diffraction and quantified by Rietveld refinement.
The results showed that the corrosion process of alumina by CaO-Al_2O_3 slag involved two mechanisms:
1) A very fast mechanism of dissolution/precipitation between molten slag and solid alumina while slag existed;
2) A slower second mechanism of solid-state diffusion between lime-alumina crystallised phases and alumina.
The slag dissolved alumina and allowed the formation of aluminate layers. Calcium diffused through aluminate layers from slag to alumina and reacted with alumina and aluminate phases making the layers to grow up. The thicker the layers, the more difficult the diffusion of calcium ions.
According to the temperature treatment and the refractory/lime-alumina-slag ratio, the thermodynamic equilibriums were not always observed, even for long time holding. With the CaO-Al_2O_3-SiO_2 slag, the thermodynamic equilibriums were reached. Due to the silica adding, the molten slag viscosity changed and the formation rate of aluminate layers slowed down.

Abstract-Number: *339*

CARBON BONDED REFRACTORY COMPOSITES

Guillo P.[1], Mazerat S.[1], Martelli S.[2], De Bastiani D.[3], Dupuy D.[4], Huger M.[4], Chotard T.[4]
[1]Vesuvius PLC, Feignies, France, [2]Vesuvius PLC, Genova, Italy, [3]Vesuvius PLC, Pittsburgh, United States, [4]SPCTS, CNRS-UMR 7315, Limoges, France

Carbon bonded refractories used for continuous casting of steel in flow control applications (submerged entry nozzles, stopper rods, ladle shrouds slide gates) need to fulfill various strict technical requirements. The refractory materials must exhibit high corrosion/erosion resistance, low interaction with steel and liquid slags, high thermal shock and oxidation resistance while providing the required mechanical strength characteristics at 1600 °C. Moreover, the ever-increasing demand for higher quality steel grades is directly linked to the improvement of the refractories properties. Naturally, these properties are deeply interdependent where improvements in one characteristic can result detrimentally in another. For these reasons, carbon bonded refractories , truly advanced heterogeneous composites, must be highly engineered to meet the harsh working conditions and ever increasing demands on refractories during steel casting operations. Any property improvement presupposes the deep comprehension of the influence of the single constituents, e.g. multiphasic bonding matrix, hard oxide and graphite reinforcement, and of the basic mechanisms ruling the composite behavior. In this paper, the composite nature of refractory products will be explored examining the link between microstructures and corresponding properties, e.g. mechanical strength and thermal expansion.

Abstract-Number: *341*

FUSED REFRACTORY RAW MATERIALS - CHALLENGING ASPECTS FOR THEIR PRODUCTION

Gelbmann G., Muehlhaeusser J., Nilica R.
RHI-AG, Corporate R&D, Leoben, Austria

For enhanced corrosion resistance one of the most important properties of refractory raw materials is their density and respectively their porosity. One possibility to obtain dense refractory aggregates is the production by fusing in an electric arc furnace. Thereby density values close to the theoretical limits can be obtained. The fusion of these materials implies a deep understanding for the process and the individual materials. For the process mass, concentration and energy balances play an important role. As the fusion is done in cooled steel shells for economic production the minimization of crust and other not molten material is essential. With respect to concentrations there may be some enrichments in different zones of the fused block, crust and dust which have an influence on the raw material quality produced.The process parameters during production are strongly cross linked by the material properties. Here properties of the solid at room temperature as well as properties of the hot solid and liquid material are of great importance. Beneath electric conductivity density, vapor pressure and solidification behavior are of interest. Some of these properties are known to a certain degree, others are unknown or only can be assumed or measured with great difficulties. The current contribution outlines industrial production of fused refractory raw materials. Balances for energy, concentrations and mass are given and shown by examples. Furthermore some material properties relevant for solidification are shown.

Abstract-Number: *342*

THE FORMATION VELOCITY OF CA HYDRATE PHASES IN REFRACTORY CASTABLES AFTER WATER ADDITION

Tischer D.[1], Krause O.[1], Kasper J.[2], Dannert C.[2]
[1]Koblenz - University of Applied Sciences, Materials Engineering, Glass and Ceramics, Höhr-Grenzhausen, Germany,
[2]Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany

The presented work is a contribution to understand the setting and hardening kinetics for hydraulic bond refractory castables more into detail.
In the recent years the measurement of the sonic velocity to monitor the setting behaviour of refractory castables is a well-accepted method and already broadly in use. However it remains still difficult to understand in detail the increase of the sonic velocity as a function of setting time. Supplementary measurements of the electrical conductivity show that behind every increase and decrease of the sonic velocity a reproducible mineralogical and physical reason can be determined.
The presentation will show recent results that assist the interpretation of the evolution of the sonic velocity during the first 48 hours. In particular the discrimination of pore water and hydration water by gravimetric methods clearly show that an increase of the sonic velocity during the first stages of setting cannot be correlated with the formation of a hydrate phases and therefore

should me not correlated with the first setting of the castables.

Abstract-Number: *343*

CHARACTERISTICS OF ALUMINA-SPINEL CASTABLE USING NEW BIPHASE ALUMINA BASED AGGREGATES

Li Z.[1], Li N.[2], Gu H.[2], Yu Y.[2], Zhou N.[3]
[1]*Jiangsu Jingxin High Temperature Materials Co. Ltd., Yangzhou, China,* [2]*State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China,* [3]*Henan University of Science and Technology, High Temperature Materials Institute, Luoyang, China*

High purity Al_2O_3-MgO castables are of important refractories for steel ladle, purging plug, etc, for which high performance is increasingly required. The concerns of possibly sharp volumetric expansion due to *in situ* spinel formation and the risk of magnesia hydration have inhibited magnesia addition in the castable. The present work has developed a biphase alumina based (Al_2O_3≥97%) sintered material with corundum as dominant phase and dotted with fine spinel crystals. It has been used as aggregates to replace regular tabular alumina in Al_2O_3-MgO castables using white fuse alumina, fused magnesia and ultrafine α- Al_2O_3 powders as the matrix and Al_2O_3-SiO_2 gelatinized powders as binder. Properties of such new type castables heated at different temperatures were investigated in comparison with the counterpart using tabular alumina as the dominant raw material. After dried at 110℃ for 24h, regular properties of the two types of castables are found equivalent. While fired at 1000℃ for 3h and 1500℃ for 3h respectively, CCS and CMOR of the former are higher than those of the latter. With regard to thermal shock resistance of the specimens prefired at 1500℃ for 3h, represented by residual CMOR after quenching from 1100℃ to water at RT for 5 cycles, the former is better than the latter. Crucible slag test at 1600℃ for 3h indicates a significant superiority of the former in slag resistance, no matter the specimens have been prefied at 1500℃ for 3h or not.

Abstract-Number: *344*

UNDERSTANDING THE INTERACTION OF CALCIUM ZIRCONATE IN CONTACT WITH TITANIUM AND TITANIUM ALLOY MELTS

Schafföner S.[1], Aneziris C.G.[1], Berek H.[1], Rotmann B.[2], Bartosinski M.[2], Friedrich B.[2]
[1]*TU Bergakademie Freiberg, Institute of Ceramic, Glass and Construction Materials, Freiberg, Germany,* [2]*RWTH Aachen University, IME Institute for Process Metallurgy and Metal Recycling, Aachen, Germany*

This contribution investigates the corrosion behavior of calcium zirconate ($CaZrO_3$) during vacuum induction melting of extremely corrosive titanium and titanium alloy melts.
The crucibles with a volume of 0.4 l were produced by cold isostatic pressing and fired at 1650 °C. The crucibles were used to melt cp-Ti, Ti6Al4V, and TiAl and were later investigated by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD) detectors. Furthermore, the crucible material was analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray diffraction (XRD), and light microscopy. Because oxygen and other impurities impair the mechanical properties of titanium materials, the oxygen and zirconium contamination of the melts was also determined by glow discharge optical emission spectrometry (GDOES) in order to study the corrosion tendency by different melts.
All crucibles withstood several melts and exhibited no cracking by thermal shock.
Due to the evaporation of calcia during the raw material production, the fused $CaZrO_3$ raw material of the crucibles contained a significant amount of cubic zirconia as a second phase. SEM analyses revealed the preferred dissolution of the cubic zirconia phase by Ti6Al4V and cp-Ti melts. The calcium zirconate phase however remained unaffected.
Thus, the raw material composition was adjusted by adding $Ca(OH)_2$ as a calcia precursor during the crucible production. An increasing $CaZrO_3$ content of the crucibles reduced the oxygen and zirconium content of the melts to very promising levels. The remaining contamination was attributed to still present residual cubic zirconia. Crucibles containing free lime, however, caused the evaporation of calcia and should be avoided.
In case of melting TiAl a significant amount of zirconium dissolved in the melt, whereas the oxygen content increased on a much lower level. SEM and XRD investigations of the corrosion front exhibited new formed calcium aluminates, whereas titanium was almost absent.

Based on the experimental results, a corrosion model will be presented that attributes the high corrosion resistance of $CaZrO_3$ in contact with low alloyed titanium melts to an in-situ formation of CaO. Alloy melts with a high content of aluminum (TiAl), however, destroy this in-situ layer by forming calcium aluminates, which finally causes a stronger corrosion of the crucibles.

Abstract-Number: *345*

HIGH PERFORMANCE REFRACTORY DEVELOPMENTS FOR CONTINUOUS CASTING OF QUALITY STEELS

Nitzl G., Krumpel G., Eglsaeer C.
RHI AG, Vienna, Austria

The production of quality steels meeting highest cleanliness standards is often challenged by the increasing demand for lower cost refractory solutions. Design, refractory and operational performance in the plant are strongly connected with reliabaility and process reproducability from raw material to finished product cast.
This paper describes problems and refractory/design solutions during continuous casting of steel to match our customers requirements of today and tomorrow.
Flow control of liquid steel transferred from ladle to mould in order to maintain cleanliness of the steel cast shrouded by refractories thereby minimizing creation of exogen inclusions is described. Latest design and refractory features to maximize refractory to end customer quality are detailed.

Abstract-Number: *346*

EFFECT OF SODIUM ON THE THERMOMECHANICAL PROPERTIES AND MICROSTRUCTURE OF CALCIUM ALUMINATE CEMENT-BONDED CASTABLES

Alex J.[1], Vandeperre L.[1], Touzo B.[2], Parr C.[2], Lee W.[1]
[1]*Imperial College London, Dept of Materials, London, United Kingdom,* [2]*Kerneos SA, Neuilly Sur Seine Cedex, France*

Fluctuations in the quality and mineralogy of raw materials used for refractory castable manufacture can significantly affect the final product performance. Increasingly, raw materials have to be obtained from new sources leading to a higher intrinsic variability. To better evaluate the consequences of this variability it is important to establish a quantitative understanding of the effect minor elements have on refractory castables. The binder phase in many castables contains Calcium Aluminate Cement (CAC). It is commonly used for applications in extreme environments. For applications up to 1400°C silica fume is often used as a filler to improve compactness in CAC-bonded castable systems. In light of the changing market for raw materials this study aims to establish how increasing levels of sodium affect the properties of the castable system. We quantify the changes in thermomechanical properties in the presence of sodium by measuring elastic modulus, thermal expansion and creep behaviour. Phase changes are quantified by Rietveld Refinement and compared to Gibbs energy minimisation modelling in FactSage. Differences in the microstructure are identified and used to clarify the observed modifications.

Abstract-Number: *347*

EFFECT OF TIO_2 ADDITION TO A CHROME-MAGNESIA BRICK ON ITS PHYSICAL, MECHANICAL AND THERMO-MECHANICAL PROPERTIES, AS WELL AS ITS MATTE PENETRATION AND SLAG CORROSION RESISTANCE

Mulange wa Mulange D., Garbers-Craig A.M.
University of Pretoria, Materials Science and Metallurgical Engineering, Pretoria, South Africa

A high quality burnt chrome-magnesia brick, ideal for use in copper and platinum converters, has been modified by adding different amounts of nanoscale TiO_2 to the raw material mixture. This was done in an attempt to improve matte penetration and slag corrosion resistance of this brick but without reducing thermal shock resistance. Bricks with 0, 1, 3, 5 and 7 wt% TiO_2 were produced and compared by evaluating the bulk density, apparent porosity, flexural strengths (MOR), cold crushing strengths (CCS), thermal expansion and microstructures. The interactions between the five types of bricks and secondary platinum converter matte and slag were analyzed at four different temperatures ranging from 1300 to 1500ºC. The microstructures of the refractory samples and the phases that formed in the high temperature experiments were characterized using Scanning Electron Microscopy (SEM) coupled

with energy dispersive spectrometry (EDS), as well as X-ray diffraction (XRD) analysis. Results indicated that the brick that contained 1% TiO_2 outperformed the other test bricks in terms of all the evaluated properties.

Abstract-Number: *348*

COMPARISON OF BLAST FURNACE PLUGGING PRACTICE IN EUROPE AND INDIA

Hubert P.[1], Berthonneau D.[2], Dromain C.[3], Schramm M.[4], Raisane D.[5], Patranabhish T.[6]
[1]Calderys France, Iron, Steel, Foundry Markets Department, Issy les Moulineaux, France, [2]Calderys France, Iron, Steel, Foundry Markets Department, Sézanne, France, [3]Calderys France, R&D centre, St Quentin-Fallavier, France, [4]Calderys Deutschland GmbH, Iron, Steel, Foundry Markets Department, Neuwied, Germany, [5]Calderys India Refractories Limited, Iron and Steel Marketing Department, Nagpur, India, [6]Calderys India Refractories Limited, R&D, Nagpur, India

Tar bonded tap-hole clays currently remain the principle material used to plug tap - holes of blast furnaces and Corex within India. This situation is very different from that of Europe for several reasons.
In the eighties, resin bonded tap-hole clays were developed in Europe to increase the productivity of single tap-hole, and twin tap-hole blast furnaces when successive casting practice were required by reducing the plug to tap time.
Tar bonded tap-hole clays require a long time to release their volatiles and harden in the tap-hole. Consequently, local and foreign tar bonded clays still show time to time back flashing during plugging, self and explosive openings, spitting and un-controllable jet stream despite a holding time of 15 minutes min and a plug to tap time of 40 minutes min.
In Europe, resin bonded tap-hole clays enable holding times to be reduced below 2 minutes and plug to tap time down to 20 minutes without the issues observed with tar bonded clays.
The purpose of this paper is to describe the tools and methods that improve plugging practice and also to explain how the design of tap clays can improve their behaviour during plugging.
In a first step, differences between European and Indian plugging practice will be described and their consequences for plugging troubles will be point out.
In a second step, the properties of tap hole clays will be related to their behaviour during plugging.

Abstract-Number: *349*

NITROGEN-FREE MONOMERS FOR FOAM CERAMIC PRODUCTS MADE BY THE GELCASTING METHOD

Lipowska B., Śliwa A., Czechowska K., Wala T., Psiuk B.
Institute of Ceramics and Building Materials, Refractory Materials Division in Gliwice, Gliwice, Poland

Due to their mechanical properties, high surface area, resistance to chemical corrosion and stability at high temperatures, foam ceramic products made by the gelcasting method are becoming widely applied in the industry. A characteristic feature of these products is the presence of spherical macropores in their structure, which reach diameters ranging from several dozen to approximately one hundred micrometres. As a result, they can be among others applied in the filtration of hot industrial gases, as the carriers of catalysts, active electrocatalyst coatings in electrolysis or in processes characterised by the high surface area of sorptive or catalyst materials. The low thermal conductivity of this kind of products, which results from their large porosity, together with high mechanical strength and stability at high temperatures, cause that they are also high-quality insulating refractory products.
Similarly to the traditional gelcasting method used to obtain compact products, it is nitrogen-containing organic monomers, characterised by high toxicity, that are used for binding the foamed suspension. Investigations into the process of obtaining porous products by this method are mainly focused on the possibility of applying biopolymers, such as gelatine, agarose, saccharose or starch. It is known, that only the application of organic monomers allowed obtaining raw casts of foamed products characterised by the strength which enables their mechanical working after drying, before the firing process.
The aim of the undertaken work was to obtain an Al_2O_3-based foam ceramic product during the manufacture of which the toxic acrylamides are replaced by a set of hydrogen-soluble monomers that do not contain nitrogen atoms in their particle: 2-hydroxyethyl acrylate and poly(ethylene glycol) diacrylate.
We determined the type and amount of additives (liquefier and surface active agent) as well as alumina content in the suspension, which enable obtaining a stable, maximally aerated foam. The polymerization of foamed suspensions was carried out in the nitrogen atmosphere in order to avoid the phenomenon of oxygen inhibition. The obtained half-finished products were fired at

1500 ÷ 1700°C.
After firing, the products were characterised by determining their basic physical properties and microstructure. The obtained results indicate a possibility of using less toxic monomers to produce foam ceramic products by the gelcasting method.

Abstract-Number: *350*

HIGH PERFORMANCE SCRAP IMPACT PANEL IN CONVERTERS DEVELOPED USING INNOVATIVE TEST METHOD

Kumar V., Schilder M., Tamis P., Peereboom D.
Tata Steel, Ijmuiden, Netherlands

Scrap impact panel in converters is a critical area which requires a refractory brick with high strength and flexibility at high temperatures. Since impact panel has to bear the brunt of heavy scraps of different shapes and sizes, it is important that the refractory brick qualities have good high temperature impact strengths. The wear often limits the converter campaigns and reduces the availability of the vessels. The wear occurs predominantly due to the dynamic impact of falling scrap. Besides cracking and spalling, the sustained mechanical damage accelerates oxidation and the wear due to slag attack. The ability to select the most suitable brick for this application is essential for improved lining performance. Using standard refractory lab tests, no consistent solutions could be obtained neither from suppliers nor from literature.
Since the dynamic behaviour of refractories isn't well known, and no specific dynamic test standards exist for refractories, the reported study strives to answer if there is a possible relationship between the standard static tests like hot modulus of rupture and impact wear at high temperatures.
To this end an impact test was developed where samples were subjected to impact from steel balls at high temperature and inert atmosphere and were later analysed to determine the wear due to the impact. Hot modulus of rupture was also done on the respective qualities. HMOR strengths as well as epsilon were correlated to the impact test results. Based on this methodology a new quality of Magnesia Carbon brick was developed within Tata Steel in house brick plant (DSF). FEM modelling was done to check the stresses developed with this new quality around the impact panel. This was followed by successful trials in the converters at Tata Steel Ijmuiden, Netherlands.

