Abstracts

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1) CONTINUOUS CASTING

O01) AL2O3-C FUNCTIONAL REFRACTORIES IN STEEL CASTING APPLICATIONS BASED ON RESIN FREE BINDER SYSTEM

Gehre, P.(1); Ludwig, S.(1); Aneziris, C.(1); Braun, M.(2); Boenigk, W.(2); Jacob, C.(2);
(1): TU Bergakademie Freiberg / Institute of Ceramic, Glass and Construction Materials, Freiberg, Germany
(2): RÜTGERS Germany GmbH, Castrop-Rauxel, Germany

The continuous casting sector of steel production is a common application field of Al2O3-C refractories, where they are used as functional components. Since several decades resin binder systems are mostly applied. In terms of this contribution a resin free new hybrid binder system will be demonstrated which gives an excellent performance according to the extreme mechanical, thermal and chemical requirements of the application as stopper or submerged entry nozzle. Mechanical properties were evaluated at room and at elevated temperatures and in a first step a steel casting simulator was used to verify the interactions with a steel melt. Graphs based on computer tomography showed no cracks in spite the high thermal shock attack from room temperature to 1600 °C temperature of the steel melt. Based on the positive results demonstrators with dimensions next to real components were evaluated in an aggressive steel slag-system in a foundry. The demonstrators survived several thermal shocks and no contamination of the steel was registered. Their residual strengths post mortem open the horizon for the new binder system to be used in advanced applications such as the continuous steel casting.

O02) WHY SPRAY MIX IS STILL A DOMINANT TECHNOLOGY FOR TUNDISH COATING APPLICATION?

Corrêa, A.(1); Costa, E.(1); Brito, M.(1); Bellandi, N.(2); Resende, R.(1);
(1): Magnesita Refratários SA, Belo Horizonte, Brasil
(2): Refractarios Argentinos, San Nicolás, Argentina

Tundish is the last equipment in contact with liquid steel which is relined with refractory with the possibility of affecting the steel quality. In this equipment the working lining plays the role of thermal container. Despite the concerns about H2 pick up that can be caused by the presence of water and also an excessive consumption of gas for drying and heating, spray mixes have been a dominant technology for tundish application. Almost 90% of the plants in South America use this kind of refractory lining. In the last 20 years new technologies came up to the market with the proposition of reducing or even eliminating the need for water and gas, making the application easier and increasing tundish availability. Although these new technologies present these advantages over the spray mixes and are useful for some operational conditions, spray mixes still have a strong presence in the market mainly due to their low cost and high thermal insulation. Nowadays, some improvements have been developed regarding the dry and spray mixes in order to have a more complete and suitable technology to fit the most specific demands from the market. However, some operational conditions that ensure the desirable working lining performance are as important as having appropriate
technologies. The slag attack, stream deviation, and an application of a thin layer during the tundish relining are examples of operational variables that affect the performance of the tundish despite the technology used, and can be avoided. In this way, product technology, application procedure and process conditions are pillars of success and must move together.

003) EFFECTS OF THE SUBMERGED ENTRY NOZZLE DESIGN ON THE SLAB MOLD FLOW PATTERN AND STEEL QUALITY

Dolabella Resende, A.(1); Fraga Resende, R.(1); Nazareth Borges, R.(1); Alves Freire, R.(1);
(1): Magnesita Refractories, Contagem, Brazil

The fluid flow pattern in the continuous casting mold has a major impact on the final product quality. It transports non-metallic inclusions and argon bubbles to either the top slag layer, where they will be entrapped, or the solidification front, where they will become defects. Moreover, excessive surface level fluctuations and high meniscus velocities may cause mold slag entrapment, deeper oscillation marks and other defects. The flow pattern could also affect the liquid slag penetration in the gap and have impact on the longitudinal cracks index. One of the best ways to control the mold flow pattern and obtain high quality steel is through an optimal Submerged Entry Nozzle (SEN) design. In this work, the flow patterns for different SEN designs were evaluated through numerical simulations. The obtained flow fields were analyzed with focus on the prevention of defects in the final product. Through these studies, it was possible to understand how changes in the SEN design affect the mold flow pattern, and consequently, the steel quality.

004) INVESTIGATION OF THE CORROSION MECHANISM OF AL2O3-ZRO2-C SLIDE GATE PLATES FOR THE CASTING OF CA-ADDED STEEL.

Kato, Y.(1); Ikemoto, T.(1); Goto, K.(1);
(1): NIPPON STEEL and SUMITOMO METAL, Chiba Prefecture, Japan

The clogging of a submerged entry nozzle (SEN), caused by the alumina inclusions that precipitate from steel, is a serious problem for the continuous casting operation and steel quality. It is known that the addition of calcium (Ca) to the steel is effective for preventing the clogging because Ca reacts with alumina inclusions, forming calcium aluminates, which have low melting points and do not form precipitated layers. However, it was observed that the corrosion of Al2O3-ZrO2-C (AZC) slide gate plates increased when they are used for Ca-added steel casting. Therefore, it became necessary to improve the corrosion resistance of the AZC slide gate plates.

Based on the microscopic observation of used AZC slide gate plates, it became clear that when these slide gate plates were used for Ca-added steel casting, they developed many more pores than the original material, and calcium aluminates penetrated into the slide gate plate structure, along the pores. It was considered that because more pores developed in the structure, the corrosion of the AZC slide gate plates was accelerated.
To clarify the porosity increase mechanism of the Al2O3-ZrO2-C slide gate plate structure, the gas generation from the refractory materials was thermodynamically investigated. The thermodynamic calculation was conducted for the condition where solid state Al2O3, ZrO2, mullite and C, which are components of the refractory materials, coexisted with pure Fe or Fe-Ca in the liquid condition at 1550°C (1823K). The analysis indicated that the partial pressure of SiO gas generated in the slide gate plate material, when used with Ca-added steel, was much higher than the cases of the other steels. Therefore, it was suggested that it is necessary to suppress the gas generation from the slide gate plate materials, and maintain the dense structure, to improve the corrosion resistance of the Al2O3-ZrO2-C slide gate plates.

So, the sample refractory material which consisted of Calcium Hexaaluminate(CA6) aggregates used for suppressing the SiO gas generation because of its stableness as the solid state was tested by the corrosion test using the Ca-added steel at 1550°C (1823K). Then, it was revealed that the corrosion resistance of the sample material increased by 20% compared with the conventional AZC slide gate material.

**005) ROLES OF BORON CARBIDE IN AL2O3-C REFRACTORIES USING MWCNTS AS CARBON SOURCE**

Li, Y.(1); Liao, N.(1); Liu, G.(1); Sang, S.(1);
(1): Wuhan University of Science and Technology, Wuhan, China

B4C additive was adopted to accommodate the structure evolution of MWCNTs in Si containing Al2O3-C refractories. The corresponding phase compositions and microstructures of Al2O3-C refractories were investigated by means of X-ray diffraction (XRD), Raman spectra, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. The mechanical properties were investigated by means of three-point bending test and the thermal shock resistance was evaluated through traditional water quenching method combined with wedge splitting test. The results show that B4C additive prevents the structure transformation of MWCNTs at 1000 °C and suspends the transformation at 1200 °C attributes to the decreased SiO(g) pressure. Additionally, B4C favors the catalytic formation of new MWCNTs and quasi-graphene sheets. In comparison with the refractories containing Si additive alone, more residual MWCNTs and newly formed MWCNTs and graphene sheets in B4C and Si containing Al2O3-C refractories contribute to lower brittleness, leading to better thermal shock resistance.

**006) IMPROVEMENT OF NOZZLE CLOGGING FOR CONTINUOUS CASTING OF ULTRA LOW CARBON STEEL**

Park, Y.(1); Ki, W.(1); Ryu, S.(1); Maddalena, R.(2); Rezaie2, A.(2); Nolli, P.(2); Ahn, J.(1); Kim, Y.(1);
(1): Hyundai Steel Company, Dangjin, Chungnam, Republic of Korea (2): VESUVIUS, Pittsburgh, Pennsylvania, USA
In the continuous casting of steel, the submerged entry nozzle is used to prevent reoxidation by air during the pouring of the molten steel supplied from the tundish to the mold. The submerged entry nozzle, therefore, plays a very important role in assuring high product quality.

However, clogging of the submerged entry nozzle often occurring in the continuous casting of ultra low carbon steel, causes degrading product quality, and also can be led to stop the casting process. So, many researchers have been trying to develop the nozzle to suppress clogging. But, evaluation of the nozzle performance was difficult, because nozzle clogging is complexly affected by operation condition of steelmaking and continuous casting process.

In this paper, a new test method with the nozzle that has two different materials of inner section was used to consider performance of the nozzle only.

The testing nozzle that has conventional material (more than 20wt% carbon) and low carbon material (less than 5wt% carbon) of Al2O3, SiO2, C was used in field test. After casting, in order to evaluate performance of the nozzle material, measurements of the clogging thickness of two different materials were carried out. According to test results, Hyundai Steel Company was able to improve clogging by optimizing the nozzle material.
BFCO 1) BLAST FURNACES AND COKE OVENS 1

007) REFRACTORY CONDITION ASSESSMENT IN BLAST FURNACE HEARTH BY UTILIZING NDT, THERMOCOUPLE AND COOLING SYSTEM DATA

Ghorbani, H.(1); Chomyn, K.(1); Solteys, C.(1);
(1): Hatch, Mississauga, Canada

The blast furnace hearth refractory system is exposed to complex chemical attacks and thermal and mechanical loads. The hearth is a region of primary concern since excessive refractory failure and degradation limits the furnace campaign life due to premature and costly repairs. It is therefore essential to understand and monitor the hearth conditions including the temperature distribution as well as refractory and skull thicknesses. Acousto-Ultrasonic Echo (AU-E) and thermal modeling are widely used by the industry to non-destructively estimate the refractory conditions in the blast furnace hearth. This paper presents a novel methodology to simultaneously utilize AU-E and thermocouple / cooling system data and take advantage of both methods to improve accuracy of hearth condition predictions. Example applications of this assessment methodology on blast furnaces are discussed. This assessment methodology can be used to prolong the blast furnace campaign life.

008) ASSESSMENT OF THERMAL EXPANSION AND CONTRACTION OF REFRACTORY SYSTEM IN BLAST FURNACE HEARTH

Ghorbani, H.(1); Maleki, M.(1); Van Der Woude, C.(1);
(1): Hatch, Mississauga, Canada

The refractory system in blast furnace hearth is exposed to harsh conditions and varying high temperatures. Such temperature fluctuation may generate undesirable refractory cracking and gap formation which could decrease the efficiency of hearth cooling system. Minimizing crack and gap formation and optimizing the brick pattern, materials, and expansion allowances can improve the campaign life of the blast furnace hearth. This paper presents a novel assessment tool based on advanced finite element analysis for predicting refractory failure, mortar joint opening, and gap formation around rammimg mixture in the hearth. Using this tool, locations of potential refractory system failures during blow-in and blow-down of the furnace can be identified and mitigated during design stage. This tool can also be utilized in order to understand the cause of hearth refractory wear in existing furnaces.

009) DEGRADATION MECHANISMS OF Si3N4-BONDED SIC BRICKS INSTALLED IN BLAST FURNACE’S SHAFT

Rimoldi, M.(1); Camelli, S.(2); Vázquez, A.(2); Marinelli, P.(3); Mirabelli, J.(3);
The refractory systems of the bosh, belly and stack of the blast furnace, probably, are the most critical in terms of their impact on the operating capability of the equipment. When selecting refractories for these zones, it is imperative to evaluate the wear mechanisms to be encountered, to identify the expected operation conditions which could affect the lining life and to evaluate all external factors which will impact refractory performance.

The main wear mechanisms that are encountered in the bosh, belly and stack are chemical attack by alkalis and zinc, carbon monoxide disintegration and oxidation, abrasion by the descending burden, thermal load and thermal shock. Silicon carbide linings are used in these zones of the blast furnace due to their higher resistance to chemical attack, abrasion and thermal shock than fireclay or high-alumina refractories. SiC refractories can have several different bond types which change the physical properties of the refractory. In general, silicon nitride (Si3N4) bonded SiC has proven to be preferred over various direct bonded, self-bonded or carbon silicon bonded materials. Although the SiC grains are stable when exposed to alkalis, this is not the case with bonding systems. Ceramic bonding and even oxi-nitride are affected by potassium. SIALON (Si6-xAlOxN8-x) bonded materials have also been used for their improved alkali resistance.

In November 2015 Ternium Siderar Blast Furnace #1 was blown down after 5 years in operation (2010-2015). In order to evaluate the main wear mechanism encountered in the working lining of the middle shaft, it was performed a post mortem study of SiC bricks. These are Si3N4-bonded. The post mortem study included determination of the chemical and mineralogical composition, DT/ TG analysis and microstructural analysis by optical and electronic microscopy (SEM and EDS analyses).

The SiC bricks under study presented thermal and structural spalling. Chemical attack by alkali penetration was identified, mainly potassium oxide with the generation of new phases such as potassium hydrogen silicate. Cracks present in the material permit alkali condensation in the brick. Due to the thermal profile in brick thickness during operation, alkali content in the cold face is greater than in the hot face.

**O10) TOWARDS IMPROVED REFRACTORY LINING PERFORMANCES: A NOVEL CEMENT FREE BINDER SYSTEM AS SOLUTION FOR TILTING RUNNERS**

Duvauchelle, N.(1); Techer, R.(1); Soudier, J.(1); Meunier, P.(1);
(1): CALDERYS, Saint Quentin Fallavier, France

Iron tilting runner, one of the facilities of iron making, is employed on the casthouse floor to transfer the molten iron tapped from the blast furnace to torpedo ladles. In recent years, the performance of blast furnace has gradationally increased, resulting in high productivity and high iron temperatures. Thus, high expectations are placed on the refractory linings of tilting runners to maintain sufficient durability even under stringent operational conditions. The severe wear at the impact zone results in downtime for repairs or new linings. Even though used universally as linings for runners and tilting runners in iron industry, cement black castables suffer from several drawbacks.
especially during the drying step and show some extent for harsh conditions, high
temperatures, resulting in lower performance of the working lining. Over the past years,
investigations on sol/gel castables have been carried out aiming to reduce the drying
times, cracking and explosion and improve hot properties such as hot modulus of
rupture. Nevertheless, nanostructured bonded materials show inherent drawbacks
including the poor green mechanical strength and the sensitiveness due to ambient
conditions and/or ageing. In order to overcome these problems and suit combinations
of all requirements, a novel cement free binding system, inspired and reproducing
fundamental features of zeolites, has been developed. First and foremost, the paper
tackles the key properties of zeolites structure. The effect of this novel free cement
bonding system on rheological properties, setting and green strength development
kinetic as well as hot properties of vibratable Al2O3-SiC-C castables in comparison with
cement based castable and sol/gel castable will be addressed over a second phase.
According to the outcomes, the new cement free black castable reveals a high and rapid
development of green mechanical strength during curing, providing installers time
saving and ensuring safe demolding and mechanical operations. As for hot physical
properties, the non-cement castable shows high hot modulus of rupture, resulting in a
better resistance to the iron stream impact limiting therefore the risk of breakthrough.
The new binding system enables Al2O3-SiC-C castables to offer better performance than
ultra-low cement castables or sol/gel bonded castables regarding commissioning and
running time when blast furnace operations become more severe and/or when wear
lining sets stringent requirements on refractories, especially in the iron stream impact
zones.

O11) KEY ASPECTS ON THE THERMOMECHANICAL BEHAVIOR OF TORPEDO
LADLE BRICKS USING FEA

De Miranda Mati, A.(1); Alves Freire, R.(1); Breder Teixeira, L.(1); Alves De Moura Brito,
M.(1); Cabral Da Silva, S.(1); Gomes Brandão, P.(2);
(1): Magnesita Refratários, Contagem, Brazil (2): Universidade Federal de Minas Gerais,
Belo Horizonte, Brazil

Introduction Torpedo ladles are typically lined with alumina silicon carbide carbon
refractories. These materials withstand a broad range of temperature and undergo
severe thermal cycles during the campaign. As all bricks are assembled in a restricted
condition that retains the natural thermal expansion of the refractory, spalling effect
may occur. Many efforts have been made on the development of torpedo ladle bricks.
As it is difficult to analyze the thermomechanical behavior of constrained bricks under
typical laboratory conditions, analysis by the finite element method (FEA) can be used
as an important tool to predict the behavior of the material. The main challenge of FEA
simulations applied to refractories is the selection of the correct failure criteria for it.
Stress-strain curves and FEA simulations, Hirota et al. (1995) have proposed a spalling
mechanism for torpedo ladle bricks during operation. On the basis of this brief review,
the purpose of the present work was (i) to evaluate the effect of some variables on the
thermomechanical behavior of Al2O3-SiC-C refractories by means of FEA simulations
and thus (ii) establishing their relative importance for the development of a torpedo
ladle brick with enhanced spalling resistance. Material and Properties One typical
Al2O3-SiC-C refractory was evaluated. After curing at 200°C, 6h, the samples were characterized by thermal expansion. Heat treated samples were characterized by stress-strain curves at different temperatures under compression. The thermal conductivity was obtained by standard values provided by Magnesita Refractories. The FEA simulation was run using Ansys® Mechanical 14.0. In order to validate the data, the first step was to simulate the spalling mechanism as proposed by Hirota et al. (1995). Afterwards, different values of thermal expansion, stress and strain and thermal conductivity were inputted in the software to assess the key properties of the material in an attempt to enhance the spalling resistance. Results and Conclusion The simulations by FEA indicated that the failure criteria selected in this work are in accordance with the spalling mechanism proposed in the literature and with practical observations. As the stress values were systematically higher after the breakage of the bricks’ edges, it seems more reasonable to avoid spalling by hindering the formation of broken edges than by avoiding the phenomenon itself. The effect of key aspects on the thermomechanical behavior of Al2O3-SiC brick was simulated by FEA. It is proposed that the key variables to be controlled are the following: stress, thermal expansion, strain and thermal conductivity. The highest and lowest effects on the normal stresses and shear stress were observed when the inputted stress value was varied by ±20%. The findings of the present investigation may be useful for developing refractories with longer service life.

O12) SPRAY SYSTEM DEVELOPMENT FOR QUALITY IMPROVEMENT IN REPAIRING THE BLAST FURNACE WALL

Choi, Y.(1); Kim, W.(2); Kim, Y.(2); Han, K.(2); Park, C.(2); Kang, H.(2); Lee, S.(2);  
(1): Chosun Refractories, Gwangyang Si, S.Korea  
(2): Chosun Refractories, Gwangyang Si, S.Korea

This report is about spray system of blast furnace designed to improve furnace wall repair quality and life.

In general, there are several ways to repair furnace wall such as spraying, injection and pre-cast panel repair etc. Especially, Spraying is often used because it can repair wide range with high efficiency. But, due to enlargement of blast furnace size and distribution form of charging materials inside furnace, there are many difficulties to repair furnace wall. As a result, the need for repair quality development has been on the rise.

So, we developed brand new system which is available to evaluate repair materials, repair machine and repair quality to solve above situation. Repair materials are Silica sol bond based, and Al2O3-SiO2, Al2O3-SiC are for each part. Repair machine is developed to repair without interference of charging material but at the same time, repair ability and adhesion are enhanced. Quality evaluation facility can monitor repair state in real time. 3D Scanner evaluates rebound loss rate and repair state.

Here are results of real application. Rebound loss is under 10% with high adhesion so, reached normal operation in early stage. Especially, repairing life and repair cycle are
improved by repair quality improvement. Consequently, we can guarantee stable furnace management and productivity improvement.
MO 1) MONOLITHICS FOR VARIOUS APPLICATIONS 1

O13) ENGINEERING CALCIUM ALUMINATE HYDRATION TO MAKE CASTABLE SETTING LESS DEPENDENT ON AMBIENT TEMPERATURE

Zetterström, C.(1); Szepizdyn, M.(1); Frier, E.(1); Lacoue, F.(1); Wöhrmeyer, C.(1);
(1): Kerneos, Vaulx-Milieu, France

Setting behavior of calcium aluminate bonded refractory castables can vary in different environments, due to different dissolution and hydrate precipitation rates, as well as different mineralogical structure of hydrates that form as a function of temperature. It is quite common that a given castable will have an excessively long setting time at low temperatures, while inversely, having a too short workability and setting at high temperatures.

In this paper, a mineral based deflocculating active compound is used in an alumina spinel type castable that stabilizes the setting behavior over the temperature range 5°C to 35°C. A comparative study with a non-doped reference material is conducted, reviling the impact from the active compound on the hydration mechanisms across the temperature range.

Differential Scanning Calorimetry, X-Ray Diffraction and SEM observations are used to describe the different hydration behavior of the reference and doped castables, and to understand how the temperature stabilizing effect is achieved.

O14) CHANGE OF PROPERTIES AND HYDRATION KINETICS OF CA AND CA2 BY PROLONGED MILLING

Hueller, F.(1); Ectors, D.(1); Neubauer, J.(1); Kuiper, S.(2); Goetz-neunhoeffer, F.(1);
(1): University of Erlangen-Nuernberg, 91054 Erlangen, Germany (2): Almatis B.V., 3197 KM Botlek-Rotterdam, Netherlands

High alumina refractory cements usually contain CA as main hydraulic phase next to the more refractory but less reactive CA2. In a study by Klaus et al. [1] the influence of particle fineness on the kinetics of CA hydration was investigated. Surprisingly, a shift to later times was observed with increasing fineness. However, the grinding times were relatively short and no X-ray amorphous phase was detected in their investigated powders.

In the presented study the properties of CA and CA2, both synthesised by solid state reaction from CaO and Al2O3, were compared after equal but longer grinding times. For enabling a good workability of the pastes fine alumina was added as inert filler. The heat flows during the hydration of pastes containing pure CA or CA2 in combination with alumina filler were precisely recorded from the time of water addition over a period of at least 72 h using a TAM Air calorimeter equipped with tools which allowed a reproducible internal water injection and paste mixing (InMixEr). The dissolution of CA or CA2 and precipitation of different hydrate phases during the hydration of the
investigated pastes was analysed by highly time resolved in-situ XRD and in-situ 1H time domain NMR. This enabled a quantitative determination of the phase contents of crystalline and amorphous hydrate phases at defined points in time of hydration.

CA2 showed a higher susceptibility to grinding which was indicated by higher BET surface areas and higher amounts of X-ray amorphous phase after equal grinding times in comparison with CA. Although CA2 is indeed less reactive than CA its hydraulic activity could be significantly increased by grinding. Especially, the increasing amounts of X-ray amorphous phase and the higher BET surface areas led to an acceleration of the hydration and to an unusual well defined heat flow peak prior to the main hydration reaction. Additional thermal treatment of the ground samples led to a reduction of the BET surface area and to a transformation of the X-ray amorphous fractions into completely crystalline CA or CA2. The thermally treated samples showed significantly different hydration kinetics. Finally, the hydraulic behaviour of the investigated samples could successfully be influenced in a targeted way by different grinding and tempering procedures.

O15) THERMOMECHANICAL BEHAVIOR OF HIGH-ALUMINA REFRUCTORY CASTABLES CONTAINING PARTIALLY STABILIZED ZIRCONIA WITH DIFFERENT GRAIN SHAPES

Etzold, S.(1); Tonnesen, T.(1); Telle, R.(1); Tarabeux, J.(2); Porada, R.(3);
(1): RWTH Aachen University, Aachen, Germany (2): ENSCI Limoges, Limoges, France (3): AGH Krakow, Krakow, Poland

In many industrial processes refractory materials are exposed to considerable mechanical stresses at high temperatures. The wear resistance of refractories against these conditions is crucial to the service life of industrial aggregates. Therefore, an increased flexibility at elevated temperatures and an advanced thermal shock resistance constitute desirable properties for refractory materials. The formation of interlocking structures contributing to this behaviour can be found in nature; for instance itacolumite, a material based on interlocked quartz grains exhibiting large intergranular decohesions. This particular microstructure, reminding of a puzzle, enables itacolumite to resist large strains before failure when exposed to thermomechanical stresses. Inspired by this very special material behaviour, this study attempts to create refractory castables which are capable of resisting higher thermal shock stresses and show an improved flexibility. As a first step of this study, two chemically identical high-alumina castables were designed, which differ in the shape of the added Y-PSZ (Partially Stabilized Zirconia doped with 3 mol.-% yttria; size 0.2 - 1 mm) grains only: The first formulation mainly includes anisometric Y-PSZ particles, whereas the second formulation predominantly contains isometric Y-PSZ grains of the same production lot. Thereby, two different methods of material reinforcement, namely transformation toughening and the formation of interlocking structures, are intended. To evaluate their impact on the high temperature performance of the castables, the applied testing methods include cycling Resonant Frequency Damping Analysis up to 1500°C as well as Refractoriness under Load and Creep in Compression, Hot Modulus of Rupture (HMOR) tests between room temperature and 1500°C and a post mortem SEM analysis of the
microstructure. The examined castables showed a very similar behavior under compressive load, but considerable difference in bending behavior. Both the HMOR measurements and SEM analysis indicated that the grain shape has a strong influence on the condition of the matrix. Since heating as well as the sudden volume change of the martensitic transformation particularly lead to expansion in axial direction of the grains in case of the elongated Y-PSZ particles, a different crack network is introduced into the surrounding matrix compared to the castable containing isometric zirconia grains which expand approximately uniform in radial direction.

O16) IN-DEPTH ANALYSIS OF THERMAL PROFILES DURING INDUSTRIAL DRY-OUT OF LOW CEMENT CASTABLE

Lee, Y.(1); Johnson, K.(1); Kumar, S.(2);
(1): ArcelorMittal Global R&D, East Chicago, USA (2): ArcelorMittal Burns Harbor, Burns Harbor, USA

Low cement castable is prone to steam spalling due to low permeability during dry-out. Much contribution has been made to understand the dewatering behavior of low cement castable and avoid steam spalling. Practical questions about heating rates and holding time were raised during industrial application. The current work will present in-depth analysis of temperature profiles of low cement castable during large-scale industrial dry-out and compare them with laboratory studies.

O17) THE ROLES OF MATRIX ALUMINAS ON THE PROPERTIES OF HIGH PERFORMING CASTABLES

Samanta, A.(1); Satpathy, S.(1); Arimitsu, E.(1); Tsuyuguchi, K.(1); Panda, P.(1); Chatterjee, S.(2);
(1): TRL KROSAKI REFRACTORIES LIMITED, JHARSUGUDA, INDIA (2): ALMATIS ALUMINA PVT. LIMITED, KOLKATA, INDIA

Decades back only ground calcined alumina was the choice of high-alumina matrix products that were used in castable formulations. At that time the flow properties of castables were enhanced by the use of silica fume. However, silica fume, later was avoided in high performing castables because of inferior high temperature thermo-mechanical properties above 1400ºC. Then the development of new generation castables came by using fully ground reactive aluminas for high temperature applications such as steel ladle well blocks, seating blocks, RH snorkel or porous plugs etc. It is well established before many a times that high alumina castables (such as medium/ low/ ultralow cement castables) containing higher Na2O, especially in matrix ingredients, show inferior high temperature properties in Al2O3 – Na2O - CaO system. So, the choice of those reactive aluminas or matrix aluminas in new generation high performing castables are certainly not limited to chemical purity but mainly to the physical properties such as specific surface area (BET) and particle size distribution (PSD). A wide range of bi-modal and multi-modal reactive aluminas of different specific surface areas were selected to observe their effects on the rheology, workability, volume & structural stability and cold and hot strengths of high alumina low cement
castable. The optimum choice of such matrix formulation provides easy castable mixing and placement conditions as well as excellent mechanical and physical properties to support the demands of high temperature applications. In this present work four different kind of matrix aluminas were selected on the basis of d50 and surface areas. Rheological study, water demand, flowability along with all common properties like AP, BD, CCS, volume stability etc. were studied. Different mineralogical phases were identified by XRD and microstructure analysis was carried out by SEM for some specific samples to understand the properties after firing at different temperatures.

O18) APPLICATION OF MICROWAVE HEATING ON THE FABRICATION OF PRECAST BLOCK OF REFRACTORIES

Nishigami, Y.(1); (1): Krosaki Harima technical research center, Kitakyuushu, Japan

Processing of castable refractories is known generally as time and energy consuming treatment including both curing and drying. Typically the process consists of casting into metal-frame, curing for 1 day (24h) at ambient temperature and drying by heating with gas-burners for 2 to 3 days after de-framing. Among the castable refractories, a cement-free type has quite low productivity requiring several days for curing process. As an environmentally-friendly process innovation by energy saving through shortening the castable processing, a microwave heating system has been introduced for drying of them used for lining of ladle and container for molten steel in some steel works so far. In the heating system, the refractories are warmed-up quite efficiently with short time by heat generation from inside of material without depending on its thermal conduction. In order to make use of the above described superior feature more progressively, the microwave heating was applied to shorten the total operation times for both curing and drying of the castable refractories. Thus, precast block of refractories were fabricated by processing with the microwave heating. Comparing the properties of the material obtained from the block by the above described new process with those by the conventional process, the effectiveness of the new process was evaluated.
Introduction

The rotary kiln is the critical equipment in Portland cement clinker production. The duration of shutdowns is determined by the installation of the bricks. And the schedule of the shutdown will be determined by residual thickness of brick lining.

A promising alternative to overcome these disadvantages is the use of unshaped Magnesia based materials. This solution involves cost and time saving as well as environmental, health and safety advantages. In addition, the option of relining up to the original brick thickness by gunning, increasing their lifespan becomes an excellent solution.

However, the major challenge for MgO castables is the control of the hydration of magnesia to prevent the spalling and cracking during the curing and drying steps.

The aim of this paper is the development of the Magnesia-Spinel castables as an innovative alternative and/or complement to MgO bricks in rotary clinker kilns. The design allows the application of the castable by gunning and casting, in order to have a versatile product that satisfices all the needs of the clinker producers.

Materials and Methods

Different compositions of Magnesia-Spinel castables have been designed. Different magnesia sources and anti-hydration additives were studied. The evaluation of hydration of the Magnesia and its effects on the castables were carried out by the following techniques: macro-TGA, microscopy, XRD, dilatometry and properties of the samples (230 x 55 x 65 mm). In the second stage, bigger samples (300 x 300 x 300 mm) from the best recipes were casted.

Results

Magnesia-Spinel castables have been developed, without problems of cracking during the curing, drying or heat treatment. Installation methods used were gunning and vibrocasting. The properties of castables are good enough for the application and similar to Magnesia-Spinel bricks.

The control of the Magnesia hydration has been carried out two different ways, such as the selection of raw materials and the design of the microstructure. The chemical compatibility of old bricks and castables has been tested and the integrity of brick coated
showed no alteration. The behavior of castable during the process is similar to that of the bricks and no differences in the coating formation have been detected.

New Spinel-Magnesia castables designed are being tested in different clinker production plants, without operating problems up to date.

Conclusions

An innovative alternative for rotary Clinker kilns has been developed with promising results.

Rebuilt of the old bricks with the Magnesia-Spinel castables is an excellent solution promoting reductions in costs and maintenance shutdown time together with significant environmental, health and safety advantages.

O20) INFLUENCE OF FLEXIBILISERS ON BASIC CEMENT ROTARY KILN BRICKS

Geith, M.(1); Krischanitz, R.(2); Jörg, S.(1);
(1): RHI AG, Leoben, AUSTRIA (2): RHI AG, Vienna, AUSTRIA

Magnesiumoxide is an excellent refractory raw material basis for the lining of the thermally highest loaded part of cement rotary kilns (CRK), the so called burning zone. It is characterized by a high refractoriness and a high thermal expansion coefficient as well as thermal conductivity resulting in a rather poor thermal shock resistance and flexibility. To reduce the risk of brick hot face spalling, CRK-brick producers are using granular additives to prevent from crack formation. Refractory producers are talking of bricks with increased flexibility. Spinel-minerals are used for refractory application such as Chromite, MA-spinel, hercynite or pleonaste. Consequently magnesia chromite bricks are continuously replaced, at first by MA-spinel bricks. In the 90’s the next step was the development of bricks based on hercynite, an FeO.Al2O3 spinel, as flexibiliser. Most recently cement rotary kiln bricks with addition of pleonaste appeared on the market, which mineralogically is a (MgO, FeO).Al2O3 spinel. It can be described as hercynite with a defined, additional MgO-content of 20-50%. In case of standard MA-spinel or pleonaste as additive mainly the thermal misfit (difference in linear expansion between the flexibiliser and the surrounding magnesia matrix) causes the formation of stress centers or even microcracks. If crack propagation in service occurs these stress centers or microcracks reduce the young’s modulus and increase the energy that is needed for crack propagation – the brick flexibility is increased. If hercynite is used the thermal misfit is enhanced by a diffusion effect of Fe into the surrounding matrix causing that hercynite is the most effective additive. In product development the V-moduls, the Young’s modulus and the specific fracture energy are used to characterize the brick’s flexibility. A test series with constant flexibiliser content proved that hercynite can be assumed as the most effective additive, while MA-Spinel and pleonaste are on a quite similar, but lower level. Accordingly, in order to reach a certain level of flexibility a higher amount of these additives need to be added to achieve a similar level of flexibilisation compared to hercynite. This negatively affects other important properties such as the resistance to clinker melt infiltration. Summarized it could be shown that hercynite is
the most favourable additive to basic CRK-bricks leading to an optimum thermomechanical behavior combined with a maximized corrosion resistance for applications in the basic area of cement rotary kilns.

O21) MAGNESIA PLEONASTE BRICKS FOR ESSENTIAL REQUIREMENTS IN ROTARY KILNS

Klischat, H.(1); Wirsing, H.(1); Vellmer, C.(1);
(1): Refraterotechnik Cement GmbH, Goettingen, Germany

The essential effect of iron ions in providing oxygen to the human body by valency change in hemoglobin is well known. In a similar way, iron oxide is recognized as essential compound in cement and lime kiln refractories for providing a satisfactory lifetime under varying kiln conditions. Investigations have shown that a defined amount of \( \text{FeO(x)} \) in basic bricks is rather advantageous, e. g. for thermoplastic stress relaxation or coating formation, without affecting the necessary requirements regarding refractoriness, redox resistance, thermal shock resistance, etc. A measure for the thermoplastic behavior is the deformation in the creep under compression test where the positive influence of iron oxide is shown. Early investigations describe the effect of chrome ore and hercynite, nowadays the \( \text{Fe(II)} \) and \( \text{Fe(III)} \) species containing pleonastic spinel show the most advantageous properties. This is due to the fact that the iron ions are stable bound in the microstructure. This is shown by the redox test, where strength and volume change after alternation of reducing and oxidizing atmosphere is determined. Although a dependency is obvious, a high cold crushing strength and modulus of rupture as well as the simultaneous presence of both iron oxide species is advantageous concerning thermoplastic stress relaxation as well as all other relevant properties. The graded presence of iron species in a series of pleonaste-containing refractories allows the selection of adequate refractory material regarding the requirement to cope with the influence of higher temperatures. It has to be concluded that a balanced presence of both iron oxide species is quite beneficial for the performance of rotary kiln bricks, in several cases they outperform refractories based on very pure raw materials, especially in kilns with a high mechanical load on the lining.

O22) IMPROVING PROPERTIES OF MAGNESIA-SPINEL BRICKS FOR CEMENT ROTARY KILNS BY USING MICRO-FINE MGO PARTICLES

Hartenstein, J.(1); Gueguen, E.(2); Moulin, J.(1); Schepers, A.(1);
(1): Magnesita Refractories GmbH, Hagen, Germany (2): Magnesita Refractories SCS, Valenciennes, France

The fine fraction of particles or the so-called matrix plays an important role for the physical properties of refractory bricks. In this study micro-fine MgO particles were added to magnesia-spinel formulations. The aim was to reduce porosity and permeability as well as to improve the sintering behaviour and to promote the in-situ spinel formation. Micro-fine MgO particles were produced from very pure Brazilian magnesia sinter with a purity of typically > 98 %. The micro-fine particles had a diameter from 0.5 to 4 µm with a \( d_{50} \)-value of 1.6 µm as measured with a laser diffraction
analyzer. These micro-fine MgO particles were added to a standard magnesia-spinel formulation during mixing. Test cylinders were produced on the laboratory scale to optimise the necessary quantity to achieve the lowest possible porosity. Having found the optimum quantity test bricks were produced on an industrial scale. The standard physical properties bulk density, apparent porosity, gas permeability and cold crushing strength as well as the hot properties refractoriness-under-load (RuL), creep-in-compression (CiC) and hot modulus of rupture (HMoR) of the finished products were tested in comparison to the reference brick formulation. For a field trial the bricks were installed in the lower transition zone of a 4.8 m diameter cement rotary kiln to assess the performance of the bricks compared to the reference material. The comparison with the reference magnesia-spinel bricks revealed that the fired density of the bricks increased significantly by 0.05 g/cm³. The apparent porosity decreased by 0.7 % absolute. This trend was accompanied by a decrease in gas permeability and an increase in cold crushing strength. The RuL T05 was kept > 1700 °C. The CiC decreased to low values of < 1 % after 25 h at 1500 °C. The HMoR was measured in 100 K intervals from 1200 °C to 1500 °C and showed an increase of the values by a factor of approximately 1.6 in average compared to the reference. The maximum strain in the HMoR measurement is a measure of the flexibility of the material. The maximum strain was increased by a factor of approximately 1.7 compared to the reference. From all figures tested it can be concluded that the addition of micro-fine MgO particles to a standard magnesia-spinel brick formulation lead to a significant improvement of the physical brick properties. Finally, these improvements should increase the performance of the refractory bricks in service.

O23) INFLUENCE OF PHOSPHATE TO HOT PROPERTIES IN BASIC REFRACTORY BRICKS

Gelbmann, G.(1); Joerg, S.(1); Krischanitz, R.(1); (1): RHI AG, Leoben, Austria

The refractoriness of a basic brick is primarily defined by its secondary interstitial phases. What matters in this respect is not only the absolute quantity of interstitial phases, but also particularly which type of phases they form. The most common by-elements in magnesia and magnesia products respectively are Ca, Si, Fe, as well as Al and Cr. Depending on the bulk chemical composition these elements form different types of interstitial phases. In general the temperature of formation of melting phases decreases with increasing number of elements. The effect of the different interstitial phases on the refractoriness of magnesia products is sufficiently described in literature. The target of the study described in the present paper was the improvement of the properties of magnesia products rich in alumina and iron oxide, especially at elevated temperature. In the course of a laboratory trial iron-rich magnesia bricks were produced and fired at different temperatures. With increasing firing temperature increasing values in refractoriness under load could be detected. The same effect was observed with iron-rich magnesia-spinel bricks. On the other hand these bricks showed an increasing firing shrinkage with increasing temperature, which can cause big problems in the production of refractory bricks. The target of the trials was to counteract this firing shrinkage whilst maintaining the high refractoriness of the bricks by incorporation of certain elements...
into the interstitial phases of the brick. The addition of phosphate has proven successful for a controlled modification of the interstitial phases in order to be able to produce iron-rich and alumina-rich bricks with improved refactoriness.

**O24) MAGNESIA-SPINEL BRICK WITH GOOD COATING ADHESION AND HIGH RESISTANCE TO CORROSION AND SPALLING FOR CEMENT ROTARY KILNS**

Ohno, M.(1); Yoshikawa, S.(1); Toda, H.(1); Fujii, M.(1); Chiba, H.(1); Ozeki, F.(1);
(1): MINO CERAMIC CO., LTD., HANADA-SHI, AICHI, JAPAN

Zirconia-added magnesia-spinel bricks composed mainly of magnesia (MgO) and spinel (MgO • Al2O3) are extensively used in burning zone of cement rotary kilns because they have good coating adhesion and high corrosion resistance to the clinker melt while maintaining their high spalling resistance. Recently, however, the wear of the bricks has increased due to unstable coating conditions arising from the increasing use of waste as fuels and raw materials in the cement burning process. In this paper we present zirconia-added magnesia-spinel brick with high resistance to both corrosion and spalling as well as good coating adhesion under severe conditions. It contains approximately 90% MgO, featuring high corrosion resistance. Although magnesia-spinel bricks with less content of spinel have generally less spalling resistance, putting different types of spinel with proper size has enabled the brick to possess the trade-off properties. Moreover, adding minor amounts of two types of raw materials to the brick has made it possible to improve the coating adhesion properties and infiltration resistance to the cement constituents. The developed brick by such techniques also exhibited higher corrosion resistance than the brick without zirconia addition in a rotary slag test. The reason for these improved properties is that the brick has an enhanced bonding in the matrix and dense microstructure as well as high refactoriness compounds of calcium zirconate, leading to reduction of the cement infiltration. The developed brick was installed at the burning zone where the linings are exposed to harsh environment caused by the utilization of large amounts of waste. It demonstrated superior performance to our competitor’s brick and has been highly valued by our clients.
ESIN 1) ENERGY SAVING AND INSULATION 1

O25) BINDER SYSTEM EFFECT ON THE MICROSTRUCTURE AND PROPERTIES OF INSULATING CERAMIC FOAMS

Santos Junior, T.(1); Cogo E Silva, G.(1); Salvini, V.(1); Pandolfelli, V.(1);
(1): Universidade Federal de São Carlos, São Carlos, Brasil

Energy saving methods arise from two main routes: efficiency and conservation. The former reduces the energy required to perform a task, whereas the latter comprises all actions to reduce the losses. For high temperature processes, heat conduction is mostly carried out by radiation in the infrared range (0.7 to 100 µm). Therefore, a good thermal insulating material for high temperature application must be able to reduce the radiation intensity within the temperature of interest. Porous refractory ceramics with tailored amount and size of pores are candidates to be applied for this purpose.

Considering the different routes of processing porous ceramics, the direct foaming method results in materials with reproducible properties, narrow distribution of pore sizes and suitable mechanical strength. Nevertheless, physical effects as coalescence and drainage can take place in the liquid foam, reducing its stability and increasing the bubbles’ size. There are two ways to control this phenomena: adding surfactants that act on the bubble’s surface tension or using binders that induce the fast transition from the liquid to solid foam. In this work, aluminous foams were prepared by the direct foaming method using different inorganic binder systems and setting additives. Their microstructure, porosity, thermal conductivity and mechanical strength, were evaluated. The results pointed out that the foam microstructure was modified when different binder systems were used, influencing the mechanical and thermal properties of the material. Based on these results, the selection of the binder system has been shown as an important factor to process porous material with tailored properties.

O26) INSULATING CERAMIC FOAMS FOR HIGH TEMPERATURE FURNACE LINING

Salvini, V.(1); Binoto, J.(2); Rodrigues, J.(2); Junior, T.(2); Pandolfelli, V.(2);
(1): UFSCar - FATEC, São Carlos - Sertâozenho, Brasil (2): UFSCar, São Carlos, Brasil

The main reasons of applying insulating ceramics as furnace linings are related to energy costs and environmental concerns. From the emission point of view, most industrial furnaces operate in the infrared wavelength range (0.7 to 100 micra) where the thermal transmission by radiation is the major mechanism for the total effective thermal conductivity. This information is fundamental to design the composition and the microstructure of insulating ceramic materials. Commercial Al2O3-SiO2 and Al2O3-ZrO2-SiO2 linings present high porosity (70 to 85 vol%), but densify during use due to silica based binders. An alternative could rely on plain Al2O3 insulating lining, however it presents lower thermal shock resistance and higher thermal conductivity. In this work, alumina-based refractory foams with low thermal conductivity values (0.25 to 1.0 W/mK), high porosity (70 to 84 vol%), good compressive strength and high resistance to thermal shock were applied as insulating lining in a glass melting furnace operating at
1700°C. The performance of the insulating refractory was evaluated considering the energy consumed by the heating elements and the cycled thermal shock resistance. Power consumption indicated lower values when using foamed ceramic lining compared to the commercial ones. Additionally, the foamed ceramics performed very well under severe thermal shock conditions (DT=1700°C).

**O27) COMPARATIVE STUDY OF SLAG RESISTANCE OF AL2O3-MGO CASTABLES CONTAINING DIFFERENT LIGHTWEIGHT CORUNDUM AGGREGATES**

Zou, Y.(1); Gu, H.(1); Huang, A.(1); Zhang, M.(1); Zhang, M.(1);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, Hubei, P.R.China

Corundum-spinel castables containing lightweight aggregate has drawn many attention due to its potential for energy-saving, especially when applied in high-temperature region, such as the work lining of refining ladle. One main aspect that restricts its application is the slag corrosion performance, which is inferior when compared with traditional castables. In this study, one dense tabular corundum (denoted as TC) and two lightweight corundum (denoted as L1, L2) was chosen as aggregates to prepare three different corundum-spinel castables (denoted as CTC, CL1, CL2 respectively), and the slag resistance was compared through induction furnace corrosion test. XRD, SEM-EDS analyses, and thermodynamic and kinetics calculation was adopted for the discussion of corrosion mechanism. Results shown that the pore-size and its distribution, and the grain dimension of aggregates are importance for the slag performance, yet the effect of apparent porosity are not dominating. For castable CTC, the favorable corrosion resistance was mainly due to the larger average grain size of tabular corundum aggregates, of which the dissolution rate was slower when contacted with slag. The castable CL1 shown similar corrosion performance as CTC, which can be contributed to the relatively preferable microstructure of L1 - small pore size and no overlarge pore in the aggregates. The slag resistance of castable CL2 deteriorated as a result of the poor microstructure - larger pores and smaller grains of lightweight corundum L2.

**O28) FORMATION AND MICROSTRUCTURE EVOLUTION OF INTRACRYSTALLINE PORES IN LIGHTWEIGHT MICROPOROUS ALUMINA**

Fu, L.(1); Gu, H.(1); Huang, A.(1); Zhang, M.(1); Li, Z.(2);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China (2): Jiangsu Jingxin New Material Co., Ltd, Yangzhou, China

The goal of designing a lightweight wear lining refractory for industrial furnaces has attracted increased attention in the field of refractory materials because a high-porosity lightweight wear lining could produce better heating insulation and thermal spalling resistance. In order to achieve guaranteed slag resistance of prepared lightweight wear lining, fabrication of refractory aggregates with high closed porosity, especially intracrystalline pores, has attracted increasing attention. In the present work, nano-
alumina sol had been introduced to form a pile-up of nano–micro double-scale, and its effects on the properties and microstructure of prepared lightweight alumina was investigated. The introduction of nano-alumina sol led to the abnormal grain growth of prepared lightweight microporous alumina, and numerous straight line-distributed intracrystalline pores were observed inside of the abnormally-grew grains. Therefore, resulting in an increase in the closed porosity and decrease in bulk density. A mathematical model was proposed to investigate the formation and microstructure evolution of intracrystalline pores in lightweight microporous alumina. Calculation results showed that the nano–micro double-scale effect created partial regions in which the alumina sol collected, which showed a larger surface stress than other regions. Shrinkage occurred in the partial region simultaneously with grain growth, which led to the formation of intracrystalline cylindrical pores. Moreover, the introduction of nano-alumina sol resulted in a decrease in the closure time of cylindrical pores, then numerous straight line-distributed intracrystalline pores were formed.
Basic oxygen furnace (BOF) is the most popular process selection for oxygen steelmaking and is a relatively cheap conversion process for refining iron into steel. MgO-C is the widely accepted refractory used as working lining. BOF is the most important steel making application in terms of refractory tonnage and the new demands on low carbon steel have been increasing the oxygen volume flow and new process operation. Combination of top and bottom blowing are often used to lower operating costs through better stirring action in the steel bath. MgO-C bricks are been exposed to severe oxidation and corrosion by gases and slags, erosion due to higher emulsion agitation and thermal shock. Also normal thermal cycling due to tap to tap operation can affect the behavior of MgO-C bricks even if any other exceptional interference occurs.

Considering the complex heterogeneous microstructure of MgO-C bricks and the fact that their mechanical properties are strongly affected by in situ transformations during curing and heating process, measurements of the elastic modulus evolution with temperature may provide important information for the understanding the role of different additives and microstructure modification as well as for the development of novel products.

This work presents the evaluation of physical properties, cold and hot mechanical resistance, as well as in situ hot elastic modulus (E) measurements in the temperature range of 30 to 1400°C for antioxidants (Al, Si or Al-Mg alloy) containing MgO-C bricks in a reducing atmosphere. Cured and fired samples were evaluated throughout 1 or 2 heating-cooling cycles compared to the additive-free composition. A comparative evaluation of microstructures during thermal cycling is presented and discussed and linked to BOF operational conditions.

In the final 20% of the oxygen blow in a BOF, bath stirring decreases due to the drop in CO evolution. To help sustain slag-metal mixing and enhance thermal and chemical homogeneity in the melt, the bath is agitated by injecting inert gas through stirring elements in the vessel bottom – the Bath Agitation Process (BAP). Element designs include tuyeres and various configurations of single- and multi-hole plug, all of which promote localized wear which in many cases will limit the service life of the lining. Wear
arises from a combination of thermo-mechanical stresses associated with, for example, the operational vessel thermal cycle, local cooling by the injected gas, and molten bath circulation induced by the injected gas stream, often compounded by accretion growth, localized lining erosion and metal penetration. A comprehensive post mortem study of used BAP injection plugs shows in addition that steel bath wetting effects in current element designs may be a significant factor in the wear process. A new injection element design is proposed in an attempt to reduce the magnitude of these effects and thereby extend vessel lining life. The design is based on slotted gas channel geometry with materials selection optimized for the specific task. A prototype was tested by water modelling to establish its gas injection behaviour. The results and analysis of these tests are discussed, with indications for future work including in-plant trials.

**O31) TOTAL COST OF OWNERSHIP OF CONVERTER REFRACTORIES AIDED BY LASER SCANNING TECHNOLOGY**

Kubal, S.(1); Kirchhoff, S.(2); Thomas, G.(1);
(1): Tata Steel UK, Port Talbot, Wales, UK (2): MINTEQ International GmbH FERROTRON DIVISION, Duisburg, Germany

Total Cost of Ownership (TCO) of converter refractories is a complex subject involving material selection, reline labour, fluxes mix, process control, maintenance and production planning. Analysis of the total cost of refractories per tonne of liquid steel provides complete view when combined with material performance appraisal. This work enhances TCO analysis by employing LaCam in wear rate measurement and material performance assessment.

Laser scans provide information on refractory wear while wear trend analysis enables identification of outliers, projection of life of refractory products, and adjustment of maintenance practice. Comparison of the wear trends complemented with relevant process parameters helps identify the best performing materials and design converter lining with uniform wear rate. Furthermore, LaCam makes possible calculation of life of each converter repair, allowing appraisal of different material types and applications. As a result, fast wearing areas can be eliminated and application of refractory repairs optimised, leading to significant savings. Campaign costs analysis combines information about refractories performance, and relevant process costs e.g. reline labour, fluxes mix, availability, maintenance; and aids optimisation of all refractories related costs. Short term, the TCO model throws more light on the total cost of refractories per tonne of liquid steel, and indicates the optimum lining service life. Long term, the analysis can be used to define the cheapest converter refractories strategy including lining life requirement, use of slag splashing, selection of fluxes or application of repair materials.

Application of the TCO analysis resulted in a number of improvements at Tata Steel in Port Talbot. Cold iron was identified as the type of scrap causing heavy wear in the impact pad area, and its charge was reduced accordingly. The lining design was improved by installing pitch bonded materials from one supplier in the bottom, and resin bonded materials from another supplier in the barrel and upper cone. Selection of repairs giving the highest value in use was possible thanks to direct comparison of self-
flowing and gunning materials. Finally, the lining life expectation was aligned with appropriate costs leading to application of the refractory technology at the lowest cost possible.

The TCO approach linked the converter refractories interdependent costs – initial costs (reline labour, safety lining, working lining), process costs (scrap composition, fluxes, yield, reheating), maintenance costs (slag conditioning, slag splashing, refractory repairs) – and helped design optimum converter lining strategy.

**O32) IMPROVEMENT OF ABRASION WEAR RESISTANCE OF MGO-C BRICK FOR BOF SCRAP IMPACT AREA**

Fujiyoshi, R.(1); Iida, M.(1); Iida, A.(1); Torigoe, A.(1); Yoshioka, H.(1); (1): SHINAGAWA REFRACTORIES CO., LTD, Bizen, Okayama

As generally accepted, reduction of green house gas emission is one of the most important tasks for all industrial sectors. For integrated steel mills, increase in steel scrap as raw material is an effective measure since it decreases use of hot metal from the blast furnace which emits large amount of CO2 gas. Therefore, amount of scrap charged to the BOF has been increasing. The increase in steel scrap charging accelerates the wear of the scrap impact area. Particularly, heavy scrap charging seriously damages MgO-C bricks installed on the scrap impact area. Thus, it is considered that mechanical abrasion is the dominant factor of refractory wear there.

In order to investigate the wear in detail, the scrap drop impact test, of which 12kg cubic steel mass was dropped onto the brick-assembled structure from 2m height, was carried out. According to the observation of the brick after the test, it was verified that the abrasion wear of scrap impact area is a result of linking of cracks, which were initiated and propagated by mechanical shock induced by scrap collision. Therefore, two ways for brick improvement were suggested. One was suppression of crack initiation and the other was suppression of crack propagation.

Therefore, three materials were developed as; high strength material, matrix reinforced material and carbon bond enhanced material. Purpose of high strength materials was improving crack initiation resistance. The other two materials were designed to improve the crack propagation resistance. High strength material was obtained by optimizing metallic additive distribution status. Matrix reinforcement was achieved by suitably engineered matrix graphite arrangement. Carbon bond was enhanced by adequate utilization of pitch. HMOR and Fracture energies were measured by three point bending test at 800°C in an Ar atmosphere, the test sample were heat treatments at 1200°C for 3h in cokes breeze. HMOR of these materials are 17, 13 and 12 MPa, respectively. Fracture energies of these materials were evaluated by three point bending test and evaluated values were 0.26, 0.40 and 0.49J, respectively.

By practical application, the wear rate index of these materials were evaluated as 100, 75 and 50, respectively. Remarkable reduction in wear rate was obtained for high fracture energy material. Proportional relation between wear rate index and fracture
energy was clearly confirmed while poor relation was recognized for relation between wear rate index and HMOR.

Hence, it is concluded that suppression of crack propagation by improving fracture energy of MgO-C brick is essential for reducing abrasion wear of BOF scrap impact area.
MO 2) MONOLITHICS FOR VARIOUS APPLICATIONS 2

O33) INFLUENCE OF THE SILICA GEL TECHNOLOGY ON THE HIGH TEMPERATURE MECHANICAL BEHAVIOUR OF ALUMINA CASTABLES

Burgos Montes, O.(1); Alvarez, M.(1); De Aza, A.(2); Pena, P.(2); Baudin, C.(2);
(1): REFRACTARIOS ALFRAN S.A., Alcalá de Guadaira, Sevilla, Spain
(2): Instituto de Cerámica y Vidrio, CSIC, Madrid, Spain

One of the most successful innovations in the past decade has been the development of cement-free binders for monolithic refractories, no-cement castables (NCCs). The use of colloidal silica suspensions as bonding component has been widely extended at industrial scale. The major advantages of these castables are a low and fast dry-out, a maximum thermal shock resistance and high mechanical properties. The success of these materials is close linked to development of the microstructure that defines the behavior of the material at high temperatures. However, their installation and transport are more difficult than those of cement castables due to the use of the colloidal silica suspension instead of the water. In this context, the use of microsilica powder as a valuable alternative to silica-sol has been proposed. Recent reports disclose that the flowability behavior and mechanical properties of colloidal silica gel castables and microsilica gel castables are similar. This work deals with the study of the properties alumina castables fabricated using both silica gel technologies in terms of flowability, setting time, dry-out behavior and mechanical properties. The paper pays special attention to the high temperature strength and Young´s modulus, which determine their performance in the industrial processes.

O34) RECENT DEVELOPMENT IN USE OF SPHERICAL PARTICLES IN NCC

Myhre, B.(1); Hong, P.(1);
(1): Elkem Silicon Materials, Kristiansand, Norway

No-cement castables have the last few years become increasingly popular, particularly since the introduction of SioxX-Zero(microsilica-gel bond) and DARES (Dry Advanced Refractory System) binder technologies. In parallel with the development of these binder systems, development of highly specialized raw materials have progressed, and the current paper focuses on the use of spherical alumina for no-cement applications in general, and silica-free corundum-spinel systems in particular.

O35) DEVELOPMENT OF HIGH-PERFORMANCE NO-CEMENT REFRACTORY SHOTCRETE

Peng, H.(1); Myhre, B.(1);
(1): R&D, Elkem Silicon Materials, Kristiansand, Norge

Microsilica-gel bonded no-cement refractory castables (NCCs) have lately drawn great attention, not only because of their easier handling, storage and transportation thanks
to the “all-in-the-bag” solution, but also because of the improved setting behaviour and green strength development compared to silica-sol bonded NCCs.

The current work addresses the development of no-cement shotcrete using microsilica powder as a binder. The flow, setting behaviour, mechanical properties, hot-properties and abrasion resistance of no-cement shotcrete were compared to low-cement shotcrete. The results demonstrate that the cement-free shotcrete not only exhibits good installation properties and low rebound, but also provides enhanced hot-properties and abrasion resistance due to mullite formation at elevated temperatures.

Furthermore, a laboratory program on the effect of a speciality-drying agent on explosion and thermal-shock resistance on the shotcrete NCC composition showed that both the explosion- and thermal-shock resistance were significantly improved compared to the shotcrete LCC composition.

O36) MONOLITHIC PERMANENT LINING BASED ON SINTERED MAGNESIA

Wappel, D.(1); Wallgram, W.(1); Kollmann, T.(2); Ratz, A.(2);
(1): RHI AG, Leoben, Austria (2): RHI AG, Vienna, Austria

In this paper the devolvement progress of a monolithic permanent lining concept based on sintered magnesia for the application in the EAF, BOF and the steel ladle will be presented. The usage of such a mix will reduce the lining duration, increase safety during relining and reduce the cost. Currently for a permanent lining in the different fields of application either basic fired bricks, shotcrete mixes or dry mixes based on non-basic raw materials are used. All these applications show some disadvantages such as higher costs, higher water intake and low stability against steel or slag penetration. The approach of the new mixes is to focus on a water free, ready for use application or at least significantly reduce the water content to minimize the potential for hydratisation and to speed up the relining practice.

Based on the individual requirements of each aggregate individual mixes for the EAF, BOF and steel ladle were developed. Each aggregate requires individual properties such as binding strengths at room temperature, smoke and dust release during preheating/application, binding strength development with temperature etc. To investigate the best binding concept for each aggregate, various laboratory tests at different temperatures such as cold crushing strength (CCS), shrinking behaviour, cracking behaviour, thermo-gravimetrical analysis and refactororiness under load were determined. Based on these tests, the most usable binding agents and binder amount were selected and tested in detail. To verify the lining procedure and the developed strength at room temperature and application temperature a special laboratory lining test was carried out.

For the permanent lining of the EAF and BOF either a ready for use water free mix or a dry mix with a chemical binder (setting with small water addition) have shown the best results. For the steel ladle, where no strength at room temperature is required, a dry lining similar to a dry setting tundish mixes showed the most promising results.
Furthermore the slag resistance for different binder concepts in comparison with a standard basic permanent lining brick were investigated during a induction furnace test using a typical ladle slag. All mixes show a reasonable good slag resistance which ensures certain emergency running properties in case of a brick breakout.

Based on the successful laboratory trials, field trials at various customers for EAF, BOF and steel ladle are currently carried out, first results will be expected in Q1/2017.
EDU) EDUCATION

O37) REFRactory Corrosion A Recurrent Topic (Always To Be Considered)

Rigaud, M.(1); Poirier, J.(2);
(1): University of Montreal, Montréal, Canada (2): CNRS-University of Orléans, Orleans, France

Refractory materials are absolutely needed in various industrial sectors but they do corrode under harsh environment. Therefore, every efforts to minimize corrosion are to be structured upon a good understanding of the processes involved. Corrosion resistance is not an inherent property of a given material; it is a characteristic which depends on a multitude of parameters.

The goal of this presentation is to reveal the content of FIRE Compendium Series of books, number 2, on the theme of corrosion. This series will be constituted of 3 volumes.

For the first volume, volume 2A, freshly printed, several authors have been called to provide a deeper understanding of the complexity of the interlinked phenomena. Hence a brief description of the content of this book is to be presented. Also, previews on the other two volumes to follow will be underlined: volume 2B: The Testing and Characterization Methods, to illustrate mainly the evolution in the tools nowadays available and to present innovative (in-situ) techniques of characterization ; and volume 2C: The Impacts of Corrosion Wear, based upon selected case studies, to illustrate what can we learn from post-mortem analysis and what are the impacts on plant operation availability and products quality.

O38) Cooperative Refractory Research Programmes To Support Refractories Development

Parr, C.(1); Pandolfelli, V.(2); Sinnema, S.(3);
(1): Kerneos SA, Puteaux, France (2): UFSCar - DEMa GEMM, Sao Carlos, Brazil (3): Tata Steel, 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 aims to stimulate and reinforce international education and research programmes for the refractory industry. Its strength is a unique grouping of expertise drawn from all sectors of the refractory producing, supplying and consuming industries coupled with the world’s leading academic institutions involved in refractory research.

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. They are designed to further refractory science and provide a basis for education through academic research.
As an illustration of how cooperative research programmes can benefit the development of monolithic refractories, a data mining analysis of published papers spanning a 35 year history has been used to identify different active communities and the fields of research around Monolithic refractories on a global basis. The importance of the FIRE network and the establishment of different research communities can be seen emerging in recent years.

More specifically, the analysis provides a linkage between the different global research communities and research themes relevant to Monolithic refractories such as Raw Materials, Binders, Simulation, Carbon, mechanical tests. The paper will illustrate some of the ongoing cooperative programmes in the field of refractories research and how different disciplines can be harnessed to yield new and novel insights into the underpinning mechanisms of refractories technology.

Conclusions will be drawn from the key learnings of these multi-partner research programmes and how this can be applied to create further value through the usage chain of monolithic refractories. Future perspectives will explore the areas where further basic cooperative research on monolithic refractories could bring benefits.

**O39) INTEGRATING EDUCATION CONCEPTS – THE KOBLENZ REGION OFFERS A ONE-OF-A-KIND INFRASTRUCTURE TO LOCALIZE AND QUALIFY FUTURE SPECIALISTS IN ORDER TO ENSURE RELIABLE AND CONTINUOUS PROVISION OF BEST-SKILLED ENGINEERS TO THE REFRACTORY INDUSTRY.**

Krause, O.(1); Quirmbach, P.(2);

The refractory industry suffers a lack of young engineers in Germany. Within the past five years an integrating education concept has been developed to ensure a sustainable provision of young and best-skilled engineers to the refractory industry. The aim of this presentation is to demonstrate how the sophisticated network between education, science and refractory industry leads to efficient fulfilment of the industry’s demands.

Because of a vertically open vocational education structure as provided by public legislation it is possible to promote young people even with initial limited educational achievements to finish with an academic degree. The cooperative education network, BFZK (educational and research centre ceramics), which closely cooperates with Koblenz University of Applied Science and the University Koblenz-Landau, allows best possible utilisation of this public education structure.

Since 2010 Koblenz University of Applied Science provides a bachelor of material science and was followed by the implementation of a master degree in cooperation with the University of Koblenz-Landau. The educational system follows two major tasks: Best possible and targeted education in order to provide graduates with tailor-made abilities
for the ceramic industry. The second task is to promote science projects that are closely related to the demands of the industry.

The presentation will introduce the state-of-art master and bachelor curriculum and will briefly present recent research works.

**O40) EDUCATION ON REFRACTORIES IN EUROPE - A SURVEY**

Huger, M.(1);
(1): ENSCI-SPCTS, Limoges, France

During the 10 past years, the Federation for International Refractory Research and Education (FIRE) has significantly contributed to change the general opinion about refractory materials in Europe upon young people. As a matter of fact, refractory materials were, in the past, usually associated to old well-known materials mainly applied in heavy declining industries (for steel, cement and glass making... etc.). This negative image was the main reason which led to high difficulties in recruiting high potential students in the field of refractory materials.

To overcome this situation, FIRE aimed at implementing a new training methodology based on a relevant interconnections between the main experts within academic poles within Europe (Aachen, Freiberg, Leoben, Limoges and Orléans), but also worldwide (Nagoya, Wuhan, Rolla, Montreal and Sao Carlos) with most industrial leaders in refractory materials production (Almatis, Alteo, Calderys, Elkem, Imerys, Kerneos, Magnesita, Pyrotek, RHI, St-Gobain) and also some end user companies (Posco, TataSteel, Tenaris). In fact, most of these companies have important bases in Europe.

FIRE’s mission is to stimulate progress in research and education at Master and PhD level supporting high level international cooperation programs and promoting the mobility of the students. Starting from an inventory of trained students in the last ten years, in an European perspective, it is today time to analyze their placement and professional evolution, and also draw some perspectives for the future of education on refractories in Europe.
O41) INCLUSIONS IN STEEL WITH A HIGH AL CONTENT AND CASTING TEMPERATURE AFTER CORROSION TESTS IN CARBON FREE AND CONTAINING REFRACTORIES

Fruhstorfer, J.(1); Dudczig, S.(2); Rudolph, M.(2); Schöttler, L.(3); Rafaja, D.(2); Aneziris, C.(1);

During corrosion experiments on refractories for steel ingot casting, at the interface between refractory and steel, large ceramic aggregates were found. It seemed that the aggregates attached onto a thin layer. The purpose of this study thus is to investigate this supposedly reactive interfacial layer and its effect on the attached aggregates or inclusions for the subsequent application in steel melt filtration. Therefore, this study relates the oxygen content of the melt, the surface properties of the refractories and interface reactions as well as the amount and distribution of inclusions in the steel to each other.

The used steel was an ingot casting steel (17CrNiMo76) with a high Al content and high casting temperature of 1580 °C. The refractory crucibles were Al2O3, Al2O3-C, Al2O3 doped with ZrO2 and TiO2 (AZT), AZT-C and AZT-C with carbon nanotubes and alumina nanosheets. The corrosion experiments were conducted in a metal casting simulator under argon atmosphere. It was heated to the casting temperature, which was hold for 20, 30 or 60 min. About every 10 min the temperature and oxygen content were measured. For the investigation of the refractories mainly scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) were used. The inclusions in the steel were determined by a special Aspex-SEM.

The oxygen contents in the steel melt were generally lowest when melted in carbon containing refractories. The course of the oxygen content at the casting temperature correlated with the temperature, except for the crucibles AZT and AZT-C with nanoscaled additives. Supposedly, additional chemical reactions took place. Furthermore, the correlation between the oxygen content and the total corrosion showed strong linearity. The mean oxygen content during the holding time correlated with the total area of inclusions. This means that the inclusions respectively observed aggregates were already formed at this temperature. As the inclusion situation correlates with the mean oxygen content, the conclusions drawn from the mean oxygen content apply also on the inclusions: Carbon bonded refractories lead to considerably lower inclusions and an increasing total corrosion leads to increasing inclusion areas. In the carbon containing samples with increasing reactivity of the system by additional dopants and nanoscaled additives, the attachment of aggregates (based on alumina) increased as well as the formation of the thin layer (also mainly alumina). As also the Al contents in the steel were strongly reduced after the melting experiments compared to before, it seems that the inclusions precipitated.
Consequently, an increasing reactivity of the system by adding nanoscaled additives and dopants to the alumina increased the efficiency of collecting aggregates. Thus, AZT-carbon with multi-walled carbon nanotubes and alumina nanosheets has a high potential for steel melt filtration.

O42) MICROSTRUCTURE EVOLUTION DURING FIRING AND RESULTING MECHANICAL PROPERTIES OF STEEL FLOW CONTROL REFRACTORIES CONTAINING VARIOUS ADDITIVES

Warchał, A.(1); André, D.(2); Debastiani, D.(1); Guillo, P.(1); Huger, M.(2); Martelli, S.(1); Mazerat, S.(1); Romero-baivier, S.(1);
(1): Vesuvius, Feignies, France (2): SPCTS UMR CNRS 7315, Limoges, France

Refractory products such as ladle shrouds, monoblock stoppers and submerged entry nozzles find their application in the continuous casting of steel. They are responsible for the steel flow control and its protection against oxidation. During casting, refractories are subjected to severe thermal, mechanical and chemical conditions which may have a deleterious impact on their lifetime. Thus, seeing a need for properties improvement of these materials, the main goal of this work was to investigate the evolution of carbon-bonded refractories during firing and thereby understand their mechanical properties. The particular emphasis was put on the influence of additives, the so-called antioxidants.