Abstract-Number: *351*

CAUSES OF PHOSPHORUS MIGRATION IN HIGH CR_2O_3 GASIFIER REFRACTORIES AND THE IMPACT ON SLAG WEAR AND SPALLING

Bennett J.P.[1], Riggs B.W.[2], Nakano A.[1], Nakano J.[1,3]
[1]*National Energy Technology Laboratory, US Dept of Energy, Albany, United States,* [2]*Eastman Chemical Corporation, Kingsport, United States,* [3]*URS Corporation, Albany, United States*

Gasification is a high temperature/high pressure process used to convert carbonaceous materials such as coal and/or petcoke into CO and H_2, feedstock materials used in power generation and chemical production. The process of gasification is an important technology because of its high process efficiency and because environmental pollutants such as CO_2, SO_3 and mercury can be easily captured. Carbon feedstock sources used in gasification have impurities, called ash, which melt and agglomerate at the high gasification temperatures (1325-1550°C), becoming slag. Most slag becomes attached to the gasifier sidewall in air cooled entrained flow gasification systems, flowing down it and leading to wear of the refractory liner material used to protect the steel shell of the gasification chamber. High Cr_2O_3 refractory materials are the refractory liner material of choice to line the gasification chamber, but experience wear by spalling and slag corrosion - causing a service life below industry needs. Phosphate additions to the high Cr_2O_3 brick, a recent development, have been found to dramatically reduce refractory wear. In long term commercial use, migration of a phosphate compound ($AlPO_4$), within this type of refractory liner was noted. The migration of phosphorus migration was by an unknown mechanism, and has an unknown impact on refractory liner performance. Using high temperature TGA studies in controlled low oxygen partial pressures, the mechanism of phosphorus transfer has been identified as:
$4AlPO_4(s) \leftrightarrow 2Al_2O_3(s) + 2O_2(g)\uparrow + (P_2O_3)_2(g)\uparrow$
The phosphorus migration has been identified to be sensitive to both temperature and oxygen partial pressure, causing it to occur differently at different locations in the gasifier refractory lining. Through the post-mortem analysis of refractory samples, the mechanism of phosphorus migration was studied and related to possible impact on refractory wear. The results of field sample

analysis, laboratory testing, and thermodynamic studies will be presented and used to explain how phosphorus migration would occur in gasification or other refractory systems; and potential ways to control or take advantage of the movement.

Abstract-Number: *352*

INFLUENCE OF BINDING SYSTEM ON PROPERTIES OF HIGH ALUMINA CASTABLES INCORPORATED WITH SILICON POWDER AFTER CARBON EMBEDED FIRING

Xu D.[1], Shi K.[1], Zhou N.[2], Yu R.[2]
[1]*Henan Gengsheng Refractories Co., Ltd., Gongyi, China,* [2]*Henan University of Science and Technology, High Temperature Materials Institute, Luoyang, China*

High temperature properties of aluminosilicate castables can be enhanced by incorporating silicon and then carbon embedded heating. With bauxite, chamotte, silicon powder and fume silica as main raw materials, high alumina castables were prepared, using different binding systems for which CA cement, hydratable alumina and silica gel were adopted respectively. Prismatic specimens prepared by vibration casting were dried at 110℃, heated in carbon bed at 1450℃ for 6h, and then tested on their regular physical properties, hot modulus of rupture (HMOR) and thermal shock resistance (TSR). Microstructure of the related samples was analyzed by means of SEM and XRD. They are correlated with binding system of the castables. Properties at RT of the castables are satisfactory, regardless of the binding. Silica gel binding brings about the best HMOR and TSR. Increased addition of the cement leads to a deterioration of properties at high temperature. After carbon embeded heating, the added silicon powder is converted to *in situ* formed new nonoxides, like fiber- or whisker-like SiC or Si_2N_2O, which contributes to the stregthened bonding. CaO derived from the cement accounts for the formation of low melting phase, disturbing the formation of *in situ* nonoxide as additional bonding phase, and hence unfavorable to hot property improvement.

Abstract-Number: *353*

INVESTIGATION OF THE FACTORS INFLUENCING THE BULK DENSITY AND OPEN POROSITY TESTING RESULTS FOR REFRACTORY MATERIALS

Dahlem E.[1], Clasen S.[1], Dannert C.[1], Brochen E.[2], Quirmbach P.[2]
[1]*Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany,* [2]*European Center for Refractories gem.GmbH, Höhr-Grenzhausen, Germany*

At present, most testing standards published for the determination of physical, chemical and technological properties of refractory materials disclose no data on the precision of the measured values (“results”).
This study highlights the efforts that were undertaken for the determination of key parameters (“factors”) influencing the bulk density and open porosity testing results of refractory materials. Besides the generation of precision data, it is necessary to understand which instructions in the standard definitions are sensitive for diverging testing results and are therefore to be considered as key factors influencing those results.
For this to be possible an extensive investigation of the current methods was carried out. For 3 different refractory materials, 3 large scale designs of experiment including about 15 different factors with 2 levels, which can influence the results, were investigated in the FGF laboratory.
The investigation of the testing method to measure the bulk density and the open porosity has been done according to standard EN 993-1 for dense shaped refractory, and EN ISO 1927-6:2012 for unshaped refractory.
The testing parameters and experimental conditions, as well as the preparation of the specimens has been investigated. Then the most relevant factors influencing the results have been identified. Each measurement has been performed with targeted changes to the test parameters according to the Plackett-Burman experimental design. Then a second design of experiment which contains the four relevant factors has been studied for each material in four different laboratories. Hereby a solid estimation of the repeatability should be obtained.

Abstract-Number: *355*

IN-SITU DETERMINATION OF SINTERING PROCESSES IN REFRACTORY MATERIALS BY THE METHOD OF MONOTONIC HEATING (MMH)

Simmat R.[1], Brochen E.[1], Dannert C.[1], Krause O.[2], Rathaj M.[2]
[1]*Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany,* [2]*Hochschule Koblenz, Höhr-Grenzhausen, Germany*

The basic application of the Method of Monotonic Heating (MMH) is to measure the apparent thermal diffusivity of various materials. The advantages of the method applied to refractories are the continuous and fast assessment of the thermal diffusivity during heating up to 1600 °C and the relatively large and therefore representative format of the samples.
In addition to obtaining the thermal diffusivity, the method is also sensitive to phase transformations in the samples during heating/sintering. Reactions, like lattice transformations or melting, cause deviations in the apparent thermal diffusivity due to the accompanying heat of reaction. This sensitivity to phase transformations makes MMH a very useful tool for the thermal analysis of refractories.
Beyond that, permanent thermal diffusivity changes also measured by MMH indicate permanent modifications in the microstructure of the refractory product. Some phase transformations, like melting, go along with permanent thermal diffusivity changes. For example, a sudden or unusual and permanent increase in the thermal diffusivity of a green body refractory material often indicates the start of sintering.
This contribution will explain how the thermal diffusivity curves obtained by MMH can give valuable information on the changes within refractory materials as the temperature increases. It is the first of three contributions that together describe the detection of small quantities of melt and their effect on the thermo-mechanical properties of low cement castable. MMH can be a powerful tool to optimise refractories concerning their tolerance to thermo-mechanical stress within a given temperature range
Keywords: Monotonic heating, sintering behaviour, melt formation, refractory castable

Abstract-Number: *356*

ROTARY DRUM FURNACE FOR TESTING THE STABILITY OF REFRACTORIES USED IN CEMENT ROTARY KILNS AT THE PRESENCE OF SECONDARY FUEL RESIDUES

Simmat R.[1], Dannert C.[1], Knöpfelmacher A.[2], Rickert J.[2]
[1]*Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany,* [2]*VDZ gGmbH, Düsseldorf, Germany*

A significant amount of alternative fuels and raw materials (AFR) is being utilized for the production of Portland cement clinker today since they have been proved to be effective in terms of cost and environmental protection. In order to take further advantages of these benefits higher AFR portions in the fuel mixtures are desirable. This is directly linked to the question of its effects on refractories in cement rotary kilns clinker mineralogy and microstructure. A rotary drum furnace was set up in order to investigate the refractory stability at the presence of alternative fuel ashes during the production of cement in the laboratory scale. To simulate the combustion of secondary fuels, a burner system for the laboratory rotary drum furnace was developed for the injection of synthesised secondary fuel ashes directly into the natural gas/oxygen flame. The ashes inside the flame thus simulate the combustion of alternative fuels. The incorporation of fuel ash components can influence the viscosity of the clinker melt, what is an important factor for the infiltration of the refractories. Accordingly, the influence of alternative fuel ashes on the viscosity of the clinker melt was determined in the temperature range of 1300 °C to 1450 °C.
This contribution will discuss changes in the refractories after the tests in the rotary drum furnace under consideration of the viscosity results.
Keywords: cement production, refractory corrosion; rotary drum test; portland cement clinker; alternative fuel; secondary fuel; fuel ash; clinker viscosity, clinker melt

Abstract-Number: *357*

INFLUENCING THE THERMO MECHANICAL BEHAVIOUR OF MGO-C BRICKS; A SYSTEMATIC APPROACH

Siebring R.[1], Visser H.H.[1], Winnubst A.J.A.[2], Peekel M.J.M.[1]
[1]*Tata Steel, IJmuiden, Netherlands,* [2]*University of Twente, Inorganic Membranes, Enschede, Netherlands*

The importance of thermo mechanical properties of refractories is rapidly increasing in optimising the performance of refractories in the steel industry. Specially engineered refractory behaviour is necessary to further improve the life of the steel making vessels

like converter and steel ladles. Small differences in flexibility can have big effects on the performance in for instance steel ladle slagline and around the tuyeres in the converter.
To improve the materials a better and more systematic understanding of material behaviour at the different temperature regimes is required. Therefore several MgO-C bricks with pure raw materials and without anti oxidants are made with varying amounts of graphite and grain size distributions. The effect of the graphite variation on for instance thermal expansion, strength development and flexibility is investigated. Based on the investigations on thermo mechanical behaviour, the MgO-C refractories can be divided in 3 groups, with different behaviour at the different temperature zones.

Abstract-Number: *359*

NATURAL GRAPHITE RAW MATERIAL TRENDS TO 2020

Satterthwaite K.
Roskill, London, United Kingdom

By far the largest market for natural flake graphite is the manufacture of refractories for use in steelmaking, non-ferrous metals, and a wide range of other high-temperature industrial processes. Amorphous natural graphite is also used in refractory production but in smaller volumes (176,000t in 2013). Of the 511,000t of natural graphite consumed in refractories in 2013, more than 200,000tpy is consumed in China.
This market sector accounted for around 57% of total flake graphite demand in 2013 and will account for at least 54% of flake graphite demand by 2020, a slightly lower proportion of the total natural flake graphite market. By 2020, demand for natural flake graphite in refractories is expected to reach 437,000t. The refractories sector is consistently the largest volume market sector for large/jumbo flake graphite. It is only expected to grow at an average of 3.9% py to 2020 as material substitution gains for flake graphite in this application are expected to be tempered by 3.0% py growth rates for crude steel production to 2020 and by lower specific consumption rates for refractories in terms of refractory consumption per tonne of industrial product. The trend towards higher quality refractories production benefits large flake graphite consumption driven by the increased use of higher quality flake graphite in magnesia carbon and alumina-magnesia-carbon refractories. However, the trend simultaneously prolongs refractory life leading to lower overall unit consumption.
The major refractory producers (by refractory revenues) are concentrated in Europe, Japan and Brazil and these companies are keen to make sure that their flake graphite supplies are not threatened by flake graphite supply restrictions from China or increased competition for available flake graphite from the growing batteries market.
Roskill has more than three decades of experience in analysing this market and would be honoured to be chosen to present its latest research on trends affecting the market to 2020.

Abstract-Number: *361*

REFRACTORY GEL-BONDED CASTABLES WITH REDUCED AMOUNT OF WATER AND HIGHER FLOW

Myhre B., Peng H.
Elkem Silicon Materials, Kristiansand, Norway

Self-flowing castables have been around for two decades now and the various refractory producers use different strategies to improve self-flow. Common is to increase water addition in combination with more fine material, typically by lowering the so-called q-value of the particle size distribution. By doing this, normally the amount of finest fractions is increased. In this paper another perspective is chosen, and this way of re-arranging PSD will typically lead to higher flow at sometimes reduced water addition. Further, by using knowledge on the relationship between particle shape, flow and rheology, unwanted side-effects as dilatancy can be reduced or even removed for those mixes, even at very low water additions. By using these principles, castables with water additions down to below 3% have been produced while still being placeable and without using big or heavy aggregates. The castable system that is used is based on microsilica-gel bonding, a bond system that allows for fast firing and excellent hot-properties.

Abstract-Number: *363*

ASSESSING THE CHEMICAL WEAR RESISTANCE OF BLAST FURNACE CERAMIC CUP MATERIALS AT TATA STEEL IN IJMUIDEN

Small J.A., Liefhebber J.J., Zinngrebe E.W.
Tata Steel, IJmuiden, Netherlands

At Tata Steel in IJmuiden, different types of ceramic cup materials are being evaluated in terms of their thermo-mechanical properties and resistance to chemical attack from hot metal and blast furnace (BF) slag. There are many aspects in the selection of ceramic cup materials, and this paper focuses on the experiments that have been set up to test slag and hot metal (HM) attack and the subsequent microstructural investigations.
Chemical wear experiments have been performed by heating HM, BF slag, or a combination of both, under controlled gas atmospheres in cups (50 mm outer diameter, 50 mm height, 30 mm inner diameter and ~35 mm inner height) made directly from the refractory materials of interest. Several different refractory castables and bricks have been evaluated, all containing alumina as the main aggregate but having different binders and additives. The focus has been on comparing the refractories' chemical wear behaviour under the different extremes of conditions that could be expected in the BF hearth. For each material, three types of experiments were performed: 1) with (C-saturated) iron under 100% CO atmosphere to create reducing conditions, 2) with BF slag under 90% CO and 10% CO_2, also reducing conditions, 3) with both iron and BF slag under relatively oxidising atmosphere (70% CO and 30% CO_2). All experiments were carried out at 1550°C, a temperature likely to correspond to the conditions of a ceramic cup in the BF hearth, based on tap temperatures of ~1470°C and (proprietary) thermal modelling of the hearth. Cross-sections through samples were later investigated with optical and electron microscopy and micro-analysis. The wear mechanisms in these experiments are now largely understood in terms of the crucial role of the binders and additives in the chemical wear resistance.

Abstract-Number: *366*

HIGH TEMPERATURE BEHAVIOUR OF CARBON BONDED MAGNESIA (MGO-C) AT TEMPERATURES UP TO 1500 °C

Solarek J.[1], Adlmeier F.X.[1], Aneziris C.G.[2], Biermann H.[1]
[1]*Technische Universität Bergakademie Freiberg, Institute of Materials Engineering, Freiberg, Germany,* [2]*Technische Universität Bergakademie Freiberg, Department of Ceramic, Glass and Construction Materials, Freiberg, Germany*

In the Priority Programme 1418: Initiative to Reduce Emissions “FIRE” new methods are developed to reduce emission of carbon in high temperature applications like steel converters and steel ladles. For this purpose resin bonded Magnesia with a maximal grain size of 2 mm and 10 % graphite was tested using quasi static, creep and stress relaxation tests in tension, compression and bending. For testing two new high temperature testing machines, equipped with inductive heating and inert atmosphere chambers have been used at temperatures between room temperature and 1500 °C. For microstructural characterisation, scanning electron microscopy was used. The tests have shown tensile strength between 0.20 and 0.85 MPa and an elongation of fracture between 0.02 and 0.10 % at both room temperature and 500 °C. The presence of bending forces is an important issue during tensile tests of ceramic materials. Due to exact specimen alignment, bending forces were eliminated. This was proven by instrumented strain measurements.

Abstract-Number: *367*

EFFECTS OF AL_2O_3 CONTENT ON THE PROPERTIES OF MAGNESIA-MAGNESIUM ALUMINATE SPINEL MATERIALS USED IN RH SNORKEL

Li J.[1], Zhao H.[1], Xu Y.[1], Cui J.[2], Mu S.[2], Lv Y.[2]
[1]*Wuhan University of Science and Technology, The State Key Laboratory of Refractories and Metallury, Wuhan, China,* [2]*Zhengzhou Huite Group Co., Ltd, Zhengzhou, China*

Magnesia-chrome brick is the main products for RH snorkel. With more attention in pollution of Cr^{6+}, new materials such as magnesia-magnesium aluminate spinel (MgO-MA) materials for their excellent performances become attractive. Five different Al_2O_3 content MgO-MA specimens which would be used in RH snorkel were prepared using high-purity magnesia, fused magnesia and magnesium aluminate spinel sintering at 1650℃ to investigate the effects of different Al_2O_3 content (0, 7, 8, 9, 10wt.%, by changing

the amount of addictives of MA) on densification, mechanical properties, mineralogical phases formed, thermal shock resistance and microstructure of MgO-MA specimens. Results suggested that: the content of Al_2O_3 had significant influence on MgO-MA material's properties. And optimum properties were achieved in 8 wt.% Al_2O_3 content compared to other compositions.

Abstract-Number: *368*

IMPROVEMENT AND APPLICATION OF AL_2O_3-MGO GUNNING MIX IN REFINING LADLES

Shen M., Ma Z., Xue J., Fang B.
Zhejiang Zili Company Limited, Shangyu, China

In recent years, with the development of high purity and high cleanliness steel, high quality secondary refining and high treatment rate of molten steel in the ladles are required, which lead to a dramatic deterioration of the ladle refractories. In order to improve the life of the refractories in refining ladles, reduce costs and reduce labor intensity, the gunning repair of the refining ladles was alternative to the renewal of the complete lining and the effect of certain additives on the material properties was analyzed. According to the rheology theory and the actual service condition of refractories in refining ladles, the workability, sintering property and high temperature performance of corundum based Al_2O_3-MgO self-flow gunning mix for repairing of refining ladle were improved. The experimental results showed that the optimized gunning mix showed the features of good flowability, suitable setting time, labor-saving, high-strength, long service life, good insulation, high bending adhesion strength, superior resistance to thermal shock resistance and slag corrosion. The industry trials also showed a good promising repair material for the working linings of ladles.