Model materials having simplified composition compared to the real industrial ones were investigated in order to facilitate the comprehension of interactions between different constituents (alumina, graphite, binder, additives). The influence of four different antioxidants such as boron carbide, a metallic additive and two low melting point compounds were studied.

The evolution of Young’s modulus during firing was followed thanks to an ultrasonic pulse echography device. Damage occurrence within the material was registered by the acoustic emission technique. X-ray diffraction measurements with Rietveld refinement enabled identification and quantification of phases after firing. Stress-strain curves were obtained by tensile testing at room temperature.

Obtained results show that the carbonaceous binder undergoes transformation into pyrolytic carbon and that micro-cracks in material’s matrix are created during firing. It results in a non-linear stress-strain behavior. What is more, boron carbide transforms partially into boron oxide and carbon which does not have important influence on the mechanical properties. The metallic additive reacts with surrounding carbon to form carbides which rigidify the refractory. One of the low melting point compounds forms a liquid phase at high temperature which causes micro-cracks healing thereby leading to a stiffening of the material. The second one undergoes irreversible softening and only slightly modifies the mechanical properties.

Antioxidants are added to carbon-bonded refractories so as to protect all forms of carbon from oxidation. Nevertheless, this study showed that even a small quantity of
certain additives might significantly modify their mechanical properties and thus have an influence of their reliability and performance.

O43) THE INFLUENCE OF LIMESTONE CONTAINING REFRACTORIES ON THE ELEMENT CONTENT AND TOTAL OXYGEN CONTENT OF MANGANESE STEEL AT 1873K

Wei, Y.(1); Li, N.(1); Wang, Y.(1); Ye, C.(1); Liu, Z.(1);
(1): Wuhan University of Science and Technology, Wuhan, China

Reactions between CO2 gas from limestone containing refractories and [Mn], [C] in molten steel and its influence on carbon content, manganese content and total oxygen content of steel are investigated via vacuum medium frequency induction furnace. Limestone containing MgO-CaO refractory crucibles and manganese steel are used in this study. Experimental results are analysed with the assistance of thermodynamic analysis. The interesting result shows that the total oxygen content of steel did not increase with the increment of limestone content in refractory crucible always, the latter continues release CO2 gas under high temperature, but the carbon content of steel is continue increased. It can be concluded that the elements in steel were consumed by the reaction with CO2 gas and the oxidation products were absorbed by refractory lining.

O44) INTERACTION BETWEEN TUNDISH GUNNING MATERIALS AND LIQUID STEEL

Liu, Y.(1); Li, G.(1); Wang, L.(1); Zhang, Z.(1); Yang, Z.(2); Rao, J.(2);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China (2): Wuhan Iron and Steel Company Limited, China Baowu Steel Group Limited, Wuhan, China

To clarify the interaction mechanism between MgO and Al2O3 based tundish gunning materials (GM) and liquid steel. SEM, EDS, XRD and chemical analysis were carried out for steel and GM to investigate the change of chemical composition of steel in contact with GM and the interface microstructure between steel and GM after high temperature holding experiments. The steel cleanliness in terms of inclusion number density, size and size distribution was evaluated. It was found that the reducible impurities, low-melting-point phases and the pores in GM were passageway for steel penetration. Quartz and hematite in gunning materials are reduced by the dissolved Al, Ti, Mn and Si in molten steel, and then liquid steel penetrated into the sites where they located, resulting in steel infiltration. The pores and low melting point phases in gunning materials also provided the passageway for steel infiltration. The steel infiltration damaged the integrity of gunning materials, as a result, the refractory materials particles fell into liquid steel to become large-sized inclusions. The Al2O3 GM was less prone to steel penetration due to its poor wetting and the dense transition layer. MgO GM provided more oxygen and showed a stronger oxidizing capacity due to its higher content of reducible oxide impurities (10.5 wt.% SiO2+2 wt.% Fe2O3). The use of Al2O3 GM
resulted in an improved steel cleanliness and consequently could be a promising refractory for the tundish lining.
SLSM 1) STEEL LADLE AND SECONDARY METALLURGY 1

O45) EFFECT OF MICROSTRUCTURAL MODIFICATIONS AT HIGH TEMPERATURE ON THE WORK OF FRACTURE OF MAGNESIA-GRAFTHITE REFRACTORIES

Gass, S.(1); Tomba Martinez, A.(2); Galliano, P.(3); Bellandi, N.(4); Baudin, C.(5);
(1): Instituto de Cerámica y Vidrio, CSIC/ INTEMA, Madrid / Mar del Plata, Spain /
Argentina (2): INTEMA, Mar del Plata, Argentina (3): Tenaris REDE AR, Campana,
der Cerámica y Vidrio, CSIC, Madrid, Spain

Graphite containing refractories are highly resistant to mechanical and thermal cycles. The mechanical parameter that determines the resistance of the materials to crack development under subcritical conditions is the work of fracture. This parameter depends on the microstructure of the materials and, particularly, on the nature of the matrix. As-fabricated, unfired MgO–C and MgO-C-antioxidant bricks have very low porosity (<5 %), determined by the characteristics of the raw materials and the type of binder. The loss of volatile components of the binders, the inherent instability of the bricks caused by the carbothermal reduction of MgO that yields CO and Mg(g), and the oxidation of residual carbon from binders and of graphite flakes lead to increases in porosity during thermal treatments. Moreover, new phases that depend on the atmosphere could be formed at high temperature due to reactions between the components of the brick. Therefore, the nature of the matrix of the graphite containing refractories experiences significant changes during use. These changes will determine the mechanical performance of the materials. In this work, non-commercial MgO-C and MgO-C-antioxidant model materials have been used to determine the relationships between the microstructure and the work of fracture. Main composition was 83-85 wt% of magnesia (fused/sinter: 70/30) and 12 wt.% of graphite flakes. The effect of three different organic binders, phenolic resin, a new eco-binder and a chemically modified pitch has been evaluated. Fully microstructural evaluation of the “as received” and thermally treated (up to 1450ºC) materials has been done. The work of fracture has been determined using controlled fracture tests. Relationships between the microstructure and the obtained work of fracture values are presented and the effect of the different binders and the antioxidant is established.

O46) IMPROVEMENT OF MAC BRICKS FOR STEEL LADLE WITH CAO-MGO-
AL2O3 AGGREGATE: A NEW PERSPECTIVE FOR CEMENT APPLICATION

Pagliosa, C.(1); Souza, P.(1); Hama, N.(1); Wohrmeyer, C.(2); Zetterstrom, C.(2);
Evangeliista, P.(3);
(1): MAGNESITA S.A, Contagem, Brazil (2): KERNEOS Aluminate Technologies, Paris,
France (3): KERNEOS Aluminate Technologies, São Gonçalo, Brazil

Magnesia-Alumina-Carbon (MAC) and Alumina-Magnesia-Carbon (AMC) bricks have been consolidated as a product for the metal line of the steel ladles in a majority of the
integrated steel shops worldwide. Spinel MgO-Al2O3 formation during ladle operation allows to an expansive reaction that can prevent metal and slag infiltration and also promotes better corrosion resistance.

The requirements for steel quality depend on the steel shop process. Refractory indication follows operational conditions of each customer in order to optimize the campaign with acceptable cost/benefit. Better performance is the driven force for searching innovative solutions to MAC bricks in order to fulfill the performance even in particular conditions, as in both Al and Si killed steel ladles.

This work presents the development of the MAC bricks with addition of a cement CaO-MgO-Al2O3 aggregate as an alternative technological solution for the ladle metal line. A comparative evaluation was performed to show the potential of this new raw material. Product properties, physical and thermodynamic evaluation and customer trials are presented in this paper.

**O47) CORROSION MECHANISM OF AMC LADLE BRICKS BY POST MORTEM STUDY AND LAB CONDITIONS**

Camelli, S.(1); Dignani, M.(1); Marsiglia, N.(1); Marinelli, P.(2); Labadie, M.(2);

Alumina – Magnesia - Graphite (AMC) bricks are used in the metal zone of steel ladles in Ternium Siderar steelmaking. These bricks are based on different types of alumina aggregate, carbon in graphite form and have magnesia as an additive. When heated, the spinel is formed to ensure sufficient residual thermal expansion. This behavior closes the joints between the bricks and the slag penetration is reduced.

The wear mechanism of the lining refractory bricks for steel ladle metal line corresponds to a combination of different chemical (carbon oxidation, steel and slag attack), thermal (heating and cooling cycles) and mechanical stresses. In the current work, a post mortem study of different suppliers AMC bricks was performed through optical and electronic microscopy (SEM) and EDS analysis. By using these techniques the refractory microstructural changes were evaluated.

Also, five different grades of AMC bricks are comparatively characterized and their degree of spinel formation in –situ are determined as a temperature function. Immersion tests or "dipping test" were done in air atmosphere at 1600° C for 1 hour using steel and ladle slag. Corrosion mechanisms were analyzed.

As a result, the correlation between the laboratory test and the post mortem study defined the most important parameters to select AMC bricks for steel ladles.
O48) EFFECT OF THE CURING CONDITION ON THE DURABILITY OF THE INJECTION REFRACTORIES FOR RH DEGASSER REPAIR

Tsutsui, Y.(1); Sato, M.(1); Saito, Y.(1);
(1): Nippon Steel & Sumitomo Metal Corporation. Oita Steel Works., Oita, Japan

In the steelmaking process, the RH degasser is a major facility for improving steel cleanliness, by removing gases and non-metallic inclusions from the molten steel. To improve the productivity of the RH degasser, it is necessary to extend the life of the lower vessel and snorkels to reduce the time loss that occurs when they are exchanged. Injection refractories are widely used to repair the lower vessel and snorkels of the RH degasser. At Oita Steel Works, alumina-magnesia (Al$_2$O$_3$-MgO) castable refractories are used as the injection refractories. It is well known by lab investigations, that the performance of alumina-magnesia castables is influenced by the curing conditions, such as the curing temperature and time, but the optimum conditions for RH repair in the steel works have not been clearly defined. This study focused on the effect of the curing temperature and time on the lifetime of the injection refractories in the actual RH degasser.

In the actual RH degasser, the temperatures of the injection refractories in the upper, middle and lower part of the snorkel were measured using thermocouples, during the curing and drying processes. The temperature of the injected refractories at 10 hours after injection was 200°C in the upper part of the snorkel, and 50°C in the lower part of the snorkel. So the curing temperature of the lower part was less than 100°C, which indicated that the free water in the injection refractories did not completely dehydrate, whereby the injection refractories were exposed to high temperature steam during the curing time.

Therefore it was necessary to clarify the influence of the high temperature steam on the properties of the alumina-magnesia castable refractories. Alumina-magnesia castable samples (40×40×160mm) were cast in steel molds after mixing, sealed with a steel lid, and cured at 100°C, and 200°C, similar to the curing condition in the actual RH degasser. For a comparison, other samples were cured without being sealed with a steel lid.

The bending strength of each sample was measured at 1, 3, 6, 10, 24 hours after casting. It appeared that the bending strength of the samples exposed to high temperature steam increased up to 3 hours, and then decreased thereafter. The strength reduction was considered due to the slaking of MgO, caused by the high temperature steam. On the other hand, without the sealing lid on the mold, the bending strength of the injection refractories increased continuously, even after 3 hours.

The test results made it clear that the high temperature steam caused the strength deterioration of the alumina-magnesia castable refractories, because of the slaking of MgO. To suppress this strength deterioration, the curing including dehydration should be completed within 3 hours. By applying this new, controlled curing condition in the
field, the wear rate of the injection refractories in the actual RH degasser was reduced by 14%.

**O49) IMPROVEMENT OF BOTTOM IMPACT PAD LIFE FOR STEEL LADLES AT KIMITSU STEEL WORKS**

Kubota, Y.(1); Takeuchi, H.(1); Ito, S.(1);
(1): Nippon Steel & Sumitomo Metal Corporation. Kimitsu Works, kimitsu, Japan

The service life of the impact pads installed in the bottom of ladles at Kimitsu Steel Works was not long enough. So it was necessary to extend the repair interval of the ladles to improve the bottom impact pad life, so three improvements were made for this purpose.

The first one was to improve the strength of the impact pad, because of the damage caused by the impact/abrasion of molten steel during charging. Alumina-magnesia castable, the material of the impact pad, was densified as one of the improvements. So an improved bottom impact pad refractory was developed for use, which had roughly two times higher strength than the previous impact pads.

The second one was better control of the thermal expansion of the bottom refractories installed around the impact pads. The thermal expansion was decreased to prevent the damage caused by high expansion pressure between the impact pads and the surrounding bottom refractories. That is to say, the amount of magnesia of the alumina-magnesia castable, the material of the bottom refractory, was decreased to suppress too much expansion which occurred when alumina and magnesia reacted over 1200°C and formed Spinel.

The third one was optimization of the structure of the bottom area refractories. The impact pad and the bottom refractories were installed to provide a flat bottom surface, because the height difference of these refractories generated stress concentration at the interface where the lower height bottom refractories contacted the side face of the higher height impact blocks.

Success was achieved, with doubling of the life of the impact pads, by making three improvements.
MO 3) MONOLITHICS FOR VARIOUS APPLICATIONS 3

O50) SOLELY PRECISE DOCUMENTATION OF THE MATERIAL PREPARATION CONDITIONS LEADS TO REPRODUCIBLE AND TRACEABLE RESULTS IN THE RESEARCH OF REFRACTIVE CASTABLES

Krause, O.(1); Kasper, J.(2); Tischer, D.(3); Holleyn, F.(1); Dannert, C.(2);

This presentation contributes to a better understanding how sample preparation influences technological parameters. Over the last ten years research in the field of rheology, setting and curing behavior and strength evolution clearly shows that the obtainable results are strongly dependent on the sample preparation conditions. Firstly the flow properties of refractory castable are not only affected by the water addition but also by the mixing conditions. Imprecise adjustments of the power input significantly change the flow properties and in consequence the densification of the material. On the one hand for material development in the laboratory this requires mixing devices where the mixing energy input can be monitored and adjusted precisely at least for the set of samples prepared for a single material development. On the other hand mixing conditions on site should be checked carefully for the reason that it is common knowledge that often the mixing devices available in the users industry do not cover the requirements for a proper mixing of highly dispersed refractory castables therefore castables will behave different.

In principle it is not necessary to mention that curing time and ambient curing conditions impact the technological properties measured thereafter. However it is worth to mention that even small deviations of the curing conditions show a strong impact on the results. Special care has to be taken with regard towards the relative ambient humidity. Even if the relative humidity is adjusted to 95 % as recommended by ISO 1927 a significant loss of pore water is recordable. Less pore water leads to a significant increase of the green strength. It is highly recommended to adjust not only the curing temperature but also the prevailing relative humidity because it affects the dry-out behavior over the curing time. At this point it is important to reflect the mixing conditions again, because at this early stage of preparation this high-energy input changes the temperature of the admixture and already leads to a significant loss of mixing water.

In the presentation we will demonstrate and conclude that reliable and reproducible results can only be obtained if all preparation parameters are adjusted to constant conditions and also point out that only proper documentation will lead to transparent results. This is necessary for a stringent material development in a laboratory and should also be part of every publication in the refractory castable research.
O51) THE ROLE OF GRANULOMETRY AND ADDITIVES IN OPTIMISING THE ALUMINA MATRIX IN LOW CEMENT CASTABLES

Kiennemann, J.(1); Chabas, E.(1); Ulrich, C.(1); Dumont, D.(1);
(1): 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.

A systematic approach has been conducted to investigate different ways to optimize granulometric packing in Low Cement Castable formulations thanks to the use of different kinds of aluminas. Typical average particle size for these aluminas ranges from 0.3µm to 6µm.

The potential of a new alumina product has been explored as a competitive alternative to reactive alumina. It has a median particle diameter (d50) around 3µm and has a monomodal granulometry. Dinger and Funk’s packing model has been used to optimize packing design of the castable with this alumina. In many cases use of this alumina alone in the formulation can be fully satisfying for the application. In other cases, the combination with a reactive alumina (d50=0.5µm) is useful to further improve rheological properties.

Bimodal aluminas are usually found to be very efficient to achieve good rheological properties and high levels in applicative refractory tests. The effects of the granulometric curve and process additives have been investigated to understand the impact on castable properties. Flowability behavior and torque evolution during mixing have been followed to characterize rheology. It will be shown that differences between various aluminas can be associated or compensated for by usage of specific additives.

O52) HIGH-ALUMINA CHEMICALLY-BONDED REFRACTORY CASTABLES CONTAINING LIQUID OR POWDERED BINDERS

Da Luz, A.(1); Lopes, S.(1); Gomes, D.(2); Pandolfelli, V.(1);
(1): Universidade Federal de São Carlos, São Carlos, Brazil (2): Petrobras, Rio de Janeiro, Brazil

Phosphate-bonded refractories may be applied as repairing materials due to their fast setting time and good thermo-mechanical properties in the 30-1000°C temperature range. Phosphoric acid and monoaluminum phosphate (MAP) solutions are commonly used as main binder additives in chemically-bonded compositions, but solid phosphate compounds can also be applied for this purpose. This work addresses the design of vibratable high-alumina castables containing MAP (liquid) or magnesium monophosphate (powder) as binding agents. Various experimental tests (flowability, setting time, cold and hot mechanical strength, thermal shock resistance, and others) were carried out and the developed compositions were compared with commercial
products of different refractory producers. According to the attained results, both evaluated additives (MAP solutions or magnesium monophosphate) are very effective and they have the advantage of not inducing the castables’ temperature increase (such as the case of mixtures prepared with phosphoric acid) during the mixing and curing steps. Furthermore, the addition of a sintering additive (boron-based compound) to the evaluated formulations resulted in enhanced thermo-mechanical performance (mainly cold and hot mechanical strength, thermal shock and erosion resistance) in the 600-1000°C temperature range.

**O53) ROBUST CASTABLE BEHAVIOUR - HOW CAN IT BE ACHIEVED?**

Schmidtmeier, D.(1); Zacherl, D.(2); Buhr, A.(3); Schnabel, M.(3); Kockegey-lorenz, R.(1); Klaus, S.(3); Zhou, Y.(4); Zhang, J.(4); Kaneko, T.(5); Dutton, J.(6);

The behaviour of refractory castables with regard to wet mixing, flow over time, and setting and strength development depends on the composition of the mix and external factors such as ambient temperature, water quality, intensity of mixing, etc. Variation of the castable behaviour in those properties mentioned above can challenge the whole installation and trigger countermeasures on site. Sometimes these countermeasures are detrimental for the performance of the installation, e.g. through increased water demand and higher porosity as consequence. In general, conventional castables can be considered more robust due to their higher cement content when compared to low and ultra-low cement mixes. The latter ones provide higher performance in use but are more sensitive for changes in installation conditions. Their formulation is also more complex with various fine matrix components and additives for dispersion and setting control. The raw materials especially in the matrix fines can have a significant influence on the robustness of low and ultra-low cement castables. Trace contaminations and homogeneity in raw materials, under- or over-dosage of small additive amounts, aging behaviour in the ready dry-mix, and different wet-out times depending on the mixing intensity are just examples here. In order to overcome problems with too low or too high ambient temperatures during the installation, sometimes heated or cooled water is used, even if the effect might be questionable. Trials in the laboratory were performed under defined conditions for systematic investigation of dry mix and mixing water temperature influence. They also provide information on the robustness of additive systems at these different ambient temperatures. In addition, experiences and results with matrix compounds including cements are reported, which can contribute to higher robustness in installation of more sophisticated low and ultra-low cement castables.

**O54) SOLBONDED ALUMINA-SILICA MONOLITHICS – NEW DEVELOPMENTS, RECENT EXPERIENCES AND FUTURE POSSIBILITIES**

Blajs, M.(1); Pribil, B.(1); Reif, G.(1);
(1): RHI AG, Leoben, Austria
In the last years a new generation of castables, shotcreting and gunning mixes with colloidal silica bonding technology has provided enormous advantages in terms of processing and material properties, the most important being an easy-drying behavior, excellent thermal shock resistance, low brittleness, as well as hot erosion and corrosion resistance. As a consequence, in many different industries like cement, steel, non-ferrous, energy, environmental and chemistry applications, these materials show significant performance improvements and lifetime increases compared to commonly used cement bonded castables. Nevertheless, continuative research and development efforts in the field of solbonded monolithics lead to further improvements and innovations.

The sol-binding system provided the basis for further developments in the field of new and innovative matrix design for Alumina monolithics. For the carbon containing Oxycarbide-mixes colloidal silica function as the initial binding system. By increasing temperature various in-situ phase formations provide an extraordinary strong refractory matrix with non wetting properties against steel and slag. The mixes show impressive results in several hot metal and steel industry applications.

Another example are “Mullite-bonded” mixes, which represent the latest innovation in the field of cement-free refractory castables. The material properties are tailored to the very demanding conditions experienced in the EAF-roof lining, which include high thermal radiation, mechanical wear and thermal shocks.

Till now, the major disadvantage of solbonded mixes was that the commonly used sol-binder is water based and therefore freezes below 0°C. Frost irreversibly destroys the liquid binder. This problem had to be bypassed via logistic means like heat transport and heat storage at customer site. Therefore a new frost-proof solbinder was developed that allows storage and transport at very low temperatures, even below -30°C without harming the binder.

The paper provides the fundamentals of recently developed solbonded materials with innovative matrix design, the advantageous properties are illustrated by presenting the results of extensive research work and comparative results from different application areas are shown. Furthermore research efforts and results from the devolpment of a frostproof solbinder are presented.
ENRE) ENVIRONMENTAL AND RECYCLING

O55) HIGH-PERFORMANCE REFRactory CERAmICS FROM WASTE MATERIALS

Koshy, P.(1); Koszo, A.(2); Sorrell, C.(1);
(1): UNSW Australia, Sydney, Australia (2): Vecor Australia Pty. Ltd., Sydney, Australia

Waste materials such as fly ash and bottom ash are increasingly being produced in high volumes owing to the dependence of numerous industries on coal-derived electricity. Even though a small fraction of these materials are being used in the construction industry, large volumes are dumped in landfill and man-made lakes, which negatively impacts on the environment and health. Work at UNSW on waste material utilisation has resulted in the development of a patented materials and processing technology for the fabrication of interconnected and percolated mullite fibre network using aluminosilicate waste materials. Importantly, these materials have shown remarkably outstanding long-term stability at high temperatures, which makes it ideal for use as refractory ceramics. Furthermore, the characteristics of these unique ceramics can be further tailored to create ceramic composites with outstanding corrosion resistance and thermal shock properties, through careful control of chemical additions and processing conditions.

O56) A REVIEW ON RECYCLING OF REFRACTORIES FOR THE IRON & STEEL INDUSTRY

Madias, J.(1);
(1): metallon, San Nicolas, Argentina

Refractory materials are essential for the production of iron and steel. They are used in the direct reduction modules, coke oven batteries, blast furnaces, hot metal transport and pretreatment, oxygen converters, electric furnaces, steel ladles, recirculation degassers, tundishes, casting systems, reheating furnaces, heat treatment units and other downstream equipment.

Global demand for refractory materials has been estimated in 46 Mt for the year 2016. The steel industry consumes about two-thirds by weight of refractory production. It is estimated that the refractory material remaining after use is 30% of the material applied. This means that around 9 milions tons of spent refractories per annum are available for recycling or land refilling.

Taking the second half of the twentieth century as a parameter, while steel production quadrupled, the total consumption of refractories fell by half. This has been influenced by the adoption of new processes for the production of steel and improvements in the quality of refractories and application technologies.

The generation of millions of tonnes of refractory waste materials is a major challenge for the environmental performance of the steel and the refractories industries. The
adoption of recycling practices, due to their complexity, is site-specific. Experience has shown that strong internal or external incentives are required for them to be put into practice.

This paper discusses the current characteristics of the recycling of refractory materials for steel use and presents various successful experiences of recycling in steel companies of Europe, Asia, the USA, and Latin America.

**O57) APPLICATION OF RECYCLED REFRACTORY MATERIALS TO A HEATING FURNACE IN A HOT ROLLING MILL.**

Takahashi, N.(1); Itakusu, M.(1);
(1): Nippon Steel & Sumitomo Metal Corporation. Yawata Steel Works, Kitakyushu City, Japan

In general, the used refractories in a steelmaking works are disposed as the waste materials. We have worked on the recycle use of these used refractory materials to reduce the amount of the waste materials.

It was well known that the used refractory materials were used again as the castable or gunning refractory materials but we tried to use them as the hearth bottom lining material of a heating furnace in a hot rolling mill as a new application of the recycled refractories. We thought that it would be good to make the scale removal work on the surface of the hearth bottom easier by using the recycled materials there and, in addition, we expected to cut down the repair bricks cost.

After several trials, we established a new application technology of the recycled refractories, and the cost of the hearth refractories was reduced and the scale removal work became easier.

**O58) INFLUENCE OF MATRIX ON THE CORROSION RESISTANCE OF ALUMINA-CHROMIA BRICKS FOR ROTARY TYPE WASTE MELTING FURNACES**

Chiba, H.(1); Toda, H.(1); Kawaguchi, S.(1); Ohno, M.(1); Ozeki, F.(1);
(1): MINO CERAMIC CO., LTD, HANDA-SHI, AICHI, JAPAN

Waste melting furnaces play a vital role in Japan because they make it possible to incinerate and melt industrial and household wastes at high temperatures, contributing to solution of landfill shortage problems and establishment of resource recycling society. Waste melting furnaces are classified depending on the type of waste and disposal process and the properties required for the refractory lining vary according to the furnaces. Since refractory lining is exposed to intensive corrosive conditions at high temperatures, alumina-chromia brick is typically applied in waste melting furnaces. For alumina-chromia brick used in rotary type waste melting furnaces, it is necessary to have both corrosion resistance to molten slag and spalling resistance to mechanical stress during rotation and thermal shock. In general, the higher the content of chromia in alumina-chromia brick, the weaker the spalling resistance. In order to achieve a longer
lifetime of the brick in actual kilns, it needs to contain a smaller amount of chromia but have high corrosion resistance.

In this study, we investigated the relationship between chromia content in the matrix of alumina-chromia brick and the corrosion index from the rotary drum corrosion test. The test results demonstrated that the corrosion resistance was improved with increasing matrix chromia content. In the test samples, a reaction zone consisting of iron oxide, alumina and chromia was observed at the brick-slag boundary. The microstructure observation revealed that brick with higher matrix chromia content has a wider reaction zone with well densified structure, leading to enhancing corrosion resistance. Employing this technique enabled us to develop the alumina-chromia brick with both high corrosion and spalling resistance.

O59) CO-UTILIZATION OF SLAGS FROM DIFFERENT INDUSTRIAL PROCESSES TO GENERATE FUEL GASES, REDUCE CO2 EMISSIONS, AND THE POTENTIAL IMPACT OF SLAG CHANGES ON REFRACTORY WEAR

Nakano, J.(1); Bennett, J.(2); Nakano, A.(1);

Iron & steelmaking and slagging gasification processes utilize carbon feedstock such as coal and petroleum coke (petcoke) in the production of metal, power, and/or chemicals; but they also generate large quantities of greenhouse gases (high in CO2) and slag as by-products. The chemistry of slags, whenever possible, is adjusted to maximize refractory service life. Other uses for slag beyond refractory service life need to be considered in the future, especially those that may reduce greenhouse gases. Typical iron & steelmaking slags are rich in calcium oxide while petcoke slags from gasification are rich in trivalent vanadium oxide. This study discusses a potential method to simultaneously use gasification and metallurgical slags to generate gaseous fuels (CO and/or H2) by utilizing strong chemical affinity of calcium oxide to vanadium oxide under certain conditions. If metallurgical and gasification slags were mixed at a specific ratio in the presence of industrial process waste including H2O and CO2, then the calcium would influence valence of vanadium changing from 3+ to 5+, forming calcium orthovanadate (3CaO·V2O5) while converting waste gases to H2 and CO. The vanadate formation is expected to occur by removing oxygen from the surrounding gases, following:

\[ 3\text{CaO} + \text{V}_2\text{O}_3 + 2[(\text{H}_2\text{O})_{1-x} + (\text{CO}_2)x] \rightarrow (\text{CaO})_3(\text{V}_2\text{O}_5) + 2[(\text{H}_2)_{1-x} + (\text{CO})x] + \text{excess heat} \]

Excess heat generated from the reaction can be used in other processes such as ore reduction, gas turbine power generation, and synthetic liquid/gaseous fuel production. In the present work, in-situ experiments were conducted using a synthetic slag mixture of calcium rich metallurgical slag and vanadium rich petcoke slag in a CO2 rich environment. Conversion of CO2 to CO rapidly occurred between 1400 °C and 1450 °C with a CO2 conversion rate of 97%. H2 is expected to be generated from H2O using the same mixed slag approach. The final slag volume would decrease to about 30% of the
original volume, lightening burden imposed on landfill sites, and would reduce process emissions of CO2.

Thermodynamic computational simulations are discussed to explore optimal conditions for the conversions, including temperature, slag composition, and slag/gas ratios. It was found that appropriate compositions of the slag mixtures needed to maximize the conversion will alter slag chemistry – potentially impacting refractory service life and/or producing a slag of different viscosity.
O60) THERMO-MECHANICAL MODELING OF A STEEL LADLE USING THE PERIODIC LINEAR HOMOGENIZATION TECHNIQUE

Teixeira, L.(1); Gasser, A.(2); Rekik, A.(2);
(1): Magnesita Refractories, Contagem, Brazil (2): Univ. Orléans - PRISME, Orléans, France

In the Steelmaking industry and in many others that involve the processing of molten metal, the metallurgical vessels can be lined with refractory bricks, with and without mortar. The design of these linings poses a complex problem, since the material itself is non linear regarding the mechanical behavior and the bricks/joints subsystem imposes considerable computational problems due to the large amount of interfaces between them. The Periodic Linear Homogenization (PLH) is a technique that allows the consideration of the expansion joints effect in the reduction of the stresses, providing a better estimation of the applicability of a given lining to the thermo-mechanical loads imposed by operational conditions. In this work, the PLH is coupled to a commercial Finite Element Analysis software and a complete steel ladle is simulated, considering the working, safety and insulating linings.

O61) ADVANCES IN PURGING PLUG DESIGN FOR SOFT PURGING: A WATER MODELING STUDY

Trummer, B.(1); Viertauer, A.(1); Fellner, W.(2); Hackl, G.(2); Kneis, L.(1);
(1): RHI AG, Steel Division, Vienna, Austria (2): RHI AG, Technology Center, Leoben, Austria

Soft purging has turned into an indispensable process step in Secondary Metallurgy for the production of low inclusion steel grades. The effectiveness of soft purging depends considerably on the design of the purging plugs used for this purpose. Water modeling studies comparing different plug designs have been carried out and the main parameters for optimum soft purging have been identified. Based on these parameters a quantitative description and ranking of the suitability of several plug types for soft purging will be given. Finally a roadmap for the development of improved soft purging plugs will be outlined.

O62) FUSED DOLOMA CONTAINING BRICKS FOR THE STAINLESS INDUSTRY

Gueguen, E.(1); Macvinnie, R.(2); Schimd, U.(3); Stenger, J.(1);

Fired dolomite is the preferred refractory for stainless converters worldwide. It is typically produced from sintered doloma and is often blended with magnesia to enhance its prosperities.
Lining wear is usually caused by three mechanisms: (a) chemical attack i.e. the infiltration of slag which are unsaturated in CaO, (b) mechanical erosion, abrasion and (c) thermal attack i.e. softening at elevated operating temperatures, spalling via thermal cycling. The tuyere zone represents the highest wear rates due to a combination of high localized temperatures, severe thermal cycling, The slagline / trunnion above the tuyeres is a high wear area due to abrasion from solid decarburisation slags, alloy impact & high velocity flow currents. Ultimately therefore the wear rate of these two areas determines the refractory lifetime of the converter and consequently demands the use of refractories with enhanced properties.

The addition of sintered magnesia to doloma refractory is typically used to increase the volume stability and the corrosion resistance. Replacing sintered components with fused increase the crystal size which improves the corrosion resistance.

Adding fused doloma rather than magnesia reinforces the brick matrix, which is critical in terms of corrosion resistance. This is reflected in the final product whose physical properties are similar to those of traditional magnesia doloma bricks – however the wear resistance is significantly improved.

A tuyere grade based on fused doloma and sintered magnesia was developed. The high concentration of fused component increases the corrosion resistance and reduces the shrinkage at high temperatures and therefore joint opening. Furthermore it lowers the glassy phase content of the brick which increases the thermal shock resistance.

The slagline / trunnion covers a much larger area than the tuyere zone and suffers from less localized high temperatures and thermal cycling. The fused doloma containing brick developed for this application was therefore optimised in terms of performance versus cost. It is a blend of fused and sintered doloma and sintered magnesia.

To date the fused doloma containing tuyere grade has been tested in over 35 linings at 10 different customers with AODs ranging from 12 - 180Mt, realizing a reduction in wear of upto14%. The fused doloma containing slagline grade has been trialled in over 15 linings in units ranging from 50 - 180Mt at 6 customers. The wear rates were typically reduced by 4 - 30% compared to conventional magnesia doloma.

Based on the field trial results it can be concluded that the fused doloma containing tuyere and slagline grades allow increasing the performance in the critical areas of stainless converters and reduce the overall specific refractory cost.
TOR 1) TESTING OF REFRACTORIES 1

O63) NON-DESTRUCTIVE TESTING (NDT) AND MONITORING OF REFRACTORY LINING IN OPERATING FURNACES

Sadri, A.(1); Ying, W.(1); Chataway, D.(1); (1): Hatch, Mississauga, Canada

The refractory lining in a smelting furnace is crucial to providing structural integrity to the furnace and protecting the furnace exterior from the molten metal inside. Refractory bricks used in smelting furnaces are designed to withstand extreme mechanical, chemical and thermal stresses; however, soon after the start-up of a furnace, the lining inevitably suffers from wear and deterioration. Usually, critical loss of refractory is the main reason for the repair or reline of furnaces, which results in expensive maintenance costs and loss of production. Due to the nature of smelting furnaces it is nearly impossible to drill into the lining while the furnace is in operation and directly determine the remaining lining thickness and evaluate the refractory condition. Due to this need, several non-destructive testing (NDT) or indirect methods were developed. These select NDT techniques can measure refractory lining thickness and can evaluate refractory quality by determining if any chemical changes, hydrations, cracking, oxidation or metal impregnation have occurred within the refractory. The accuracy of these indirect NDT methods relies largely on the quality and homogeneity of the refractory bricks in the lining. Experience and knowledge of smelting furnaces in addition to understanding refractories as a composite ceramic is required to understand the variation in the mechanical properties of the refractory bricks in the lining and, as a result, accurately analyze the NDT measurements. In this paper, the available furnace refractory lining NDT and monitoring techniques will be reviewed and discussed. The advantages and disadvantages of the various techniques will be shown through examples and case studies. Finally, this paper will demonstrate how monitoring refractory lining can help extend the campaign life of a smelting furnace and save furnace management millions of dollars in production loss and maintenance costs.