Abstract-Number: *369*

EFFECT OF ADDITIVES ON THE SINTERING PERFORMANCE OF TITANIUM CALCIUM ALUMINATE-CALCIUM ALUMINATE-CALCIUM TITANATE MULTIPHASE MATERIALS

Wang L.[1], Zhao H.[2], Yu J.[2], Zhang H.[2], Feng L.[3], Liu Y.[3]
[1]*Wuhan University of Science and Technology, Wuhan, China,* [2]*Wuhan University of Science and Technology,The State Key Laboratory of Refractories and Metallurgy, Wuhan, China,* [3]*Jinzhou Guotai Idustial Co.Ltd, Jinzhou, China*

Titanium calcium aluminate-calcium aluminate-calcium titanate multiphase materials is Titanium-iron slag, a by-product of Ferrotitanium smelting. In order to improve its resource utilization and reduce the environment pollution, it was carried on the comprehensive performance and structure analysis. In this study, the effects of CeO_2、 Ni_2O_3、 SiO_2 as additives on sintering performance and microstructure of the multiphase materials were studied. Results indicated that: SiO_2 accelerated the sintering of samples more obviously than the others. Meanwhile, the bulk density and shrinkage rate in dimensions increased with the additions of SiO_2 increasing. The samples' bulk density and shrinkage rate in dimensions slightly changed when the percentage of SiO_2 is above 0.9%.At the same time, additives made the multiphase materials grain grow faster and pore smaller with pore closing gradually.

Abstract-Number: *372*

INFLUENCES OF CRUDE BIOGAS ON REFRACTORY MATERIALS IN THE GLASS MELTING PROCESS

Wuthnow H.[1], Dannert C.[1], Giese A.[2], Fleischmann B.[3]
[1]*Forschungsgemeinschaft Feuerfest e.V., Hoehr-Grenzhausen, Germany,* [2]*Gas- und Wärme-Institut Essen e.V., Essen, Germany,* [3]*Hüttentechnische Vereinigung der Deutschen Glasindustrie e.V., Offenbach, Germany*

Thermal processes in the modern industry such as melting of glass and firing of ceramic products need enormous quantities of natural gas. Under ecological aspects it is important to reduce the emissions of CO_2 and to increase the amount of renewable energies. An interesting solution is the use of biogas. This alternative energy can be produced using biogenic materials as well as residues. But in untreated biogas a certain level of impurities occur which can lead to corrosion reactions in contact with refractory materials.
These influences on the behavior and the properties of different refractory materials and therefore on their lifetime were investigated. Ceramic materials like silica, mullite and AZS for the use in glass melting tanks at temperatures of about 1500 °C and

magnesia zircon, developed for the use in the regenerator of glass melting tanks below about 1350 °C during cooling of the exhaust gas and condensing of salty products, were fired with different crude biogases and examined after use. The results showed that in general it is possible to use crude biogas for firing in the glass melting process. The refractory materials showed no failure but some differences in reaction kinetics and structure.

Abstract-Number: *373*

NEW DEVELOPMENTS FOR STEEL LADLE BOTTOM IMPACT PAD

Souza Ramos V.P.[1], Frasson S.C.[1], Sako E.Y.[1], Galesi D.F.[2], Lima H.A.A.[2], Rodrigues F.A.[1]
[1]Saint-Gobain do Brasil, Refractories Technical Department, Vinhedo, Brazil, [2]Saint-Gobain do Brasil, Refractories Application Engineering, Vinhedo, Brazil

A new alumina-magnesia-carbon product has been developed to overcome the strong wear at impact pad on steel ladles bottom. Characteristics as hot modulus of rupture and thermal shock resistance has been improved resulting in higher life of the steel ladle equipment.

Abstract-Number: *374*

INVESTIGATION INTO FACTORS INFLUENCING THE COLD CRUSHING STRENGTH RESULTS OF DENSE SHAPED REFRACTORIES

Czechowski J.[1], Podwórny J.[1], Gerle A.[1], Dalhem E.[2]
[1]Institute of Ceramics and Building Materials, Refractory Materials, Gliwice, Poland, [2]FGF, Forschungsgemeinschaft Feuerfest, Höhr-Grenzhausen, Germany

Compressive strength is commonly used for characterising the properties of refractory materials. There are a number of standards which specify the methodology applied for testing dense shaped materials, insulating materials and unshaped materials. They contain requirements regarding the shape and size, the dimensional tolerance of test pieces, the manner of their preparation, the load rate and preload applied, the hardness and roughness of loading plates as well as the use of packing. These requirements are not fully defined in all the standards. Moreover, there are factors not defined in standards which can influence the obtained results of cold crushing strength (CCS).
The article presents investigations conducted within the framework of ReStaR project, aimed at determining the influence of factors related to the CCS determination procedure on the results.
In order to identify factors having the greatest influence on CCS determination of dense shaped refractory materials the experimental design was applied. Tested factors has been set on two levels. In the first step of investigations from 14 analysed factors a few with the strongest impact were identified. On the base of it four factors were selected for more detailed studies during interlaboratory comparison tests. The results were used to formulate proposal of changes in dense shaped refractories cold crushing strength determination procedure.

Abstract-Number: *375*

VIBROCAST SHAPES FOR GLASS APPLICATIONS

Reiter V.[1], Dietrich M.[2], Postrach S.[2]
[1]RHI AG, Leoben, Austria, [2]RHI Glas GmbH, Wiesbaden, Germany

The size and the complexity of refractory blocks produced by pressing and hand ramming is limited. The vibrocast technology can overcome these limitations and complex shapes with a height of up to 400 mm and a length of more than 2000 mm can be produced. This means, blocks may have a weight of 1 ton or even more. With vibrocasting the supply of high-quality, high-fired glass furnace parts for applications in container glass and fiber glass furnaces is possible. The main application fields are large and heavy blocks as elements of the forehearth (e.g. channel and feeder cover) or the furnace superstructure (doghouse arch). The method enables also the production of complex structured elements like burner blocks or large shapes for the hot repair of furnace crowns.

The main requirements on refractory material in feeder channels are an excellent corrosion resistance against glass melts and a very low potential for glass defects, whereas in the feeder superstructure beside the resistance against vapors the hot properties are essential. Adapted to the various requirements in glass furnaces a portfolio of several grades based on different raw material concepts has been established. As the corrosion mechanism strongly depends on the chemical composition, mineral phases, microstructure (texture, cracks), porosity, the surface quality and chemical impurities (e.g. iron oxide, titanium oxide), carefully selected raw materials with high purity are used. Fired precast shapes composed of zirconium mullite, tabular alumina, andalusite, fused silica and chrome corundum are available. The precast shapes are based on ultra low cement and low cement castables with a maximum CaO content of 0.2-1.8 wt.%. During production special emphasis has to be placed on the drying and firing process of the pre-cast shapes as the firing temperature and the firing intensity strongly affect the product quality. Flexible and complex temperature programs are necessary to adjust the temperature curves to the product properties (e.g. format and grade composition).
The vibrocast shapes exhibit excellent characteristics for the different application areas and show even for complex geometries and large shapes a homogeneous structure as well as a high surface quality. In the paper the physical and thermo-mechanical properties (refractoriness under load, creep resistance) of the available portfolio are presented. Additionally, emphasis is placed on the results of corrosion and alkali vapor tests.

Abstract-Number: *377*

RESONANT FREQUENCY YOUNG'S MODULUS DETERMINATION OF CYLINDRICAL SAMPLES WITH INCONGRUOUS GEOMETRY

Manhart C., Marschall H.U., Urbanek G.
RHI-AG, Leoben, Austria

The aim of this work is to find a way to get the Young's Modulus of cold crushing strength cylinders (acc. to ISO 10059) by the resonant frequency method according to ASTM 1259-14. The incongruous geometry of the cylindrical samples with a diameter of 50 millimeters and a height of 50 millimeters causes an increase of the uncertainty in the resonant frequency determination.
The measurement result is a frequency spectrum on which the resonant frequency couldn't be certain identified. For the resonant frequency identification there are two challenges given: The amplitude height of the resonant frequency depends from unknown material factors and the frequency values of the vibration modes are very near to each other. This causes an uncertainty for identification and calculation of the Young's Modulus.
The aim of the described investigation is to remove or reduce the uncertainty by the resonant frequency determination. The investigation contains resonance frequency calculation by the standardized Young's Modulus formulas for the vibration modes, a finite element simulation to identify the resonant frequencies of the vibration modes and a number of specimens measured to get the real frequency values. All results superimposed to get an overview.
The calculation, finite element simulation and measurement data reveal for each vibration mode a typically resonant frequency relation. This relation values are unique for the cylindrical geometry. The resonant frequencies can found by the relation identification method in the frequency spectrum. This is a certain way to determine the Young's Modulus of cylinders with an incongruous geometry. Now the resonant frequency relation identification method reduces the measurement uncertainty successfully.
In the RHI the resonant frequency method can now be used as a specimen selection tool for Round Robin Tests of crushing strength cylinders. It helps to select specimens with a suitable Young's Modulus range for each participating laboratory. RHI supported the ReStaR-Project with this tool too.

Abstract-Number: *378*

ADVANCED PRECERAMIC PAPER DERIVED MULTILAYER REFRACTORIES WITH INTEGRATED $LACRO_3$ BASED SENSORS FOR ON-LINE STRUCTURE HEALTH MONOTORING

Bonet A., Travitzky N., Greil P.
University of Erlangen-Nuremberg, Erlangen, Germany

Due to superior thermal stability and high electrical conductivity at high temperatures as well as tailorable materials properties, lanthanum chromite based electric sensor structures integrated in multilayer composite devices might offer a high potential for

structure health monitoring in advanced refractory components. For example, lanthanum chromite resistance grids integrated in refractory alumina/zirconia based multilayer devices (e. g. nozzles) can be used to detect thermal shock induced crack formation and corrosion reaction controlled melt infiltration into the refractory components used in metal melt casting. Since those components suffer from very short lifetime of less than 24 h, due to high degradation and safety aspects in steel casting, structure health monitoring might offer longer service life. Major challenges arise from co-sintering of lanthanum chromite - alumina/zirconia multilayer composites, matching of coefficient of thermal expansion to prevent misfit stress generation upon thermal cycling and microstructure stability over long term operation at elevated temperatures. $LaCrO_3$ based sensor structures were screen printed on preceramic papers, laminated and co-sintered to multilayer refractory components. Thermal, chemical and mechanical stability of the composites during thermal cycling and long term operation at 1600°C was investigated. Integrated sensors were tested in view of on-line detection of thermal shock induced crack formation and corrosion reaction controlled melt infiltration of an industrial CaO-Fe_2O_3-SiO_2 slag.

Abstract-Number: *379*

HIGH-TEMPERATURE CORROSION OF ZIRCONIA REFRACTORIES BY LIQUID STEEL AND SLAG

Szczerba J.[1], Wiśniewska K.[1], Madej D.[1], Grabowy M.[2]
[1]*AGH University of Science and Technology, Ceramic and Refractories Materials, Krakow, Poland,* [2]*Zakłady Magnezytowe "Ropczyce" S.A., Ropczyce, Poland*

One of the possible applications of zirconium oxide is metering nozzle in tundish for continuous steel casting. The nozzle is mounted at the bottom of the tundish and it is exposed to corrosive effect to liquid steel and slag at temperature up to 1600°C.
In this study the corrosion behavior of the zirconia metering nozzle after service in continuous steel tundish were investigated. The Mg-partially stabilized zirconia nozzles were isostatically pressed and fired under industrial condition. The nozzles after various service times in tundish were compared with nozzle 'as delivered'.
The phase composition and chemical composition were investigated by X-ray diffraction (XRD) and X-ray fluorescence (XRF), respectively. The microstructure of the nozzles was observed using the Scanning Electron Microscope (SEM) coupled with an energy dispersive x-ray system (EDS). Compactness was measured by Archimedes method.
The major phases present in the metering nozzles were monoclinic zirconium oxide and Mg-stabilized zirconium oxide. In each of the corroded nozzle was possible to distinguish two zones, light zone- uncorroded area of the nozzle and dark zone from the "hot face" of the nozzle. Furthermore, cracks along the surface of the brick were present in all corroded nozzles. SEM/EDS investigation confirmed that during corrosion process liquid steel and slag infiltrate the zirconia nozzle. The XRF analysis showed that the amount of components such as: MgO, CaO, Fe_2O_3, Al_2O_3 has changed with increasing time of corrosion test.

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Abstract-Number: *382*

PERFORMANCE OF REFRACTORY IN EXTREME SERVICE CONDITIONS IN REFINERY AND PETROCHEMICAL INDUSTRIES

Saha P., Lahiri P.P.
Engineers India Limited, New Delhi, India

Refractory used in process plant for to serve the two purposes, one is for conservation of heat energy and other is for to protect the casing. Refractory act as liner face for severe atmosphere, so knowledge of corrosion/erosion behaviour of refractory is utmost important for selection of refractory in severe atmosphere e.g. particle carrying through hot gases in Fluidized catalytic cracking unit, process gas nascent hydrogen directly in contact with refractory in Cold collector and process gas boiler in hydrogen reformer and Main Combustion Chamber, Incinerator in a Sulphur Recovery Unit where refractory is exposed in high temperature sulphurous atmosphere in Refinery and petrochemical industries. In many cases it has been seen that corrosion of refractory and ancillaries leads to immature failure of refractory and forces a unit to take un-wanted shut down. In this paper an effort has been made to identify the nature of corrosion of refractory for the aforesaid unit and selection/design criteria of refractory to prevent the corrosion/erosion of refractory.

Abstract-Number: *383*

EFFECT OF MGO ADDTION ON MULLITIZATION AND SINTERING BEHAVIOR OF ANDALUSITE POWDER

Li K.[1], Li L.[2], Wang Q.[2], Liao G.[2], Qian Y.[2], Ye G.[1]
[1]*Zhengzhou University, Zhengzhou, China,* [2]*Luoyang Institute of Science and Technology, Department of Materials Engineering, Luoyang, China*

It is known that the mullite formation temperature and glassy phase compositions of andalusite powder are of interest to refractories producer. The reduced temperature of mullite formation through incorporation of MgO and CaO in andalusite has been studied. In this research, the effects of MgO, Al_2O_3, TiO_2 on the amount and compositions of the glassy phase and therefore on the sintering properties of andalusite powder were investigated. Different amounts of MgO and Al_2O_3 and TiO_2 were added in andalusite, and then the samples were fired at temperatures between 1150°C and 1600°C with intervals of 50°C for 2h. The bulk density, apparent porosity and linear expansion of samples were determined and phase compositions (especially of glassy phase) and microstructures were studied by X-ray diffraction, SEM and EDS.

Abstract-Number: *388*

MONITORING TOOLS DEDICATED TO THE DRYING OF CASTABLES COUPLED TO A NUMERICAL MODEL: A POWERFUL METHOD FOR A SAFE AND FAST DRYING OF REFRACTORY CONCRETE LININGS

Abdelouhab S.[1], Martic G.[2], Cambier M.[1], Gonon M.[2], Lardot V.[1], Cambier F.[1]
[1]*CRIBC, Research and technological support department, Mons, Belgium,* [2]*UMons, Pôle Matériaux-Service Science des matériaux, Mons, Belgium*

During the drying step of refractory castables bonded by hydraulic cements, the water contained in the castable transforms into vapour. The steam pressure inside the material rises with the temperature increase and can become higher than the tensile resistance of the material. It leads to some lining damages. The present work is focused on the monitoring of the drying and the development of a numerical model to reach the final goal of a safe and faster drying of refractory concrete linings.
Monitoring drying tests were realised with large concrete samples. The slabs were instrumented with thermocouples and acoustic emission sensors. The slabs weight was also measured during tests. The heating was conducted in a furnace allowing semi-industrial heating conditions, from room temperature to 450°C during 24H. Three different heating rates were applied: 0.25, 0.5 and 1°C/min. The results obtained with a LCC castable with a 6% in weight of water added in the starting mixture show a critical temperature zone during the drying, between 100°C and 200°C. This zone corresponds to ebullition phenomena. The acoustic sensors allow the detection of the end of drying when all of the chemically bonded water is eliminated. The time at which the maximum steam pressure is reached inside the material can be determined thanks to the derivate of weight loss measurement as a function of time. The evolution of critical parameters and the different drying steps (ebullition phenomena, maximum steam pressure, etc.) in function of the heating rate applied are used to set up a numerical model which is implemented with concrete properties (tensile resistance, permeability, etc.). The numerical model developed indicated a good agreement between the simulated time at which the maximum steam pressure is reached and those determined experimentally. The maximum steam pressure can be also located according to the slab thickness thanks to the model. For this concrete it is close to the hot surface for any heating rate applied. This model can be used to apply a critical heating rate where the maximum steam pressure reached in the material during the drying is just lower than the maximal tensile strain that can be supported by the concrete.
The use of monitoring tools dedicated to the castables drying coupled to the development of a numerical model can be a powerful method in order to optimise a safe and faster drying during the first heat up leading to energy and time savings.

Abstract-Number: *389*

THE INFLUENCE OF DIFFERENT PYROLYSIS TEMPERATURES ON THE HIGH TEMPERATURE YOUNG'S MODULUS OF AL2O3-C

Werner J., Aneziris C.G.
TU Bergakademie Freiberg, Ceramics, Glass and Construction Materials, Freiberg, Germany

Carbon-bonded refractories are widely used in steel industry as functional components and as lining material (e.g. BOF). They are well known for their outstanding thermal shock behavior. The knowledge of the elastic properties at high temperatures will provide simulation of thermal shock resistance with unknown data or supports the understanding of the material microstructure.
In this work we present results regarding the Young´s modulus of elasticity (E) of carbon- bonded alumina refractories at high temperatures with variation in the pyrolysis temperature. Using the method of impulse excitation, one can accurately determine E up to 1450°C in air and inert gas atmosphere. Therefore, a sample is excited by a projectile, resulting in an oscillation. From that the resonance frequency of the material can be obtained. According to ASTM 1876, E can be calculated using that frequency. A novolac resin was used as bonding agent. The samples were coked at 700,1000 and 1400°C. To obtain possible hysteresis effects, the cycles were repeated. Additional thermal expansion measurements were carried out to compare with the Young's modulus measurements.
As a result, one can model the thermal shock and thermo-mechanical behavior of carbon- bonded materials due to the available temperature depending Youngs modulus of elas- ticity. Furthermore, the influence of firing on the thermal shock behavior can be evalu- ated.

Abstract-Number: *390*

EXPERIMENTAL STUDY OF THE COMPRESSION BEHAVIOUR OF REFRACTORY CASTABLES USING IN-SITU X-RAY MICROTOMOGRAPHY

Hubálková J., Aneziris C.G.
TU Bergakademie Freiberg, Institute of Ceramic, Glass and Construction Materials, Freiberg, Germany

This study presents results of macrostructural damage development and failure of refractory castables during mechanical in-situ testing using X-ray microtomography. The damage initiation and propagation have been investigated at different stages of compression loading. During the tomographic scans the loading was kept constant, i.e. so called interrupted in-situ testing was carried out. Two kinds of in-situ experiments were performed - monotonic and cycling loading. Using 3D image analysis software MAVI (Modular Algorithms for Volume Images), the visualization as well as the quantification of the structural and crack volume features, such as crack specific surface, can be done. The crack volume features were related to the parameters derived from the in-situ load-deformation curve.

Abstract-Number: *391*

MICROSTRUCTURE AND PROPERTIES OF ALUMINA-CARBON CASTABLES USING CARBIDE COATED CARBON

Ye J.[1], Thachray R.P.[1], Lee W.E.[2], Zhang S.[3]
[1]University of Sheffield, Sheffield, United Kingdom, [2]Imperial College London, Materials, London, United Kingdom, [3]University of Exeter, Exeter, United Kingdom

Water-wettable carbide coatings were prepared on graphite flakes and carbon black respectively by using a low temperature molten salt synthesis technique. Their effects on water demand, flowability, physical/mechanical properties, and oxidation resistance of model alumina-carbon castables were investigated. The water demand was evidently reduced from 8-10 to < 6.5 wt%, resulting in a considerably reduced apparent porosity and increased bulk density. Moreover, compressive and bending strengths of castables using coated carbon (after coking at 1500 ^{o}C) were respectively 6 and 3-5 times higher than those of castables using uncoated carbon. Microstructure examinations revealed that carbide coatings improved the compatibility between carbon materials and cement matrix and oxide aggregates. In addition, oxidation test results revealed that castables using coated carbon showed much improved oxidation resistance compared to those using uncoated carbon, which was attributed to the reduced porosity as well as effective protection from the carbide coatings.

Abstract-Number: *392*

NEW MATERIALS AND IMPROVEMENTS FOR THE GLASS INDUSTRY-PART 2

Frasson S.C., Guerra M.A.F., Ramos V.P.S., Sako E.Y., Rodrigues F.A.
Saint-Gobain do Brasil, Vinhedo, Brazil

This paper shows the development and improvement of new materials for the glass market.
These materials have 10 and 20% ZrO_2, to support the most aggressive applications in glass market
This paper will show the development of materials and details of its use in the glass industry.

Abstract-Number: *393*

CARBON BONDED MGO-C REFRACTORIES WITH LOW PAH CONTAINING BINDER SYSTEM

Weber A.[1], Ludwig S.[2], Mertke A.[2], Aneziris C.G.[2]
[1]*IMERYS/S&B Minerals GmbH & Co KG, Metallurgy, Neuss, Germany,* [2]*Technische Universität Bergakademie Freiberg, Institut für Keramik, Glas- und Baustofftechnik, Freiberg, Germany*

Due to unique mechanical, thermal and chemical properties carbon bonded MgO-C bricks are established as high refractory products in steelmaking industries in particular for applications in converters, electric arc furnaces and steel treatment ladles. In terms of this contribution different binder systems will be compared according to their physical and thermo mechanical properties. The combination of an environmental friendly artificial resin with an environmental friendly thermocarbon binder has led to improved residual strengths after one and five thermal shock cycles. Further compositions with metallic and inorganic additions based on the same binder system have been explored, but no further improvement was identified according to the thermo mechanical performance.

Abstract-Number: *394*

INFLUENCE OF FEO/SIO_2 RATIO OF ZNO-RICH FAYALITE SLAGS ON THE DEGRADATION OF MAGNESIA-CHROMITE REFRACTORIES UNDER REDUCING ATMOSPHERE

Chen L., Guo M., Shi H., Jones P.T., Blanpain B., Malfliet A.
KU Leuven, Department of Materials Engineering, Leuven, Belgium

The objective of this work is to investigate the influence of the FeO/SiO_2 ratio of ZnO-rich fayalite slags on the corrosion behavior of magnesia-chromite refractory under reducing atmosphere. These slags may occur in secondary copper smelting units, which are gaining importance in the world copper production. Rotating finger tests with a direct-bonded magnesia-chromite refractory submerged in ZnO-rich (20 wt.%) secondary smelting copper slags (ZnO-FeO-SiO_2-Al_2O_3-CaO) were performed in a vertical tube furnace under reducing atmosphere at 1200 °C for 4 h. The degradation behavior of the magnesia-chromite refractory is determined through microstructure characterization of corroded fingers with Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS). Both periclase and chromite grains are attacked more by the slag with lower FeO/SiO_2 ratio as concluded from the higher MgO dissolution and severe ZnO-containing spinel decomposition from primary chromite grains. On the other hand, formation of (Zn,Fe,Mg)O solid solution by ZnO and FeO diffusion into periclase is enhanced in the slag with higher FeO/SiO_2 ratio. The results show that from the view of furnace lining protection, use of higher FeO/SiO_2 ratio ZnO-rich fayalite slags in secondary copper smelting would be beneficial.

Abstract-Number: *395*

CORRELATION OF PHOSPHATE AMOUNT IN BIOMASS SLAGS AND THE MICROSTRUCTURAL CHANGES DUE TO CORROSION OF ALUMINA AND ANDALUSITE REFRACTORIES

Tonnesen T.[1], Loison L.[1], Hausser M.[2], Telle R.[1]
[1]*RWTH Aachen University, Institut für Gesteinshüttenkunde, Aachen, Germany,* [2]*ENSCI Limoges, Limoges, France*

Economic and environmental issues are responsible for the use of alternative fuels like biomass or waste as replacement for fossil fuels. The chemical composition of the alternative fuels influences directly the corrosive environment present in waste and biomass incineration facilities. The increased complexity of the corrosive components, mainly alkalis, sulfates and phosphates lead to higher wear level in comparison to the traditional combustion of fossils. The refractory materials used in the incineration process have to be adapted. The aim of these studies is the research of corrosion mechanisms and effects of multi component systems taking place in the biomass/waste-to-energy plants in order to achieve a technological advantage by customizing the composition and the microstructure of refractory materials. Therefore, two families of refractory materials will be tested: alumina based castables and phosphate bonded andalusite bricks. So far only few scientific works are devoted to the effect of phosphate on corrosion of refractories. In these studies the influence of phosphate on microstructural modifications of different alumina castables and andalusite bricks during laboratory corrosion tests were examined using an industrial related slag with varying phosphate amounts. A thermodynamic model, by using the software package FactSage, was worked out and applied on the different refractory compositions to predict phase formation and corrosion. Phase formation was experimentally determined with X-Ray Diffraction (XRD) and the melting behavior of the different slag samples as well as interfacial reactions were analyzed by means of hot stage microscopy. Slag and post-mortem crucible test analyses were furthermore achieved. Microstructural changes were quantitatively correlated with high temperature Young's Modulus measurements using Resonance Frequency Damping Analysis (RFDA). In order to examine the infiltration of the slag samples in the refractory microstructure and to define dissolution behaviour and high temperature reactions of the different materials corroded refractory samples were observed by means of Scanning Electron Microscopy (SEM).

Abstract-Number: *396*

MODULUS OF RUPTURE OF REFRACTORY CASTABLES: OPTIMIZATION OF TEST PARAMETERS

Wilkerson K.R.[1], Smith J.D.[2], Hilmas G.[2], Burns E.[2], Kennedy S.[2], Kuzara M.[2]
[1]*Allied Mineral Products, Inc., Columbus, United States,* [2]*Missouri S&T, Rolla, United States*

The industry standard for measuring the modulus of rupture (MOR) of refractory materials currently uses three-point flexural testing based on ASTM C133-97(2008)e1. This study is designed to optimize specimen size and number of specimens tested to determine whether or not the procedures outlined in ASTM C133 are both an appropriate and efficient method for measuring the MOR of refractory castables. Mullite-based, low-cement castable was selected as the material for the study. Initially 40 specimens, nominally 1x1x7” in size, were tested. The initial study was designed to verify the applicability of using the Weibull analysis model, as opposed to other statistical models such as the Gaussian or lognormal distributions. Further testing and statistical analysis was then performed on sample groups consisting of varying numbers of specimens (i.e. three to 40), the sizes of which were selected based on the ASTM standards for testing advanced ceramics and concrete (ASTM C1161-13 and C293/293M-10, respectively). The statistical significance and reproducibility of all sample groups were then collectively analyzed and compared.

Abstract-Number: *397*

HOT METAL CORROSION OF REFRACTORY MATERIALS FOR BLAST FURNACE HEARTH

Camelli S.[1], Rimoldi M.[1], Marsiglia N.[1], Marinelli P.[2]
[1]*Instituto Argentino de Siderurgia, Material Refractories, San Nicolas, Argentina,* [2]*Ternium Siderar, San Nicolas, Argentina*

Conditions in the blast furnace vary widely by zone and the refractories are subjeted to a variety of wear mechanisms. Particularly, the prevailing types of wear in the hearth are of chemical nature, such as alkali attack, CO-disintegration, slag corrosion, oxidation and iron penetration. Appart form the chemical wear mechanisms, the hearth lining is subjected to stress due to temperature fluctuations which can be as high as 500°C and erosion by hot metal/ slag/ coke bath.
Hearths are generally composed of varying grades of carbonaceous and ceramic materials, zoned to take advantage of the properties of each grade and to minimize wear. A variety of design concepts and materials, that withstand these wear mechanisms, eliminate hearth problems and maximize life, are avaliable to the blast furnace user. New carbon blocks have been developed, which have superior characteristics: prevention of matrix solution by adding alumina and by adding silicon, improvement of pore size distribution to reduce and avoid pig iron infiltration by improved forming method and thermal conductivity by using natural graphite.
The objetive of this work was to evaluate the corrosion behavior to hot metal attack of different carbon grades and cermic refractory materials used in blast furnace hearths. In order to evaluate the corrosion mechanism, there were performed dipping

tests with unsaturated C-hot metal at 1550°C.
The refractory materials under study were also chemical, physical, mechanical, thermal and microstrutural characterized to correlate with their corrosion resistance.

Abstract-Number: *398*

GEL BONDED CEMENT FREE SHOTCRETE

Nguyen J.[1], Volk R.[1], Caprio J.[2]
[1]*Uni-Ref Inc., Sharonville, United States,* [2]*United Refractories Company, McMurray, United States*

Gel bonded shotcrete is a cement free single component system that delivers improved performance versus cement bonded shotcrete systems. The gel bond system contains no chemically combined water allowing dry-outs to be accomplished in half the time required for cement bonded materials. Significantly improved hot mechanical properties are achieved by eliminating fluxing agents. For a typical mullite shotcrete, 1400°C hot modulus of rupture increases from 10 to 17 MPa. Relative to colloidal silica based systems, the Gel bonded shotcrete is much easier to install and more cost effective with field savings in the 10-20% range.

Abstract-Number: *399*

EFFECTS OF ADDITION OF SIC WITH DIFFERENT PARTICLE SIZE ON PROPERTIES OF SILICA BRICK

Zhang H.[1], Liao G.[2], Li L.[2], Wang L.[2], Wang Q.[1,2], Ye G.[1]
[1]*Zhengzhou University, Zhengzhou, China,* [2]*Luoyang Institute of Science and Technology, Luoyang, China*

It is well known that various properties of oxide refractory, including its mechanical property, thermal property and chemical corrosion resistance, could be affected through addition of some non-oxides such as silicon nitride and silicon carbide. In this work, by way of adding 325 mesh and 1000 mesh of SiC powder in silica brick specimens respectively and changing their addition amount, effects of different particle sizes of SiC powder on apparent porosity, bulk density, cold crushing strength (CCS), refractoriness under load (RUL) and thermal conductivity of the silica brick specimens were investigated, with the aim at increasing the thermal conductivity of the silica brick. X-ray diffraction technique was adopted to analyze the phase compositions of the specimens, and the microstructure of some typical specimens was examined by SEM.

Abstract-Number: *400*

STRUCTURAL AND MICROSTRUCTURAL STUDY ON HERCYNITE AND ITS SOLID SOLUTIONS

Jastrzębska I., Szczerba J., Stoch P.
University of Science and Technology, Faculty of Materials Science and Ceramics, Kraków, Poland

Compounds with spinel structure, so-called 2-3 spinels, like regular spinel or hercynite, are today of great technological importance due to their beneficial physicochemical and mechanical properties and because they can act as 'substitutes' in the production of toxic chrome-containing refractories. Endmembers $FeAl_2O_4$ and $MgAl_2O_4$ are the examples of the spinel minerals rarely encountered in nature and characterised by the high melting points of 1780°C and 2135°C, respectively. Although the properties of spinel sensu stricto ($MgAl_2O_4$) are well explored in the literature, the information about microstructure and high temperature behaviour of $FeAl_2O_4$ and $FeAl_2O_4$-based materials are very scarce. Therefore, this work aims to give a deeper insight into the structure and microstructure of hercynite as well as hercynite-spinel solid solutions.
It is well known that synthesis of these two spinels is not easy and requires apart from high temperature, mostly above 1500°C, also special treatment of two-stage process in case of spinel, and highly controllable atmosphere with low oxygen partial pressure when considering hercynite. Therefore, in this work synthesis of spinel compounds $Fe_{1-x}Mg_xAl_2O_4$ ($0< x\leq 1$, x=0.1, 0.3, 0.5, 0.7, 0.9) was carried out by a non-classical method of arc melting, which allowed to obtain fully reacted pure materials. The precursors of spinels used in the present study were high grade oxides Fe_2O_3, Al_2O_3 and MgO. The homogenous and stoichiometric mixtures of the proper oxides were pressed into pellets and subsequently subjected to melting in arc furnace Spekoarc 300. The obtained materials

were characterised in terms of their phase composition by XRD and structure parameters. The content of iron ions and their occupancy among tetrahedral and octahedral sites in the structure were determined by Mössbauer spectroscopy. The observation and detailed analysis of the micostructure was performed by SEM/EDS method, both on the fractures and polished cross-sections. Additionally, a mechanism of spinel crystal growth was established in this work.
It has been investigated that obtained hercynite characterises by the well ordered structure with a low inversion parameter, high purity and well developed crystals.

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Abstract-Number: *401*

FORMATION OF NANOSTRUCTURED CARBONS IN MGO-C BODIES

Khaki Hendijani A.[1], Golestanifard F.[1], Rezaie H.[1], Khalili N.[2]
[1]*Iran University of Science and Technology, School of Metallurgy & Materials Engineering, Tehran, Iran, Islamic Republic of,* [2]*Aryan Fars Refractories Co., Shiraz, Iran, Islamic Republic of*

Magnesia-carbon (MgO-C) refractories are among the most applicable refractory materials used in steel industries in basic oxygen furnaces, electric arc furnaces and steel ladles. However some drawbacks caused by high carbon content like poor oxidation resistance, excessive heat losses through furnace shell, steel temperature drop and potential of carbon transfer from lining to melt, are always known as challenges in this field of refractory materials. With lowering carbon content in MgO-C refractories, one may decrease the difficulties mentioned above, but some excellent properties such as thermal shock resistance will also decline. In this study, the possibility of In-Situ formation of nanostructured carbons (CNFs and CNTs) by catalytic synthesis, in MgO-C bodies was investigated. Different amounts of nano nickel catalyst, prepared by chemical method, were mixed with phenolic resin and micron size magnesia particles. FE-SEM micrographs demonstrated formation of CNTs and CNFs at around 1000°C in coke beded samples. Also XRD patterns confirmed the graphitization of residual carbon from resin in as mentioned samples. It was found that formation of In-Situ nanostructured carbons would lead to improve mechanical strength which can be attributed to crack arresting.

Abstract-Number: *402*

ROLE AND POSITION OF IRON IN MAGNESIA AGGREGATS

Szczerba J., Stoch P., Prorok R.
AGH - University of Science and Technology, Materials Science and Ceramics, Krakow, Poland

Magnesium oxide is a substance of versatile application, but use of MgO for specific and advanced application is limited by its purity. One of the most common admixtures coexisting with magnesium oxide are iron oxides which amount and distribution strongly influence on properties of MgO such like melting point, mechanical properties in high temperature, corrosion resistance and etc. This is particularly important in case of refractory materials, which works in hard conditions like high temperatures, reducing or oxidizing conditions, etc.
Refractories industry use relatively high purity magnesium oxide called magnesia, amount and distribution of iron oxides in magnesia depends on quality and type of starting raw materials and on the other hand on a manufacturing process. Magnesia during commercial production is usually subjected of sintering or melting techniques. This two types of heat treatment processes strongly influence on properties of magnesia in respect to amount and distribution of iron oxides. That why determination of heat treatment in terms of amount and location of iron oxides in MgO crystal structure is a very important matter.
The ^{57}Fe Mössbauer Effect, XRD, SEM+EDS, XRF measurements of sintered and fused magnesia samples at room temperature were conducted. The samples contained different amounts of Fe_2O_3 ranging from 0.2 to 8 mass. %. If the iron concentration is low most of the iron atoms are present as Fe^{2+} in octahedral coordination and substitute Mg^{2+} in MgO crystal lattice. Fe^{3+} ions are present in two different crystal sites which both are also in octahedral symmetry. One of the sites corresponds to Fe^{3+} ions which substitute Mg^{2+} but in this case in order to maintain the neutrality of crystal charge it must create a Mg^{2+} vacancy. The Mg^{2+} vacancy incorporated with Fe^{3+} ion cause a strong distortion of the second Fe^{3+} iron site. These both effects can be connected to reorganization of MgO lattice due to early stage formation of $MgFe_2O_4$ clusters. For the higher iron atoms concentration additional formation of $MgFe_2O_4$ phase is evidenced.

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Abstract-Number: *403*

PRODUCTION TECHNOLOGIES FOR AND PROPERTIES OF PLANAR AND CYLINDRICAL REFRACTORIES WITH GRADED MICROSTRUCTURE

Scheithauer U., Schwarzer E., Slawik T., Michaelis A.
Fraunhofer IKTS Dresden, Dresden, Germany

At the Fraunhofer Institute for Ceramic Technologies and Systems the principle of manufacturing of refractories with graded properties is investigated. The main goal is the production of carbon-free refractories but their properties must at least be equivalent to the carbon-containing refractories.
The manufacturing of multilayer composites by aqueous ceramic tape technology allows an environmental-friendly production of components with large dimensions and gradient structures regarding porosity and phase composition. Within the framework of the SPP 1418 “Fire I + II” funded by the German Research Foundation (DFG) carbonless refractories with different porosities in each layer are developed. The used material systems are Ca-aluminate/Al_2O_3 and MgO-stabilized ZrO_2.The resulting different properties in the gradient structure regarding thermal conductivity and capacity, density, mechanical strength, and elastic modulus shall result in improved thermal shock properties of the materials.
Not only planar structures, but also cylindrical structures with a radial gradient of the microstructure and the resulting properties can be realized by applying a winding technology known from the paper technology.
The presentation will show the production of planar and cylindrical refractories with a selected microstructure and graded porosity. Computer tomography allows searching for possible delaminations between the different tapes after the sintering process. SEM-images of the sintered components show the perfect connection between the single layers and the produced structures.