O64) APPLICATION OF DIGITAL IMAGE CORRELATION FOR THE ANALYSIS OF THE FRACTURE BEHAVIOUR OF REFRACTORIES

Khlifi, I.(1); Dupré, J.(2); Pop, O.(3); Doumalin, P.(2); Huger, M.(1); (1): Science des Procédés Céramiques et Traitements de Surface (SPCTS UMR CNRS 7315), CEC, Limoges, France (2): Institut Pprime, CNRS, Université de Poitiers, Poitiers, France (3): Groupe d'Etude des Matériaux Hétérogènes (GEMH), Université de Limoges, Limoges, France

Refractories are heterogeneous materials designed to operate in harsh working environments which sometimes lead to their premature failure. Therefore, it is necessary to enhance their properties to ensure consistent furnace performance and operator safety. Among these properties, the thermal shock resistance of refractories is a parameter of significant interest which is known to be closely related to their mechanical behaviour. In fact, an existing network of micro-cracks within the
microstructure of refractories often leads to non-linear mechanical phenomena around the crack tip which are beneficial for their crack propagation resistance and thus, their thermal shock resistance.

In the present study, refractory materials with a non-linear mechanical behaviour were chosen in order to highlight their fracture behaviour, with regard to their microstructure, by using Digital Image Correlation (DIC). The direct measurement of displacement fields between digital images of the reference state and the deformed one has provided valuable information on material deformation during loading, especially at the vicinity of the crack tip where non-linear phenomena take place. Therefore, the aim of this work is to investigate the fracture behaviour of refractories through DIC by using a refined DIC process based on a material transformation taking into account a discontinuity of displacement.

As highlighted by the results, the coupling of DIC with mechanical tests commonly applied to refractories (Wedge splitting test, Brazilian test and bending) has proven to be effective in characterizing the mechanical behaviour of these materials. The set of measured data can be used as a validation tool for numerical models and thus, bridge the gap between experiments and simulations.

**O65) RHEOLOGY AND PRESSURE SLIP CASTING OF COARSE GRAINED SUSPENSIONS FOR GRADED COMPOSITE REFRACTORIES**

Schafföner, S.(1); Fruhstorfer, J.(1); Gehre, P.(1); Thalheim, M.(1); Hubalkova, J.(1); Aneziris, C.(1);

(1): Institute of Ceramic, Glass and Construction Materials, Freiberg, Germany

Pressure slip casting is state of the art for the production of ceramics containing clay minerals such as sanitary ware and whiteware. Recently, pressure slip casting was presented as a forming technique for coarse grained oxide ceramics using a xanthan/guar gum solution as a stabilizer and binder. Subsequently, graded refractories consisting of two layers with a different maximum grain size were successfully produced by pressure slip casting.

The present contribution presents the further developments of the pressure slip casting of graded composites for refractory applications by demonstrating the manufacturing and characterizing of filter cakes with three layers, which have a maximum grain size of 3 mm, 1 mm and 0.5 mm, respectively.

To study the rheological behavior of the slips, an adapted falling sphere viscosimeter was designed, which uses the sphere’s acceleration phase to measure the viscosity of the slips. By repeated measurements, the thixotropy of the slips can be determined. Afterwards, the effect of the added amount of water, binder and dispersant on the thixotropy of the slips was evaluated using full factorial experimental designs.

Subsequently, the casting of graded coarse grained filter cakes was investigated in a pressure filtration cell, which uses pressurized air as the pressure medium. To study the
filtration behavior of the filter cakes, the effects of the filtration pressure and filtration time of the three slip layers were firstly determined. In addition, the application of a small layer of the xanthan/guar gum binder solution as a filtration aid was evaluated. Eventually, the effects of the type of the dispersant, particle size distribution and of the used refractory raw material were analyzed.

For all three particle size distributions, a slip composition with a minimal thixotropy and fast filtration behavior was developed. Later on, stable filter cakes with an excellent bonding without cracks, pores or delamination of the three filter cake layers were achieved, which was confirmed by X-ray computed tomography investigations. Finally, thermal shock resistance investigations were performed by comparing X-ray computed tomography images before and after thermal shock, whereas a special focus was a possible delamination of the three filter cake layers.
OI 2) OTHER INDUSTRIES 2

O66) TIME DEPENDENT INTERACTION BETWEEN CARBON-BONDED ALUMINA FILTERS AND MOLTEN STEEL

Schmidt, A.(1); Dudczig, S.(1); Salomon, A.(1); Zienert, T.(1); Storti, E.(1); Rafaja, D.(1); Aneziris, C.(1);
(1): TU Bergakademie Freiberg, Freiberg, Germany

The understanding of the reactions between filter material and molten steel is essential to improve the purity of casted products by filtration. Thus, this contribution illuminates the kinetics of interactions between carbon-bonded filters and molten steel. In addition, a thermodynamic model accompanies the experiments to describe the impact of carbon on the reactions. For the experiments, carbon-bonded alumina filters were coated either with pure alumina or with a mixture of alumina and 4wt% carbon (Al2O3+4C). Two methods were applied to evaluate the time dependence of the interactions. First, the coated filters were immersed in molten steel for 10s up to 120s. These short-time tests are performed using a special steel casting simulator providing close-to-reality conditions. Secondly, long-time trials up to 60min using spark plasma sintering (SPS) equipment complement the investigations. In the SPS test, the flow of molten steel is minimized, which enables an almost undisturbed examination of the chemical reactions at the interface. The phase composition and the distribution of phases at the metal/ceramic interface were characterized by means of optical microscopy, SEM with EDX, WDX and EBSD. Carbon seems to accelerate the layer buildup during steel contact, as the in situ formed layers were already observed after immersing filters coated with Al2O3+4C for 10s into the molten steel. In comparison, the in-situ formed layers were only found after 30s immersion of alumina coated samples. Furthermore, the long-term SPS experiments revealed enhanced chemical interactions of Al2O3+4C coated filters as compared to the alumina coated ones. These findings indicate that an accelerated dissolution and precipitation of alumina from steel is triggered by the presence of carbon, in excellent agreement with predictions of the thermodynamic model. Interestingly, very fine inclusions with the size of a few micrometers were found on the surface of alumina coated filters after 60s and even more of these inclusions after 120s immersion. They are considered to be deposited directly from the molten steel, which would be the desired filtration effect. In summary, the carbon content of alumina based filter material significantly influences the steel melt filtration. The thermodynamic model clarified the impact of carbon on these interactions and will be beneficial to tailor future filter material compositions.

O67) COMPARISON OF CARBON-BONDED ALUMINA FILTERS WITH ADDITION OF TITANIA AND NANOMATERIALS IN CONTACT WITH A STEEL MELT

Storti, E.(1); Dudczig, S.(1); Schmidt, G.(1); Aneziris, C.(1);
(1): TU Bergakademie Freiberg, Freiberg, Germany
Non-metallic inclusions in cast metal parts often have a negative impact on properties such as fracture toughness, tensile strength and fatigue resistance. Foundries require high purity metal melts in order to limit the casting repairs and possibly avoid rejected castings. This can be achieved by applying a filtration process after the ladle treatment. In the case of steel, ceramic foam filters (CFFs), especially those based on zirconia and carbon-bonded alumina, have been successfully employed for years. However, their potential has not been fully exploited yet: the filtration efficiency of ceramic foam filters in ferrous melts is less than 75% for inclusions in the particle size range 1-100 μm. It was reported that over 90% of the large nonmetallic inclusions with a size of 100 μm are efficiently filtered by the novel filters. In contrast, numerical simulations also showed that the filtration efficiency of small inclusions with a size of 1 μm and 10 μm is less than 10% and 18%, respectively. In order to improve the filtration efficiency, promising approaches which involve “active” and “reactive” coatings applied on the filters have been proposed.

Recently, carbon-bonded alumina filters were coated with multi-walled carbon nanotubes and immersed in a steel melt containing endogenous alumina inclusions. Microscope investigations after the test suggested a better performance of these MWCNTs-coated filters over uncoated Al2O3-C samples for short immersion times (10/30 s). Starting from this formulation, other additions of TiO2 and alumina nanosheets (in the substrate material and in the coating, respectively) were explored. In the case of titania, the reducing atmosphere of the heat treatment was expected to generate free electrons and produce point (or even surface) defects that could alter the chemical properties of the host system. The coated samples were tested for different times in contact with a corrosive steel melt clean from inclusions at 1580°C. Investigation of the filters after the test was carried out by optical microscopy, scanning electron microscopy and electron backscatter diffraction. In addition, steel samples were thoroughly analyzed with a special ASPEX-SEM to evaluate the influence of each specific ceramic filter on the steel composition and purity. Finally, the results from the different filter formulations were compared.

**O68) CARBON-BONDED ALUMINA FILTERS FOR STEEL MELT FILTRATION BY A GEL-CASTING PROCESSING ROUTE BASED ON SODIUM ALGINATE**

Wetzig, T.(1); Ode, C.(1); Dudczig, S.(1); Aneziris, C.(1);
(1): TU Bergakademie Freiberg, Institute of Ceramic, Glass and Construction Materials, 09599 Freiberg, Germany

The use of carbon-bonded alumina filters became a common way to increase the purity of steel by removing non-metallic inclusions from the melt. However, established filter processing routes such as the replica technique are restricted with regard to the mechanical strength and the pore structure of the produced filter systems. In this study, a novel gel-casting process is presented as a viable alternative. The desired filter structures have been casted using a water-based alumina-carbon slurry with sodium alginate as gelling agent. By pumping the material into a watery solution of calcium chloride dihydrate, the alginate forms a solid gel. This allows the computer-assisted manufacturing of three-dimensional lattice structures consisting of a continuous filter
strut. The produced filter structures were immersed in a steel melt at 1585°C. Afterwards, the microstructure and the chemical composition of the filter surface were characterized by digital light microscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The study showed that the developed processing route is suitable for the production of carbon-bonded alumina filters for steel melt filtration. The tested samples provided sufficient thermal shock resistance and refractoriness in contact with molten steel. Furthermore, in-situ formed layers and crystalline phases were found on the surface of the immersed filters. These observations prove the filter effect of the produced alumina-carbon structures. The novel processing route is very promising because it allows the production of full-strut filters with adaptable macro-porosity resulting in higher component strength and tailored melt flow conditions.
Introduction: The need to produce high quality but low cost magnesite-carbon refractories materials, leads us to evaluate the importance of the raw materials’ choice for these products depending on the application in iron and steel industry. Despite the wide use of magnesia raw materials, there are no recent studies that critically analyze their actual performance related to their properties. In this work, a preliminary study was carried out to investigate the most used raw materials based on MgO in refractory field. Chemical and physical-mechanical analysis were performed on specimens integrally formed from each raw material. Three classes of magnesite have been analyzed: dead burned (DBM), “seawater” and electrofused magnesite. A comparison of the results was made and it has been defined in theory the ideal field of employment of these materials in steel industry. To verify the actual performance in real application, the bricks formulas most commonly used and marketed in steelworks were reproduced in laboratory introducing the raw materials with the best theoretical properties.

Material and Methods: Six different magnesia raw materials were analyzed preparing ten specimens for each of them. The main physical-mechanical features were evaluated performing tests such as apparent porosity, density, cold crushing strength, resistance to thermal shock, refractoriness-under-load, and thermal expansion. The chemical properties of the materials were evaluated performing test such as resistance to alkali corrosion and to slag attack, X-Ray Diffraction and Fluorescence. In the second part of this work the information acquired for each raw material were used to modify the formulation of magnesite-carbon products in order to improve their performance. The study was made on different magnesite-carbon brick used in the most critical places of the steel mill, in particular converter, electric arc furnace and steel ladle. In laboratory bricks with standard formula was made with the raw materials normally used in current industry’s application and it was compared with the bricks produced with the same formula but different magnesiti.

Results and Conclusions: The study of raw materials gave us interesting information in particular for dead burned and “seawater” magnesite. These materials show good properties of resistance to chemical and mechanical stress comparable in some cases to the performance guaranteed by the electrofused. At the same time, the results obtained for electrofused are useful to discriminate which magnesite use in relation to the application. The actual performance in real application of the bricks producing in laboratory was tested and the results obtained show interesting improvements. The formulation of new products appear to be attractive for a subsequent use at the industrial level.
O70) MORPHOLOGY EVOLUTION OF \( \alpha \)-AL2O3 FROM MILLED \( \gamma \)-AL2O3 PRECURSOR WITH NH4F ADDITIVE

Sun, C.(1); Zhu, L.(1); Li, S.(1); Chen, L.(1); Ye, G.(1); Liu, L.(1);
(1): Zhengzhou University, Zhengzhou, China

Influences of precursor milling treatment, NH4F addition and calcination time on the morphology of \( \alpha \)-AL2O3 formed from commercial \( \gamma \)-AL2O3 precursor have been studied. The neck growth of \( \alpha \)-AL2O3 nuclei formed from milled precursor has been partially suppressed by the morphological change of commercial \( \gamma \)-AL2O3 precursor, oval-like shape alumina with about 500nm in grain size appeared in the sample obtained by a 1450°C calcination of milled \( \gamma \)-AL2O3 precursor without NH4F, coexisting with vermicular-alumina aggregates in the size range of 2~10 \( \mu \)m. Furthermore, the morphology of \( \alpha \)-AL2O3 was significantly changed by the introduction of NH4F addition and calcination time. Square like \( \alpha \)-AL2O3 powders with an average primary crystal size of \( \sim \)200 nm were formed from milled \( \gamma \)-AL2O3 precursor with 1wt% NH4F, while cake-like \( \alpha \)-AL2O3 powders in the size range of 0.2~1 \( \mu \)m were synthesized from milled \( \gamma \)-AL2O3 precursor with 20%NH4F addition, and the particle size distribution of \( \alpha \)-AL2O3 were further improved by increasing the calcination time from 2h to 5h. The gas intermediate compound, such as AlOF, AlO2 etc, produced from the reaction of AL2O3 precursor and NH4F addition at high temperature, may lead to an alteration of \( \alpha \)-AL2O3 growth process by a change in the scale of the developing microstructure.

O71) CONCEPTS OF ENGINEERED REFRACTORY AGGREGATES AND SOME PRACTICES IN CASTABLES

Zhou, N.(1); Shi, S.(2); Li, Z.(3);
(1): High Temperature Materials Institute, Henan University of Science and Technology, Luoynag, P. R. China (2): Materials Technology Innovation LLC, Katy, USA (3): Jiangsu Jingxin New Materials Co., Ltd, Yangzhou, P. R. China

Not being just made of fired mineral ores as conventional products, refractories are increasingly becoming sophisticated with carefully designed compositions and microstructures, for which refractories engineering is of a great necessity. Most past efforts in this aspect are focused on matrix portion. Today, attention has turned to the necessity to engineer aggregates too, as they constitute dominant part in most of refractory products. In this paper, concepts of aggregates engineering were put forwarded and possible engineered structures by purposely designed and controlled shape, surface feature, chemical and phase compositions and their distribution as well as microstructure inside and on aggregate surface were suggested. Some newly developed engineered aggregates, i.e., mullite based hollow balls, mullite based porous spherical aggregates, micro-pored sintered alumina and spherical bauxite and their adoptions in light weight and dense castables were introduced. Exceptional advantages and benefits from using them have been evidenced, highlighted by higher strength, increased flowability, reduced thermal conductivity, enhanced thermal shock resistance and improved size processing effectiveness, compared to conventional counterparts.
The direct and potential impacts by using such engineered aggregates on advancement of refractory technology were discussed.
SLSM 3) STEEL LADLE AND SECONDARY METALLURGY 3

O72) CONSTRAINTING EFFECTS ON HIGH-ALUMINA CALCIUM MAGNESIUM ALUMINATE-BONDED CASTABLES FOR STEEL LADLES

Braulio, M.(1); Morbioli, G.(2); Guilherme, P.(2); Wöhrmeyer, C.(3); Szepizdyn, M.(3); Zetterström, C.(3); Parr, C.(4); Pandolfelli, V.(2);
(1): 4Cast Technical Assistance and Consultancy on Materials, Sao Carlos, Brazil (2): Federal University of São Carlos, Sao Carlos, Brazil (3): Kerneos, Vaulx-Milieu, France (4): Kerneos, Paris, France

The main features of magnesium aluminate spinel (MgAl2O4) are related to its chemical stability and the volumetric expansion that takes place during its in situ formation. Although the volume increase can close joints and generate compressive stresses, it can also spoil the refractory’s performance if not properly designed. In order to master the expansion and improve the corrosion resistance to basic slag, a unique binder (CMA72) obtained by co-sintering calcium oxide, magnesia and alumina has been recently developed, aiming to homogeneously attain ultra-fine spinel throughout the refractory matrix. Regarding the studies associated with the expansive behavior of spinel-forming castables, they are usually conducted in free-expansion environments, which is not in tune with the working structural conditions that involve limited room for volumetric change. Considering that the restrained expansion can act as a strengthening mechanism by reducing the castables’ porosity levels, the results attained in lab-scale conditions (expansion-free situation) may not represent the practical ones, when the compositions are applied in steel ladles. In this context, this work addressed the evaluation of thermo-mechanical properties after firing the castables under constraint, for compositions containing different amounts of pre-formed spinel and CMA72 binder. After drying bar-shaped samples (25 mm x 25 mm x 150 mm) at 600°C for 5h, they were embedded by an alumina-calcium aluminate cement castable and, after that, the whole system was fired at 1500°C for 5h. The samples were then cut for thermal shock and hot modulus of rupture evaluation and their results were compared with those of samples fired with no constraint (expansion-free). The results of these two conditions were remarkably different, pointing out that the constrained expansion procedure should be adopted for the development and evaluation of advanced spinel-forming castables’ compositions aiming to improve the working life of steel ladle linings.

O73) USE OF ULTRA LOW CARBON CONTENT MAGNESIA-CARBON PRODUCTS FOR THE PRODUCTION OF LOW CARBON CONTENT SPECIAL AND STAINLESS STEELS

Hill, K.(1); Silva, S.(2); Brito, M.(2); Gueguen, E.(3);
(1): Magnesita Refractories, Dinnington, United Kingdom (2): Magnesita Refractories, Contagem, Brazil (3): Magnesita Refractories, Hilden, Germany

The production of clean steels is becoming more common and this demands the use of special refractories in order to avoid contamination of the steel. Usually, for the lining
of the ladles it is very common to use fired bricks as the carbon pick-up can jeopardize the steel quality. However, magnesia carbon bricks with very low carbon content can be an alternative to the fired brick.

This paper shows the results of steelplant customer trials using this type of product in the production of low carbon special and stainless steels. The advantage of using this type of brick is a lower wear rate, lower cost and they don’t show structural spalling at the same frequency as the fired bricks. A further advantage of the ULC brick is the lower thermal conductivity, which reduces the heat losses and the steel shell temperature.

In addition this paper compares the properties of resin and pitch bonded ULC content bricks illustrating the different characteristics imparted by using these different binder systems and the effect these have on product performance.

**O74) EVALUATION OF CARBON DEPOSITION IN THE STRUCTURE OF A HYBRID PLUG USED IN A STEEL LADLE FOR GAS STIRRING**

Dutra, P.(1); Figueiredo, A.(1); Cunha, M.(1); Zamagno, J.(1);
(1): Magnesita, Contagem, Brasil

Porous plugs are used in secondary metallurgy for the production of high purity steels. It can improve steel cleanliness, homogenization of composition and temperature. The porous plug is usually assembled on a metal can that is connected to a gas inlet pipe. Then this porous plug is fitted in the bottom of the ladle and through it nitrogen or argon is blown into the molten metal bath. To ensure a good performance of the stirring system, the plugs are tested for leakage and outflow behavior. Nitrogen is used to test the leak-proofness of the entire stirring system on the ladle and a hydrocarbon gas like propane and natural gas can be used to check the flame pattern of the porous plug. Several wear mechanisms of the plugs have already been studied and reported in the literature, like abrasion due to back attack of the gas, slag and FeO corrosion, peeling and cracking due to thermal shock and infiltration of molten steel. But little has been said about the decrease in gas permeability due to carbon deposition in the porous structure of plug. According to this study it was confirmed that during the life of the plug, when it is submitted to gas flame test pattern, the propane and natural gas can be cracked and cause carbon deposition, what can decrease the efficiency and as a consequence the life of the plug. After conducting a test with a hybrid plug in a customer, it was removed from the ladle and sent to the lab for a post-mortem analysis. The test results shown a carbon deposition throughout the entire extension of the plug. The characterization of the plug was performed using chemical analysis, optical microscopy, density, porosity, permeability and total carbon. After checking the quality control parameters of the plug and making sure it was produced according to the specification, comparative measurements of total carbon and permeability have been performed along the used plug. It was observed by this analysis that there is a direct correlation between carbon deposition and permeability decrease. The greater the carbon deposition, the lower the permeability of the plug. The carbon deposition has been originated from the hydrocarbon gas cracking used to check the flame pattern on the porous plug. It was also influenced by the long time spent for the flame test.
According to the results, the carbon deposition directly influences the plug performance by reducing its permeability and therefore decreasing the gas injection efficiency.

**O75) STUDY ON THE PROPERTIES AND PERFORMANCE OF BASIC REFRACTORY MIXES FOR EBT TAPHOLE SLEEVE: EFFECT OF SINTERING AIDS**

Satpathy, S.(1); Samanta, A.(1); Naofumi, K.(1); Arimitsu, E.(1); Panda, P.(1);
(1): TRL KROSASKI REFRACTORIES LIMITED, JHARSUGUDA, INDIA

Repair of a furnace taphole is usually done on hot condition free from molten metal. Typically, refractory sleeves are placed in the taphole. With increased number of tapping the thickness of the sleeve reduces invariably and therefore it is essential to repair the sleeve on regular basis. Repairing around the sleeves is preferred simply because to replace the entire taphole block after it is worn out would require shutting down the entire furnace which usually requires at least 8 to 10 hours of down time. In order to achieve the original taphole diameter, the space inside the sleeve is filled with a basic repairing mix. Therefore, for reasons of economics, the industry has developed an inconvenient procedure of frequent repairing of taphole sleeves. It has been found that a repairing mix which works well for emergency repairs to the taphole sleeve is preferred. The usual time required for emergency repairs of a taphole sleeve is about 30 minutes. The need clearly exists for a longer lasting maintenance material which requires less frequent repair. These materials should have easy installation, high bulk density, fast sintering, excellent resistance against molten metal penetration, and superior erosion/corrosion resistance.

The present study is based on the effect of different sintering aids on the properties of basic repairing material and its performance during application. The hot setting behavior of the dry mass depends on the sintering aids, binder content and curing temperature. Grain sizes and material chemistry are carefully controlled to allow for proper density and sintering. Trials were done with chromate, sulphate and phosphate bonded additives and sintering study was carried out both in rammed as well as site conditions at temperatures ranging from 600°C to 1400°C. The Bulk Density, Porosity, Strength and other high temperature properties of samples were evaluated for all the trials and it was found that at intermediate temperatures the sintering aids plays a vital role during application. The developed material has been tested at different integrated steel plants and the performance is satisfactory.

**O76) EFFECTIVENESS OF FIRED ALUMINA-SPINEL BRICK IN SECONDARY METALLURGY**

Chatterjee, S.(1); Buhr, A.(2); Kockegey, R.(3); Pal, A.(4); Singh, B.(4);

Alumina-Spinel fired refractory brick for steel ladle metal zone lining is one of the recent innovations over last decade. The purpose of such innovation was primarily to cater the
growing need of advanced metallurgy for ultralow carbon and automobile grade of steels to reduce Carbon pick-up from refractory body to liquid steel. Even as alternative to other C-free refractories, the newly developed alumina-spinel fired brick is another superior generation fired refractory for achieving high performance in highly corrosive metallurgical environment (such as C/S=1.5, 5% CaF2, 2% MnO2). Such Alumina Spinel brick is manufactured by using proper granulometry of high purity synthetic alumina aggregate (Tabular alumina or white fused alumina or mixed), Mag-Al spinel in finer fractions (Al-rich or Mg-rich) and calcined alumina in matrix. The present work describes the effect of these raw materials and their granulometry on product properties such as density, porosity, shrinkage, cold and hot strengths as well as on the properties such as abrasion, slag corrosion, thermal spalling which are of prime focus of end users for evaluating refractories for predicting higher performances. SEM studies and pore size distributions are analyzed to understand the roles of raw materials on properties. It is seen in industrial applications that refractory lining life has increased significantly with Alumina-Spinel lining compared to previously used MgO-C lining due to superior resistances to abrasion, corrosion and spalling. Although the cost of refractory lining has increased compared to traditional MgO-C linings, however the overall cost of refractory per ton of liquid steel for the steel plant has reduced due to higher lining life in metal zone. The present paper describes the effectiveness of this newly developed fired alumina-spinel refractory in terms of refractory manufacturing (formulations and property evaluations) as well as steel production (application and performance).

O77) THE LIFE STABILIZATION FOR RH-SNORKELS BY COOLING OF STEEL SHELL

Nakamura, Y.(1); Hosohara, S.(1); Takahashi, K.(1);
(1): JFE Steel Corporation, Fukuyama, JAPAN

Recently, the demand against high purity steel becomes higher and the secondary refining rate for molten steel becomes larger. Keeping the working ratio of RH-degasser has become one of the most important tasks for steel production lines.

One of the shortest refractories life part in RH-degasser is a snorkel. Especially, sudden damage of an upleg snorkel requires unscheduled replacement of it that harms stable steel production.

In most cases of the sudden damaged snorkels, the deformation of steel shell of snorkel are observed. Therefore, the risk of sudden damage of the snorkels might be reduced by prevention of the shell deformation.

It is well-known strength of steel decreases along with temperature increase, and this degradation has negative influence to the shell deformation.

In this study we tried to cool the steel shell by using gas flow pipes, used for lifting molten steel.
Two types of test snorkels were prepared for the actual equipment experiment, and the steel shell’s temperature were measured continuously. Type1 had gas pipes placed on almost all area of steel shell, and type2 had that intensively placed near the lower area of steel shell.

Both type of test snorkel were kept lower temperature than conventional one. Especially, the test snorkel type2 showed the drastic effect for cooling, and deformation occurred in very limited area near the lower edge. It suggests that the cooling effect is increased by concentrating cooling near the lower edge of steel shell.

The deformation rate of the steel shell were decreased, and their lifetime were prolonged. Their lifetime was 140% in type1 and 160% in type2 compared with the average life of conventional snorkels, respectively.

The relationship between the temperature and deformation of steel shell of RH-snorkels is strongly indicated and possibility of sudden damages will be reduced under 1230 K.
TOR 2) TESTING OF REFRACTORIES 2

O78) A CONTRIBUTION TO THE UNDERSTANDING OF THE FAILURE MECHANISM OF HIGH ALUMINA REFRACTORY CASTABLES UNDER PRACTICE-ORIENTED THERMAL SHOCK CONDITIONS

Brochen, E.(1); Dahlem, E.(1); Dannert, C.(1); Krause, O.(2); Holleyn, F.(2);
(1): Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany (2): Hochschule Koblenz, Höhr-Grenzhausen, Germany

In service, refractories endure steady and/or transient thermal loading, which induces thermal stresses that are able to damage refractory components, even leading to failure of refractory structures. The assessment of the thermal shock resistance (TSR) of refractories is therefore of central concern for both refractory manufacturers and users.

Traditional methods and techniques to investigate the TSR of refractory systems still strongly rely on rather unrealistic testing conditions (e.g. descending thermal shocks, low temperatures) when compared to their industrial applications.

When considering refractory castables, it is additionally important to keep in mind that this type of refractory system is highly heterogeneous over the thickness of the lining, where only the first few centimetres can develop a ceramic bond, followed by a dehydrated and thus mechanically weak transition zone. Finally at the cold face even hydrate phases may still be found. For reasons of practicality, classical approaches to investigate their TSR largely ignore this key feature. Test pieces made from castables are, on the contrary, usually completely and homogeneously pre-fired before testing for TSR with standardized methods.

Thanks to an innovative testing device, which enables thermal cycling at high temperatures, the TSR of high alumina refractory castables can be investigated under practice-oriented thermal shock conditions and compared to the behaviour of test pieces from high alumina bricks. The damaging was assessed quantitatively and with ultrasonic velocity measurements as well as optical observations.

Compared to the refractory bricks, sintering processes during the thermal shock strongly impact the TSR behaviour of the tested castables. While in test pieces made from fired bricks the damaging is more pronounced and concentrated near the hot face where thermal cycling takes place during testing, the damaging of test pieces made from unfired castables tend to occur at first in the weak bonded “cold part” of the test pieces whereas important sintering takes place near to the hot face. By increasing the number of thermal cycles, damaging near the hot face increases. Pre-fired castable test pieces basically behave like refractory bricks.

These results broaden the knowledge obtained from traditional methods and techniques to investigate the TSR of refractory castables and highlight the necessity to develop smart testing devices and enhanced castables with tailored properties in the transition zone/dehydrated zone.
O79) ACOUSTIC EMISSION ANALYSIS TO RECOGNIZE THE FRACTURE PATTERN OF REFRACATORY MATERIALS DURING THERMAL SHOCK

Dahlem, E.(1); Dannert, C.(1);
(1): Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany

Refractories are essential for all highly industrialized processes which are performed at elevated temperatures. When in use, the temperatures at which these processes are run tend to change more often and more rapidly, as large scale industrial processes become more flexible to the availability of raw materials and the demand for products. Repeatedly cooling down and heating up the refractory linings (thermal shock) can cause severe damages to them and their service life and thus the uninterrupted operation time of the equipment are considerably reduced. Consequently, it is necessary to develop new refractory lining materials which have a good resistance to thermal shock, which in addition to long service life also leads to improved corrosion resistance at high temperatures.

To support the development of new refractory products with a higher thermal shock resistance, a new advanced testing device was developed based on the disc irradiation method. It is able to determine the critical thermal shock induced stress of refractory materials under ascending thermal shock conditions. The disc-shaped test pieces are irradiated centrally on both sides using focused halogen lamps. Within a few seconds, a circular temperature field is generated in the test piece. The heating-up regime causes a higher thermal expansion at the heated centre of the test piece compared to its edge, inducing a stress gradient. When the maximal tensile stress is reached at the edge of the test piece, fracture occurs and propagates towards to the centre.

With an appropriate in situ damaging detection using microphones, the disc irradiation method can be used to investigate the fracture process taking place within refractory test pieces during thermal shock. Using in situ detection of the acoustic emission during cracking, fracture pattern in the stressed test pieces were identified (through the matrix, the grains, the interface) by evaluation of the complex noises of the fracture during the thermal shock procedure. This fracture analysis can contribute to the development of new generations of refractory linings with a higher thermal shock resistance.

O80) EXCAVATION METHOD FOR A 2.4 M DIAMETER PILOT-SCALE FURNACE

Chetty, J.(1); Steenkamp, J.(2);
(1): Mintek, Johannesburg, South Africa (2): Mintek ,

An important part of pilot-scale test work, with the intention to design and build an industrial-scale furnace, is the evaluation of refractory materials. Information on wear of the working refractory lining, obtained during excavation of the pilot-scale furnace, can be used to improve designs in future. Therefore, reliable measurement of the wear profile and accurate sampling of refractory materials, are useful methods to apply during furnace excavations. The methods described in this paper, address these requirements. As furnace excavations (both pilot- and industrial-scale) often produce the opportunity
to study process materials in more detail, a method of encapsulating a large sample of process material in resin, is also described.

In 2016 Mintek conducted a pilot-scale study on the production of high carbon ferro-manganese (HCFeMn) using DC-arc furnace technology in sub-merged arc furnace (SAF) mode. The furnace containment system was originally designed for ilmenite smelting trials, conducted in the early 1990’s, and consisted of magnesia-based ramming material installed in the hearth, and magnesia bricks installed in a water-cooled shell as the sidewall-lining. Magnesia-based refractory is not suitable for HCFeMn production, due to the corrosive nature of the slag, and carbon-based working linings are typical for HCFeMn production on industrial-scale. The design of the furnace containment system was therefore adapted to install carbon-based cold ramming paste as working lining in the hearth and lower sidewalls. As back-lining, magnesia-based ramming material in the hearth, and magnesia-based refractory bricks on the sidewall, was retained. Furthermore, the magnesia-based refractory bricks were extended vertically to form the upper sidewall lining.

The furnace steel shell had an internal diameter of 2 470mm. After installation, the lower sidewall had a diameter of 1 700mm in the hearth, and a height of 537 mm. The upper sidewall lining had a height of 570mm and internal diameter of 2 004mm. In the past, manual excavation methods, including wear profiling and sampling, were applied. After the campaign in which HCFeMn was produced, new methods to excavate and sample the burden, to profile refractory wear, and to sample the refractory materials were developed and implemented. The development and implementation of these methods are described in this paper.

The method consists of three sub-sections:

1. Casting of the burden (process material) in resin and excavation of the block of resin encapsulated burden.
2. Three dimensional (3D) scanning of the wear profile of the refractory working lining and superimposing the results onto the model of the refractory design to create a set of detailed drawings.
3. Core drilling samples of the refractory working lining in the hearth.

For each sub-section the method includes sourcing and description of materials used, equipment and detailed steps.