Abstract-Number: *404*

THERMAL, CHEMICAL AND MECHANICAL EVALUATION OF AL_2O_3-MGO-C BRICKS UNDER OXIDANT CONDITIONS

Muñoz V.[1], Benavidez E.[2], Brandaleze E.[2], Tomba Martinez A.G.[1]
[1]INTEMA, Mar del Plata, Argentina, [2]Universidad Tecnológica Nacional - Facultad Regional San Nicolás, San Nicolás, Argentina

Al_2O_3-MgO-C (AMC) refractories are used in steelmaking ladles, where they are part of the working lining's bottom and walls. Taking into account the conditions during the operation, refractories with high-melt corrosion resistance, oxidation resistance and good mechanical properties are required to provide good service performance.
In this work, the main results of a comprehensive evaluation of three commercial AMC bricks used under near-service conditions are reported. Previously, the bricks were characterized by XRF, ICP-OES, XRD, DTA/TGA, density, porosity, PLC and permeability measurements, mercury intrusion porosimetry, optical microscopy and SEM/EDS. These materials have different sources of alumina and amounts of MgO, but similar contents of phenolic resin and aluminium. In the three bricks, the amount of graphite was lower than 3.6 wt.%.
The AMC refractories were evaluated in relation with: a) their thermal evolution, regarding the compositional, microstructural and textural changes occurring when temperature increases, b) their chemical wear in contact with oxidant atmosphere and liquid slag at high temperature and c) their hot mechanical behaviour. The testing was accomplished up to 1450°C, in air atmosphere.
To study the thermal evolution, isothermal treatments of brick fragments were carried out. The cup-test was employed to analyze the slag corrosion resistance, with a basic slag from an industrial plant. Moreover, isothermal treatments in air were performed on cylindrical samples to determine the resistance of AMC materials to be oxidized by oxygen from the atmosphere. Mechanical testing was carried out by stress-strain curves under uniaxial compression. Furthermore, the post-testing evaluation of the materials was accomplished by XRD, porosity measurements and SEM/EDS analysis.
The AMC brick with the higher amounts of MgO and open pores (AMC2) exhibited the worst mechanical and chemical performances. On the other hand, the material containing bauxite besides tabular and brown electrofused alumina as raw materials, and having the lowest porosity (AMC3), did not show the impoverishment of mechanical properties showed by the other two bricks at 1000°C. Furthermore, this brick showed the lowest loss of graphite by direct oxidation in air. The third material (AMC1), which has the highest amount of tabular alumina and intermediate apparent porosity, showed a high tendency to form spinel and exhibited the best resistance to slag corrosion.

Abstract-Number: *405*

PREPARATION OF SIC-ZRSIO$_4$ POROUS COMPOSITES AND ITS HIGH TEMPERATURE OXIDATION BEHAVIOR

Akashi T.[1], Kobiyama K.[2]
[1]*Hosei University, Faculty of Bioscience and Applied Chemistry, Tokyo, Japan,* [2]*Hosei University, Graduate School of Science and Engineering, Tokyo, Japan*

To prevent the cracking due to phase transition of cristobalite in SiO_2 layer on SiC-based porous materials, the alternative $ZrSiO_4$ layer to SiO_2 layer was intended to form on each SiC grain in the porous materials. The advantage of $ZrSiO_4$ over SiO_2 is its thermal stability without phase transition from room temperature to 1676 ^oC, but one of the obstacles is an extremely slow rate of the $ZrSiO_4$ formation by solid state reaction between ZrO_2 and SiO_2, which is drawback to its processing. In this study, the effect of Ni addition was investigated on the formation of SiC-$ZrSiO_4$ porous composites and its high temperature oxidation resistance.
A solution containing silicon tetraethoxide, zirconium tetra-n-butoxide, and nickel nitrate was mixed with SiC powder with 1 µm-diameter, and dried by a rotary evaporator. For comparison, a solution without nickel nitrate was also prepared and dried to obtain powder. The dried powder was mixed with polyethylene glycol as a pore-forming agent, uniaxially pressed to form a powder compact, and sintered to obtain SiC-$ZrSiO_4$ porous composite. X-ray diffraction analysis indicates that $ZrSiO_4$ was formed only for SiC-based porous composite with Ni addition, which implies that Ni promoted the formation of $ZrSiO_4$. The effect of Ni addition on the formation of $ZrSiO_4$ was verified by XPS analysis. The relative densities of SiC-based porous composites with and without Ni addition were approximately the same, but the specific surface area was decreased from 4.98 m^2/g to 4.07 m^2/g by Ni addition. The Brinell hardness of the SiC-based porous composite was increased by Ni addition. These results indicate that the sintering of SiC-based porous composite was promoted by Ni addition. The high temperature oxidation resistance of the porous composites was evaluated by thermogravimetry. The weight gain of SiC-based porous composite with Ni addition was smaller than that of the composite without Ni addition, implying the high temperature oxidation resistance of SiC-based porous composite was improved by Ni addition. A kinetic analysis indicates that rate-controlling step of the high temperature oxidation was diffusion of a component species in the product oxide layer formed on each SiC grain.

Abstract-Number: *406*

INFLUENCE OF ANTIOXIDANT ON ABRASION RESISTANCE OF SIC CONTAINING CASTABLES

Kannabiran S.[1], Alibasic E.[1], Yiakoumi A.[2]
[1]*Höganäs Bjuf AB, Research and Development Centre, Bjuv, Sweden,* [2]*Höganäs Bjuf AB, Marketing, Bjuv, Sweden*

Al_2O_3-SiO_2-SiC castable finds widespread use in various applications such as cement, incinerators, boilers etc. Addition of SiC improves the resistance against alkali, abrasion and thermal shock in applications. A major problem with this kind of castable is oxidation of SiC leading to expansion and deterioration of structure. The application temperature of alumino-silicate castables containing various amounts of SiC can go up to 1300°C and this affect the performance of castables due to oxidation. To overcome the oxidation problem, antioxidants are often used and thus retain the properties of castables. This study explores the effect of an antioxidant on the cold and hot abrasion of SiC containing castables up to 1300°C. The correlation between amount and type of antioxidant on the abrasion resistance has been established.

Abstract-Number: *407*

DESIGN OF CHEMISTRY OF HOLLOWWARE REFRACTORIES FOR INGOT CASTING APPLICATIONS

Kannabiran S., Flodman L., Wijk G.
Höganäs Bjuf AB, Research and Development Centre, Bjuv, Sweden

Hollowware refractory used for ingot casting is one of the potential sources of exogenous inclusion in steel though re-oxidation of alloying elements in reaction with refractory phases and erosion of refractories. The inclusions size, volume fraction, chemistry and morphology strongly influence the mechanical properties of end products such as fracture toughness, ductility and fatigue resistance. Extrusion and shaping is one of the routes for manufacturing hollowware refractories which is using higher level of clay to facilitate the manufacturing process. Firing of hollowware containing clay is resulting in free silica in the matrix, which is a potential source of inclusion generation. Also, the addition of more clay in the hollowware reduces the refractoriness and erosion resistance while casting at high temperature.

This study attempts to explore the design of chamotte and bauxite based hollowware refractories of 55-70% Al_2O_3 contents with optimal addition of clay and shaped by extrusion. A suitable testing methodology for evaluating reaction and erosion of hollowware refractories with steel in laboratory has been identified and the tests have been conducted to simulate the performance in field conditions. The field trials with the products of increasing alumina contents have resulted in drastic reduction in amount of exogenous inclusions of refractory origin in the steel, confirming the validity of product design and characterization technique used for testing hollowware refractories in lab.

Abstract-Number: *408*

PROPERTIES IMPROVEMENT OF MULLITE BASED LIGHTWEIGHT CASTABLE BY ADDING RAW AND LIGHT-CALCINED COAL MEASURE KAOLIN

Bi Y., Zhou N.
Henan University of Science and Technology, High Temperature Materials Institute, Luoyang, China

To achieve high performance of Al_2O_3-SiO_2 lightweight castables at high temperatures, weaknesses of shrinkage and insufficient hot strength need to be overcome. For this purpose, raw coal measure kaolin and its lightly calcined small aggregate were introduced in a mullite based lightweight castable, taking the advantage of mullitization and *in situ* mullite formation of the kaolin when heated to compensate the shrinkage and enhance hot strength. The lightweight castable was prepared, using micropored porous mullite as aggregates and Al_2O_3 60% sintered mullite, CA cement and microsilica as the matrix. Up to 10% of the raw kaolin powder (-200 mesh) and 5% of the 1-0mm aggregate calcined at 700ºC to remove structural water were respectively added in the castables to replace correspondingly the sintered mullite powder and the porous mullite aggregate, and meanwhile adequate amount of a bauxite with Al_2O_3 83% lightly calcined at 600ºC to remove structural water was incorporated to maintain an equivalent Al_2O_3/SiO_2 ratio. Specimens were prepared by vibration casting, dried at 110ºC for 24h and heated at 1000ºC for 3h, 1350ºC for 3h and 1400ºC for 3h respectively. Properties in terms of BD, AP, CMOR, CCS, HMOR, PLC and reheated linear change were tested and microstructure was analyzed by means of SEM and XRD. It is confirmed by this work that by adequately adding raw and light-calcined coal measure kaolin, HMOR of the lightweight castable can be significantly improved and linear shrinkage after heating at 1400ºC can be avoided.

Abstract-Number: *409*

STUDY ON BASIC CERAMIC BINDER

Szczerba J., Prorok R., Śnieżek E.
AGH - University of Science and Technology, Faculty of Material Science and Ceramics, Krakow, Poland

The MgO - SiO_2 - H_2O phase system, has a potential wide application in refractory materials, as well as in building materials. This is connected with the MSH phase, which may constitute a modern bonding system. The aim of this study was to investigated phase evolution in MgO - SiO_2 - H_2O phase system in samples ageing at room temperature.
The paste was composed of sintered magnesia and microsilica, in 1:1 molar ratio and water, in water to solid ratio equal 0.5. The obtained mixtures were homogenized by mechanical mixing. After preparation, samples has been ageing at 20˚C.
The samples of pastes were studied and analyzed by DTA-TGA-EGA, XRD, FTIR and NMR analysis. Performed analysis revealed that products of reaction in mixture of MgO, SiO_2 and water was a poorly crystalline layer magnesium silicate.

Abstract-Number: *410*

THE CORROSION BEHAVIOR OF MGO/$CAZRO_3$ MATRIX IN CONTACT WITH PORTLAND CLINKER

Szczerba J., Sniezek E., Prorok R.
AGH University of Science and Technology, Department of Ceramics and Refractories, Krakow, Poland

The aim of this work was to investigate the chemical corrosion between Portland clinker and MgO-$CaZrO_3$ refractories. The Portland clinker consists of various calcium silicates, including tricalcium silicate (Ca_3SiO_5) and dicalcium silicate (Ca_2SiO_4). Tricalcium aluminate ($Ca_3Al_2O_6$) and calcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$) are other common components. Static chemical attack test by these

phases were conducted for evaluating corrosion resistance of MgO-$CaZrO_3$ matrix and MgO-$CaZrO_3$ materials with selected aluminate addition.
In this study, corrosion behaviours of MgO-$CaZrO_3$ and MgO-$CaZrO_3$-aluminate refractories in contact with Portland clinker are investigated to determine their corrosion mechanisms at 1200-1500°C. The materials were obtained from sintered MgO, pre-synthesized $CaZrO_3$ and aluminate. The mixture consisted of variable amounts of MgO (max. 85 vol%) and $CaZrO_3$ (max. 30 vol%) and 4 vol% of aluminate. Homogenized mixtures were pressed uniaxially in the hardened steel die at a pressure of 80 MPa and were sintered using the one-step heat treatment at 1580°C. The obtained materials were grinded, mixed with cement Portland clinker and pressed into pellets. The pellets were heat treated in different temperature corresponding to conditions in the transition and sintering zone in cement rotary kilns. The mixture of MgO-$CaZrO_3$-aluminate, after heating in the required temperatures, were studied.
The intentional introduction of aluminate phases into the magnesia-zirconia materials affects on their properties. The presented studies indicate that aluminate phases were located at the boundaries between MgO and $CaZrO_3$ grains and up to 1300°C reaction between Portland cement clinker and samples has not been started in significant way.
Acknowledgement: The work was partially supported by the grant no. INNOTECH-K2/IN2/16/181920/NCBR/13

Abstract-Number: *412*

REAPPRAISAL OF CURRENT STANDARD TESTING METHODS FOR THE DETERMINATION OF THE MODULUS OF RUPTURE (MOR) OF REFRACTORY PRODUCTS

Erauw J.-P., Mastroianni I., Lardot V., Cambier F.
Belgian Ceramic Research Centre, Mons, Belgium

Since the adoption of former PRE recommendations as EN standards, most testing methods used for the determination of critical mechanical and physical properties have not been thoroughly reassessed whereas in the meantime, refractory products have evolved drastically. The adequacy of current testing standards to fulfil today´s requirements of the market has become questionable. In particular, current documents lack any statement regarding the accuracy and precision that can be expected from the test methods described. This is in particular true for the test methods used for the determination of the modulus of rupture (MOR) of refractory products.
Accordingly, within the framework of the European project ReStaR, "Review and improvement of testing Standards for Refractory products", the current EN standards for the determination of the MOR of dense shaped, insulating (EN 993-6) and monolithic (EN ISO 1927-6) refractory products have been re-evaluated. After screening, through factorial designs of experiments and subsequent ANOVA analysis, the various test parameters susceptible to influence the test results, a set of three parameters has been selected for further analysis. Their criticality has been investigated on the three types of products through interlaboratory round robin tests. On the basis of the outcome, improvement of the current standard requirements have been drafted that will in a later stage be proposed to the relevant CEN Technical Committee. Concurrently, a set of precision data has been generated that could be incorporated in the future version of the standards.

Abstract-Number: *415*

INFLUENCE OF $CACL_2$ ADDITION ON THE HYDRATION BEHAVIOR OF CALCIUM MAGNESIUM ALUMINATE CEMENT AT ROOM TEMPERATURES

Wang Q.[1], Zhang C.[2], Shang X.[2], Mu Y.[2], Liao G.[1], Li L.[1], Ye G.[2]
[1]*Luoyang Institute of Science and Technology, Luoyang, China,* [2]*Zhengzhou University, Zhengzhou, China*

Calcium aluminate cement containing microcrystalline magnesium aluminate spinel has been used as the binder in the castables, resulting from the fact that the homogeneously distributed spinel in the cements can bring about the improved corrosion and penetration resistance of castables for steel ladle applications. However, the calcium magnesium aluminate cement often presents a longer setting time than the calcium aluminate cement (containing 70wt.% Al_2O_3) without spinel at room temperatures due to the presence of the spinel in the cement. Considering the formation of cement hydrates determined by the concentrations of the Ca^{2+} and $Al(OH)_4^-$ ions in solution, a higher Ca^{2+} concentration in the solution may induce the less soluble hydrates and accelerate the cement setting. Therefore, different contents of $CaCl_2$ were added in the cement pastes to control the hydration and setting rates of the calcium magnesium aluminate cement. The hydration behavior of the cement was analyzed through the hydration heat evolution using the semi-adiabatic method. And the ongoing hydration of the cements was arrested by vacuum freeze drying and

the hydrates were characterized by X-ray powder diffraction with the aim to illustrate the effect of $CaCl_2$ addition on the hydration behavior of calcium magnesium aluminate cement at room temperatures.

Abstract-Number: *417*

THE OPTIMAL BASIC INSULATING SPRAYING REFRACTORY DESIGN FOR TUNDISHWITH THE PREDICTABLE FIELD RESULT

Chul-Eui K., Jae-Won K., Dong-Ha L., Je-ha L., Byeong-su K.
POSCO CHEMTECH, Inorganic Materials R&D Group, Pohang, Korea, Republic of

This investigation describes the optimal product design as control the test conditions with the unique high temperature erosion test method. The basic insulating spraying refractory must be attributed for tundish, essentially, such as an easy installation, a good erosion resistivity, a proper thermal conductivity and reducing infiltration of liquid metal and slag. Especially, the easy dismantlement of the used insulating spraying refractory from the tundish saves the time and the cost could be wasted during the steel making process. Test specimens of basic magnesia insulating spraying refractory were prepared with the different porosity, from 20% to 60%, as adding pore control additives. And also, the specimens having different porosity were employed for the surface coating layer with the thickness range of 10 to 30 mm. After that, the erosion test was carried out at the high temperature, typically at 1,550℃, with the specially assembled specimens which are consisted of two types of refractories, for example, magnesia coated material and high alumina castable. Additionally, the thermal conductivity of the specimens also was measured. Finally, the optimal basic insulating spraying refractory design was compared and discussed with the result of the infiltration rate into the coated material, the adhesive statement between coated material and permanent lining, the erosion rate of coated material and the thermal conductivity on the coated material thickness versus the materials' porosity.

Abstract-Number: *418*

SPECIALLY TREATED GRAPHITE FORTIFIED ALUMINA-SILICON CARBIDE-CARBON REFRACTORIES

Singh K.[1], Singh B.[1], Lodha R.[1], Adak S.[2], Behera S.K.[3], Sathiyakumar M.[2]
[1]Govt. College of Engineering & Technology, Ceramic Engineering, Bikaner, India, [2]TRL Krosaki Refractories Ltd, Research & Development, Belpahar, India, [3]National Institute of Technology, Department of Ceramic Engineering, Rourkela, India

This work showcases specially treated graphite (STG) as carbon source to partially replace flaky graphite in Al_2O_3-SiC-C (ASC) refractories to study the effect of its addition on the microstructure and mechanical and thermo-mechanical properties of tempered as well as coked specimens.
The compositions developed using these specially treated graphite exhibited excellent hot strength, thermal shock resistance, slag corrosion resistance and oxidation resistance.

Abstract-Number: *419*

NEW LIGHTWEIGHT AGGREGATES AND INSULATING CASTABLES COMPRISING OF THEM

Zhou N.[1], Bi Y.[1], Hu S.[1], Wang C.[1], Bai H.[2], Liu C.[3]
[1]Henan University of Science and Technology, High Temperature Materials Institute, Luoyang, China, [2]Yanshi Zhongyue Refractories Co., Ltd., Yanshi, China, [3]Henan Zhongyuan Special Refractories Co., Ltd., Xinmi, China

Lightweight (LW) castables are of important part of monolithic refractories, and their high performance is required for refractories to play the role in energy saving and reducing material consumption. Concepts for high performance of LW castables were put forwarded, i.e. high purity, high strength, high service temperature, high resistance to the attack by corrosive furnace atmosphere, low thermal conductivity and low shrinkage at working temperatures. Approaches to meeting such challenges are introduced. Newly developed LW aggregates in Al_2O_3-SiO_2, MgO-SiO_2, Al_2O_3-MgO, Al_2O_3-CaO-MgO and Al_2O_3-SiO_2-CaO systems were adopted in LW castables with BD ranged from 1.0 to 2.0g/cm^3, featured by hollow ball and/or micropore structures to enable efficient thermal insulation, sufficient strength and other required properties. Newly developed LW Al_2O_3-SiO_2 castables have been used as steel ladle back lining, water cooled skid and post lining of reheating furnace and back lining of tin bath hearth in glass industry, with encouraging results.

Abstract-Number: *420*

THERMAL SHOCK BEHAVIOR OF CARBON-REDUCED REFRACTORIES

Böhm A.[1], Fruhstorfer J.[2], Mertke A.[2], Aneziris C.G.[2], Malzbender J.[1]
[1]*Forschungszentrum Jülich GmbH, Jülich, Germany,* [2]*TU Bergakademie Freiberg, Freiberg, Germany*

Fracture resistance and thermal shock behavior of novel carbon reduced refractories were assessed within the framework of the DFG SPP Fire. Wedge splitting tests permitted a determination of the R-Curve behavior and the thermal-shock parameter R''''. The test set-up was modified compared to the well-known set-up developed by Tschegg to permit testing of small specimens (20 x 20 x 20 mm³ and 40 x 40 x 20 mm³). The results showed good agreement with complementary compact tension tests for the studied Al_2O_3 material. Since cooling thermal-shock tests are not representative of the typical application conditions and hence might induce different failure modes, fast electron beam heating thermal-shock experiments were carried to permit a direct characterization of the materials thermal-shock behavior without interaction with steel or slag as additional characterization method. However, since electrical conductivity of the samples is necessary tests were limited to MgO-C and Al_2O_3-C materials. Optimization of the electron beam operation parameters permitted a homogeneous application of the thermal-shock onto the sample surface. The measured and simulated surface temperature distribution showed a good agreement. The damage state was evaluated by post-test microscopic observation. Additional SEM investigations of sample cross-section yielded information on the sub-surface damage.

Abstract-Number: *421*

EFFECTS OF DIFFERENT ADDITIVES ON THE SETTING BEHAVIOR AND GREEN STRENGTH OF COLLOIDAL SILICA BONDED AL_2O_3-SIC-C CASTABLES

Ma J.[1], Zhang Y.[2], Zhu L.[1], Shang X.[1], Zhou W.[1], Ye G.[1]
[1]*Zhengzhou University, Zhengzhou, China,* [2]*Henan University of Technology, Zhengzhou, China*

It is hard for colloidal silica (CS) bonded castables to set or harden and acquire enough green strength, due to the high ζ-potential of CS. It was noticed that the addition of sodium tripolyphosphate (STP), sodium hexametaphosphate (SHP) and citric acid all decreased the ζ-potential of CS, which consequently accelerated the coagulation of CS, and shorten the setting time of the castables. In this work, the above additives were used to control the setting time of CS bonded castables and to raise the green strength of the castables. The change of ζ-potential, pH, and conductivity of CS with the additives and time were tested by a Zeta potential analyzer (ZetaProbe, Colloidal Dynamics, America). Apparent viscosity variation of CS with additives and time was carried out by a rheometer (R/S Plus, Brookfield, America). The green strength of the castables was tested using 40*40*160 mm bars after curing for 24 h at room temperature.

Abstract-Number: *422*

CRITERIA FOR APPLICATION OF EXTERNAL RECYCLED SCRAPS IN REFRACTORY PRODUCTS

Monsberger G.
RHI AG-Technologie Center Leoben, DRL-Alumina Silica Bricks, Leoben, Austria

Refractories are used in many industries like steel, cement, glass and others and for years they have ended in landfills or been stored on site at work facilities, without a clear plan. But in the last 6 years, the recycling practice of refractories has been intensified, due to its increasing reuse but also to meet stringent international environmental regulations.
Due to their different mineral composition and its extended range of properties a lot of different refractory materials are applied together in the lining of the furnaces.
At the end of the service life, refractory's were broken out but mixed with the adhering slag's and melts from process mainly to time lack. Hence they have to be carefully separated, selectively recovered and cleaned for its reuse in refractory's applications.
The object of the present study is to examine, which essential requirements have to be considered for the reuse of these recycling materials in refractory's products and which measures are necessary to meet the requirements

Abstract-Number: *423*

PREPARATION OF MICRO-SIZED α-AL_2O_3 PLATELETS FROM MILLED $AL(OH)_3$ PRECURSOR WITH NH_4F AND NH_4CL ADDITIVES

Zhu L., An Z., Wu L., Yu X., Ye G.
Zhengzhou University, Zhengzhou, China

Alumina is one of the most important raw materials used in refractory industry, because of its excellent chemical, mechanical and thermal properties. α-alumina (α-Al_2O_3) hexagonal platelets can be both used as main raw material in Al_2O_3-C, Al_2O_3-SiO_2-C and Al_2O_3-Cr_2O_3 system, but also introduced into other high alumina unshaped refractory as alumina-rich composition. In this work, Single-crystal α-Al_2O_3 hexagonal platelets with a diameter of about 1.0 ~ 5.0 μm were synthesized by heating a mixture of gibbsite ($Al(OH)_3$), ammonium fluoride (NH_4F) and ammonium chloride (NH_4Cl) additives at high temperatures. The decomposition process of $Al(OH)_3$ precursor with different NH_4F and NH_4Cl addition were investigated using Differential Thermal Analysis (DTA), Fourier Transform Infra-Red Spectroscopy (FTIR) and X-ray Diffraction (XRD); and the effect of NH_4F and NH_4Cl composite additive on the morphology evolution of α-Al_2O_3 were studied by Field-emission Scanning Electron microscope(SEM).

Abstract-Number: *426*

REACTIVITY OF SEMI-ANTHRACITE COAL AND SINTERED MGO-CHROME REFRACTORIES IN ROTARY KILN

Lim Y.-T.
POSCO CHEMTECH, R&D, Pohang, Gyeongbuk, Korea, Republic of

Sinterd MgO-Chrome bricks have been main refractories especially in the burning zone of Rotary kiln to fabricate sea water magnesia clinkers. The life cycle of these refractories can be decreased by unexpected thermal spalling and coating materials formed along the burning zone.
Recently much effort to search and apply relatively low-cost fuel sources has been conducted for high temperature kilns to produce raw materials of refractories. Pet (Petroleum) coke is one of the commonly used energy source for rotary kilns to produce cement and also sea water magnesia by substituting bunker C heavy oil. Another candidate for buker C heavy oil is semi-anthracite coal with much less environmental contaminants such as sulfur and nitrogen. However, semi-anthracite coal has much ash components which Al2O3 and SiO2 are main chemical compositions.
In this study, the interactions between semi-anthracite coals and sintered MgO-Chrome refractories according to the various high temperatures up to 1550℃ in an electric furnace are assessed by heating semi-anthracite samples on the plate type and in the trench type MgO-Chrome refractories samples. The properties of the microstructural (SEM) and chemical changes (XRF) on the refractories surface are estimated and the thermochemical calculations are conducted with the software package FactSage. Finally the feasibility to use semi-anthracite coal in a rotary kiln as a primary energy source will be discussed.

Abstract-Number: *428*

INFLUENCE OF THE COUPLED EFFECT OF THERMAL GRADIENT AND CHEMICAL ATTACK ON THE SPALLING BEHAVIOR OF AN ALUMINA REFRACTORY CASTABLE

Loison L., Tonnesen T., Telle R.
RWTH Aachen, Institute of Mineral Engineering, Aachen, Germany

Refractory materials used to line industrial furnaces are simultaneously exposed to high temperatures and a corrosive environment. The complexity of this combined load intensifies the difficulty to understand the behavior of refractory when submitted to both thermo-mechanical stress and chemical wear. Indeed, the cracking of a refractory brick can be caused by both temperature gradients and thermal expansion variations from the reaction with slag, leading to a loss of the material stiffness. If the failure of the refractory is a consequence of the stresses caused by creating zones of different compositions and properties as a result of the slag penetration, the term structural or chemical spalling is used. This work aimed to examine the coupled effect of chemical and thermal load on the deterioration of a refractory microstructure. The experimental setup attempted to submit a refractory sample to a thermal gradient while being in contact with a slag. Samples of basic alumina low cement castable (LCC) composed of tabular alumina and reactive alumina were prepared to react with a calcia rich industrial slag. Temperature along the refractory sample was

measured to draw the thermal profile inside the brick. In order to better understand the microstructural changes taking place at the different temperatures endured by the refractory brick, corrosion tests at single temperatures were carried out in parallel. The damages of the microstructure were examined through elastic properties measurements by means of Resonance Frequency Damping Analysis (RFDA). The microstructural modifications were observed with Scanning Electron Microscopy (SEM) to characterize the infiltration into the refractory samples and to estimate the penetration depth of the corrosive chemical elements contained in the industrial slag.

Abstract-Number: *429*

INFLUENCE OF ZIRCONIA DOPING AGENT ON THE FATIGUE OF HIGH ALUMINA REFRACTORY CASTABLES AT ELEVATED TEMPERATURE

Traon N., Etzold S., Tonnesen T., Telle R.
RWTH Aachen, Institute of Mineral Engineering, Department of Ceramics and Refractory Materials, Aachen, Germany

Partially Stabilized Zirconia (PSZ) or Fully Stabilized Zirconia (FSZ) are commonly added to standard high alumina refractory castable formulations in order to enhance the toughening properties of the material. Indeed, progressive nucleated cracks, generated by thermal shock experiments or by other external mechanical stresses, are either deviated by zirconia particles in case of cubic phase or those cracks can also result in the martensitic transformation of zirconia grains in case of tetragonal phase. Both mechanisms considerably consume energy and therefore contribute to the fracture energy improvement of the material.
From this standing point, zirconia grains (0,2 - 1mm) were incorporated in a model tabular alumina refractory castable formulation with maximal grain size of 3mm. Three raw materials were used in the study herein to examine the influence of monoclinic, tetragonal and cubic phases on the toughening property of the material: the first one was doped with 3% CaO, the second one with 3% MgO and the last one with 8% Y_2O_3. A tabular alumina based castable was considered in this study as reference and all the following testing measurements were compared to those of that reference. Cycling Refractoriness under Load tests were performed on each formulation for 7 days according to DIN EN ISO 1893 in a temperature range between 900°C and 1500°C as well as between 600°C and 1200°C, as refractory materials are conventionally subjected to such kinds of thermal gradients. The interpretation of the creeping behaviour of the castables was completed by cycling Young's modulus measurements carried out in the same temperature ranges with help of a Resonant Frequency Damping Analysis according to ASTM C 1548-02. Toughness and stiffness of the tested formulations could be correlated with regards to long term measurements with the aim of evaluating the mechanical and elastic fatigue of the castables. Furthermore, the examination of the damping behaviour of the castables subjected to cycling measurements could provide further information related to friction phenomenon due to crack nucleation.
Three point bending tests were also performed on the refractory samples for 7 days at elevated temperatures, namely the same temperature ranges as described before, to study the deformation of the tested formulations under tensile stresses. Cracks generated at the grain boundaries of the zirconia grains have considerably influenced the strain behaviour of the castable.

Abstract-Number: *430*

FUTURE CHALLENGES OF REFRACTORY RESEARCH AND INDUSTRY

Geigenmüller A.[1], Lenk K.[1], Aneziris C.G.[2]
[1]*Ilmenau University of Technology, Marketing, Ilmenau, Germany,* [2]*Freiberg University of Technology, Freiberg, Germany*

Refractory industry is facing enormous economic, political and social challenges, including slower growth rates, mature markets, intense competition, and price sensitivity among customers. This requires strategic activities in several fields, ranging from technology and innovation to human resources management and promotion of the industry.
This paper presents results of a roadmapping process that captures perceptions and expectations about future developments in refractory industry, research, and education. Originated from corporate strategic planning, roadmaps are used traditionally to monitor, forecast and communicate technological developments, in order to link technologies, products, and market opportunities. Science and technology roadmaps are utilized to predict the long-term future of science and technology, including economic and societal issues. Although the instrument of roadmapping has already been applied to several fields of materials research, to our best knowledge, a roadmap for refractory research and industry is lacking.
Therefore, this paper aims at developing a science and technology roadmap for refractory research and industry that predicts

strategic objectives, market requirements and, consequently, future research needs in refractories. To this end, the study employs an extensive review of existing roadmaps, strategic papers, reports, and presentations in the fields of materials science and engineering, ceramics, glass, metals, metallurgy, and refractory applications. Furthermore, in-depth interviews with national and international experts from academia, industry and professional associations provides judgments about future research trends and estimates about their time of occurrence.
The study identifies strategic key variables with an impact on refractory research and industry as well as economic and market-related factors. From this, critical functions and principles are derived, which eventually drive future research areas, including novel materials compositions as enablers for improved or extended materials properties, new approaches for materials preparation, forming and processing technologies. Furthermore, substantial research gaps considering aspects of emission reduction, approaches to functionalize materials and components as well as methods for materials testing, simulation and modeling of refractories are revealed. The paper concludes on strategic challenges of the refractory industry.

Abstract-Number: *432*

NUMERICAL TREATMENT OF THE INELASTIC BEHAVIOUR OF REFRACTORY MATERIALS

Penasa M.[1], Piccolroaz A.[1], Bigoni D.[1], Dal Corso F.[1], Romero-Baivier S.[2]
[1]*University of Trento, Trento, Italy,* [2]*Vesuvius Group S.A., Ghlin, Belgium*

The collaboration between University of Trento and Vesuvius Group aims to develop material models for proper description of the behavior of refractory materials at high temperature and their implementation in FEM codes. The research results are expected to improve the design of Vesuvius metal flow engineering products used in foundry industries.
The most important issue in the design of ceramics devices for high-temperature applications is the proper constitutive modelling of mechanical behavior, but routines taking into account the correct thermoplastic behaviour of these materials, for use with finite element method, are still not available.
Elastoplasticity in refractory materials can be analysed using the yield functions recently proposed by Bigoni and Piccolroaz. An important feature of this function is the possibility to describe the elastoplastic behavior of several materials, depending on 7 characteristical parameters. Unfortunately, this extremely flexible yield function is not defined outside the yield locus, so that 'gradient-based' integration algorithms of elastoplasticity cannot be directly employed.
Therefore, our research group developed two algorithms: a finite-step integration scheme based on a forward Euler technique with a 'center-of-mass-return' correction and a cutoff-substepping return mapping integration.
Iso-error maps and comparisons between the two algorithms with an exact solution, have shown that both the proposed algorithms perform correctly for all possible yield function parameters, but the latter is computationally more efficient than the former.
The further developement of the constitutive model treats the modelling of coupled thermoelasticity. Temperature changes as a consequence of volumetric deformation is usually neglected in the most common FEM Software. For this reason the 'fully' coupled thermoelastic equations have been implemented in an 'ad hoc' definited finite element. The element performance has been tested comparing analytical solutions and numerical simulations of some simple examples.
In order to investigate the accuracy of the FEM subroutines in a wide range of cases, the simulations have been carried out using proper model parametrisation and automatic execution. This procedure paves the way to optimization studies that could provide important design improvements to our industrial partners.

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Abstract-Number: *433*

THERMAL EXPANSION AND PHASE CHANGES IN HIGH ALUMINA ULTRA-LOW CEMENT CASTABLE REFRACTORIES

Singh B., Lodha R., Singh K.
Govt. College of Engineering & Technology, Ceramic Engineering, Bikaner, India

In this work, the phase transitions of high alumina ultra-low cement castable refractories are correlated through differential thermal analyses, thermo-gravimetric analyses, dilatometry and X-ray diffraction. The changes in phase and structure correlate to the loss of physical and chemical bonded water, organic additives and phase changes resulting in the development of properties at

816°C and further changes at 1200°C.
The current work explores the development of properties of these castables are correlated to the temperature dependent changes and time-temperature paradigms.

Abstract-Number: *434*

LAB EVALUATION OF LADLE LINING GRANULAR MATERIALS UNDER IN SERVICE CONDITIONS

Bourahima F.[1], Blond E.[1], Gasser A.[1], van Beurden P.[2], Sinnema S.[2], Simaro T.[3], Musante L.[3], Galliano P.[3]
[1]Université d'Orléans, INSA-CVL, PRISME, Orleans, France, [2]Ceramics Research Centre, TATA Steel Europe, IJmuiden, Netherlands, [3]Tenaris REDE AR, Campana, Argentina

Steelmaking ladle performance during operation strongly depends on refractory lining design and corresponding materials in-service properties. Both shaped bricks and castable working and safety linings are present in any ladle design. In some cases, dry granular materials can additionally be used as an intermediate layer between working and safety linings. Main aim is to promote a close contact between both linings and to avoid the presence of gaps that could be filled with liquid steel and/or slag if the working lining happens to fail. The presence of this intermediate lining may also enhance ladle integrity by reducing heat transfer and stress transmission to the external shell under operation. The impact can be even more critical when this type of dry granular materials is used as a single material for safety lining assembling, instead of as an intermediate backfill. In order to thoroughly evaluate the effect of these materials on the general ladle performance, a sound characterization of these materials is required, as well as a deep understanding of the thermal evolution during ladle cycling. In this paper, two types of granular materials are characterized through various lab tests, with special focus on their thermal evolution under in-service conditions. Main focus of the tests is to simulate both thermal and loading conditions of the ladle during operation. For that purpose materials sintering of these materials is evaluated under loads between 0.2 and 5 MPa. The effect of sample vibration during sample preparation was also evaluated. Results show that materials densification begins at temperatures around 700 ºC. Moreover, mechanical response of these systems has been evaluated through compressive stress-strain curves and showed that results are mainly affected by the sintering phenomena. This complete understanding of the reversible and non-reversible thermal evolution of these properties is critical in order to obtain reliable numerical simulation of the ladle thermal profile and stress distribution during operation.