**O81) EFFECT OF CORROSION ON THE PERMEABILITY OF HIGH ALUMINA REFRACTORIES**

De Bilbao, E.(1); Loison, L.(2); Brassamin, S.(3); Tonnesen, T.(2); Poirier, J.(1);
(1): CNRS - Univ. Orléans, Orléans, France (2): RWTH Aachen, Aachen, Germany (3): CNRS, Orléans, France

Permeability is a very important property of refractory materials. For example, it plays a key role in the dewatering of refractory castable, in the oxygen pick up by submerged
nozzle during the steel continuous casting or in corrosion of refractory linings by gases (Na2O, K2O,...). On the other hand, permeability to liquid plays a key role in the resistance to the penetration of corrosive fluids. For example, the corrosion of high-alumina refractory bricks and alumina-magnesia in situ spinel castables used in steel ladles by slag involves reactive impregnation where the slag impregnation is driven by the capillary suction and limited by the liquid permeability.

Dedicated permeameter has been designed to perform gas permeability measurements. The pressure drop and the flow rate can be controlled to perform test in viscous conditions and active Klinkenberg’s effects. Liquid permeability can therefore be accurately derived from gas permeability measurements.

The objectives of this work were:

i) To demonstrate the reliability of the new permeameter and the possibility to measure accurately the permeability. The measurements were carried out on an alumina based refractory Low Cement Castable (LCC).

ii) To evaluate the impact of the corrosion on the gas and liquid permeability of the LCC by measuring the property before and after corrosion. The corrosion tests were performed with industrial slags coming respectively from steel and energy production. The permeability measurements were complemented with microstructural examination by means of Scanning Electron Microscope (SEM) and porosimetry measurements. Finally the characterization of the pores configuration and the permeability results could be correlated.

The infiltration behavior was observed to depend strongly on the basicity of the slag. In the case of a low basicity, the reaction of the matrix with the corrosive species is accompanied by the penetration of the molten slag into the refractory castable, filling and clogging the porosity. The corroded microstructure exhibited consequently a decreased permeability, which could be established accurately thanks to permeability measurements performed in viscous conditions.

O82) KINETICS OF CORROSION OF HIGH ALUMINA REFRACTORIES BY MOLTEN OXIDES WITH TIME-RESOLVED HIGH-TEMPERATURE X-RAY DIFFRACTION

De Bilbao, E.(1); Dombrowski, M.(1); Pillière, H.(2); Poirier, J.(1);
(1): CEMHTI - Univ. Orléans, Orléans, France (2): ThermoFisher Scientific, Artenay, France

This original work aimed at quantifying the time-dependent indirect corrosion of high alumina refractories by Al2O3-CaO-SiO2 secondary steelmaking slag. The main objectives were:

i) To determine corrosion kinetics based on time-resolved X-ray diffraction at high temperature combined with Rietveld quantification;
ii) To propose a reaction model based dissolution/precipitation/diffusion mechanism for numerical simulation.

The tests were performed at temperature ranging from 1500 °C up to 1650 °C. Two different tests were performed: Ex situ experiments to obtain long time treatment (up to 24 hours) and in situ experiments to analyse the phase changes in the early first moments (less than 5 minutes).

The ex situ corrosion tests associated with quenching method, XRD and high temperature XRD were performed in order to determine the Al2O3/CA6/CA2/CA contents vs time.

The in situ experiments at high temperature were the most innovative part of this work. The tests were performed on a diffractometer equipped with a dedicated furnace allowing for very fast heating. Alumina powder was mixed with crushed slag and put on the especially designed heating strip. The mixture alumina/slag was heated up to 1600 °C in less than 5 minutes to prevent solid/solid reaction before the slag melts. A full 2θ pattern was recorded every 5 s by means of a Curved Position Sensitive detector (CPS120). Rietveld refinement was carried out and crystallised phases were quantified. The liquid phase content was evaluated from stoichiometric balance. In addition, Scanning Electron Microscopy (SEM) was performed to analyse the microstructure of the corroded grains.

This original approach allowed for quantifying the time-dependent indirect dissolution of the alumina grains while mono-mineral calcium aluminates precipitated as well known in literature. The results show that the corrosion process is very fast and that it involves two mechanisms: i) the solid-state diffusion of calcium cations through the successive aluminate layers observed with SEM analyses; ii) the dissolution of the outer layer at the interface with slag providing slag exists. Due to silica adding, the molten slag viscosity changed and the formation rate of aluminates layers slowed down. As a result the thicknesses of the layers change according to amount of slag. Finally, numerical simulations were carried out taking into account the both mechanism and showed relative good agreements with experimental data.

O83) STUDY OF WEAR MECHANISMS OF DELTA ROOF REFRACTORIES IN EAF

Chiartano, S.(1); Prigent, P.(1); Pinard, S.(1);
(1): TRB, Decines, France

Introduction

One of the most common technologies used in steel-making industries is Electric Arc Furnace (EAF). The EAF consists of a refractory-lined vessel, covered with a roof. The centre of the roof is called the delta and made of refractory product. Since more than 20 years, TRB is designing and producing deltas for EAF. The delta is composed of a refractory precast shape.
The wear mechanisms of delta roofs are not well known. This is one of the most affected parts of the EAF as it is subject to all kind of stresses, e.g. thermal, chemical and mechanical. The delta bottom surface is exposed to temperature by radiation and slag splashes. It is also exposed to corrosive action of slag and metal oxides. Since the design is also complicated because of the openings of the electrodes, water cooling arrangement etc. it is subjected to considerable mechanical stresses and thermal shocks causing spalling.

**Material and methods**

In order to contribute to a better knowledge of the processes of degradation, temperature measurements of a delta roof were performed on several campaigns. Measurements were made in different heights and positions using thermocouples. A data logger was used to record temperatures.

Temperature observed during one campaign isn’t very high, reaching a maximum of 700°C at 130 mm of the working lining. Knowing the thermal conductivity of the refractory, we expected the temperature on the hot face to be less than 1150°C. This result was confirmed by post mortem analysis of refractory on the hot face: mineralogical phases observed after the campaign were formed between 1000°C and 1100°C.

Secondly, numerical simulation using finite element analysis helped us to understand the thermomechanical behaviour of the delta in operation. The results point out some specific location where we found stress concentration due to the cooling system or other process factor.

**Results and conclusions**

Thus, the instrumentation of delta roof allowed a better correlation between degradations and the process in service conditions.

On the other hand, temperature measurement and numerical simulation allow the development of new solution better armed to withstand against the stress level present in EAF roof.
A constant focus on the technical applications and in particular on the economic saving potentials in several industries results in numerous flexible, efficient and reliable innovations in the development of refractory concretes. As a result the share of monolithic products of the world wide refractory market increases year by year. Cement-containing refractory concretes are considered to be standard in many industries and applications, although a major drawback of these materials is their long and complex curing and drying phase. The heat-up of such linings may cause higher energy costs and longer downtimes of the furnace. Thus, in linings designed with shaped and monolithic refractories the typical cement bonded products limit the efficiency of the refractory commissioning procedure. At present the development of preferentially two different no cement castable concepts, namely cement-free refractory concretes which are installed simply with water or with a highly reactive liquid binder, represents a significant technical advance. This paper presents a comparison of cement containing refractory concretes, where the novel no cement concepts embody an optimized microstructure. In this context the easy and simple applying, a faster drying and heating with a reduced risk of explosion damage, a shorter time for re-commissioning, veneering aspects as well as a stress-reduced performance and improved high temperature properties of these cement-free refractory concretes are accentuated. A constant focus on these multifaceted and closely interconnected demands has resulted in new refractory concrete concepts, which allows simple handling with safe installation and high performance in highly stressed plant areas of different industries in the foreground.

Due to the in situ spinel and calcium hexaluminate formation, alumina-magnesia cement-bonded castables present excellent properties such as slag and thermal shock resistance. However, the expansion derived from in situ reactions is a key issue for keeping the integrity of castables. Normally, mineralizing compounds were used to control the overall expansion as well as the phase and microstructure evolution of castables. In this work, the influence of BaTiO3 addition on the expansion of alumina-magnesia cement-bonded castables was investigated by combining of the effects of BaO and TiO2. The phase composition and microstructure of castables with BaTiO3 addition after calcining at 1150-1450 ºC were characterized by X-ray diffraction and scanning
electron microscope. By comparison with the reference, lower expansion and higher strength for castables with addition of 1wt% BaTiO3 calcined at 1450 ºC were achieved. The results show that element Ba and Ti played a role in enhancing the bonding and increasing the expansion respectively.

**O86) EFFECT OF GRAIN SIZE DISTRIBUTION ON THE ABRASION RESISTANCE OF LOW CEMENT CASTABLES.**

Kannabiran, S.(1); Zhang, M.(1);  
(1): HÖGANÅS BJUF AB, BJUV, SWEDEN

Abrasion resistance is a key concern for castables used in various applications in cement and boilers, where the temperatures vary between 800-1100°C. The current study is evaluating the effect of grain size distribution on the abrasion resistance of low cement castables commonly used in such applications that fails due to lack of abrasion resistance. Experiments have been conducted both at room and high temperatures to simulate the conditions existing in reality. Studies have revealed the fact that the varying grain size distribution has a strong influence on the abrasion resistance of castables while keeping the other variables such as chemistry, cement content etc., at the same level.

**O87) A NOVEL FREE CEMENT BONDING CONCEPT FOR ADVANCED REFRACTORY CASTABLES**

Meunier, P.(1); Soudier, J.(1); Techer, R.(1);  
(1): CALDERYS, Saint Quentin Fallavier, France

Over the last decades, with an accelerating trend over the past years, intensive research has been carried out, aiming at developing alternative bonding systems to Calcium Aluminate Cements (CAC) for refractory castables, respectively aiming at buffering CAC inherent drawbacks. Even if used successfully and widely as primary bonding constituent for refractory castables, CAC intrinsic chemistry and hydration mechanism result in limitations when combination of ultra-tailored properties such as high refractoriness, robust and conditions independent placement behaviour, long workability followed by rapid development of high green strength level and safe drying are needed for refractory castables. Academics, raw materials suppliers and refractory makers have thus designed alternative bonds, mainly based on Sol-Gel concepts or on hydrated gels formation such as Magnesia-Silica or Alumina-Magnesia hydrated gels. On a parallel way, tremendous efforts have been done for developing additives to CAC, respectively for modifying CAC, in order to extend its range of applications. These attempts permit to solve some of the upper listed drawbacks efficiently, but barely permit to achieve combinations of all targeted ultra-tailored properties at the same time. Based on that statement, a novel bonding system has been developed for permitting such a simultaneous combination of properties in refractory castables. Unlike nanostructured and geopolymer bonded materials, this new generation of castables, once mixed with water, develops a clear set leading to a microstructure mimicking zeolites microstructures. After a brief recall of key properties of zeolites structure, the present paper focusses on the effect of this novel
free bonding system on rheological properties, setting and green strength development kinetic, mechanical properties, and refactororiness of vibratable alumina castables compared to state of the art bonding systems. According to the results, the prepared formulations yield outstanding placement properties and show high refactororiness resulting in higher maximum service temperature of the monolithic lining and its load bearing ability on job site.

**O88) EFFECT OF PARTICLE SIZE OF CALCIUM ALUMINATE CEMENTS ON STRENGTH OF CASTABLES AT 110°C AND 800°C**

Zhang, Y.(1); Tian, X.(1); Ding, D.(1); Chen, L.(1); Ye, G.(1);
(1): Zhengzhou University, Zhengzhou, China

The particle size of calcium aluminate cements (CAC) has a close relationship with the morphology and distribution of hydration products. In this work, two types of cements with and without grinding were used and the influence of particle size distribution of CAC on strength of castables was investigated. Matrixes containing different particle size distribution of CAC have been analysed by XRD and SEM to investigate the relationship between morphology and distribution of hydration products and strength of castables at 110°C and 800°C.

**O89) INFLUENCE OF SiC CONTENT ON MICROSTRUCTURES AND PROPERTIES OF LIGHTWEIGHT CORUNDUM-SPINEL CASTABLES**

Yan, W.(1); Ma, S.(1); Lin, X.(1); Wu, G.(1); Chen, Z.(1); Li, N.(1);
(1): Wuhan University of Science and Technology, Wuhan, China

Corundum-spinel castables have been widely used as working lining in ladle due to their excellent properties and easy installation. With increased demand for saving high-quality resources and energy, more attention has been devoted to the researches on the lightweight refractories for working linings of industrial furnaces. In order to fabricate the lightweight corundum-spinel castables, the bulk density of dense aggregate must be decreased. The decreasing bulk density of aggregate may affect the strengths and slag resistance of castables, which determines whether the lightweight castables could be used as working lining of ladle or not.

In the early work, the porous corundum-spinel ceramics have been prepared through an in-situ decomposition pore-forming technique, which is an excellent lightweight aggregate for fabricating lightweight refractories. In order to improve the slag resistance of lightweight corundum-spinel castables, additives are needed to adjust the microstructure and composition of the matrix. SiC has lower wettability by molten slag, and can increase the SiO2 content of the penetrated slag after reaction with slag to increase the viscosity of slag, and thus inhibits the penetration of the slag. But until now, when the porous corundum-spinel ceramics are used as aggregates to prepare lightweight corundum-spinel castables, the effect of the SiC content on the slag resistance still has not been understood. This will be addressed in the present work.
O90) EFFICIENT HOT METAL DESULPHURIZATION LADLE

Viertauer, A.(1); Trummer, B.(1); Dott, K.(2); Spiess, B.(1); Hackl, G.(3); Skala, K.(4); Pellegrino, M.(4);  
(1): RHI-AG, Vienna, Austria (2): RHI-AG, Muehlheim-Kaerlich, Germany (3): RHI-AG, Leoben, Austria (4): RHI-AG, Munster, USA

Short Abstract:

The paper gives an overview about refractories for a highly efficient hot metal ladle. Based on economic aspects for the lining concept, low thermal conductivity and advanced purging during deslagging are the key issues in this paper. The sulfur rich contaminated slag has to be removed thoroughly. The amount of the remaining slag and iron losses should be as low as possible. The optimal location of the plugs was determined with CFD-analysis and is presented in the paper too. Finally some safety issues are rounding up the topic.

O91) NEW ANTI-OXIDATION TECHNOLOGY FOR TROUGH AND RUNNERS CASTABLES: A SUCCESSFUL SOLUTION AT ARCELOR MITTAL TUBARÃO BLAST-FURNACE NO.02

Sako, E.(1); Alves, W.(1); Rangel, B.(1); Januario, N.(1); Rodrigues, F.(1); Galesi, D.(1); Fujiwara, H.(2); Komatsu, T.(2); Tasaki, H.(2); Costa, C.(3);  
(1): Saint-Gobain, Vinhedo, Brazil (2): Nippon Crucible Co., Toyota, Japan (3): Arcelor Mittal Tubarao, Serra, Brazil

One of the main difficulties in the operation of trough and runners at Arcelor Mittal Tubarão (AMT) Blast-furnace no.02, which is limited by two tap holes, is the reduced amount of time available for repair procedures. The consequence is that the castable installation in main troughs must often be performed during hot conditions. The most critical issue which must be addressed is that the installed castable could easily detach from the base material during the early stage of operation. This could result in exposing the previously oxidized base material to molten iron and corrosive slag attack. When events like this happen, emergency repairs must be executed, resulting in increased refractory unit consumption and an unplanned shutdown of unit operation. Highly oxidation resistant materials were demanded in order to avoid a decline in the efficiency of the furnace operation and increase refractory unit consumption. This would achieve a reliable campaign without any risks, and also reduce the number of hours spent in trough repairs. Considering these targets, Nippon Crucible Co. and Saint-Gobain HPR Brazil have developed a high-performance Al2O3-SiC-C composition based on an entirely novel anti-oxidation technology. Oxidizing reactions could be attenuated by using a special deflocculant in combination with carbon black addition. As a result, the water required for castable installation was significantly reduced in addition to reducing its open porosity values. The new material was tested on one of the main troughs at AMT BF no.02, resulting in a 50% improvement of campaign life in terms of passing pig
iron when compared with the regular castable. An analysis of this life improvement showed successful results for the material after 250 days of campaign. We determined that the main reason for such successful results was that the deterioration caused by the oxidation was significantly less and that this change made on the high cohesive structure of the base material was maintained for a long time. The attained results allowed Arcelor Mittal Tubarão to achieve longer trough campaigns, and avoid any unplanned stoppages with zero breakdown risks.

O92) MICROSTRUCTURAL AND THERMAL PROPERTY CHANGES OF CASTABLES AFTER CORROSION WITH BLAST FURNACE SLAG AT DIFFERENT CONDITIONS

Tonnesen, T.(1); Loison, L.(1); Telle, R.(1); Baas, F.(2); Firsbach, F.(2); Senk, D.(2);
(1): RWTH Aachen University, Institute of Mineral Engineering, Aachen, Germany (2): RWTH Aachen University, Institute of Ferrous Metallurgy, Aachen, Germany

Slags from iron and steel production are important byproduct, which can be processed to be used for instance in road construction or as fertilizer in agriculture. For application in the production of cement, amorphous solidified blast furnace slag is used, also referred to as slag sand. The blast furnace slag exhibits a tapping temperature up to 1700°C, however this stored thermal energy cannot be retrieved yet. In order to develop industrial facility for the heat recovery, the selection of corrosion resistant refractory materials is crucial.

Different refractory castable materials were tested in contact of molten blast furnace slag in order to describe the mechanisms of corrosion and their suitability for the application process. Materials based on alumina as well as SiC based castables have been examined. A thermodynamic model, by using the software package FactSage, was worked out and applied on the different refractory and slag compositions to predict phase formation and corrosion. The microstructural properties of the monolithic samples were characterized after firing by means of porosimetry and permeability measurements and Scanning Electron Microscopy (SEM) examinations. Static as well as dynamic corrosion test have been performed on the refractory materials, in particular finger test methodology as described in the European standard (DIN 15418). Time and temperature coordinates have been changed as well as the rotation speed to examine kinetic data and dissolution and erosion behavior. The corrosion experiments were applied on the matrix materials (cements, calcium aluminates, SiC fines) as well as on grog aggegates and full castable mixes. Subsequent to the macroscopic evaluation performed on the infiltrated samples, microscopic characterization and structural changes of the corroded microstructure have been carried out with SEM/EDS and XRD.

The SiC based refractory product was strongly infiltrated, while the high alumina specimen exhibited a high resistance against the molten slag. The microstructural analyse of the high alumina sample revealed the dissolution of the matrix and precipitation of new phases in the blast furnace slag, however with slower kinetics than the SiC based sample. For SiC and other carbon constituents the oxidation behaviour was of importance. Finally the impregnation and the microstructural change are
discussed in regard of changing thermal properties such as expansion, permeability and strength.

**O93) STUDY OF THERMAL, THERMO-MECHANICAL AND MINERALOGICAL CHANGES OF USED SILICA BRICKS AFTER MORE THAN 40 YEARS OF LIFE IN COKE OVEN BATTERY-3 OF TATA STEEL**

Sarkar, A.(1); Mukherjee, A.(1); Mishra, P.(1); Panda, B.(2); Swain, S.(2); Prasad, B.(2);
(1): TATA STEEL, JAMSHEDPUR, JHARKHAND, JAMSHEDPUR, INDIA (2): OCL, RAJGANGPUR, ORISSA, ORISSA, INDIA

After completion of campaign life more than 40 years, the coke oven battery no-3 of Tata Steel was dismantled and silica bricks were collected for full investigation. It has been found that, though the outer appearance remain same as it was before use, there is a substantial change inside the brick making it denser especially in the area exposed to flue side. These bricks were tested for chemical, physical (AP, BD, TSG), thermal (RTE), thermo-mechanical (Creep-in-compression, RUL) and mineralogical (XRD, Microscopy) studies. It has been found that these used bricks have low amount of cristoballite phase and more amount of tridymite and glassy phase. These changes are found more predominant in the area which are towards flue gas side.

The present paper not only deals with the study on the mineralogical changes that happened in these bricks after use for 40 years but also tries to establish a correlation between its laboratory test results after use with the original brick composition.

**O94) MICROSTRUCTURAL AND THERMO MECHANICAL BEHAVIOUR OF SiC REFRACTORIES IN BLAST FURNACE APPLICATION**

Ravikumar, N.(1); Dey, R.(1); Paul, S.(1); N, T.(1); R, R.(1);
(1): Carborundum Universal Limited, Chennai, INDIA

Silicon Carbide based Refractory materials are commonly used in Blast Furnace of iron making application. They compose part of Lower Stack, lower and upper bosh regions in Blast Furnace. Refractories are subjected to severe thermal gradients, Alkali attack, high oxidation atmospheres, high abrasion and Carbon monoxide attack. These refractories also play important role in converting thermal energy to generate electrical energy as by product as well in formation of protecting layer due to high thermal conductivity.

SiAlON bonded SiC materials are advanced over Nitride bonded SiC (NBSiC). In this paper, advantages of SiAlON bonded SiC over NBSiC are discussed. Microstructures and thermo mechanical properties of NBSiC and SiAlON bonded are investigated in order to understand their behaviour in Blast Furnace application. The resulting microstructure deals with SiC grains bounded with Silicon Nitride and SiAlON phases with a high degree of complexity. Microstructural properties of NBSiC and SiAlON bonded SiC refractory are studied by X-ray diffraction for phase identification and by Scanning Electron Microscope for phase morphology. As these material are used in severe atmospheres of
carbon monoxide and alkali, effect of CO-Disintegration and Alkali attack resistance properties also investigated along with long term oxidation.

Overall comparison of microstructural and thermo mechanical properties of NBSiC and SiAlON bonded SiC are studied with illustrations of uses in blast furnace application.

**O95) UNIQUE & INNOVATIVE METHOD FOR HOT OVEN REPAIR IN NON-RECOVERY COKE OVEN**

Mathai, R.(1); Theepan, T.(2); Sairama Krishna, N.(2); Kumar, S.(2);
(1): JSW Steel ltd., Salem, India (2): JSW Steel Ltd, Salem, India

**ABSTRACT**

JSW Steel Limited (JSWSL), Salem Works, is an integrated steel plant, which operates a Coke oven plant, produces 0.5 million tons per annum of metallurgical coke to cater two mini blast furnaces with a combined production capacity of 1.0 million tons per annum of hot metal.

This technical paper describes brief about implementation and benefits of the innovative and Unique method of online hot refractory repair in JSW Salem non recovery coke oven.

The healthiness of ovens depends on the proper maintenance of oven inside temperature and intact refractory works. It was observed that some silica bricks of oven no: 85 has disoriented in the flue gas intake holes. The effect was studied and prominently visualized in recent years and condition assessment comparison reports indicated possibility of further deterioration and complete chocking of flue path resulting to a dead oven. The challenge was to repair the oven intake hole from inside the oven in hot condition without losing production.

The aim was to do online hot repair of the collapsed silica with the help of in-house insulated cage (7Mx3.5Mx1.5M) made of Ceramic blankets, which inserted into the oven. The damaged silica bricks replaced by high alumina bricks The activities carried out within the stipulated time period and maintained 650°C wall temperature.

**CONCLUSION**

A new window is opened towards in-house restoration of problematic oven and delayed further deteriorating process, enhanced oven life. Significant cost saving by eliminating external agency repair cost and avoided production loss through blanking method of the oven.
ESIN 2) ENERGY SAVING AND INSULATION 2

O96) LIGHTWEIGHT ALUMINOSILICATE AGGREGATE FOR HIGHER TEMPERATURE REFRACTORY APPLICATIONS

Graddick, S.(1); Beiter, C.(1); Frulli, D.(2);

For years, refractory producers have struggled to find an insulative/lightweight (LW) aggregate to use in bricks and monolithics for applications above 2500F (1370°C): petrochemical, power, cement dry calciners, steel ladle covers, preheaters, etc. Imerys is developing a range lightweight aluminosilicate calcines (the initial product is called Mulcoa 43LW), that can be used in light weight formulations capable of reaching 2800F (1540°C) and beyond. Obviously, the main feature of these products is the exceptional refactororiness, associated with a density significantly lower than regular aluminosilicates. But, these materials are also quite interesting in that their open porosity is generally quite low, allowing for casting/gunning/pumping at lower than normal water content than for products based on most other insulative materials. In comparison, this positively affects the dry-out and re-heat shrinkage characteristics, at elevated T, of formulations based on Mulcoa M43LW.

These new LW aggregates allow for the development of a range of finished products: Reduced Cement Insulating Castables, Traditional Insulating Castables and Gunning Castables where, in practice, Mulcoa 43LW acts very similar to normal Mulcoa aggregates.

This study examines the properties of conventional and low cement castable formulations based on Mulcoa M43LW.

O97) STEEL LADLE ENERGY SAVINGS BY REFRACTORY LINING DESIGN

Santos, M.(1); Moreira, M.(1); Campos, M.(1); Pelissari, P.(1); Angelico, R.(2); Sako, E.(3); Pandolfelli, V.(1);
(1): Federal University of Sao Carlos, Sao Carlos, Brazil (2): University of Sao Paulo, Sao Carlos, Brazil (3): Saint-Gobain Ceramics, Vinhedo, Brazil

The secondary metallurgy is a high energy-intensive step in steelmaking process as it requires an accurate adjustment of the composition and temperature of the molten metal during the ladle refining. In this context, the steel ladle lining plays an important role on the process energy consumption, as the refractory thermal properties are strictly related to the ladle ability to keep the molten metal temperature constant. Aiming to improve the process energy efficiency, reducing both the costs and the environmental effects, many studies have been recently carried out, using numerical simulation tools, analytical models and experimental data, to predict the heat transfer mechanisms in the ladle operational cycle. Nevertheless, few of them highlight the refractory role on those mechanisms. Based on a transient numerical analysis using temperature dependent
refractory properties, the present work proposes a holistic process view in order to help the refractory design of steel ladles, according to their saving energy capability. The numerical model was developed using a commercial software (Abaqus) to simulate one ladle cycle (pre-heating, holding and waiting steps). Distinct working layer materials and the presence of an insulating one were considered and investigated. The temperatures of molten metal and ladle shell were compared to evaluate the energy efficiency of the different lining configurations. The numerical simulation results indicated that the configurations containing an insulating layer significantly reduced the energy needed for reheating the molten bath. The distinct refractory working layer materials also had a great impact in the process energy consumption due to their different thermal conductivity and heat capacity. In summary, saving energy in steelmaking is a key factor to improve the process efficiency and, when supported by a thermal and energy balance tool, new materials and optimized lining configurations could be explored, leading to a higher performance of the steel plants.

**O99) FABRICATION AND PROPERTIES OF SI3N4 FIBER MATERIAL IN A NOVEL METHOD**

Gang, W.(1); Jianshen, H.(1); Bo, Y.(1); Binbin, D.(1); Kuo, C.(1); Hongxia, L.(1);
(1): Sinosteel Corporation Luoyang Institute of Refractory Research Co., Ltd., Luoyang, China

In this paper, Low-cost Si3N4 fiber material was synthesized by heating silicon porous body prepared via direct foaming method at 1400°C for 5h in a flowing N2 atmosphere. The influence of addition of foaming agent on the properties of Si3N4 fiber material was studied. The results showed that with the addition of foaming agent increased from 1 wt % to 4 wt %, the bulk density of Si3N4 fiber material reduced from 0.76 g/cm3 to 0.37 g/cm3, the compressive strength reduced from 6.1 Mpa to 1.6 Mpa and the thermal conductivity at 1000°C descended from 0.494 W·M-1·K-1 to 0.216 W·M-1·K-1. After staying in the cryolite steam at 1000°C for 50h, the properties of Si3N4 fiber material changed little. These indicate that Si3N4 fiber material has excellent thermal insulating performance and erosion resistance.
EVALUATION OF THE DEGRADATION OF LF SLAG AND ITS IMPACT ON THE DECARBURIZATION OF THE LADLE REFRACTORY LINING

Moliné, M.(1); Galliano, P.(2); Tomba, A.(1); (1): División Cerámicos, INTEMA - CONICET, Mar del Plata, Argentina (2): Departamento de Tecnología de Refractarios, Tenaris REDE AR (CINI), Campana, Argentina

MgO-C and Al2O3-MgO-C bricks are widely used as working lining in the steelmaking ladles. Due to their carbon content they are particularly susceptible to high temperature oxidation in contact with ambient oxygen. These refractories are exposed to such conditions after casting end and during its pre-heating previous to the next heat.

At the end of each heat, LF slag remains partly adhered to ladle walls, generating a coating that exerts a barrier effect, protecting the refractory to subsequent decarburization. This slag suffers different transformations according to environmental thermal conditions, including degradation processes caused by hydration and/or spalling, which can affect its protective capacity to the refractory bricks.

For this reason, physico-chemical characterization of a steelmaking ladle slag and the evolution of its integrity over time under different conditions are carried out in this work. The degradation of the slag by weathering is evaluated through its granulometric evolution at different times for several months. In each case, samples were also characterized by different techniques: X-ray fluorescence (XRF), X-ray diffraction (XRD), differential thermal (DTA) and thermogravimetric analyses (TGA).

The obtained results show the hydration of different phases present in the slag. At short time, degradative processes of CaO are observed, and in lesser degree, the degradation of MgO. At longer time, changes in the calcium aluminate present in the system are also detected. These transformations involve volumetric expansions and then, the slag disintegration. This strongly affects the characteristics of the slag protective capacity to prevent decarburation of ladle working lining refractories in empty ladle conditions during its campaign.

DEVELOPMENT OF MORE EFFICIENT STRUCTURES FOR LADLE AND TUNDISHES MONOLITHIC COVERS

Gonzalez Bernaldo De Quiros, J.(1); (1): CUARIBAR SA, Tortuguitas, Argentina

After years of working and researching at the steel industry, we had found some weaknesses in designs and structures of monolithic covers for melt steel containing vessels. We have developed and successfully tested a low cost design for steel ladle covers and we are expanding this technology not only to steel industry but to other
industries too. For this design we use alumina silica castables with a steel structure and stainless steel anchors.

Our design consists of light and ventilate structures that allow the user to work on a lower temperature on the metallic structure preserving the refractory and achieving a prolonged performance that the designs that have been used for more than 40 years.

Since the first test this product have reached more than two times the life cycles of the traditional alternative. For this reason and because of the low cost we are expanding this development to other applications expecting better results on each area.

O102) INTERACTION BETWEEN MOLTEN METAL AND MGO-C REFRACTORY DURING THE RH DEGASSING PROCESS IN STEELMAKING

Ji, H.(1); Hong, Y.(1); Ahn, J.(1); Chung, Y.(2);
(1): Hyundai Steel Company, Dangjin, Republic of Korea (2): Korea Polytechnic University, siheung, Republic of Korea

Magnesia–carbon brick was applied to improve the lifetime of refractory for lower vessel and snorkels in RH degassing process. The reaction between molten steel and MgO-C refractory was evaluated and compared with conventional MgO-Cr2O3 refractory for RH process. In this paper, cup tests were performed at 1600 °C during 3 hours in air and vacuum conditions. In order to analyze corrosion reaction, microstructure was analyzed by SEM. Nondestructive inspection (NDI) was carried out to observe interface between molten steel and refractory by X-Ray CT. By this experiment, reaction area and inner part of the sample were examined closely without damage of sample. In this Lab test, a dense MgO-layer was observed at an interface between molten steel and refractory. And it shows that this layer is very effective to protect additional oxidation. Based on this observation, MgO-C refractory will be tested in RH lower vessel and snorkels soon.

O103) CHARACTERISTICS OF CASTABLE REFRACTORIES FOR STEEL LADLE HEATED UNDER RESTRAINT

Nakabo, K.(1); Nishida, S.(1); Kitamura, M.(1);
(1): Shinagawa Refractories co., ltd., Bizen, Okayama, Japan

Alumina-magnesia castable refractories, which mainly used for the steel ladle, show large permanent linear change in high temperature accompanied by the spinel formation reaction. This reaction makes the material porous, when heated without restraining, however the materials in actual use is restrained two dimensionally by the surrounding structure, which should cause different structure and characteristics of the material comparing to the laboratory evaluations. In this study, the authors investigated the influence of two-dimensional restraint on structural, physical and chemical characteristics of alumina-magnesia castable using the specimens heated under restraint for correct understanding of the properties in actual use. The authors also made investigations into the influence of the magnesia content on the characteristics of
alumina-magnesia castable heated under restraint condition. To prepare two-dimensional restrained specimens, alumina-magnesia castable refractories were surrounded by other high strength castable and heated at 1000°C, 1300°C and 1500°C. Then various characteristic evaluations and the microstructure observations were carried out. The permanent expansions of restrained specimens were drastically suppressed to approximately zero, which can be used as evidence that the restraint during heating was satisfactorily carried out. The restraint during heating affected the material strength. The strength rose greatly especially after high temperature heating. The apparent porosity was decreased and the pore size became smaller. It is suggested that the increase of strength is caused by densified structure. Under unrestrained condition, the expansion after heating enlarged as the magnesia content increase. On the other hand, under restraint condition, any specimens did not substantially expand. Nevertheless, the apparent porosity of restrained specimens also rose by heating; this may indicate that the specimens expanded in the unrestrained axis direction.
MO 6) MONOLITHICS FOR VARIOUS APPLICATIONS 6

O104) MONOLITHIC REFRACTORIES DESIGN WITH IMPROVED STRENGTH DUE TO SMART PARTICLE DISTRIBUTION IN SIZE AND SHAPE

Erbar, L.(1); Krause, O.(1); Holley, F.(1); Dahlem, E.(2); Dannert, C.(2);
(1): Hochschule Koblenz, Hoehr-Grenzhausen, Germany (2): Forschungsgemeinschaft Feuerfest e.V., Hoehr-Grenzhausen, Germany

Particle interlocking plays the most important role in the formation of physical and mechanical properties and is dependent on optimized particle distribution in size and shape composing in the refractory monolithic formulation. The aim of the project is to define a procedure that allows individual adjustments for the grain size distribution with special consideration to the aspect ratio of the grain size, that are analysed with computerized particle analysis (CPA). In this early project stage, sinter and fused corundum and sintered and fused mullite were adjusted to the best possible packing and interlocking of particles. The optimization process was investigated by means of working properties e.g. mixing properties by measuring the energy input, water demand, rheology, densification, drying shrinkage and green strength. The detailed and quantified results of this optimization process provided a much deeper understanding of how the particle size, shape and surface roughness influence the working properties of refractory monolithics and therefore provide comprehensive information about improved particle size distribution. The systematically correlation of the particles’ nature with the optimized grain size distributions result in optimized workability to obtain refractory monolithics with the best possible physical and mechanical properties. Furthermore, the results of this project will enable flexible reaction of refractory producers to changes in particle shape of raw materials, which already ran through a process (recyclate).

O105) PRE-SHAPED REFRACTORY CASTABLE FOR REHEATING FURNACE BURNER BLOCKS

Domiciano, V.(1); Inocêncio, E.(1);
(1): Magnesita Refractories, Contagem-MG, Brazil

Reheating furnace is the equipment that mostly dictates the speed of production of a melt shop, since a furnace that frequently stops for maintenance forces an interruption of the plant production and, in the case of an integrated mill, can also entail an output reduction in the blast furnace. Within this important equipment on the steel production flow, the burner blocks play a crucial role in the furnace operation since they are responsible for heating the billets/plates so that they reach the temperature required for lamination. Besides compromising the reheating furnace operational safety, worn or damaged burner blocks can cause uneven heating of the steel products, consequently requiring longer residence time causing the loss of productivity and possibly the overheating of some billets/plates that can lead them to melt. On the other hand, poorly heated billets/plates can breakdown during lamination process, causing an emergency stop and the loss of production in addition to materials losses, labor waste and lost
profits until the operation is resumed. The performance of Magnesita’s reheating furnace burner blocks used to last for a year, when spalling and/or cracks were observed in the pre-shaped refractory castable blocks which necessarily require a furnace stoppage for their replacement. This paper presents the main characteristics and properties of a new refractory castable developed for pre-shaped burner blocks, including raw materials and grain size distribution adjusts, physico-chemical properties and thermo-mechanical behavior, which allowed to significantly improve the burner blocks performance. Tests carried out in 3 different melt shops have shown that the new refractory castable was able to endure severe and unstable reheating furnace operating conditions extending the service life of the refractory burner blocks from 1 year to more than 3 years showing perfect conditions to continue operating for a longer period.

**O106) THE INFLUENCE OF MICRO SILICA ON THE HYDRATION OF CALCIUM ALUMINATE CEMENT**

Liu, Y.(1); Fu, X.(1); Tian, X.(1); Zhang, Y.(1); Chen, L.(1); Ye, G.(1);
(1): Henan Key Laboratory of High Temperature Functional Ceramics, Zhengzhou University, Zhengzhou, China

Many different sources of microsilica with varied compositions and properties are used in calcium aluminate cements (CAC)-containing castables in China and can have different effect on the hydration behavior of calcium aluminate cements (CAC). The electrical conductivity, PH value and impurity content of microsilica from four different sources were tested in this work. Then the influence of microsilica from the four sources on the hydration of CAC was investigated. The exothermic temperature development of cement pastes at various curing temperatures was monitored by semi-conductive measurement. The hydration process of cement pastes was halted by a freeze vacuum drying method to examine the evolution of phase composition and microstructure of hydrates with XRD and SEM, respectively. The setting time and demoulding strength of mortars were also tested at 20 °C.

**O107) INFLUENCE OF REACTIVE MICRO ALUMINA CONTENTS ON THE MICROSTRUCTURES AND MECHANICAL PROPERTIES OF GEL BONDED CORUNDUM-SPINEL REFRACTORY CASTABLES**

Nana, X.(1); Yuanbing, L.(1); Qingheng, W.(1); Hao, W.(2); Shujing, L.(1); Ruofei, X.(1);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China (2): Alteo Shanghai Co., Ltd, Shanghai, China

Corundum-spinel refractory castables were prepared by using tabular alumina aggregates, fused magnesia, reactive micro alumina, calcined micro alumina and gel powder as starting raw materials. While the different contents of calcined micro alumina were instead of reactive micro alumina, effects of the reactive micro alumina content on the microstructures and mechanical properties properties of the castables were investigated by means of X-ray diffractometer (XRD), scanning electron microscopy (SEM) and elastic modulus tester, etc. The slag resistance was tested by means of crucible test, and the results indicated that the slag penetration resistance increases and
slag corrosion resistance decreases with increases in reactive micro alumina content. More irons of the penetrated slag can be absorbed on lattice vacancies in the in-situ spinel because of its smaller grain size and higher lattice distortion, and viscosity of the penetrated slag increase thus inhibiting further penetration.
To remove nonmetallic inclusions and ensure the requirements of high purity metal castings, ceramic filters have been used in metal casting applications such as foundries for several years. These inclusions are responsible for the strength, the elongation, the fracture toughness and the fatigue performance of the metal components. During loading, stress concentrations are generated in the proximity of inclusions. In order to meet the increasing demands for high purity metals such as high security steels, ceramic foam filters (CFF), especially those based on zirconia and carbon bonded alumina, have been successfully employed for years. Zirconia filters, however, have the disadvantage of exhibiting creep, which decreases the flow rate during casting because of the changing filter geometry. In contrast, carbon bonded systems exhibit negligible creeping due to the high amount of carbon.

In terms of this contribution calcium aluminate composition coatings containing carbon will be explored. Such kind of functional coatings on a carbon bonded filter substrate provide a number of advantages for capturing fine alumina and calcium aluminate inclusions. If calcium aluminate compositions containing carbon come in contact with steel melt following mechanisms are activated:

I) The calcium aluminates react with the carbon, form calcium aluminate suboxides or also calcium and aluminum which are deposited on a calcium aluminate decarburized or partially decarburized zone in contact with the metal melt and generate a thin very active calcium aluminate layer due to the reaction of these suboxides with the oxygen of the steel melt. This thin very active layer between the decarburized zone and the steel melt is contributing as an active collector for endogenous inclusions.

II) In addition the high vapor pressure of calcium with an associated intense bath stirring promotes collision and coalescence of the alumina fine inclusions in the melt. With the aid of calcium vapor and the resulting coalescence of the alumina inclusions through collision, their removal from the steel is enhanced compared to the small non-buoyant alumina inclusions which must first cluster on their own before they are able to be separated by the liquid steel.

III) Depending on the applied composition of calcium aluminates the softening point and or the melting point of the mixture can be adjusted in order to promote an additional capturing by increasing the roughness of the thin active layer which copies the surface of the carbon free calcium aluminate layer below. A higher roughness leads to higher wetting angle against the iron melt which promotes a higher agglomeration via collision of the fine inclusions.
IV) The endogenous inclusions are trapped mechanically better during their collision on the active surface and more contacting surface is available for sintering fixing of the inclusions on the surface of the thin active layer.

O109) CONTRIBUTION OF MOLTEN METAL FILTERS WITH THERMAL AND SLIP SPRAYED ALUMINA COATINGS TO THE CLEANLINESS OF STEEL

Gehre, P.(1); Schmidt, A.(1); Dudczig, S.(1); Anezirinis, C.(1); Child, N.(2); Delaney, I.(2); Rancoule, G.(3); Debastiani, D.(4);

Ceramic filters play an essential role relating to the cleanliness of cast steel bodies; they smooth the fluid steel flow and interact with, and capture inclusions contained within the molten steel as it enters the mould. A coating on such a filter is able to increase their mechanical strength and enhance the mechanisms of inclusion capture. In this study, commercially available Al2O3-C filters were coated by two techniques: with an alumina slip via cold spraying, and with alumina via flame spray technology. The cold sprayed alumina coating requires an additional thermal treatment at 1400 °C, whereas filters with a flame spray coating can be directly used after the coating process. The microstructures of the coatings have been investigated by light microscopy, SEM, and CT and the phase composition has been analyzed by x-ray diffraction. The effect of the filters, with and without coating, on the cleanliness of steel was evaluated in a metal casting simulator by dipping and rotating the filters into molten steel (Grade 1.6587) at 1580 °C for 20 seconds. The levels of inclusions contained in the steel before and after filter interaction have been counted, and the chemistry and size identified with PSEM. In addition, the surface of the filters has been analyzed in order to identify the amount and type of trapped inclusions.

After the additional thermal treatment, the cold spayed coating is composed of homogenous corundum (α-Al2O3) particles and exhibits a porosity of about 35%. The alumina coating interacts with the Alumina-C filter substrate forming an in situ alumina-layer, which promotes the deposition of inclusions during casting. However, there is some interaction between the metal and the base filter structure, that can negatively impact on the casting quality. In contrast, flame spraying results in a coating composed of overlaid γ-Al2O3 droplets. The flame sprayed coating is comparatively dense with a porosity of 7%, this prevents any interaction of the filter substrate with the molten steel. It has been found that the Al2O3-C filter with cold sprayed coating has the highest inclusion filtration efficiency by trapping very small inclusions with diameter < 1 µm. Without alumina coating the Al2O3-C filter overall shows a good filtration of inclusions in range of 1 – 5 µm. A thermal spray coating is recommended for filtration of cast steel products that require a particularly high level of cleanliness.
O110) CORROSION RESISTANCE OF HIBONITE BASED LOW CEMENT CASTABLE AGAINST BIOMASS SLAG

Loison, L.(1); Tonnesen, T.(1); Telle, R.(1); To, E.(2); De Bilbao, E.(3); Poirier, J.(4);
(1): RWTH Aachen University, Aachen, Germany (2): ENSCI Limoges, Limoges, France (3): CEHMTI Université d’Orléans, Orléans, France (4): CEHMTI Université d’Orléans, Orléans, France

Refractory linings used in incinerators for energy production have to adapt to the energy transition, where fossil fuels tend to be replaced by biomass, exposing the lining to different ranges of chemical compositions. The use of alternative combustibles impacts the life expectancy of the refractory products due to corrosion reactions, whose complexity originates in the variety of the biomass sources. Andalusite, Al2O3-Cr, or SiC based refractory products have been heretofore used in incinerators, however refractory containing hibonite (CaO·6Al2O3) could be an alternative, because of its high refractoriness and high resistance against alkali attack. This work aims to describe and understand the chemical resistance brought by the presence of hexaaluminate of lime in a Low Cement Castable (LCC).

In order to outline the degradation mechanisms induced by biomass, this study focuses on the impact of wood ash and aims to understand the effect of its main oxides, namely CaO, SiO2 and K2O on the high temperature corrosion. Therefore, model slags were synthesized to isolate the influence of the different chemical species and enable the comparison with the effects observed by corrosion with the original wood slag. The reaction of hibonite with the model slags were characterized by means of in situ HT-XRD performed on the ground refractory powder mixed with the slag. Furthermore, hibonite raw materials were conserved in molten slag at high temperature in order to study the dissolution behavior through post-mortem SEM examinations performed on quenched microstructures. The crucible test was performed on a formulation of LCC designed with the hibonite raw materials, whose grain size ranges from 0-3 mm, to evaluate the resistance to reactive infiltration of a calcium hexaaluminate based refractory product.

Due to its high chemical resistance against different biomass slag compositions, the use of hibonite in the formulation of refractory castables could be a solution to prevent early breakdown of refractory lining, with high performance against the aggressive environment of biomass incinerators.

O111) INVESTIGATION ON THE INTERACTIONS BETWEEN MULLITE AND LI-ION BATTERY CATHODE MATERIALS DURING CALCINATION

Zhai, P.(1); Gu, W.(1); Li, Y.(1); Chen, L.(1); Li, S.(1); Ye, G.(1);
(1): Zhengzhou University, Zhengzhou, China

To identify the interactions between Li-ion battery cathode materials and the mullite sager matrix during the industrial calcinations, mixtures of mullite powder (0.074mm) and commercial Li-ion battery cathode materials were fired at different temperatures between 800 °C and 1100 °C. The phase development in the interactions between
mullite and Li-ion battery cathode materials during heat treatment were investigated by X-ray power diffraction (XRD). The characteristic morphologies of the formed products from interfacial reactions were obtained by scanning electron microscopy (SEM). Additionally, the eutectic temperature and mass loss during calcination process were confirmed by means of thermo gravimetric-differential thermal analysis TG-DTA. Based on these experimental results, the corrosion mechanism of mullite sager matrix by Li-ion battery cathode materials is discussed.
TOR 3) TESTING OF REFRACTORIES 3

O112) EVALUATION OF INTERACTIONS BETWEEN REFRACTORY MATERIALS AND STEEL MELT BY USING A STEEL CASTING SIMULATOR

Dudczig, S.(1); Schmidt, G.(1); Hubalková, J.(1); Aneziris, C.(1);
(1): Institute of Ceramic, Glass and Construction Materials, TU Bergakademie Freiberg, Freiberg, Germany

For investigations of interactions between different refractory materials and steel melt, a so called steel casting simulator is used. Different kinds of experimental setup can be applied to investigate the interactions between refractory components and steel melts with different various compositions. Porous filter or dense prismatic materials can be dipped and rotated in steel melt which contains a defined amount of endogenous inclusions. In case of this setup it’s possible to removed and cool down the test materials under oxygen free conditions to exclude atmospheric reactions, e.g. carbon oxidation in the case of carbon containing materials. These experiments enable the investigation of filter materials with different surface chemistry and attached non-metallic inclusions after steel melt contact. It has been shown, that carbon bonded alumina filter materials forms a secondary alumina skin-like layer which intensify the deposition of inclusions. Crucible Tests are performed under the same inert conditions with various steel melts under the aspect of long-term stability of new developed materials under reproducible conditions. The simulation of metal casting through model nozzle components allows investigating clogging phenomena simultaneously at two model samples at each trial. The recorded mass flow during the test, the solid steel before and after as well as the pre and post mortem characterisation of the model nozzles show significant influences of the surface chemistry to the clogging properties.

O113) FRACTURE PROCESS ZONE DEVELOPMENT IN A MAGNESIA AND A MAGNESIA SPINEL REFRACTORY AS OBSERVED BY DIGITAL IMAGE CORRELATION

Gruber, D.(1); Dai, Y.(2); Harmuth, H.(1);
(1): Chair of Ceramics, Montanuniversitaet Leoben, Leoben, Austria (2): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China

Introduction

Magnesia and magnesia spinel materials show a completely different fracture behaviour. For the latter one, due to pre-existing microcracks, cracks initiate easily in the magnesia spinel material, but the development of the process zone enhances the resistance to crack propagation. This is related to the considerable brittleness reduction by spinel addition.

Materials and Methods
In this research, a magnesia spinel material and a pure magnesia material are studied by digital image correlation to investigate the fracture process. A wedge splitting test was applied for both materials. During the test strains as well as the crack propagation were detected by digital image correlation. Fracture mechanical data have afterwards been determined from the load/displacement curves.

Results and Conclusions

The microcrack network already present in a virgin magnesia spinel material supports the formation of a pronounced fracture process zone. The mechanical properties measured by the wedge splitting test indicate a reduction in strength and an increase in fracture energy for the magnesia spinel material. The special microstructure characterized by pre-existing microcracks increases the strain bearing capacity, which is very important for improving the thermal shock resistance. For pure magnesia, no pronounced fracture process zone could be detected. Crack propagation in magnesia refractories commences immediately after reaching the maximum load. For magnesia spinel, the fracture process zone development starts in the pre-peak region. The fracture process of magnesia spinel is characterized by the development of the fracture process zone and the subsequent development of the macro-crack. The transition is indicated by a change of the fracture process zone dimensions. Due to the closure of the microcracks and propagation of the macro-crack, the fracture process zone width and height both decrease. The onset of the macro-crack is in the post-peak region when the load has already decreased to 66% of its maximum value. The fracture process zone of magnesia spinel contributes to the large post-peak region, stable crack propagation and high strain tolerance before failure. All of these properties are associated with lower material brittleness.

Q114) YOUNG’ S MODULUS OF ELASTICITY OF CARBON-BONDED FOAM STRUCTURES AT ELEVATED TEMPERATURES

Werner, J. (1); Aneziris, C. (1); Luchini, B. (2); Pandolfelli, V. (2);
(1): Technical University Bergakademie Freiberg, Freiberg, Germany (2): Universidade Federal de Sào Carlos, Sào Carlos, Brazil

Carbon-bonded foam structures are used for metal melt filtration, especially in the steel and iron metallurgy. A recent approach is coating the filters with so called “active” and “reactive” layers. Besides the usual mechanical filtration effect, these layers were effective to withdraw the impurity particles by surface energy effects (“active”) or due to reactions with the filter substrate, the coating and gases or alloying elements in the melt (“reactive”).

In this investigation the influence of such surface coatings on carbon-bonded foam structures were evaluated by Young’s modulus ($E$) at room and high temperatures using the impulse excitation method, where a prismatic sample is excited by a projectile, resulting in an oscillation. By this technique the resonance frequency of the material can be obtained and used to accurately determine $E$ up to 1450 °C in air and inert gas atmosphere, according to ASTM 1876.
Alumina, alumina-carbon and a carbon-nanotubes containing carbon coating, were applied on the ceramic substrate and the samples were heat treated at 1400 °C in a pet coke filled retort.

These measurements and their evaluation are key aspects to provide a better understanding of the thermo-mechanical behavior of carbon-bonded foams during metal melt filtration.

O115) TOWARDS A POTENTIAL STANDARDIZATION OF THE SPLITTING TENSILE-STRENGTH TEST FOR DENSE SHAPED REFRACTORY PRODUCTS

Erauw, J.(1); Mastroianni, I.(1); Abdelouhab, S.(1); Lardot, V.(1); Cambier, F.(1);
(1): BCRC (Belgian Ceramic Research Centre), Mons, Belgium

Reliable mechanical strength values of refractory products are relevant parameters with respect to the design of durable and safe installations and accurate tensile strength values are in this context of paramount importance. Whereas CCS method enables to correctly evaluate the compressive strength, bending strength values (i.e. MOR values) are unfortunately not sufficiently representative of the actual tensile strength of the products. Accordingly, a simple, standardized method able to reliably approach the true tensile strength of the products appears still needed.

The splitting tensile-strength test could be such a method. It consists in loading diametrally a right-circular cylinder till the fracture strength of the material is reached and the specimen splits along its vertical diameter. The splitting tensile strength is subsequently calculated from the measured maximum load sustained and the dimensions of the specimen.

The main advantages of this test stems from its ease of implementation. It allows indeed for the use of simple specimen geometry compared to what would be needed for pure tensile test, readily obtained by drilling, and compatible with other, already standardized test methods for refractory products (CCS, density/porosity). Thereupon, the stress state in the specimen during the test is well documented in the literature: the diametral loading induces a uniform tensile stress normal to the loading axis across a rather large part of the anticipated fracture plane whereas relatively high compressive stresses develop around the loading points. This method has for long been applied for the indirect determination of the tensile strength of concrete and has already been standardized in the civil engineering sector.

In the current study, the parameters susceptible to influence the test have been thoroughly screened through factorial designs of experiments and subsequent ANOVA analysis. Practically, the effects of both specimen size and testing conditions (preload level, loading rate, use of load bearing strips and characteristics thereof) have been investigated experimentally on three representative dense shaped commercial products: two high alumina grades with respectively 76 and 81 % alumina, and a magnesia-carbon bonded grade with a carbon content higher than 9 wt.%. A total of more than 250 splitting tests have been performed. By far the largest effect observed is the one
related to the use of bearing strips, the role of which consists in distributing the load applied along the length of the cylinder and preventing compressive-stress failure near the loading points.

All by all, sets of optimum conditions have been identified with regard to repeatability. These will be further evaluated with respect to reproductibility through interlaboratory round robin tests and, if proven satisfactory, drafted as potential EN standard.

O116) ADVANCED CORROSION TEST APPARATUS FOR REFRACTORY DEVELOPMENT

Chen, M.(1); Cui, Z.(2); Contreras, L.(3); Zhao, B.(1);
(1): School of Chemical Engineering, The University of Queensland, Brisbane, Australia
(2): Dongying Fangyuan Nonferrous Metals Co., Ltd, Dongying, China (3): National Copper Corporation of Chile, Santiago, Chile

Refractories are widely used in all high temperature processes and provide resistance to the thermal stress, physical wear and chemical corrosions. Development of the advanced refractory is always a great challenge to the researchers as the tests of refractories in the lab is difficult to truly reflect the operating conditions of the industrial furnaces. It is practically difficult to directly test the new materials in the furnace as the replacement of the refractories will need to stop the operation, which will cause significant productivity losses. It is necessary to develop a reliable technique to perform the corrosion test of the refractory with simulated operating conditions, which includes temperature, oxygen partial pressure, flowing melts and reaction time. An accurate simulation of the refractory corroded in the melt will provide the first hand information for the further development of refractory materials, such as the corrosion mechanism and wearing rate.

In the present study, a new dynamic corrosion test apparatus was developed to simulate the corrosions in the furnace. A vertical tube furnace is employed as well as a gas-tight chamber enclosed at the top of the furnace. The crucible holding melt sample is suspended using alumina tube with Pt wires, and located in the hot-zone of the reaction tube. The refractory sample prepared is suspended by an electric stirrer through an alumina tube, and the rotation speed of the refractory sample can be adjusted by a computer connected to the stirrer. The platforms holding the melt and refractory can move by independent motors. The atmosphere in the furnace and chamber can be controlled by inert gas or gas mixtures. After certain reaction time at a given temperature, the refractory sample can be rapidly raise to the cold end of the furnace and the crucible with melt can be directly dropped into ice water. This way the reactions between the refractory and the melt are stopped and the microstructure and compositions of the phases present are freezed. The retained microstructures and compositions of the refractory and melt can provide accurate information at high temperature. The quenched refractory sample and melt are sectioned, mounted, polished and carbon coated for electron probe X-ray microanalysis (EPMA). The depth of the penetration, phases present and their compositions can be accurately measured by EPMA.
Examples have been given to demonstrate the advantage of the present apparatus with features of accurately controlled atmosphere, temperature, reaction time, rotation speed followed by quenching both refractory and melt. The magnesia-chrome refractory and the synthetic MgO-Al₂O₃ spinel material have been tested with copper smelting slag and melted Cu₂O respectively.
**SLSM 5) STEEL LADLE AND SECONDARY METALLURGY 5**

**O117) FREE AND LOW CARBON ALUMINA-MAGNESIA BRICKS FOR STEEL LADLE METAL LINE**

Ramos, V.(1); Lima, H.(1); Galesi, D.(1); Sako, E.(1); Frasson, S.(1); Nascimento, A.(1);
(1): Saint-Gobain do Brasil Ltda, Vinhedo, Brazil

IF (interstitial free) steels are defined by the ultra-low carbon content, which ensures good ductility and plasticity, important properties for a good mechanical shaping and energy releasing during impact. Those properties are essential needs for automotive applications. Currently refractory solutions for steel ladle in Brazil are based on magnesia-carbon system, applied for slag lines, and alumina-magnesia-carbon, applied for metal lines. Both systems, which includes carbon levels generally above five percent weight, assure good performance, but are questionable considering carbon pick-up levels. Based on customer needs to produce low carbon IF steel, new families of free and low carbon alumina-magnesia bricks were developed. Wall and bottom metal line solutions were based on carbon-free alumina-magnesia system, with high corrosion resistance, high penetration resistance, adjusted in situ expansion and low thermal conductivity, which also assure no carbon pick-up into the steel. For the specific case of impact pad, a low carbon alumina-magnesia brick, with high hot mechanical strength, was developed to improve local erosion resistance and to reduce carbon pick up possibilities. Both solutions allowed the costumer the possibility to increase steel ladle life to 130 heats, safely working to avoid carbon pick-up in ultra-low carbon steel production.

**O118) DEVELOPMENT OF MGO-C REFRACTORIES DOPED WITH CARBON NANOFIBERS**

Castaño-laviana, D.(1); Campello-garcía, J.(1); Miranda-martínez, M.(1);
(1): FUNDACIÓN ITMA, Llanera, España

This work develops and characterizes a new family of magnesia-carbon refractory bricks (MgO-C) bonded with a new pitch modified by the addition of carbon nanofibers (CNFs), thus producing a MgO-C-CNФ refractory.

Steel makers and refractory suppliers rely on MgO-C bricks for some of the most aggressive industrial applications. This research, by fully characterizing a reference formulation, suggests the use of a CNF doped pitch, while maintaining its characteristics as a binder and source of carbon, increases the MgO-C resistance to oxidation and thermal shock. The conclusion is that CNF doping modifies the pitch microstructure, and hence the refractory microstructure, introducing a number of new mechanisms for thermal stress absorption.
O119) IMPROVEMENT OF LADLE REFRACTORY PERFORMANCE THROUGH OPTIMIZATION OF REFRACTORY QUALITY AND OPERATING PARAMETERS

Ghosh, G.(1); Biswas, S.(1); Panigrahi, P.(1); Singh, B.(1); Pal, A.(1);
(1): TATA STEEL, TATANAGAR, INDIA

Steel ladle life is one of the key performance indicating factors for steel plant from the operational and refractory performance point of view. Different varieties of Carbon containing refractory are used in the working lining of the steel ladle. To improve the performance of steel ladle life, refractory quality optimisation is done through in depth analysis of the refractory lined. After optimising the quality of magnesia carbon refractory different operating conditions are monitored and suitable change in the ladle design was performed.

The present paper deals with the comparative analysis of different working lining brick properties and performance used in the ladle. Chemical and physical properties are investigated of magnesia carbon bricks supplied by three different suppliers. Oxidation resistance is measured in TG DSC machine along with evolve gas analysis to understand the oxidation reaction in the bricks. Thermal expansion in inert atmosphere, high temperature creep at 1500 deg C temperature and pore size distribution are measured for comparison of the bricks. HMOR and MOE measurement conducted at 1400 degree centigrade on different quality of magnesia carbon bricks. Static slag corrosion in crucible and rotary slag corrosion test was conducted to understand the corrosion behavour of the magnesia carbon materials. Rotating finger test at 1600 degree centigrade was performed in induction melting furnace using plant slag. Detail morphology of the materials was studied by SEM with EDAX. With the continuous improvement in the steel ladle, 20% life improvement achieved in flat product and long product shop in our steel plant.

O120) EVALUATION OF THE REFRACTORIES FOR APPLICATION TO THE RH DEGASSER

Tomita, Y.(1); Tanaka, M.(1); Taira, H.(1);
(1): Krosaki Harima Corporation, Kitakyushu, Japan

Refractories used in the side wall of the RH degasser lower vessel have often been attacked by both oxides of Al and Si in the molten steel which is processed by the operation such as an oxygen blowing and a powder blowing for refining to purified high grade products. Both magnesia-chrome and magnesia-carbon refractories were investigated for application to the above mentioned lower vessel using a molten steel stirring test system. After stirring in the molten steel incorporated with both oxides, the damages of the refractories samples were observed and analyzed using the optical microscope and scanning electron microscopy (SEM) with the EPMA system. For the case of molten steel with Al oxide, although the magnesia as a component reacted with the oxide and formed a reaction layer of about 0.5mm thickness at the working surface in the magnesia-chrome refractories, the chromium oxide retained without reacting the oxide. The magnesia in the refractories also reacted with Si oxide in the molten steel
and formed reaction layer of about 0.01mm thickness at the surface with some penetration of the oxide into the inside of the refractories. However, the chromium oxide kept in the structure without reacting the oxide. In the case of the magnesia-carbon refractories, relatively dense reaction layers of about 0.01mm thickness were formed at the working surface in the refractories by an activated reaction of both metal oxides with Mg vapor generated in the refractories under the circumstance of the elevated temperature with contacting of the molten steel for both cases including Al and Si oxides, respectively. As a comparison of the refractories for molten steel including the above mentioned metal oxides, the magnesia-chrome was superior in the erosion with remaining chromium oxide phase stably in the refractories. The damages of the refractories by the attack of the metal oxides in the molten steel for use of the RH degasser were apparently different by the kind of materials used for the refractories.

O121) IMPROVEMENT OF CASTABLE REFRACTORY FOR STEEL LADLES AT KASHIMA STEEL WORKS

Ishikawa, A.(1);
(1): Nippon Steel & Sumitomo Metal Corporation, Kashima,Ibaraki,314-0014, Japan

Alumina-magnesia (Al2O3-MgO) castable refractory has been used in the sidewall of the molten steel ladles at Kashima Steel Works, Nippon Steel & Sumitomo Metal Corporation. The life of the ladles depends on the wear and residual thickness of the sidewall castable in the ladles. According to the observation of the sidewall refractories through the ladle campaigns, it was revealed that the decrease of the sidewall thickness did not become large until reaching about 70 charges, and thereafter, the sidewall thickness decreased stepwise with spalls ranging from 20-50 mm in thickness. It was considered that the sidewall refractories were not seriously damaged by slag corrosion, but the thickness was reduced sharply by spalling. Based on the field observation of the damage condition of the sidewall refractories, and the laboratory investigation of the used refractory materials, the following three modified castables were selected for trial, with the intent of improving the life of the ladle sidewall.

Castable 1. To reduce the thermal spalling, the grain size distribution was changed, which decreased the elastic modulus and thermal expansion coefficient.

Castable 2. To reduce the structural spalling, the dispersing agents were changed and the amount of the water addition was decreased, which decreased the pores in the refractories, and thus decreased the pathways for slag to penetrate into the castable.

Castable 3. To reduce the structural spalling, fine Al2O3 powder was added, and MgO was reduced, which decreased the slag penetration depth.

These three castables were tested in the ladle sidewall at Kashima Steel Works. The field results showed that all three castables showed better residual thickness than the castable used previously. The castables tested were mainly damaged by spalling, similar to the previous castable, but the first spalling occurred some charges later, and the average thickness of the spalling layer was about 15% thinner than the previously used
castable. Castable1 was selected as the new standard refractory for the ladle sidewall, with an increased average service life of 30 heats.
In all discontinuous driven thermal processes refractory linings are exposed to thermomechanical stress that is often responsible for a premature wear. This is especially significant for monolithic refractory materials that are typically in green state prior to the first heat-up. Spinel has been identified as a valid countermeasure to overcome material damage caused by thermal stress a long time ago. Especially spinel forming high alumina refractory monolithics show a significant improvement. However in service monolithic linings are exposed to a temperature gradient that only forms a sintered layer at the hot face. In deeper zones the monolithic lining remains in an unfinished state due to lower temperatures that are dependent on the thermal conductivity of the material. Here the material suffers of an unfinished ceramic structure. Especially the zone beneath the sintered zone is critical because here the thermo-mechanical impact is still high. Thermo-mechanical induced spalling is typically initiated in this zone. The proposed presentation will demonstrate that a smart matrix design including the particle size distribution and the spinel precursor materials allows to adjust the formation velocity and the appearance of the spinel in dependence of the temperature. Distinct amounts of low temperature spinel enables a goal oriented strengthening of the described weak zone in the lining. In matrix formulations Mg-delivering precursors were chosen due to their ability to form spinel and their workability in the mixture. The choice was taken for a dead burned magnesia (MgO) and a raw magnesite (MgCO3). The precursors were implemented in different amounts into cement-containing and cement-free concretes. The influence on physical properties like CMoR, open porosity or the yield of spinel formed was measured. Investigations of the spinel formation kinetics confirm, that generally the higher the firing temperature and the finer the particles, the more efficient is the spinel formation. However, the state of agglomeration, the particle size distribution and presence of impurities seems to play a decisive role in the spinel formation. By adding the spinel precursors to high alumina concretes the CMoR is influenced. In comparison to MgCO3, MgO seems to be more efficient to promote a spinel formation. Overall these information will provide very valuable information for an intelligent matrix design for an improved spinel formation adjusted to service conditions.
O123) INNOVATIVE REFRACTORY PRODUCTS TO LINE AND TO REPAIR HEAVILY LOADED AREAS

Tassot, P.(1); Kesselheim, B.(1); Schemmel, T.(1); (1): Refratechnik steel GmbH, Düsseldorf, Germany

Increased worldwide globalization in term of economy and competition imposes innovative measure for the steelmaker and other producers targeting cost reduction in order to have the ability to withstand the pressure of the market.

High reliability and availability of the main vessels used for the process are key factors in the choice of a technology. In the last decades a lot of innovation from the monolithic side has enabled to establish these products worldwide. Some areas still stays as a weak point due to such cumulative stresses during operative conditions as high temperature, thermal shocks, high abrasion and corrosion.

REFRAWIRE® precast technology is giving the answer to these multi-task operations. This new generation of refractory composite material offers a combination of strength, high refractoriness, abrasion resistance and reasonable corrosion resistance. For answering the requirements of the market we have developed a range of refractory self-flowing material allowing working in such different environments as iron and steel making, nonferrous industry, incineration, power plant and cement industry.

Additionally to new performant lining it is essential to propose some efficient easy hot repair possibility to our customer. This can be achieved with REFRASPRAY®, here also constituted by a customized line of products enabling a hot repair by spraying. Applied very successfully in the foundry sector, we can save significant time for the repair of ladles or runners.

O124) IMPACT OF PARTICLE SIZE OF CALCIUM ALUMINATE CEMENT ON ITS HYDRATION PRODUCTS AT 40°C

Shang, X.(1); Tian, K.(1); Liu, Y.(1); Chen, L.(1); Ye, G.(1); (1): Zhengzhou University, Zhengzhou, China

In this work, the effect of particle size of calcium aluminate cement (CAC) on its hydration products during hydration at 40 °C was studied. The cement hydration at the designated times was terminated by the freeze-vacuum method. The phase development and microstructure evolution during the cement hydration were investigated by XRD and SEM, respectively. It was found that the quantity and the degree of crystallinity of C3AH6 increases with the reducing particle size of CAC after hydration at 40 °C. Moreover, the mechanism of such phase development was discussed.
O125) EFFECT OF ADDING A KIND OF SURFACTANT ON PORE SIZE DISTRIBUTION AND PROPERTIES OF ALUMINA-SPINEL CASTABLE

Li, J.(1); Zhou, N.(2); Gao, Q.(1); Bi, Z.(1);
(1): Henan Haiger High Temperature Materials Co., Ltd., Luoyang, Henan, China (2): High Temperature Materials Institute, Henan University of Science & Technology, Luoyang, Henan, China

Properties and quality consistency of refractory castables are closely associated with porosity and pore size distribution. More uniform pores distribution under equivalent porosity is preferable. In this work, a kind of surfactant was introduced into alumina-spinel castable for making steel ladle integral purging plugs by pre-casting for the purpose of avoiding big pores and improving properties. The surfactant was absorbed by alumina based powders by pre-mixing them, so that it can be better dispersed in the castable by adding such powdery additive. The addition was set at 0, 1%, 2% and 3% respectively. Properties of the castables in terms of water demand, flow value, hot modulus of rupture and permanent linear change were investigated and microstructure of the samples dried and fired at different temperatures were observed by SEM. The incorporation of such agent can influence the flow behavior, properties and microstructure of the castables, while little effect on the original shaping and drying process as well as volumetric stability at high temperature. The introduction of this additive is helpful to reducing bleeding phenomenon of the castable and avoiding segregation. Hot modulus of rupture at 1400℃ can also be enhanced from 14.3MPa to 16.8MPa at 1% addition of the additive, which can be attributed to a reduction of big vacancies and an increase in smaller size pores which are more uniformly distributed in the matrix. Field test of the improved alumina-spinel castable with addition of 1% of the additive was carried out as pre-cast integral purging plugs in a 90t stainless steel ladle in Taiyuan Iron & Steel (Group) Co., Ltd. and positive results were obtained, evidenced by reduced late stage cracking and prolonged durability.