Abstract-Number: *436*

THE INFLUENCE OF HEATING RATE ON TORSION STRENGTH OF REFRACTORIES AT ELEVATED TEMPERATURES

Ge S., Zhu Q., Yin Y., Liu Z.
The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China

A new apparatus for the determination of torsion strength of refractory materials at elevated temperatures has been developed. As the employment of a induction heating unit, this apparatus allows us to carry out torsion strength test at high temperatures with fast heating rate up to 200°C/min. Torsion strength of high alumina bricks, magnesite bricks, Si_3N_4 bonded SiC bricks and high alumina castables has been tested separately, with different heating rate of 10°C/min, 100°C/min and 200°C/min. Results indicate that, for high alumina bricks, magnesite bricks, and high alumina castables, the tested torsion strength with heating rate of 10°C/min is very closed to that of 100°C/min. However, their tested torsion strength with heating rate of 200°C/min is dramatic different from that with heating rate of 10°C/min and 100°C/min. This might imply too fast heating rate would damage the structure of refractory materials with normal thermal shock resistance, or have some effect on the sintering process of unburned materials, and thus decrease the torsion strength. But for refractory materials with excellent thermal shock resistance, such as Si_3N_4 bonded SiC bricks, it seems that their tested torsion strength is almost not affected by the heating rate, even up to 200°C/min.

Abstract-Number: *441*

POTASSIUM ALUMINATES AS REFRACTORY MATERIALS

Brachhold N., Schönherr K., Schlegel E., Aneziris C.G.
TU Bergakademie Freiberg, Freiberg, Germany

Corrosion of refractory materials due to interactions with substances containing alkali compounds is a central problem in refractory applications. In present day technology, especially in the cement industry, the problem became even more significant because of the increasing use of secondary fuels such as waste material and biomass. These fuels contained higher amounts of alkali substances than conventional ones. Additionally, the counter currant of the raw material flow and the combustion gases caused an enrichment of alkali components in the furnace which increased the corrosion processes strongly. Therefore, the development of new refractory materials is necessary. The analysis of corroded material from industrial applications showed regularly the formation of alkali containing oxidic compounds. Therefore, these alkali containing phases seemed to be stable under high temperatures in environments with a high alkali load.
In the phase diagram K_2O-Al_2O_3 the potassium based compound $KAlO_2$ exists and has a melting point of 2260 °C. The eutectic between $KAlO_2$ and Al_2O_3 is reported to be at 1910 °C. These properties make materials containing $KAlO_2$ interesting for high temperature applications.
This study presents basic investigations of compositions in the system $KAlO_2$-Al_2O_3 with regard to their application as a refractory material. Synthesizing experiments up to 1600 °C were performed. Aluminium hydroxide and potassium carbonate were used as raw materials. The resulting reaction products were analysed by X-ray diffraction and tested with regard to alkali corrosion. Furthermore, the hydration resistance of the synthesized products was investigated. Promising materials were transferred to coarse grained material to manufacture refractory castables. Basic properties were characterized such as refractoriness under load and cold modulus of rupture.

Abstract-Number: *443*

LOWERING OF THE REFRACTORY CORROSION IN HIGH TEMPERATURE PROCESSES

Weigand R.[1,2], Hessenkemper H.[1], Rössel A.-K.[1], Tritschel D.[1]
[1]*TU Bergakademie Freiberg, IKGB, Freiberg, Germany,* [2]*ancorro GmbH, Großschirma, Germany*

The attack of refractory is a well-known problem in any kind of furnace worldwide in high temperature processes. As a result of the high temperature and the aggressive conditions the corrosion of refractory takes place in direct contact with the melt and also with the atmosphere and the dust. In the past a lot of developments were done to optimize the composition and structure of the refractory. E.g. for glass furnaces the content of ZrO_2 rises in the bricks. Since 2008 a new technology to lower the refractory corrosion was developed at TU Bergakademie Freiberg (Germany). With the surface treatment technology the corrosion of refractory can be lowered up to 90%. The mechanism of the treatment was detected in typically laboratory tests (e.g. finger test, crucible test). In detail the lower interaction after the special treatment of the bricks causes by a higher surface tension and viscosity of the melt in the boundary layer. So the interaction between brick and melt slows down significant. The surface treatment technology can be used on every porous refractory brick worldwide. The effect of the treatment depends on the application of the brick and the conditions in the furnace. With the surface treatment technology porous refractory bricks reach the same corrosion level as fused cast one. For the future it will be possible to use more and more porous refractory and lower the energy consumption of the furnaces. During different industrial tests the measured results of the laboratory tests were confirmed. Also calculations of the saving potential of high temperature processes were done.

Abstract-Number: *444*

ON THE WEAR OF A BLAST FURNACE WALL AND THE DETECTION THEREOF, A FINITE ELEMENT NODAL WEAR APPROACH

Put P., Sinnema S., Liefhebber J., Hes R.
Tata Steel, IJmuiden, Netherlands

In the majority of cases, the hearth wall of blast furnaces will show progressive wear and tear during its service life. A difficult topic for blast furnace operators is the assessment of the remaining hearth lining.
It is economically and technically not feasible to directly inspect the lining on a regular basis during its life span. Normally the only view on the lining is through an array of thermocouple readings. These readings may provide health monitoring of the lining system as a whole, but care should be taken since the density of the thermocouple array is directly related to the size of lining damage features that can be assessed.

The thermocouple readings can provide us with: - information on the remaining lining thickness, -process information like locally persistent iron flow velocity, -structural health information like gap formation between lining and shell.
Here we show how Finite Element (FE) models can be used to provide us with useful information on the interaction of lining wear, iron velocity, gap formation and monitoring possibilities.

Abstract-Number: *447*

FLOW CONTROL REFRACTORY DESIGN OPTIMISATION BY MODELLING AND SIMULATION

Hackl G.[1], Ehrengruber R.[2], Tomas M.[1], Eglsäer C.[3]
[1]*RHI AG, Leoben, Austria,* [2]*Stopinc AG, Hünenberg, Switzerland,* [3]*RHI AG, Wien, Austria*

The design of refractory components for the continuous casting process plays an important role in terms of process controllability and has an impact on the quality of the product. Contamination of steel, which may occur when the liquid steel is transferred from the ladle to the mould, needs to be avoided as much as possible. Therefore, considerable effort is constantly undertaken to further improve the functionality of refractory products for the continuous casting process, in order to precisely control the flow of liquid metal and/or gas. Examples of these products are slide gate systems, flow modifiers in the tundish as well as stopper rods or submerged entry nozzles.
This paper presents how different modelling techniques, such as CFD and water modelling, are applied in order to deepen the understanding of the process and derive measures to optimize the design of the refractory components for continuous casting. Several examples of product improvements as well as innovative product developments, are shown.

Abstract-Number: *448*

MODIFIED RADIATIVE HEAT TRANSFER IN COMBINATION WITH A HIGHER SERVICE LIFE OF THE SILICA CROWN IN GLASS FURNACES

Weigand R.[1,2], Hessenkemper H.[1], Rössel A.-K.[1], Tritschel D.[1]
[1]*TU Bergakademie Freiberg, IKGB, Freiberg, Germany,* [2]*ancorro GmbH, Großschirma, Germany*

The corrosion of the silica crown in the glass furnace is still a problem which do not enable a higher temperature of the superstructure. So the aim of this study was to transfer the developed surface treatment technology which increases the service life of porous refractory to the superstructure of the furnace. With the combination a higher service life of the refractory and a higher radiative heat transfer should be possible. As a result of the treatment of the superstructure the problem of the temperature sink after the change of the flames should be lowered. By using the surface treatment technology a better heating of the glass and batch will be possible in the future. The corrosion tests were done with NaOH at 1200°C for different hours. After treating the silica material the service life increases up to 15%. To detect the corrosion attack of the bricks a 3D scanner was used for the measurement. After the surface treatment of the bricks the modified radiative heat transfer was measured by using an IR camera and a pyrometer. The radiative heat transfer rises after the treatment of the porous refractory. The values of these tests were used for a simulation of the furnace properties. Savings in the range of a few hundred thousand euros per year and furnace can be generated.

Abstract-Number: *449*

INVESTIGATION OF THERMAL SHOCK BEHAVIOUR OF REFRACTORY CERAMICS BASED ON THE CALCIUM-ALUMINATE

Zhang W.[1], Doynov N.[1], Ossenbrink R.[1], Michailov V.[1], Scheithauer U.[2], Michaelis A.[2]
[1]*Brandenburg University of Technology Cottbus-Senftenberg, Department of Joining and Welding Technology, Cottbus, Germany,*
[2]*Fraunhofer IKTS Dresden, Dresden, Germany*

Thermal shock testing of fabricated Ca-Aluminate/Al_2O_3 samples with different porosities were carried out in a plasma test stand: only one side of the ceramic disks were heated in the center until failure occurred; besides measuring the temperature field on the

opposite side the crack initiation and propagation were traced by a high speed video camera. Subsequently the temperature and stress distribution were determined by means of thermomechanical simulation. Assessment criteria from the combined experimental testing and FE-simulation methods such as time to failure, critical temperature and tensile stress, crack initiation and origin of the fracture are suggested and proved. They could be used to characterize and compare the thermal shock behaviour of various refractory ceramic component parts.
The samples were produced by multilayer technology where ceramic green tapes were casted and stacked to multilayers. By adding different kinds and amounts of pore forming agents the resulting porosity can adjust for each layer to produce samples with homogenous or graded porosity.

Abstract-Number: *451*

HIGHER EDUCATION IN THE FIELDS OF CERAMICS - POSSIBILITIES AND LIMITATIONS

Häußler K.
TU Bergakademie Freiberg, Institute of Ceramics, Glass and Construction materials, Freiberg, Germany

The present state of education in the field of ceramics at the Technical University Bergakademie Freiberg is described. There are different possibilities of study: diploma program and master programs.
The possibilities of study are given, but are there used by young people? How to interest them for engineering, for the special field of ceramics? How the industry can and should support universties in marketing for ceramics? Visions and wishes....

Abstract-Number: *452*

INFLUENCE OF ADDITIVES ON THE CRYSTALLISATION OF CALCIUM SILICATE HYDRATES UNDER HYDROTHERMAL CONDITIONS

Schickle B.[1], Tonnesen T.[1], Telle R.[1], Opsommer A.[2], Abdul-Kader O.[2], Ceulemans E.[2]
[1]RWTH Aachen University, Institute of Mineral Engineering, Aachen, Germany, [2]Promat Research and Technology Centre N.V., Tisselt, Belgium

Calcium silicate insulating materials are produced in a wide range of bulk density from 50 to over 1500 kg/m^3. They are made from lime, silica, fibres, additives, and water under hydrothermal conditions in an autoclave. Several technologies are used for the production of light calcium silicate hydrates. They can be divided in different shaping methods and different types of hydrothermal treatment. Common combinations are:
· Hydrothermal synthesis in a stirring autoclave followed by filter pressing
· Pre-reacting of raw materials, filter pressing and post autoclaving
· Slurry casting followed by post autoclaving
The technological properties of calcium silicate hydrates strongly depend on their crystal structure, which can be influenced by several process parameters as well as raw materials. Furthermore, additives can help to set the favoured phases. The present work shows the effects of additives on the formation of calcium silicate hydrates in the hydrothermal process and their influence on the technological properties of the products. Therefore, several tests were performed using the above-mentioned technologies to also clarify if the additives react in a different way under the specific conditions of each process.

Abstract-Number: *453*

ALTERNATIVE ADVANCED ALUMINAS FOR REFRACTORY CASTABLES (PART 2)

Jérôme K.S., Chabas E., Ulrich C.
Alteo, Gardanne, France

Fine particles play not only a major role in the flowing characteristics of castables but also in the final properties of the castable in application. To optimize the particle packing of the castable, different kinds of fine aluminas can be used to form the matrix: calcined, semi-reactive, monomodal reactive or multimodal reactive aluminas. In a previous study PFR40 and PBR bimodal aluminas were found to be very efficient at achieving high performance levels in applicative refractory tests. This paper will present a new

alumina product named FLO-2 with a median particle diameter (d_{50}) about 3µm that can be classified as a lower cost alternative reactive alumina. It has been tested in silica free tabular alumina Low Cement Castable (LCC). In order to investigate its multifunctional potential, two kinds of matrix configurations have been investigated. For both matrices, in order to get a low water requirement and good compactness, formulations have been optimized with Dinger and Funk's packing model.
In the first configuration, FLO-2 is included in a matrix with ground calcined alumina. It has been compared to two commercially available aluminas on the market: a monomodal reactive alumina and a bimodal reactive alumina. It appears that with an appropriate FLO-2 ratio in the matrix, not only the flowability of the castable but also its cold properties after firing (density, porosity, cold crush strength) can reach the same performance level as the commercially available aluminas.
In the second configuration, FLO-2 is included in a 100% reactive matrix and has been compared to the bimodal commercial reactive alumina. Obtained castables were characterized according to standard refractory tests:
· Physical evaluation after drying and after firing: density/porosity, dimensional linear change.
· Mechanical properties: cold flexural resistance, sinterability under load, refractoriness under load.
· Thermochemical evaluations with standard corrosion cup test. For that purpose an industrial slag has been selected with the following main elements Fe_2O_3, CaO, SiO_2, MgO, MnO and P_2O_5.
These applicative tests show that in a 100% reactive matrix configuration, FLO-2 can be at the same level as a reactive bimodal alumina. It confirms that FLO-2 can also be a reference solution in the refractory market alongside with PFR40 and PBR.

Abstract-Number: *454*

MECHANICAL CHARACTERISATION OF CARBON BONDED ALUMINA (AL_2O_3-C) AT TEMPERATURES UP TO 1500 °C

Solarek J.[1], Bachmann C.[1], Klemm Y.[1], Aneziris C.G.[2], Biermann H.[1]
[1]Technische Universität Bergakademie Freiberg, Institute of Materials Engineering, Freiberg, Germany, [2]Technische Universität Bergakademie Freiberg, Department of Ceramic, Glass and Construction Materials, Freiberg, Germany

In the Collaborative Research Center 920 “Multi-Functional Filters for Metal Melt Filtration - A Contribution towards Zero Defect Materials”, fine grained, pitch bonded alumina (Al_2O_3) with a maximal alumina grain size of less than 10 µm and approximately 32 wt.-% residual carbon is used to develop new, enhanced filter materials for steel melt filtration. For this purpose, quasi-static tests as well as creep and stress-relaxation tests in both compression and bending have been performed on compact bulk specimens. Therefore a modern high temperature testing machine with inductive heating and inert atmosphere chamber was used to test the mechanical properties at temperatures between 700 and 1500 °C. The microstructure was characterised with scanning electron microscopy. The results show a significant rate of creep at temperature above approximately 1200 °C. Moreover, already above 700 °C small amounts of plastic deformation due to creep deformation were observed. At room temperature, viscoelastic behaviour of the refractory material was found.

Abstract-Number: *455*

SHOTCRETING CASTABLES FOR BLAST-FURNACE HOT REPAIRS

Sako E.Y.[1], Rodrigues F.[1], Frasson S.C.[1], Ramos V.P.S.[1], Januario N.[1], Bomfim D.A.[1], Neves E.S.[2], Sousa P.C.S.[2]
[1]Saint-Gobain do Brasil, Vinhedo, Brazil, [2]Companhia Siderurgica Nacional - CSN, Volta Redonda, Brazil

Blast-furnace working life can be extended when hot repairs procedures are performed on upper and middle stacks. During such repairs, new bricks installation is time-consuming and, therefore, is not considered as a feasible option. As an alternative, gunning monolithic refractories could be chosen for a quick and easy hot application, but its relatively high rebound rate is a severe concern for the customer, as it might strongly affect the slag composition during the blast-furnace restart. In this sense, shotcreting castable technology is the one which suits better the purposes of such repairs. In the present work, three different shotcreting castable compositions developed at Saint-Gobain (two cement-bonded materials and a colloidal silica-based one) were compared and evaluated in partnership with Companhia Siderúrgica Nacional (CSN) in order to define the best solution for blast-furnace hot repairs. Due to its fast drying behavior, low rebound rate and excellent mechanical properties, the latter composition proved to be the right choice for middle stack repair. On the other hand, cement-bonded compositions, when properly designed, could provide materials with excellent abrasion resistance at lower temperatures, increasing significantly the upper stack working life.

Abstract-Number: *456*

EQUILIBRIUM PHASE RELATIONS IN THE AL_2O_3-CAO-CR_2O_3 SYSTEM IN AIR

Song S., Garbers-Craig A.M.
University of Pretoria, Materials Science and Metallurgical Engineering, Pretoria, South Africa

Cr_2O_3 can be present in refractory monolithic castables either as a specific addition or as a residual element present in certain raw materials. The transformation of Cr(III) to Cr(VI) during the use of refractory monolithics can cause subsequent problems with disposal of the used refractory lining. It is therefore important to study the degree of Cr(VI) formation as well as its formation mechanism from a fundamental perspective. This study investigated a simplified system around Al_2O_3 and CaO in the presence of Cr_2O_3, representative of a system commonly found in refractory castables. Equilibrium phase relations in the Al_2O_3-CaO-Cr_2O_3 system in air were investigated in this study. Samples were prepared by varying the Al_2O_3 contents in the range of 50-80 wt%. Cr_2O_3 concentrations up to 4 wt% and equilibrium temperatures up to 1923K were used. After equilibrium was reached, the samples were quenched in a water cooled copper coil. The chromium distribution, oxidation states of chromium and phase compositions in the quenched samples were studied using SEM-EDS/Microprobe, XPS and XRD analyses. The results indicated that Cr-containing phases with chromium in different oxidation states exist in this system. The soluble Cr(VI) in the quenched samples was quantified using the diphenylcarbazide spectrophotometric method according to the TRGS 613 and BS EN 196-10 standards.

Abstract-Number: *457*

CHEMICAL INTERACTION BETWEEN MAGNESIA-CHROMITE REFRACTORY BRICKS AND PRIMARY PGM MATTE

Garbers-Craig A.M.[1], Cromarty R.[1], Lange M.[1,2]
[1]*University of Pretoria, Materials Science and Metallurgical Engineering, Pretoria, South Africa,* [2]*Anglo American, Coal, South Africa*

Magnesia-chromite bricks have traditionally been used in the tapholes of primary PGM smelters. The main wear mechanism associated with these taphole bricks has been matte penetration. With increasing amounts of chromium present in the concentrate that is fed to the smelter, operating temperatures have steadily increased. Chemical thermodynamics predict that increasing operating temperatures will result in chemical interaction between the matte and magnesia-chromite bricks. This study subsequently examined matte - magnesia-chromite brick interaction at temperatures from 1300 to 1750°C. Experiments consisted of heating cylindrical samples of refractory material in matte, which was contained in high-density alumina crucibles, in an induction furnace. SEM-EDS analysis of the refractory samples confirmed that at temperatures above 1500°C refractory wear proceeded by both matte penetration and chemical interaction between the matte and refractory. The Fe-Ni-Cu-S matte reacted with the brick by disintegrating the fused magnesia-chromite grains and sulphidising the chromite. This resulted in chromium and FeO pick-up in the matte.

Abstract-Number: *460*

IMPACT OF DRY GUNNING ON THE DRYING PROPERTIES OF REFRACTORY MONOLITHS

André L.
HEPHA, R&D, Saint-Benoit, France

Major attention is paid to novel formulations able to be quickly dried. This legitimate need is mostly dedicated to save production time or to adapt the refractory lining to the specificity of a process. Nevertheless, it is commonly known and demonstrated that dry gunning introduced interconnected porosity which facilitate the elimination of water in cement bonded castables. This global work has for goal to define the case of utilization dry gunning product instead of casting vibrating or quick drying. In order to evaluate the *in situ* impact of this setting way, we have put in place a gunning station with 10 m^2 of setting surface. This station enables us to test gunning on wall, roof and inclined surfaces in the same conditions. Our study is based on the projection of low cement castables. Porosity, water removal, physical and mechanical properties has been investigated. The comparison of these results with those obtained with casted references allows us to identify dry gunning as a good solution for many industrial applications.

Abstract-Number: *462*

ENHANCEMENT OF PERMEABILITY FOR A RAPID DRY-OUT OF REFRACTORY CASTABLES

Zetterström C., Auvray J.-M., Wöhrmeyer C., Parr C.
Kerneos SA, Vaulx Milieu, France

One of the key parameter in assessing a safe and easy dry out procedure is the intrinsic permeability of the refractory castable. There has been an increasing interest in different technologies to achieve a sufficient permeable microstructure such as colloidal binders or organic fibers to release water at a drying temperature as low as possible. Nevertheless, these solutions still suffer some disadvantages such as a slow strength development in the case of cement-free solutions, difficulties to dose automatically and homogenize polymer fibres in a castable dry-mix. Furthermore, the melting temperature of the polypropylene fibres might be too high to fully eliminate the risk of castable explosion during the dry-out phase.
This paper discusses about the dry-out ability of different castable formulations relative to the level of permeability measured at 110°C. Different permeability enhancing systems are investigated and compared with respect to their impact on placing properties and mechanical strength development at early stage Moreover, it will be shown a comparison of dewatering mechanisms associated with the different permeability enhancing systems used. Results are based on both, uni-directional as well as multi-directional drying procedures and take into account results from macro-TG measurements of blocks of different sizes as well as the associated changes in phase composition and microstructure during the dry-out phase.

Abstract-Number: *463*

RELATION BETWEEN STRUCTURE, MICROSTRUCTURE AND CORROSION RESISTANCE TO SLAG OF REFRACTORIES IN TEEMING LADLES - ROLE OF PERMEABILITY

Collignon B., Perrot C.
ICAR S.A., Moncel les Luneville, France

The corrosion resistance in steel ladle refractories is a function of wetting abilities of the slag on the material, transport phenomenon in the porous network, as well as the chemical reaction that dissolves the magnesia grains and modifies the fine matrix. Basic parameters that control corrosion speed are temperature, slag chemistry, refractory properties and residence time as well.
Few papers treat the corrosion considering the structure and its evolution during heating of the material. This is of course less important for magnesia carbon refractories, since the low wetting of slag, thanks to graphite additions, strongly limits the corrosion speed.
Porous network is of prime importance in the corrosion kinetics, when the mass transfer is the limiting step of the global corrosion reaction. This is the case for carbon free refractories, but also in MgO-C bricks when decarburization occurs, especially during empty ladle steps: the mass transfer is controlled by permeability of the material that means the connection and the size or pores.
This work attempts to clarify the relation between permeability, related microstructure and slag corrosion kinetics. As the permeability is changing during heating process of refractories, we adopt a method that takes into account this evolution, for magnesia concrete and MgO-C bricks, that are taken as references, for 2 types of slags representing flat carbon and long carbon steelmaking.
For carbon containing refractories, the permeability is being modified during 2 operations: the firing of the material in coke-bed media, and then the decarburization of carbon during empty stage of the ladle. The corrosion is the result of these permeability adjustments since the mass transport of slag occurs in a third step before the dissolution of mineral phases. The permeability evolution during this long process is evaluated and correlated with a kinetic model in porous media.
For concretes, the permeability determines the pore creation due to drying in the first step of material life, and thus the mass transfer in the modified structure. As for carbon containing refractories, the global corrosion process is the result of combined mass transfer and chemical dissolution of mineral phases in slag. Once more, the permeability evolution through these operations is correlated with a global kinetic model.
The final objective of this work can help material industrial optimization for a better corrosion resistance in steel process.

Abstract-Number: *464*

THE IMPACT OF PERMEABILITY ENHANCERS IN RAPID DRYING CASTABLES ON THERMOMECHANICAL PROPERTIES AND WEAR RESISTANCE

Auvray J.-M., Zetterström C., Wöhrmeyer C., Parr C., Kebli F.
Kerneos SA, Vaulx Milieu, France

The initial dry-out is one of the most critical steps of the installation process of refractory castables. The prediction of a safe and controlled drying of refractory castables remains today a challenge so the intrinsic and external parameters are numerous to explain the explosive spalling of a castable. In any case, a key concern is to limit the internal vapor pressure to a value below the tensile strength of the structure. Therefore, an increase of permeability is an efficient way to facilitate the removal of free and bounded water from the structure. Nevertheless, a good compromise needs to be found between a well permeable microstructure promoting the drying process and the applicative performances of the refractory materials at service temperature and in contact with liquids and gas.
This paper presents the relationship between the dry-out ability and the applicative performances at high temperature of refractory castable formulations with different permeability levels. Experimental simulations of dry-out under safe conditions with one-sided heating as well as the more traditional furnace based approach are conducted. The relationship between the type of permeability enhancing system and the thermo-mechanical properties will be discussed. Effects on thermal expansion and elastic modulus at high temperature will be presented. Moreover, the consequence of this specific permeable microstructure formed during the dry-out stage upon the corrosion resistance at high temperature will be investigated for different fast drying refractory solutions.

Abstract-Number: *466*

THERMO-MECHANICAL BENEFITS OF A RIGID INSULATION LAYER ON IRON AND STEEL LADLE SHELL LIFESPAN

Rebouillat L.[1], Lee Y.M.[2], Hodren G.[3], Kumar S.[4]
[1]Pyrotek Inc., Drummondville, Canada, [2]ArcelorMittal Steel, Global R&D, East Chicago, United States, [3]Pyrotek Inc., Spokane, United States, [4]ArcelorMittal Steel, Burns Harbor, United States

Ladles are used to transport molten iron and steel between the different stations of the metallurgical process. The ladle shell is submitted to various stress cycles including thermal shock, charging/discharging, lifting/drop. Most of the time, the steel shell is at high temperature during these cycles and during long steady stages. ArcelorMittal Burns Harbor recently experienced some ladle shell vertical cracking. The effects of the temperature during service on the fatigue of the steel shell have been investigated thanks to a finite element modeling. To reduce the impact of the temperature on the lifespan of the ladle shell, the use of a rigid insulation layer has been modeled and implemented. The benefits of the rigid insulation layer will be presented.

Abstract-Number: *467*

COMPARISM OF MECHANISMS AND CORROSION RESISTANCE OF MG- AND Y-STABILIZED ZIRCONIA IN SILICATE SLAGS

Hemberger Y., Berthold C., Nickel K.G.
Mathematisch-Naturwissenschaftliche Fakultät, Angewandte Mineralogie, Eberhard Karls Universität Tübingen, Tübingen, Germany

The corrosion of cubic and tetragonal ZrO2 with 10mol% MgO, 8 and 3mol% Y2O3 by model silicate slags was investigated in dependency of temperature and time to evaluate the mechanisms and kinetics of Zirconia degradation in refractory or thermal barrier applications. The silicate slags we report here come from the systems Na_2O-Al_2O_3-SiO_2, CaO- Al_2O_3- SiO_2 and CaO-MgO-Al_2O_3- SiO_2. They were chosen, because they are very reactive model slags with simple compositions.
In order to investigate the corrosion processes on the sub grain-scale we performed combined crucible-single crystal test in a special test setup with an upright standing FSZ single crystal.
We observed the dissolution of the stabilizing Y_2O_3 into the molten phase and according phase transformations from the fully stabilized cubic zirconia into tetragonal and monoclinic modifications. As a consequence we observe a disintegration of individual grains. The transformation sequence (c-ZrO2) à t-ZrO2à m-ZrO2 was detected by Raman-spectroscopic mapping, chemical analysis of the corroded ceramic and the adherent slag were done by wavelength dispersive spectroscopy (WDS).
Besides the chemical differences we found a strong dependency of corrosion rate on the grain size of the poly crystalline materials. We will discuss the corrosion kinetics of stabilized ZrO_2 materials as a function of stabilizing agent, time, temperature and grain size.

Abstract-Number: *468*

SIMULTANEOUS PHASE AND CHEMISTRY ANALYSIS IN YSZ BY RAMAN SPECTROSCOPY

Hemberger Y., Wichtner N., Berthold C., Nickel K.G.
Mathematisch-Naturwissenschaftliche Fakultät, Angewandte Mineralogie, Eberhard Karls Universität Tübingen, Tübingen, Germany

The relationship between Y_2O_3 content in tetragonal and cubic ZrO_2 phases and the shift of the Raman band at ~645cm^{-1} was investigated. A dependency of the vibrational frequency of tetragonal E_G and the cubic F_{2G} mode with varying Y_2O_3 content was observed. This dependency, first described by Yashima et al. 1996[1], was found to reach from the related structures of low Yttria stabilized tetragonal modifications (PSZ and TZP) to include both the transition zone with the t´´ modification and the fully stabilized cubic modification. A model showing the dependency of Yttria content and Raman band position is introduced by comparing several partially and fully stabilized poly and single crystalline zirconias with different Yttria concentrations. Thus it is possible to determine the Y_2O_3 content of any YSZ by determing the exact band position only.
This method combines the advantages of a true structural analysis and an indirect chemical analysis. It provides a high lateral spatial resolution, comparable to electron micro probe analysis and simultaneously distinguishes between all ZrO_2 polytypes very easily. In addition, the method is quick and does not require any special preparation step. Accordingly thin transformation layers can be phase mapped and the chemical variation of Y_2O_3 within grains or layers can be determined simultaneously. We will present some examples of application from the refractory corrosion field.
[1]Yashima et al. (1996), J.PhysChem.Solids **57**: 17-24

Abstract-Number: *469*

INFLUENCE OF SECONDARY PHASES ON CARBOTHERMIC REDUCTION IN MAGNESIA-CARBON BRICKS

Redecker L.[1], Sax A.[1], Quirmbach P.[1], Jansen H.[2]
[1]*University of Koblenz-Landau, Chemistry, Koblenz, Germany,* [2]*Refratechnik Steel GmbH, Düsseldorf, Germany*

Thermal degradation of magnesia-carbon bricks through carbothermic reduction of MgO at temperatures of about 1400°C and low partial pressure of O_2 is a known phenomenon. However, the influence of secondary phases in the magnesia on the carbothermic reduction reaction has been unattended so far. In the present study, the role of the main mineral secondary phases in magnesia as monticellite, merwinite and belite in carbothermic reduction processes are studied by thermogravimetric and microstructural analysis of MgO-C formulations with different synthetic secondary phases.

Abstract-Number: *470*

OPTIMIZATION OF THE STEEL LADLE TOP TING AT HKM

Tassot P., Rzepczyk J., Strutzik M., Stahl S.
REFRATECHNIK Steel, Düsseldorf, Germany

Hüttenwerke Krupp Mannesmann's plant (HKM) is located in Duisburg (Germany). It is an integrated steel plant with an annual output of approx. 5 million tonnes.
HKM has specialized in the production of slabs for flat products and in steel rounds for tube-making.
The highly sophisticated metallurgical treatment of the liquid steel during secondary metallurgy is operated in steel ladles with 280 tonnes capacity. Two ladle tank degassers and three argon stirring stands nowadays provide an optimum secondary metallurgical processing. The treatment in the vacuum tank degasser is particularly tough needing a high free-board up top 950mm. Key parameter in this process is consequently a reliable steel ladle with an optimum performance.
At HKM the weakest point is the top ring of the ladle cumulating a very high temperature (tapping temperature up to 1720°C) and corrosion with the slag during the heavy treatments but also submitted to a high mechanical stress by removing of the skull.
An innovative solution has been jointly developed after detailed analysis of the main sources of stress allowing the required performance for an equilibrated wear profile. Furthermore the new material based on Nanobond sol-gel technology is enabling a safe and very quick preheating of the ladle, improving the availability of the ladle fleet without any risk of cracks or explosion. The performance of the ladle has improved significantly through this measure.

Abstract-Number: *475*

A NEW FIRING TECHNOLOGY FOR RAW MATERIALS CONTAINING HIGH ENERGETIC ADDITIVES

Appel F., Reschke W.-H., Siefke C.
Hans Lingl Anlagenbau & Verfahrenstechnik GmbH & Co. KG, Krumbach, Germany

In the manufacturing process of porous products e.g. light weight insulating refractory bricks the desired properties of a low raw density and a high insulation value are achieved by the addition of additives like polystyrene, sawdust or paper pulp. However, the maximum amount of these additives is limited, because too high contents of these additives lead to uncontrolled ignition and firing of the organic carbon at temperatures starting even at around 230 °C - 300 °C. This leads to extreme heat peaks in the preheat-zone, with consequences such like local overheating with loss of product quality due to cracks and even product melting damages. In extreme cases the kiln is no longer controllable. In any case the dissipating energy in the preheat zone cannot be used in the process and thus is deteriorating the energy consumption of the kiln.
The presented new firing technology allows by means of a temperature- and oxygen-regulated process a controlled firing process of raw materials with high-energetic additives.
This is achieved by a pyrolysis process of the containing organic carbon under a low oxygen atmosphere in the preheat zone. The refined solid residues (carbon) during this process are afterwards oxidized in the firing zone, which contributes to reasonable energy savings.
Due to a controlled and gentle heat-up process the product parameters are significantly improved. Impulse burners or high-temperature recirculation units are used to improve the temperature distribution in the preheat- and cooling zone firing channel. By means of this new process it is possible to add a larger content of high energetic additives while the kiln remains fully controllable.
Another important aspect of this new firing technology is a sensible usage of the process excess energy created during the firing process. Dependent on the plant and product the energy can be used for
· production of preheated combustion air
· production of steam respectively hot water
· hot air supply for the dryer
· production of electric power for example with an ORC plant

Abstract-Number: *476*

TESTING OF MGO-C BRICKS FOR BOF: FROM LABORATORY TO INDUSTRIAL TESTS

Cordonnier T.[1], Le Ruyet T.[1], Blumenfeld P.[2]
[1]*ArcelorMittal Maizières, Maizières-les-Metz, France,* [2]*ArcelorMittal Maizières, Fos-sur-Mer, France*

Following several decades of use of pitch-bonded products, European flat carbon steelplants recently opened to the evaluation of resin-bonded MgO-C for BOF applications.
To assess suppliers' products, a comprehensive laboratory study was performed on 30 products from 6 suppliers, with focusing on trunnions, impact, cylinder and cone areas. Results showed a high convergence of products, whatever the supplier, country of production or binder type.
To furthermore improve confidence for industrial trials, some delivery audits have also been done before new supplier trials. Careful attention should also be paid to process parameters analysis during trial campaigns.

Abstract-Number: *477*

IMPROVED CASTABLE FOR STEEL LADLE BOTTOMS

Speiran T.[1], Rodrigues-Schroer A.[2]
[1]*U. S. Steel Research & Technology, Munhall, United States,* [2]*Wahl Refractory Solutions, Research and Development, Fremont, United States*

The sidewalls and bottoms of ladles handling molten steel at U. S. Steel have been traditionally lined with brick. In the last 15 to 20 years, alumina-magnesia-carbon brick was preferred. However, the process of installing and repairing brick linings is labor intensive and limits the contour that can be achieved for increasing yield, for example. Since 2013, in a project to reduce installation time, several plants in U. S. Steel have been experimenting with one-piece pre-cast bottoms, which can be lowered by crane into position. Suppliers were provided with a specification to provide a bottom that meets certain physical property requirements. A castable formulation was developed that surpassed the specified properties and trials of ladle bottoms were initiated at U. S. Steel. The refractory is capable of completing a full ladle campaign (approximately 200 heats) without patching. In order to further improve the wear rate of the bottom refractory castable, the supplier introduced several types and sizes of refractory aggregates to the base mixes. Samples were provided to U. S. Steel Research for slag resistance testing. In both the 80% and 90% alumina castable formulations, the addition of large aggregates resulted in better slag resistance compared to the base mix. The microstructures of the rotary slag samples were examined to see the penetration and reaction between the aggregate and matrix. Improved formulations will be trialed to determine the impact of the large aggregate.

Abstract-Number: *478*

INVESTIGATION OF THE EFFECT OF TIO_2 ADDITION ON CORROSION BEHAVIOUR OF MGO-SPINEL COMPOSITE REFRACTORIES

Aksel C.
Anadolu University, Department of Materials Science and Engineering, Eskisehir, Turkey

The effect of TiO_2 incorporation in various amounts into MgO-spinel (M-S) composite refractories at different compositions on corrosion behaviour was examined. Density and open porosity values were measured and evaluated. Corrosion tests of refractories were carried out statically under standard conditions using cylindrical shaped samples in terms of determining the interaction with cement clinker. Corrosion resistance was determined by measuring the values of penetration, depth and width of the corroded regions of refractories. The influence of corrosion resistance based on the microstructural changes occurred as a result of solubilities of constituents in the interface of clinker-refractory for various regions was examined using SEM and the results were evaluated using EDX analysis. It was observed that there was an increase in density values and decrease in porosity data for some of the compositions obtained from the addition of TiO_2 to MgO-spinel. As a consequence of microstructural characterisation performed at the interface of clinker-refractory, the observations made were determined as follows: i) the formation of Mg_2TiO_4 phase among the MgO grains during sintering, ii) prevention of penetration by the new phase formed that make a barrier effect against clinker with the improvement in densification, and iii) the decrease in the amount of CaO based on the EDX analysis made from clinker to refractory in a corroded region. The incorporation of TiO_2 into MgO-spinel reduced the values of penetration, depth and width of the corroded regions of refractories and improved the corrosion resistance.
The penetration of clinker to refractory showed a minimum level for the composition of M-5%S-30%TiO_2 and the improvements within the range of 33% and 48%, as compared to M-30%S and M-5%S, respectively. This development is combined with a long service life of M-S-TiO_2 containing composite refractories for industrial uses, as well.
Keywords: MgO; Spinel; TiO_2; Composite; Refractory; Corrosion