O155) VALUE ENHANCEMENT FOR REFRACTORY CASTABLES BY DEFLOCCULANTS BASED ON COMB POLYMER TECHNOLOGY

Wutz, K.(1);
(1): BASF Construction Solutions GmbH, Trostberg, Germany

The paper presents Polycarboxylate ethers (PCE) with comb polymer structure, the new generation of dispersants for refractory castables, in respect of chemical structure and mode of action. The molecular design of the Polycarboxylate ethers is crucial for their performance, but the comb polymer architecture can be tailor-made in a very broad range for various refractory materials and requirements. The investigations focus also on the understanding of polymer interaction with refractory materials.

Polycarboxylate ethers adds remarkable value to the refractory industry as these advanced polymers supports the trend from shaped to unshaped refractory products. Successful production and installation of self-flow castables at low water contents is enabled by the application the latest Polycarboxylate ether technology.
The benefits of the comb polymer deflocculants are twofold by influencing positively both fresh and hardened properties of refractory castables. Hence, these polymers contribute sustainable in the further improvement of refractory materials and future installation technology.
The recycling of aluminum provides high efficiency in terms of ecologic and economic aspects. To ensure high quality products for both secondary and primary aluminum, appropriate and effective procedures have to be applied for the removal of non-metallic inclusions. A simple, relatively cheap, and efficient process to reduce non-metallic inclusions is the usage of ceramic foam filters during the casting process.

The present study focuses on the effect of the filter surface chemistry on the filtration behavior. Five different oxide filter surface chemistries (alumina (Al2O3), spinel (MgAl2O4), mullite (3Al2O3·2SiO2), silica (SiO2) and titanium dioxide (TiO2)) were tested with the aluminum alloy AlSi7Mg with regard to their filtration behavior.

The filtration experiments were conducted on a laboratory scale with a filtration pilot plant at Constellium C-TEC (Voreppe, France), which allows appropriate filtration durations (40 to 76 min) using a 730 kg aluminum furnace. During these trials the amount and size of the non-metallic inclusions were quantified with LiMCA (Liquid metal cleanliness analyzer). The test set-up allows the simultaneous use of two LiMCAs (before and after the filter) from which the filtration efficiency can be calculated.

All filter natures were quite efficient in terms of inclusions removal (85 to 95%). The test results showed the coatings to rank in the following sequence (from highest to lowest): Al2O3, MgAl2O4, 3Al2O3·2SiO2 and TiO2. The analysis of the removal efficiency as function of the inclusion size shows that the Al2O3 and the MgAl2O4 filters are comparable (efficiency closed to 100% for inclusions larger than 90 µm) while the 3Al2O3·2SiO2 filter possesses the lowest filtration efficiency for the larger inclusions (> 110 µm). In these trials, the 3Al2O3·2SiO2 filter showed the highest filtration efficiencies for smaller inclusions (< 60 µm). The TiO2 filter showed the lowest filtration efficiencies.

The spent filters were metallographically analyzed at the SEM in order to observe the interactions between the inclusions and the filter surface. Only limited interaction between inclusions and the four different coating natures were observed, regardless of the chemistry of the coating.

The development of carbon nanofiber reinforced pitch for carbon electrodes for electric arc furnaces provides significant benefits in terms of improved electrical conductivity and mechanical properties. The use of carbon nanofiber as a reinforcement material enhances the performance of the electrode, leading to reduced energy consumption and increased efficiency. The study focuses on the optimization of the pitch composition and the integration of carbon nanofibers to achieve the desired properties.
Many industrial processes involve the use of carbon electrodes in electric arc furnaces (EAF). Söderberg electrodes are extensively used and while other types of electrodes are subjected to thermal treatment before use, Söderberg electrodes are formed in situ, consuming a carbon paste that is transformed during operation. In general terms the paste is composed of calcined anthracite, petroleum coke and coal tar pitch as binder.

This work evaluates the use of carbon nanofiber (CNF) reinforced coal tar pitch in the production of Söderberg paste. The effects of CNFs are evaluated both for the coal tar pitch itself and for the Söderberg paste. A hypothesis explaining the effects of CNFs on the paste behavior has been tested by means of a reference formulation that has been thoroughly characterized.

O128) INCREASING REFRACTORY LIFE IN A PIERCE-SMITH CONVERTER THROUGH NUMERICAL SIMULATIONS

Dolabella Resende, A.(1); Terra Elias, F.(1);
(1): Magnesita Refractories, Contagem, Brazil

The converter, in copper metallurgy, is a reactor where molten sulfides (matte) are oxidized in order to obtain blister copper (99% Cu). The Pierce-Smith converter is the most common vessel for this process and its refractory wear and converting efficiency are strongly influenced by the flow pattern of the matte and the blown air. In this work, numerical simulations were performed to study the dynamics of gas injection under different tuyere line configurations. The influence of design variables such as the size, number and position of tuyeres was evaluated regarding the amount of bubble overlapping between tuyeres, blown air penetration, contact region between the air and matte and turbulence. By comparing these results, it was possible to improve the tuyere line design towards reduced refractory wear and enhanced converting efficiency of the vessel.

O129) IMPACT OF ALUMINIUM PHOSPHATE ADDITION TO REFRACTORY CASTABLES ON MAGNESIUM-ALUMINIUM SPINEL FORMATION IN CONTACT WITH MOLTEN ALUMINIUM ALLOY

Reichert, W.(1); Tonnesen, T.(1); Miriuta, M.(2); Loison, L.(1); Telle, R.(1);
(1): RWTH Aachen University, Aachen, Germany (2): ENSCI Limoges, Limoges, France

Refractories used in the aluminium industry undergo severe corrosion due to reaction with molten aluminium. The high wettability by aluminium melt is suspected to be a key factor for degradation and infiltration, hence anti-wetting additives such as BaSO4, CaF2 or AlPO4 are added to the refractory to limit the contamination of the melt. The conditions as well as the mechanisms of the improved corrosion resistance are not yet well understood. In particular the behaviour of phosphor at the interface between refractory and aluminium melt is subject of current research. The present work is aims at improving the corrosion resistance against molten aluminium of an alumina based no cement castable with addition of AlPO4. It has been shown that for an anti-wetting effect a high amount of 10 wt% AlPO4 is needed. Furthermore the use of additives leads
to worsening of the refractory microstructure especially when sintered at high temperatures, presumably due to rheological issues. Nevertheless, an improved corrosion resistance was obtained even at fewer addition of AlPO4 around 6 wt%. This study intends to examine the impact of varying AlPO4 addition to an alumina no cement castable to the MA-spinel formation at the interface between aluminium alloy Al 7075 and the refractory castable. The applied methods include a first characterization of the material with open porosity, density and permeability measurements, examination of spinel formation mechanisms by SEM and XRD as well as a study of the reactivity with aluminium melt during a dynamic laboratory finger test according to standard CEN/TS 15418. The efficiency of the addition and its impact on the microstructure including Young’s Modulus as well as the possible improvement of the infiltration resistance are discussed.

Q130) INVESTIGATION ON THE INTERACTIONS BETWEEN AL2O3-CHROMITE REFRACTORIES AND ZNO-CONTAINING FAYALITE SLAGS

Chen, L.(1); Guo, M.(1); Blanpain, B.(1); Malfliet, A.(1);
(1): KU Leuven, Leuven, Belgium

Al2O3-chromite refractories have been proven to be more resistant against fayalitic (FeO-Fe2O3-SiO2) slags than MgO-chromite refractories in the primary copper smelting process. It is therefore expected that such Al2O3-chromite refractories could be used in the lining of secondary copper smelters to extend the lifetime of these furnaces. However, secondary raw materials are introduced in secondary copper production processes compared to primary copper production, leading to changes in the composition of the slag. ZnO, for example, can be present in the secondary smelting slag forming a ZnO-containing fayalite (ZFS) slag. With ZnO present in the slag, both the physical and chemical properties of the slag are varied, which can consequently affect the corrosion behaviour of Al2O3-chromite refractories. Therefore, the interactions between Al2O3-chromite refractories and ZnO-containing fayalite slags was investigated in this work by static refractory finger tests and Al2O3 crucible tests at 1200 °C under Ar atmosphere. The microstructure of the corroded refractory samples and the slag composition were analyzed by electron probe micro-analysis equipped with wavelength dispersive spectroscopy (EPMA-WDS). The influence of the ZnO level on the Al2O3 dissolution and the Al2O3/slag interfacial reactions was studied. The experimental results from the Al2O3 crucible tests were interpreted and supported by thermodynamic calculations.
The microstructure of refractory materials exhibit grains with a very large size distribution, from some µm to some mm. This prevents automatic, fast and accurate description of the whole microstructure from microscopic observations. However, today, it exist automatic methods allowing image analysis, which are currently used in some other scientific subject such as biology. Optical microscopy allows the observation of large particles (aggregates), however electronic microscopy is suitable to observe finer particles (matrix or bonding phase). Moreover, due to similar composition, it exist few contrast between grains and grain boundaries are not clearly defined. This also prevents thresholding which is necessary to automatically detect grains with the aid of an image analysis method. Actually, it doesn’t exist method allowing the quantitative description and the control of the refractory materials whole microstructure.

In this work, different complementary methods were used to describe as well as possible the whole microstructure of refractory castables. A skill was developed to obtain special large size samples. They were prepared by drilling, cutting, surface machining and polishing. This large size allows including a lot of large whole particles (aggregates) in the samples and to reduce the “cut” ones at the edge. Optical and scanning electronic microscopy where used for picture acquisition at different magnification. Optical microscopy was used for aggregates observation whereas electronic microscopy was used for fine particles observation. “Panorama” software was used for pictures assembly leading to larger pictures showing a “sufficient” number of particles with high accuracy. Some artefacts such as ink impregnation were used to enhance contrast between different phases and to promote grains recognition by image analysis software. Method was applied to different castables with different particle size distributions. Results show that it is possible to obtain a description of the microstructure including a “particle size distribution”. Today, the progress of the work leads to a finger print of the materials which could be used to check and to compare materials.
samples with different geometries must be tested. First of all the sample scale is large at Refractory bricks, after shaping the geometry size is small at laboratory samples. The Young’s Modulus determination by the Resonant frequency method described, e.g. in ASTM C1259-08 is time and money consuming. Because the measurement and analysis procedure contains many steps. This time must be multiplied by the number of samples and necessary measurement repetitions. Therefore, a way was searched to reduce the time demand at the Resonant Frequency based Young’s Modulus determination. A solution was found. It is based on the analysis of the frequency spectrum of all vibration modes of a specimen. The vibration modes are excited by the standardized impulse hammer and direction. The alternative Young’s Modulus determination method uses the principle of free vibration of all wave types and orders in a specimen geometry. By a software the Young’s Modulus values of all significant frequency peaks of all measured spectra are computed. A search algorithm determines the plausibility of the Young’s Modulus of each resonant frequency combination of all wave types and orders. If a plausible Young’s Modulus combination was found, the result is given out by the search algorithm. This alternative resonant frequency Young’s Modulus determination method was verified by several ways. It was done at different sample geometries and Refractory material types. For a methodical verification the Standard Resonant Frequency method according to ASTM C1259-08 and the Ultrasonic transmission method are used to determine the Young’s Modulus values. For a theoretical verification the Finite Element Eigenfrequency calculation was applied at different geometries and material properties. At the Eigenfrequency data the alternative Young’s Modulus was applied and the results compared with the Finite Element Simulation parameters of the data set. The Finite Element Simulation was done by the Simulation Department of the RHI. The verification was successfully finished. The described alternative Young’s Modulus determination Method can be automatized and computes the Young’s Modulus values of all available wave types and frequency orders of a spectrum in a split second. By this alternative procedure a significant time reduction of the Young’s Modulus computation procedure is possible. In future this method can also used to determine the poisons ratio automatically.

**O133) MECHANICAL BEHAVIOUR OF CARBON BONDED MAGNESIA (MGO-C) AT TEMPERATURES UP TO 1500 ℃**

Solarek, J.(1); Aneziris, C.(1); Biermann, H.(1); 
(1): Technical University Freiberg, Freiberg, Germany

Carbon-bonded magnesia (MgO-C) with maximal magnesia grain sizes of 2 mm and a graphite content of 10 % was investigated regarding its mechanical properties. Therefore quasi-static and fracture mechanical tests were carried out at temperatures up to 1500°C under inert atmosphere. The tests were complemented by analysis of microstructure, density, porosity and dynamic Young’s modulus. The results showed change of mechanical behaviour in dependency of temperature. Besides changes in course of both stress-strain curve and force-crack displacement curve, a change of fracture mechanism was found. Investigations of microstructure revealed a change from fracture through matrix and MgO grains at low and intermediate temperatures to fracture only through the carbonaceous matrix at high temperatures.
O134) HIGH TEMPERATURE BEHAVIOR OF CARBON-BONDED FILTER STRUCTURES

Solarek, J.(1); Klemm, Y.(1); Aneziris, C.(1); Biermann, H.(1);
(1): Technische Universität Freiberg, Freiberg, Germany

In the Collaborative Research Centre 920 “Multi-Functional Filters for Metal Melt Filtration - A Contribution towards Zero Defect Materials”, filter structures of fine-grained, carbon-bonded alumina (Al2O3-C) are used to improve purity of metal melts. To improve understanding of behaviour of the filters, compact specimens as well as filter specimens were investigated regarding their mechanical properties at temperatures up to 1500°C. Therefore, quasi-static tests and creep tests were carried in compression. The tests were complemented by investigations of microstructure by scanning electron microscopy, Raman spectroscopy and light microscopy. The experiments showed brittle behaviour of the material at low and intermediate temperature. The filter specimens showed fracture of single struts, leading to drop of stress in stress-strain curves. At higher temperature, softening of the filter occurred, leading to smooth stress-strain curves and a maximum of strength at ap. 1400°C. The softening was accompanied by microstructural changes leading to formation of highly orientated graphite, which was proven by Raman spectroscopy.

O135) CHEMICAL ATTACK EVALUATION OF ALUMINA-MAGNESIA-GRAFPITE BRICKS BY DYNAMIC TESTS AND THERMODYNAMIC SIMULATION

Calvo, A.(1); Muñoz, V.(1); Camelli, S.(2); Gutiérrez Campos, D.(3); Tomba Martinez, A.(1);
(1): INTEMA (instituto de tecnología en materiales), Mar del Plata, Argentina (2): IAS (instituto argentino de siderúrgia), San Nicolás, Argentina (3): Universidad Simón Bolívar (departamento de ciencia de los materiales), Caracas, Venezuela

Alumina-magnesia-carbon (AMC) refractories used in the steelmaking ladles support temperatures up to 1600-1700°C and are also exposed to the attack of melts (liquid metal and slag) and oxidant gases of the atmosphere. On the other hand, the high degradation of the bricks under real conditions in-service is difficult to reproduce at laboratory scale. For this reason, a combination of analytical methodologies is convenient to face the problem.

In this work, the corrosion of commercial AMC bricks by molten slag is studied by a combination of methodologies in order to achieve a deep understanding of the corrosion mechanisms and its relationship with refractory characteristics such as composition, microstructure and texture.

The dipping-test, which reproduces the relative movement between the slag and the refractory, is used together with the thermodynamic simulation of the system by a commercial software. Prismatic specimens extracted from the brick are subjected to the corrosion test at 1600°C during 30 min, and a sample speed of 25 rpm. A typical industrial slag is evaluated with a CaO/SiO2 ratio of 10.6. After the test, the sample wear is evaluated by dimensional variations, XRD, DTA/TGA, density and porosity.
measurements. Also, optical and SEM/EDS microscopies are employed. A previous characterization of the commercial bricks is performed by the same analytical techniques in order to use this information as reference. The thermodynamic simulation of slag-refractory system is carried out using FactSage 7.0 commercial package and the chemical composition of the slag and the brick. An iterative procedure is employed until the amount of equilibrium liquid is null. The specimen wear as well as the identification of the new phases formed at the slag-refractory interface (mainly different calcium aluminates and MgO.Al2O3 spinel) are used as indications of sample corrosion. Moreover, the equilibrium calculations brings good prediction with regard to the phases present at the slag-refractory interface, and the degree of corrosion wear taking into account number of steps from the iterative process, and the amount and viscosity of the equilibrium liquid, among others.

From these results, the main steps of the corrosion process (mechanisms) are inferred, as well as the relationship between chemical attack and AMC bricks characteristics (raw materials, periclase, graphite content, type of antioxidant, etc.).

**O136) MECHANICAL BEHAVIOR OF MGO-C REFRACTORY BRICKS THERMALLY TREATED IN LOW TEMPERATURE RANGE**

Gass, S.(1); Tomba Martinez, A.(1); Galliano, P.(2); Bellandi, N.(3);

Steelmaking refractories performances have a strong impact on critical aspects of the industrial process, such as production costs and steel quality, between others. In this paper, the effects of thermal treatments on the mechanical behavior of MgO-C refractory materials are assessed using two types of atmospheres, argon flow and graphite bed, in addition to combination of both of them in different stages.

Non-commercial bricks with and without antioxidants are evaluated using cylindrical testing specimens (diameter: 30 mm, length: 45 mm). Microstructural and textural changes as consequence of heat treatments at temperatures < 1000ºC during 1h or 3h prior to mechanical test were analyzed by X-Ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM/EDS). As received materials, as well as those thermally treated, are mechanically tested in compression between room temperature and 1000ºC (in Ar) to obtain the stress-strain relationship in each case.

Stress-strain curves change according to alterations in the microstructure and texture of the brick, due to the events taking place during the different stage of thermal treatments prior and during mechanical tests (heating, permanence and cooling). Furthermore, the time of exposition is considered as a variable to evaluate the effect of different advance in the processes which occur during the thermal treatment. In the range of low temperatures (T < 1000ºC), the organic binder is the main component affected by thermal variations; however, the antioxidant additive actually affects the mechanical behavior even its reaction occurs at temperatures above 600ºC. The results obtained in the range of low temperatures can be interpreted taking into account factors such as
mass losses (volatile elimination and carbon oxidation), thermal shrinking and expansion, and cracks healing.
RM 1) RAW MATERIALS 1

O137) SOME CONSIDERATIONS REGARDING THE GRAIN SHAPE OF REFRACTORY RAW MATERIALS

Moehmel, S.(1); Kurz, B.(1); Dietze, C.(2); Schafföner, S.(2); Fruhstorfer, J.(2);
(1): Center for Abrasives and Refractories Research & Development GmbH, Villach, Austria
(2): Institute of Ceramic, Glass and Construction Materials, TU Bergakademie Freiberg, Freiberg, Germany

The particle size distribution (PSD) is an essential characteristic of raw materials. This feature is taken into account by nearly all aspects related to the development and optimisation of refractory products. Nevertheless, not only the PSD itself is important but also the shape of the grains. This has long been neglected especially within the field of refractories. For building materials and abrasives e.g. it is common practice to characterise raw materials not only regarding their size distribution but also concerning their shape.

Like the particle size distribution also the grain shape is already determining several important properties of the raw material itself as well as of their mixtures. This might be reflected in the behaviour of a material discharged from a silo, the miscibility of different raw materials, the flowability of a readily mixed composition into a mould, the compactibility etc. Moreover, the properties of refractory products such as porosity, strength, abrasion, corrosion as well as creep resistance might be significantly influenced not only by the size distribution but also by the shape of the raw material particles. Finally it is well known that the reactivity of a particle is determined by its specific surface area and this again is depending on the shape.

Therefore in a first part of this work some general considerations regarding the definition of grain shape, its measurement and the targeted production of raw materials with certain grain shapes will be presented. A second part is then dedicated to the influence of differently shaped raw materials on the properties of refractory castables and bricks. As a result it is shown that raw materials with identical size distribution but with differently shaped grains can influence the physical, mechanical and thermo-mechanical properties of refractories.

O138) COMPARISON OF FUSED AND SINTERED HIGH ALUMINA REFRACTORY AGGREGATES - PERCEPTIONS, CHARACTERISTICS, AND BEHAVIOUR IN DIFFERENT REFRACTORIES

Zacherl, D.(1); Schnabel, M.(2); Klaus, S.(2); Buhr, A.(2); Schmidtmeyer, D.(3); Chatterjee, S.(4); Dutton, J.(5);
(1): Almatis, Inc., Leetsdale, United States
(2): Almatis, GmbH, Frankfurt, Germany
(3): Almatis, GmbH, Ludwigshafen, Germany
(4): Almatis Alumina Private Ltd, Kolkata, India
(5): Stourbridge, United Kingdom
There are many perceptions in the market about the most appropriate refractory aggregate for a particular application. Opinions about the relative benefits of the fused and sintered versions of synthetic high alumina materials are set and often difficult to discuss and refute. However, changes in the refractory raw materials market over the past few years have influenced the properties of the currently available synthetic high alumina materials and triggered the development of new aggregates. The purpose of this paper is to outline the differences between high alumina fused and sintered raw materials. The focus will be on physical properties such as density, porosity and grain shape, but the influence on the final properties of refractory formulations such as bricks, castables or dry vibratable mixes is also discussed.

**O139) INFLUENCE OF MINERAL PURITY ON MULLITE AND ANDALUSITE BASED REFRACTORIES**

Frulli, D.(1); Möhmel, S.(2); Graddick, S.(3); Ahouanto, F.(4);

Andalusite and Mullite are widely used as raw materials for many different applications in the refractory industry. These minerals are well known to provide high thermo-mechanical stability, therefore enhancing key properties such as thermal shock resistance and refractoriness under load. However, the performance of the refractory products based on mullite and andalusite can be strongly affected by the amount and the type of impurities associated with the main mineral.

This paper presents the results of several studies comparing the performance of different types of andalusite and mullite grades. A broad range of commercial products was deeply characterised regarding chemical and mineralogical composition, as well as dilatometry and heating microscopy.

Refractory bricks and castables were produced from each type of andalusite and mullite in a laboratory scale, in order to establish a correlation between the raw material purity and the refractory performance.

For instance, low ferric oxide and alkali/alkali-earth oxide content in certain materials yield outstanding hot properties and CO resistance for the refractories in which they are used. The processing that goes into their production participates in the superior performance, playing an important role in the densification of the material, thus impacting key properties, such as water demand and flowability.

Thermo-mechanical properties such as refractoriness under load, creep resistance and Hot MOR were investigated, with a particular focus on the impact of impurity level, its enrichment in the matrix, and its influence on the microstructure.
**O140) EFFECT OF PROCESSING PARAMETERS AND ADDITIVES IN THE GRAPHITIZATION OF PHENOLIC RESINS**

Da Luz, A.(1); Renda, C.(1); Lucas, A.(1); Aneziris, C.(2); Pandolfelli, V.(1);
(1): Universidade Federal de São Carlos, São Carlos, Brazil (2): TU Bergakademie Freiberg, Freiberg, Germany

Most of the thermosetting resins are classified as non-graphitizing carbon sources. However, the chemical resistance and thermo-mechanical properties of refractories bonded with resole or novolak resins depend on the presence of crystalline carbon phases (preferentially with features close to graphite ones) in their compositions. Consequently, there is major interest in finding routes to induce the graphitization of such components at temperatures and conditions similar to the ones that refractories are submitted to in service. This work evaluates the role of processing parameters (mixing, curing and firing temperature) and additives (ferrocene, boric acid and graphite) on the graphitization process of two commercial resins (resole and novolak) and a synthesized one (modified-novolak). X-ray diffraction, Raman spectroscopy and thermogravimetric analyses were carried out to identify the microstructural evolution of the compositions. According to the results, carbon graphitization was already detected after firing the samples at 1000°C for 5h under reducing atmosphere. Ferrocene addition favored a more effective graphitization of the selected resins, but H3BO3 also induced the rearrangement of the carbon derived from the commercial novolak product. The mixing and curing procedures used during the compositions’ preparations proved to be very important steps as they affected in a greater extent the resulting graphitization degree of the fired samples.

**O141) ACTIVATION OF CALCIUM ALUMINATE BASED AQUEOUS SLURRIES**

Santos Junior, T.(1); Zetterström, C.(2); Wöhrmeyer, C.(2); Parr, C.(2); Pandolfelli, V.(1);
(1): Universidade Federal de São Carlos, São Carlos, Brazil (2): Kerneos Aluminates, Vaulx-Milieu, France

The dispersion of calcium aluminate (CAC) in water is considered a challenge due to the hydration step which takes place when their particles are exposed to the aqueous media. In order to induce the dispersion, a new technology to stabilise CAC aqueous slurries, was developed. Based on this, suspensions containing up to 75 wt% of CAC and fillers, such as alumina, can be produced. After stabilisation, they can be easily reactivated by changing the pH, allowing the CAC particles to hydrate. The kinetics of hydration can be adjusted by adding some lithium source, so the time of solidification can be adjusted for different applications, such as feedstock for additive manufacturing techniques or for the production of dense and insulating refractories. In this work, the activation of stabilised slurries containing 75 wt% of Secar 71 or 15 wt% of Secar 71 and 60 wt% of alumina, was carried out. Sodium hydroxide and lithium sulphate solutions were selected to adjust the pH and the lithium content, respectively. The effect of the temperature was characterised in the range between 20°C and 50°C. Oscillatory rheometry, ultrasound speed evolution and temperature measurements were carried out in order to evaluate the microstructural changes in the reactivated slurries.
According to the results, increasing the pH and the amount of lithium sulphate induced a faster solidification of the systems, which was followed by heat release associated with the precipitation of CAC hydrates. The temperature increase had a similar effect, speeding up the solidification. As it was observed in this study, CAC-stabilised slurries could be reactivated and the time of solidification could be tailored. Due to this flexibility to adjust the liquid-solid transition and the advantages of having dispersed CAC particles in an aqueous and non-toxic media, these slurries have a great potential to be used in different refractory applications.

**O142) IMPROVED OXIDATION RESISTANCE AND MECHANICAL PROPERTIES OF AL2O3-C REFRACTORIES WITH ADDITION OF BORON-DOPED EXPANDED GRAPHITE**

Wang, Q.(1); Li, Y.(1); Sang, S.(1); Xu, Y.(1);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China

Born (B)-doped expanded graphite (EG) has been synthesized by annealing the synthetics, which were obtained from the suspensions of EG and boric acid. After that, the B-doped EG were introduced into Al2O3-C refractories to partially replace graphite flake. The ratio of the G and D bands of B-doped EG in first-order Raman spectra curves was significantly larger than as-received EG, indicating more graphitization of B-doped EG due to doping effect. Meanwhile, the B1s XPS spectrum of B-doped EG could be composed of several peaks at 187.2, 188.9 and 190.3 eV, being attributed to the presence of B atom in B4C, B-sub-C and BC2O, respectively. In comparison with as-received EG, the B-doped EG appeared better oxidation resistance via non-isothermal kinetics analysis. In addition, the mechanical properties such as modulus of rupture (CMOR), flexural modulus (FM), force and displacement and thermal shock resistance of Al2O3-C specimens with 0.5 wt% B-doped EG were improved in comparison with those with only graphite flake. Besides, the Al2O3-C specimens appeared significantly better oxidation resistance due to addition of B-doped EG.
The mechanism of carbon monoxide decomposition, called the Boudouard reaction, which results in the deposition of solid carbon (\(2\text{CO} \Leftrightarrow \text{CO}_2 + \text{C(solid)}\)) causes premature degradation of refractory linings. This reaction occurs at temperature ranging between 400 to 900°C with a maximum intensity around 600 °C, and is highly favoured by the presence of catalytic particles such as iron and iron oxides. Fe\(_x\)O\(_y\) particles are present in the refractories as impurities in raw materials and by attrition of the mixing devices while blending the refractory formulation.

The CO resistance is usually improved by the selection of raw materials with a low content of iron particles and by raising the refractory sintering temperature. Unfortunately, these solutions are not always very effective for new industrial applications where refractories are subjected to CO and H\(_2\) reducing atmospheres (biomass and coal gasification, new generation of blast furnaces with low CO\(_2\) emission....).

The aim of this study is to understand the mechanisms of carbon formation at a micro- and macro-scale and to find an efficient refractory solution to inhibit the Boudouard reaction. In these extreme conditions, the effect of the iron oxide valence (i.e., oxidation degree: Fe, FeO, Fe\(_3\)O\(_4\) and Fe\(_2\)O\(_3\)) and grain size (nanometre to millimetre size) on the carbon deposition amount in different CO + H\(_2\) gas mixtures was investigated, using thermogravimetric measurements and in situ Raman spectroscopy. After cooling, the samples were characterised using various methods: X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscopy (TEM). Two different carbons are formed. In pure CO gas, the carbon has a high quality with significantly coherent domains. The addition of H\(_2\) (CO + H\(_2\) mixture) favored a more disordered sp\(^2\) carbon and the production of carbon nanofibers.

An inhibition mechanism in a CO + H\(_2\) gas mixture is proposed and validated. Sulfur inhibits the carbon monoxide dissociation on contact with iron and iron oxides. At 600°C and under CO+ H\(_2\) atmosphere, the behavior of iron sulfides was investigated and the inhibiting effect of the sulfur in contact with iron oxides was demonstrated. The conclusions of this study were applied to develop new CO/H\(_2\) resistant industrial refractories. The practical solution consists in introducing a very small amount of sulfur compounds (pure S, BaSO\(_4\), ...) into refractories.
BIO INSPIRED REFRACTORIES BASED ON NACRE STRUCTURE

Batistel Galiote Brossi Pelissari, P.(1); Bouville, F.(2); Luz, A.(3); Pandolfelli, V.(3); Studart, A.(2);
(1): Universidade Federal de São Carlos, RIBEIRAO PRETO, BRAZIL (2): ETH Zürich, Zürich, Switzerland (3): Universidade Federal de São Carlos, São Carlos, Brazil

Structural ceramic materials are usually strong or tough, although both properties are required for high temperature applications. During the past decades, intensive research has been carried out to engineer the ceramic’s microstructure, which allowed the development of advanced materials with improved toughness (due to the action of different toughening mechanism) while maintaining their strength. Other approach consisted on mimicking the structure of natural materials, as these can be strong and tough (despite the fact that they are comprised by brittle constituents). One example is the mother of pearl shell (Abalone Nacre) with approximately 95 % of calcium carbonate platelets imbedded in 5 % of protein layers. This material presents strength and toughness 20 times higher than its constituents and do not follow the rule mixture of properties. This behaviour is only possible due to the nacre structure which presents high level of organization from nano to micro scale. Considering these aspects, this work addresses the design of alumina refractories with nacre-like structure, based on the use of the Magnetically Assisted Slip Casting (MASC) technique and the Transient Liquid phase sintering (TL) procedure. Cold and hot mechanical tests were carried out to evaluate the prepared samples. The nacre-like refractories (NLR) had a structure comprised by alumina platelets with aluminium borate as a second phase. The latter played two important roles: (i) stabilized the structure, and (ii) enhanced the mechanical properties by increasing the bond strength between the platelets. The NLR showed average flexural strength of 672 MPa, fracture toughness of 11 MPa.m1/2 at room temperature and stable crack propagation. Crack branching, deflection and bridging were the main toughening mechanisms responsible for this improved behavior. The samples evaluated at 1200°C presented high mechanical strength (280 MPa) and fracture toughness of 6 MPa.m1/2. The same toughening mechanisms observed at room temperature as well as stable crack propagation (throughout the entire tested range of the load versus displacement curve) were identified in the measurements carried out at high temperature (1200°C). When compared to Ceramic Matrix Composites (CMCs), the prepared NLR presented twice the specific strength of these ceramics in the temperature range of 750-1200°C. Therefore, due to their enhanced performance, nacre-like refractories can be considered as novel structural materials for specific high temperature applications.

PLATELET ALUMINA: A POTENTIAL STRUCTURAL REINFORCEMENT FOR HIGH PERFORMANCE REFRACTORIES

Shi, S.(1); Zhou, N.(2); Li, Z.(3);
(1): Materials Technology Innovation, LLC, Katy, USA (2): High Temperature Materials Institute, Henan University of Science and Technology, Luoyang, P. R. China (3): Jiangsu Jingxin New Materials Co., Ltd., Yangzhou, P.R. China
Platelet alumina is a kind of 2D corundum synthesized at relatively lower temperatures by specific technologies different from that for tabular alumina. The well-known application of platelet alumina is in automobile industry as pearlescent pigments. However, more attention is paid to the use for materials strengthening. Like 1D structural reinforcement elements such as whiskers, rods and needles, such 2D elements should have a similar capability to resist crack propagation in material matrix. Examples of polymer, glass and bioceramics strengthened by platelet alumina have been evidenced in many literatures. The authors attempted to use such platelets to strengthen Al2O3-SiO2 based ceramics and significant increase in split tensile strength has been observed. Synthesis of platelet alumina with low cost aluminum hydrate was also attempted and the results have shown implications for refractory applications. Ideas and suggestions were put forwarded for further efforts.

O146) CHEMICAL REACTION BETWEEN POTASSIUM ALUMINOSILICATES AND AGGREGATES AT DIFFERENT TEMPERATURES

Yin, Y.(1); Li, Y.(1); Li, S.(1); Zhai, P.(1); Chen, L.(1); Ye, G.(1);
(1): Zhengzhou University, Zhengzhou, China

Kalsilite/kaliophilite (KAlSiO₄, KAS) could be used in saggars for the calcination of Li(NixCoyMnz)O₂ ternary battery materials because kalsilite has high melting point (1750°C) and could be chemically resistant to such ternary battery materials. However, the compatibility of KAS with the commonly used aggregates in the saggars is not clear. In this work, KAS was synthesized using potassium carbonate (K₂CO₃), silica and alumina. Then the as-synthesized KAS fine powder was mixed with four kinds of aggregates (alumina, mullite, cordierite and magnesia-alumina spinel) respectively. The mixtures were fired at temperatures between 700°C and 1200°C and subsequently examined by means of XRD and SEM to investigate the reaction between the KAS fine powder and various aggregates.

O147) EFFECTS OF DIFFERENT DISPERSANTS ON THE CHANGE OF CHEMICAL BOND OF COLLOIDAL SILICA

Feng, T.(1); Guo, B.(1); Liu, Y.(1); Chen, L.(1); Ye, G.(1);
(1): Zhengzhou University, Zhengzhou, China

This work aims to study the relationships between dispersants types, addition amount and the change of chemical bonds of the particles of colloidal silica. The impact of dispersant types (phosphate, citric acid, polycarboxylate) on the chemical bond changes of the colloidal silica (solid content of 30%) was investigated during the dehydration condensation reaction. The chemical bonds of the particles and phase transformation of colloidal silica were investigated by Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). Moreover, the change of Si 2p and O 1s binding energy of colloidal silica with different dispersants was analyzed by energy spectrometer for chemical analysis (XPS) in different curing conditions.
For thermomechanical modelling of industrial vessels with the Finite Element Method (FEM), refractories should be seen, at macroscopic scale, as a homogeneous continua. However, at microscopic scale these refractory materials involve sophisticated microstructures that mix several phases. Generally, these micro-structures are composed by a large amount of inclusions embedded in a brittle matrix that ensures the cohesion of the material. In some cases, these materials can advantageously exhibit complex non-linear mechanical behaviors that result from the interactions between the different phases that compose the composite micro-structure. Following this idea, the macroscopic behaviour of these media may be predicted from the fine knowledge of their micro-structure. This paper proposes to study the impact of the diffuse damages that result from the thermal expansion mismatch between the phases in presence. These phenomenon involves a high amount of discontinuities and can not be tackled easily with the Finite Element Method (FEM). The Discrete Element Method (DEM) naturally accounts for discontinuities and is therefore a good alternative to the continuum approaches such as the FEM. However, the difficulty with DEM is to perform quantitative simulations because the mechanical quantities can't be described in terms of the classical continuum theory such as stresses or strains. This study will describe the approach used here to tackle this fundamental difficulty. The results given by the proposed approach are compared to experimental data obtained on simplified refractory materials. The results are compared in terms of macroscopic parameters such as the apparent Young's modulus and the thermal expansion coefficient that can be strongly affected by the presence of diffuse damages.
NFM 2) NON-FERROUS METALLURGY 2

O149) A NEW GENERATION OF CHROME FREE REFRACTORIES FOR COPPER PRODUCTION

Stein, V.(1); Schemmel, T.(1); Jansen, H.(1);
(1): Refratechnik Steel GmbH, Duesseldorf, Germany

Magnesia-chromite refractories are the essential refractories for copper making since several years. High stability against various environments and a high corrosion resistance are key properties for the application as wear lining in copper production furnaces. Weak points are their heavy infiltration during copper making with process melts like matte or copper, poor thermomechanical resistance, high risk of spalling, a high density of the material, corrosion by fayalitic slag and also the environmental aspect of chromite based refractories. Based on these weak points the present work introduces a new family of refractory materials that combine an effective infiltration barrier with a very good corrosion resistance and thermomechanical resistance. Furthermore, they have a lower density than magnesia-chromite bricks. Several industrial trials have proved the high potential of this new refractory material family.

O150) POST MORTEM ANALYSIS OF A TAPPING CHANNEL FROM A PLATINUM SMELTER

Du Toit, J.(1); Garbers-craig, A.(1);
(1): University of Pretoria, Pretoria, South Africa

Platinum group metal (PGM) matte, a nickel-copper rich sulphide melt with high iron and low cobalt contents, is tapped through an alumina-chrome brick lined tapping channel in a platinum smelter. Penetration of PGM matte into these tap-hole bricks leads to detrimental refractory wear which can cause furnace breakouts. Multiple factors affect the extent of penetration, with the superheat of the matte being a significant factor. PGM furnaces in South Africa typically smelt blends of concentrates from the Merensky Reef, UG2 Reef and the Platreef. As supplies of Merensky concentrate are decreasing, increasing amounts of UG2 concentrate (which is rich in chromite) are used. The high chromium content of the UG2 concentrate increases the slag liquidus temperature. As the smelters operate above the slag liquidus temperature, the slag operating temperatures can range between 1460-1650°C depending on the feed composition. These high slag operating temperatures result in matte superheats of 300-650°C, which implies the matte is extremely fluid, can easily penetrate the refractory bricks and thereby increase refractory wear. The extent to which matte penetration and chemical interaction takes place were investigated through a post mortem study of a tapping channel removed from the Anglo American Platinum Mortimer smelter in South Africa. Matte penetration in regions surrounding the hole in the refractory tapping module was the main focus. The investigation also included determining whether residual tap-hole clay is present in the tapping channel. The excavated bricks were analysed in centimetre sections from the tap hole towards the edge of the brick, using SEM-EDS analysis. XRD analyses were done on samples taken
from the position of the new tapping module condition as well as the worn hole, both on the tap hole side of the brick (the hot face) and at the edge of the brick (the cold face). It was found that upon solidification, the penetrated matte crystallised to form sulphides with different concentrations of iron, copper and nickel, or combinations of these elements. Chalcopyrite (CuFeS2), pentlandite ((Fe, Ni)9S8) and pyrrhotite (Fe1-xS) were the dominant phases. A significant amount of iron oxidation was observed and to a lesser extent the oxidation of copper. This resulted in the formation of a CuFe2O4 – Fe3O4 solid solution spinel phase in the areas surrounding the worn hole, and a more complex Cu-Fe-Al-Cr-based spinel phase in the position of the original hole. Residual tap-hole clay could not be identified. SiO2 observed in the bricks is associated with CaO and MgO, which indicates that slag also came in contact with the matte tap-hole bricks. Matte penetration was more significant toward the bottom of the tap hole than towards the side, indicating that gravity aided matte penetration.

O151) APPLICATION OF SIC-BASED REFRACTORIES IN COPPER INDUSTRY

Chen, M.(1); Tang, F.(2); Chen, J.(3); Feng, L.(4); Zhao, B.(1);
(1): University of Queensland, Brisbane, Australia (2): University of Queensland, Brisbane, Brisbane (3): University of Science and Technology, Beijing, China (4): LuZhong Refractory Pty Ltd, Zibo, China

In the modern copper industry, it is important to achieve continuous operation to increase the productivity and reduce the environmental problems. Launder is one of the essential components to rapidly transfer molten matte and copper in different processes. In most of the copper-making plants, castable alumina-silicate refractories have been used for the launder materials. However, these refractories cannot meet the requirements of the continuous operation as the molten matte and copper metal can react with the refractory causing serious damage. Development of new launder materials with good resistances and environmental friendly is urgent for the copper industry.

SiC has some unique properties like high hardness, toughness, chemical and thermal stability and, in particularly, low wettability to matte and copper metal. SiC-based ceramics have been proposed to be the alternative material for the launders and it can also be potentially used as lining for refining furnace and ladel. However, SiC is hard to be sintered directly and suitable bonding phase is required to make strong and cheaper refractories. In the present study, SiC-based refractories will be prepared by various methods with different bonding phases. These refractories will be evaluated with molten matte and copper respectively.

The Si3N4 bonded SiC materials can be prepared by carbothermal reduction of silica under controlled conditions. Reaction temperature, time and partial pressure of N2 have been tested to achieve an optimum condition. The silicates bonded SiC can also be prepared starting from accurately controlled oxygen partial pressure, temperature and time to form a required layer of SiO2 on the surface. The pre-oxidised SiC powders were then mixed with Al2O3 and heated under controlled temperature and time. The silicate formed acts as the bonding phase to join the SiC particles. Static corrosion resistance
tests were carried out to test the resistances of the new materials to molten matte and copper. The sample to be tested was placed in an Al2O3 crucible with matte or Cu. The sample was heated to high temperatures for a required period in Ar gas flow. After reaction the material was quenched into water for electron probe X-ray microanalysis (EPMA). The depth of the penetration, phases present and their compositions can be accurately measured by EPMA.

The careful analyses of the microstructures clear reveal the reaction mechanisms of the SiC-based materials with matte and copper. The performances of these materials show the possibility to be used as the launder material or linings for ladle and refining furnace in copper industrial.

O152) REACTION AND SINTERING OF (Ni,Mg)(Al,Fe)2O4 MATERIALS AND THEIR CORROSION PROCESS IN NA3ALF6-ALF3-K3ALF6 ELECTROLYTE

Xu, Y.(1); Li, Y.(1); Yang, J.(1); Sang, S.(1);
(1): Wuhan University of Science and Technology, Wuhan, China

The application of ledge-free sidewalls in the Hall-Héroult cells is preferred as it potentially reduces the energy requirement of aluminum production by about 30%. However, this approach requires new types of sidewall materials to replace the currently used Si3N4 bonded SiC sidewalls. In the present paper, (Ni,Mg)(Al,Fe)2O4 materials were prepared using fused magnesia, reactive alumina, nickel oxide and ferric oxide powders as starting materials. The sintering behaviors of specimens as well as their corrosion resistance to molten electrolyte have been investigated by means of X-ray diffraction (XRD), scanning electron microscope (SEM). The results show that after firing at 1400 to 1600○C, all the specimens prepared are composed of single-phase (Ni,Mg)(Al,Fe)2O4 composite spinel, whose lattice parameter increases with increasing Fe3+ ion concentration. Increasing the ferric oxide content enhances densification of the specimens, which is accompanied by the formation of homogeneously distributed smaller pores in the matrix. The corrosion tests show that corrosion layers consist of fluoride and Ni(Al,Fe)2O4 composite spinel grains are produced in specimens with Fe/Al mole ration no more than 1, whereas for specimens with Fe/Al mole ration more than 1, dense Ni(Al,Fe)2O4 composite spinel corrosion layers are formed on the surface of the specimens. The Ni(Al,Fe)2O4 composite spinel layers formed effectively improve the corrosion resistance of the specimens by inhibiting infiltration of electrolyte and hindering chemical reaction between the specimen and electrolyte.

O153) STUDY ON HOT AL RESISTANCE OF AL2O3-SIO2 CASTABLES WITH DIFFERENT AL2O3 CONTENT

Wang, Z.(1); Zhang, S.(1); Hu, S.(2); Li, S.(1); Shi, H.(1); Cao, X.(1); Yu, L.(1);
(1): State Key Laboratory of Advanced Refractories, Sinosteel Luoyang Institute of Refractories Research, Luoyang, China (2): Henan University of Science and Technology, Luoyang, China
The working linings of melting furnace and holding furnace in aluminum industry are usually damaged by the attack of hot Al and its alloy. In order to improve service performance of the lining, hot aluminum resistance of Al2O3-SiO2 castables with different Al2O3 content was investigated by crucible method and immersion method. The microstructure of Al2O3-SiO2 castable corroded by hot aluminum was also analyzed by means of SEM and EDAX. The results showed that: (1) With the increase of Al2O3 content, the hot aluminum resistance of the castable indicates better. (2) The hot aluminum resistance of the castable seems worse with the heat treatment temperature 1100°C compared with 110°C, 800°C and 1400°C. (3) After hot aluminum penetrated into the interior of castables, Al and even Mg react with SiO2 in quartz and mullite, and SiO2 is reduced to Si, but Al and Mg are oxidized into Al2O3 and MgO; MgO further reacts with Al2O3 to produce spinel resulting in structural damage of the sample. For the Al2O3-SiO2 castable with higher Al2O3 content, the layer of the formation of spinel is densified and could prevent hot aluminum from penetration further.

O154) A SYSTEMATIC APPROACH TO THE DEVELOPMENT OF SELF-HEALING SLAG REFRACTORY SYSTEMS

Fallah Mehrjardi, A.(1); Hayes, P.(1); Azekenov, T.(2); Ushkov, L.(3); Jak, E.(1);
(1): Pyrometallurgy Innovation Centre, University of Queensland, Brisbane, Australia (2): KAZZINC, Glencore, Kazakhstan, (3): KAZZINC, Glencore, Kazakhstan, Kazakhstan

In conventional pyrometallurgical reactors, aggressive liquid slags, salts and metals attack refractory materials leading to the continuous dissolution of the refractory. Refractories are mainly used as a thermal insulator as well as providing resistance to the chemical corrosion. The presence of corrosive slags, forced convection, and high process temperatures in the pyrometallurgical reactors can lead to the rapid degradation of the lining; imposing extra costs on processing in terms of downtime and repair costs.

The focus of the present study is on the detailed characterisation of the phase chemistry and slag interactions with refractories. As a result of characterisation of end-of-life industrial refractory samples and selected experimental studies a new methodology has been developed that can be used to enhance refractory life. The systematic approach includes the analysis of “as received” slag samples from smelters, post-mortem analysis, isothermal laboratory tests under controlled conditions, and FactSage predictions in order to predict the conditions for minimum refractory wear.

The chemical dissolution of refractory into the slag occurs through infiltration of liquid into refractory via pores as well as selective attack of the refractory components. As a result of the refractory slag interaction, the chemical reaction products are a new solid phase(s), or a liquid phase (direct dissolution), or a combination of both liquid and solid phases. This study focuses on the modification of the slag chemistry to prevent the direct dissolution of refractory components into the slag and also to block the pores with newly formed solid phases. It has been shown that with accurate information on the slag/refractory phase equilibrium self-healing refractory systems can be designed and operated by judicious selection of the slag composition to obtain optimum slag/refractory combinations.
O156) AN INVESTIGATION ON THE CORROSION RESISTANCE OF ALUMINA-SPINEL REFRACTORY CASTABLE CONTAINING CALCIUM MAGNESIUM ALUMINATE CEMENT

Tan, X.(1); Li, N.(1); Yan, W.(1);
(1): Wuhan University of Science and Technology, Wuhan, China

This work addressed the using alternative binders (calcium magnesium aluminate cement (CMA) or calcium aluminate cement (CAC)) in alumina-spinel castables containing different microsilica content (0 wt% or 1 wt%), in order to evaluate the influence of microstructure evolution on the corrosion resistance properties of final products. The static crucible test by convert slag (C/S=2) were conducted, and XRD, SEM and thermodynamic calculation etc. were carried out. The results showed that adding microsilica (1wt%) decreased the apparent porosity and the median pore size of matrix of castables in the same binder system. Meanwhile for same microsilica content, the apparent porosity and the median pore size of matrix in the CMA-bonded castables were smaller than that of CAC-boned castables. Furthermore, the results indicated that CMA-boned castables shown better corrosion resistance than that of CAC-boned castables. The optimized matrix distribution of micro-crystal spinel and reasonable pore size distribution were obtained in CMA-boned castables. And the refine texture was responsible for the improvement in the corrosion resistance performances.
O157) OPTIMIZATION OF LADLE REFRACTORY LINING, GAP AND CRACK DETECTION, LINING SURFACE TEMPERATURE AND SAND FILLING OF THE LADLE-TAPHOLE BY MEANS OF A 3D-LASERPROFILE-MEASUREMENT-SYSTEM THAT IS IMMERSED IN TO A HOT LADLE TO EVALUATE THE ENTIRE CONDITION

Lamm, R.(1); Kirchhoff, S.(1); (1): Minteq International GmbH, Duisburg, Germany

The new developed Laser-Measuring system shows a unique way to measure refractory lining thickness and 3D-profile in hot steel casting ladles from inside the ladle. The Laser-measuring system has an innovative, yet simple and rugged design that allows immersion of a laser head into a hot Steel Casting Ladle with surrounding temperatures of more than 1100 °C and surface temperatures up to 1700°C. The system’s laser-beam rapidly scans the lining thickness of the entire surface, collecting millions of data points that are generated in a wide range of computer displays from simple tabular reporting to a virtual walk-through of configurable 3D images. Due to the optimal Scan Angle Gap and crack detection is possible as well as Determination of critical areas below the slag line which cannot be seen by conventional laser technology from outside the ladle. By means of precise determination of the taphole-geometry an automated sand filling of the tap hole can be made. This new development allows steel makers to measure refractory-lining thickness in Steel casting ladles in less than three minutes, This measuring system can provide steel makers with improved safety, increased ladle availability and capacity, extended refractory life and cost savings in energy, material and the maintenance of hot Steel Casting Ladles.

O158) MECHANISMS OF PT-RH THERMOCOUPLE FAILURE BY GASEOUS PHOSPHOROUS IN HIGH TEMPERATURE PROCESSES

Nakano, A.(1); Nakano, J.(1); Bennett, J.(2); (1): U.S. Department of Energy National Energy Technology Laboratory; AECOM, Albany, USA (2): U.S. Department of Energy National Energy Technology Laboratory, Albany, USA

Thermocouples are the sensor of choice for monitoring high temperature process. Sensor failure can be caused by a number of reasons related to severe service environments; including slag attack, abrasive wear, shear, protection tube failure, and vapor attack. Depending on the industrial process being monitored, post-modern analysis of a failed thermocouple assembly to determine causes of failure cannot always be conclusive because process disruption is not always possible. The gasification of coal occurs at temperatures from 1300-1575 °C, with H2 and CO (syngas) production being critical for power or chemical generation. In severe service environments thermocouples are placed in protection assemblies that are in contact with refractory
liners and the process. Refractory lining shifts or the nature of the process can cause breakage or failure of the thermocouple protection assembly, allowing the corrosive gaseous environment of a process to contact thermocouple wires. Corrosive gases in gasifier originate from the carbon feedstock or refractories - materials that can contain arsenic, sulfur, phosphorous and other impurities. Current research investigated the effects of phosphorous gas on the Pt-Rh thermocouple degradation. Gaseous phosphorous interactions with a type-B thermocouple conducted non-isothermally by heating to 1500 °C and isothermally at 1012 °C in high temperature resistance furnace. CO and CO2 gases were used to simulate reducing environment similar to those in industrial gasifier and to promote evolution of phosphorus gas. Separately, individual Pt wires with varying Rh contents were tested isothermally in the phosphorous rich reducing environment with different exposure times. The analysis revealed the material degradation was caused by a combination of Pt liquidus lowering and the intermediate phase formation at grain boundaries or gas/solid interfaces. The phosphorous diffusion in the Pt-Rhx alloys depended on Rh contents. In the low Rh (0, 6, 10 wt.%) alloys, intergranular diffusion was dominant, while intragranular diffusion was governing the P transport in the high Rh alloys (30 wt.%) due to higher interactions with Rh. Upon isothermal P exposure, the Rh2P intermediate phase formed in all the wires containing Rh, and the pure Pt wire extensively melted at grain boundaries due to phosphorous enrichment within one minute exposure contributing to material degradation. Mechanisms of ultimate thermocouple failure by phosphorous are proposed.
PCH) PETROCHEMICAL

O160) CHARACTERISATION OF THERMO-MECHANICAL BEHAVIOUR OF HIGH ALUMINA REFRACTORIES FOR SECONDARY REFORMER APPLICATION

Dey, R.(1); Neelapu, R.(1); V T, E.(1); Paul, S.(1);
(1): CARBORUNDUM UNIVERSAL LIMITED, CHENNAI, INDIA

In the secondary reformer, high density, high alumina (99% & more) refractory used in hot face from the burner down to the diffuser cone and to the catalyst dome support. High Alumina hexagonal target tiles are commonly used in the secondary reformer as bed topping media. Refractories are subjected to severe reducing atmosphere, Corrosion, Thermal Gradient and Load Deformation. Therefore the refractory has to be made specially with high purity & careful selection of raw materials & adequate process control.

The high alumina content, low impurity such as silica and high strength of high alumina refractory is ideal for high temperature and steam applications. Processing of high alumina refractories discussed here with various high purity raw material aggregates. Effect of Sintering temperatures vis-à-vis mechanical strength properties studied. Characterisation of microstructural properties and thermo-mechanical properties of developed high alumina refractory shared in this paper.
PO) POSTER

P01) THE DAMAGE MECHANISM OF SiC-MULLITE BRICK IN CEMENT INDUSTRY

Zhou, Y.(1); Liu, X.(1); Wang, J.(1); Chen, S.(1); Yuan, L.(1);
(1): Ruitai Materials Technology, Beijing, China

SiC-Mullite bricks is widely in upper and latter transitional zone of cement kilns, due to excellent thermal shock resistance, abrasion-resistance and erosion resistance. This essay will focus on SiC-mullite 1680 in the transition zone of 5000 t/d large dry-process cement rotary kiln and explore erosion mechanism by layers connected with Portland cement clink in the upper transitional zone. The brick (the thickness is 220mm) is divided into four parts equally, XRD and SEM is employed to analysis phases changes and relative variable in chemical composition (including mullite, SiC, Fe2O3, K2O and Na2O) of different depth of the SiC-mullite brick; and reaction products between cement clinker and the brick. The results reveal that potassium contained in alkali salt reacted with corundum and mullite phase to produce KAlSi2O6 and KAlO4 of low melting point, which severely influence alkali-resistance and thermal-shock resistance of this brick. Moreover, SiC contained in the reaction layer was oxidized seriously, and the difference of thermal conductivity in different depth of the brick lead to the formation of distortion strain. Therefore the impact of alkali salt and partly oxidation of SiC are the main causes for damage of SiC-mullite brick.

P02) APPLICATION OF ALTERNATIVE ENERGY IN CEMENT INDUSTRY

Liu, X.(1); Zhou, Y.(1); Yuan, L.(1); Wang, J.(1); Chen, S.(1);
(1): Ruitai Materials Technology, Beijing, China

One of the main characteristics of the second generation new dry process cement technology is wates disposal harmless and resources utilization technology, which point out that the utilization rate of alternative energy in cement industry reaches 40% for developed countries, while China cement groups do not have experience in managing alternative fuels. This essay discussed application of alternative fuels, such as petrol coke, used tire and municipal solid waste, and their impact on refractory.

P03) PREPARATION AND CHARACTERIZATION OF LOW COST POROUS CERAMISITE ADSORBENTS BASED ON FORSTERITE POWDERS AND PORCELAIN INSULATORS WASTES

Li, G.(1); Li, S.(2); Li, Y.(1); Xu, N.(1);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan, (2): The State Key Laboratory of Refractories and Metallurgy, Wuhan, China

The high cost of activated carbon adsorbents and secondary pollution produced by modified adsorbents encourage experts to search for more environmental friendly
adsorbents. In this work, Novel porous ceramisites adsorbents with high porosity and strength were prepared using low cost forsterite powders and porcelain insulators wastes as main raw materials. The paper attempts to discuss the effects of compositions and firing temperature on the physical properties, especially the influences of liquid phases. When the firing temperature is 1050 °C, the ratio of forsterite powders to porcelain insulators wastes is 36:54, samples show better complex properties with strength of 119 N, apparent porosity of 51%, closed porosity of 2.12%, bulk density of 1.27 g·cm⁻³, water adsorption ratio of 40.17%, solubility in hydrochloric acid of 7.59%. The porous ceramisite adsorbents are able to remove Cu²⁺ in the polluted water. The adsorption between adsorbent and adsorbate is well fitted with Freundlich model, indicating that the adsorption of Cu²⁺ on the surface of adsorbent belongs to multilayer adsorption. The work has a broad application prospect in sewage treatment and comprehensive utilization of resources. The high cost of carbon adsorbents and second pollution of modified adsorbents encourage experts to search for more environmental friendly adsorbents. In this work, Novel porous ceramisites adsorbents were prepared using low cost forsterite powders and porcelain insulators wastes as main raw materials with high porosity and strength. The paper attempts to discuss the effects of compositions and firing temperature on the physical properties, especially the influences of liquid phases. The sample with forsterite powders and porcelain insulators wastes ratio of 36:54 firing at 1050 °C have better complex properties with strength of 119 N, apparent porosity of 51%, closed porosity of 2.12%, bulk density of 1.27 g·cm⁻³, water adsorption ratio of 40.17%, solubility in hydrochloric acid of 7.59%. The porous ceramisite adsorbents are able to remove Cu²⁺ in the polluted water. The adsorption between adsorbent and adsorbate is well fitted with Freundlich model, indicating that the adsorption of Cu²⁺ on the surface of adsorbent belongs to multilayer adsorption. The work has a broad application prospect in sewage treatment and comprehensive utilization of resources.

P04) REACTION OF SOME OXIDE CERAMICS WITH MOLTEN ALUMINUM

Ohya, Y.(1); Ishii, Y.(1); Ban, T.(2);
(1): Gifu University, Gifu, Japan (2): Gifu University, Gifu, Japan

Introduction

Molten aluminum is very reactive and it reduces many oxide ceramics. In order to prevent and/or expect the reduction reaction of oxides by molten aluminum, an “Ellingham diagram” offers crucial guide and is usually used for a selection and modification of the refractory materials. According to the Ellingham diagram, TiO₂ should be reduced and, MgO and Y₂O₃ should not be reduced by molten aluminum. In an actual reaction of the oxide ceramics with molten aluminum, a reaction interface between them is very important and should influence the reaction. Here we report our results of the reaction of TiO₂, Y₂Ti₂O₇, Y₂O₃, and MgO ceramics with molten aluminum.

Material and Methods
Raw materials used were TiO2, Y2O3 and MgO powders of high purity and they were CIPed into disks of 10mm diameter by 100MPa and then fired at 1500°C for 2h to obtain dense ceramics. The relative densities of the TiO2, Y2O3 and MgO ceramics were 85, 94 and 93%, respectively. Y2Ti2O7 ceramic was fabricated by mixing TiO2 and Y2O3 in a ball mill, and CIPed, then fired at 1500°C 2h. The resultant Y2Ti2O7 ceramic was 83% of its theoretical density. The fired ceramic was set in an alumina tube. Aluminum rod of 99% pure was set on the ceramic in the alumina tube. Then it was heated at 1000°C for 25h in N2 gas flowing atmosphere. After the reaction experiment, it was cut and polished for microstructural observation using SEM and EDX. Another sample after the reaction was treated with aqueous NaOH solution to remove aluminum and the sediment was analyzed.

Results and Conclusions

Among the four oxide ceramics tested, TiO2 and Y2Ti2O7 ones were not reacted severely. It is attributed to a formation of corundum layer at the interface between the ceramics and molten aluminum. The thickness of the corundum layer formed on the TiO2 ceramic was only 1-2mm. Obviously the corundum layer was the result of the reduction of Ti4+ by aluminum and the layer prevented further reduction of TiO2 and Y2Ti2O7 ceramics.

Y2O3 ceramic was reacted with molten aluminum to form intermetallic compound of YAl3, which was detected in the precipitate after aqueous NaOH treatment. The remains of the ceramic consisted of YAlO3 and Y3Al5O12, and aluminum also existed inside the remains. It means that Y3+ ion was reduced by molten aluminum to form YAl3, which melted at the experiment temperature of 1000°C. This is not expected from the Ellingham diagram, because the diagram does not include any information on intermetallics, such as YAl3.

MgO ceramic reacted with molten aluminum and spinel layer was formed at the interface. The thermodynamic calculation, 4MgO + 2Al → MgAl2O4 + 3Mg, is 66kJ at 1298K. In order to realize a reason of the formation of spinel, a formation of melt consisted of aluminum and magnesium should be a key.

P05) RESEARCH ON SLAG RESISTANCE OF AL2O3-CR2O3 REFRACTORIES UNDER TEMPERATURE FLUCTUATION CONDITION

Honggang, S.(1); Hongxia, L.(1); Pengtao, L.(1); Shixian, Z.(1);
(1): Sinosteel Luoyang Institute of Refractories Research Co., Ltd., Luoyang, China

Al2O3-Cr2O3 refractories have been widely used in the harsh areas of thermal equipments such as petrochemical and steelmaking due to their excellent slag corrosion resistance. Molten slag, which is the primary cause of Al2O3-Cr2O3 refractories degradation, has great effect on the corrosion of refractories at high temperature with thermal fluctuation. To discuss the comprehensive effects of chromium oxide content, additives and microstructure on the slag resistance of Al2O3-Cr2O3, eight kinds of commercial Al2O3-Cr2O3 refractories were selected with Cr2O3 mass fraction of 10%,
12%, 30%, 50%, 60%, 75%, 90% and 95%, respectively. Some of the specimens had small amount of zirconia as an additive, and some had the microstructure with microporous. All the specimens were installed in the same rotary slag-resistant furnace, using intermittent heating process to realize the test temperature fluctuated between 200 °C and 1600 °C. By adding CaO-SiO2-Al2O3-Fe2O3-MgO slag as the corrosion slag, the corrosion resistance of Al2O3-Cr2O3 refractories was researched under the simulated thermal fluctuation condition. The erosion degree and thermal shock fracture of corroded refractories were evaluated through observation and measurement. The microstructure and chemical composition of the specimens were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The pore size distribution of virgin refractories were measured by mercury porosimetry. The interfacial reactions of refractory materials with slag were investigated by thermodynamic modeling using FactSageTM software. The results showed that the degradation of Al2O3-Cr2O3 refractories was affected by comprehensive factors, including chemical erosion, physical dissolution, thermal spalling caused by penetration. With the increase of Cr2O3 content, the slag corrosion rate of Al2O3-Cr2O3 material decreased, which indicated that the Cr2O3 content played a decisive role in the slag resistance of Al2O3-Cr2O3 material. Dense spinel layer was formed by the reaction of Cr2O3 with Fe2O3 and MgO, which had a high melting point and prevented the further infiltration of slag into the materials. Thermodynamic evaluation also showed that the content of Cr2O3 in refractories had a significant influence on the formation of dense spinel layer. Moreover, the additives had benefit on improving the slag penetration resistance because it effectively suppressed the microcrack propagations under the condition of temperature fluctuation. Additionally, microporous structure improved the slag penetration resistance and thermal shock resistance of the materials. Therefore, it will be also an effective way to promote slag resistance of Al2O3-Cr2O3 refractories with lower content of Cr2O3 by the designation and preparation of microporous structural materials.

**P06) EFFECT OF PARTICLE SIZES OF PREHEATING ANDALUSITE AGGREGATE ON THE PROPERTIES OF MULLITE-BASED REFRACTORY**

Wang, Q.(1); Tang, W.(2); Wang, X.(1); Li, L.(1); Liao, G.(1); Ye, G.(2); (1): School of Materials Science and Engineering, Luoyang Institute of Science and Technology, Luoyang, People’s Republic of China (2): School of Materials Science and Engineering, Zhengzhou University, Zhengzhou, People’s Republic of China

In this work, the different particle sizes (5-3mm, 3-1mm, <1mm) of andalusite aggregate were preheated at 1400°C for 3h to substitute the same size of mullite aggregates in mullite-based refractory. And the cold mechanical strength and thermal shock resistance of these mullite-based samples, after firing at 1430°C for 3h, were investigated in the light of phase evolution and microstructure development. The results showed that the residual andalusite in the preheated andalusite aggregate played the role on the properties of fired samples. And the increased particle size of andalusite aggregate induced the improved thermal shock resistance and the deceased mechanical strength, due to the microcracking network resulting from the anisotropic characteristic of andalusite crystals.
**P07) INFLUENCE OF PORE SIZE DISTRIBUTION OF ALUMINA BRICK ON STRENGTH BY REGRESSION ANALYSIS METHOD**

Yang, X.(1); Deng, C.(1); Zhu, H.(1); Yu, C.(1); Ding, J.(1);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China

Influence of pore size distribution of alumina brick on its modulus of rupture (MOR) and cold crushing strength (CCS) at room temperature was studied with regression analysis method, respectively. The pore size distribution of specimens were characterized by scanning electron microscope (SEM), mercury intrusion porosimetry (MIP), and the strength was tested by universal strength tester. The results show that the pore size distribution of alumina brick was not homogeneous, though the apparent porosity (A.P) almost no difference. The little difference of pore size distribution of specimens contributed immeasurably to dispersion of MOR, especially of CCS. At the end, analyzed the influence coefficient of each interval of pore size distribution to MOR and CCS.

**P08) CHARACTERISTICS AND CORROSION BEHAVIOR ON REFRACTORIES OF MOLTEN SLAG UNDER ELECTROMAGNETIC FIELD**

Lian, P.(1); Huang, A.(1); Gu, H.(1); Zou, Y.(1); Wang, Y.(1); Fu, L.(1);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, P.R.China

Electromagnetic technology has been widely used in metallurgical process of high quality steel and alloy material. It can improve the cleanliness of molten steel, ensure the quality of steel and increase productivity. However, electromagnetic smelting seriously affects the high temperature corrosion behavior of molten slag, which not only reduces the service life of refractory materials, but also has a negative effect on the quality of molten steel. In the paper, a resistance furnace with controllable electromagnetic field was design and made, the numerical simulation in combination with the high temperature thermal simulation experiment was applied, the slag properties such as viscosity was investigated under the conditions of high temperature and electromagnetic field, the influence of slag composition and the emulsified metal were discussed. And the slag corrosion behavior on refractories was analyzed by means of the X-ray diffraction and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX). The results show that, the spreadability and viscosity of the molten slag can be improved by optimizing the slag composition and the magnetic intensity; In the electromagnetic field with proper parameters, the slag containing a certain magnetic metal has a relatively large viscosity, show smaller spreading area at the bottom of the crucible and slight infiltration and corrosion on refractory materials.

**P09) DETERMINATION OF QUANTITATIVE PHASE ANALYSIS RESULTS OF SINTERED MULLITE BY RIETVELD FULL SPECTRUM FITTING**

Xu, J.(1); Zhou, S.(1); Yin, Y.(1);
(1): Wuhan University of Science and Technology, Wuhan, P.R.China
Mullite, \( \text{Al}_2[\text{Al}_2+2\text{Si}_2-2x]\text{O}_{10-x}(0.17 \leq x \leq 0.59) \), is a non-stoichiometric compound in \( \text{Al}_2\text{O}_3\)-SiO2 system, represents a series of alumina silicate minerals without certain chemical compositions, which also cause the different X-ray diffraction patterns of mullite. Therefore, 5 different mullite references were given in the databank of commercial software of Siroquant for quantitative phase composition analysis of materials. When performing quantitative phase composition analysis of sintered mullite, the test results of mullite contents are always different from each other if a mullite reference or combination of them was selected. With the addition of spike phase, such as ZnO, the glass contents determined by siroquant were also present big divatation by inputing the weighted content of spike phase initially. This may indicates difference between the used reference mullite structure and actual mullite structure of sample affect the analysis results significantly. With the aim to improve the accuracy of phase composition analysis results of sintered mullite by Siroquant software, ZnO was added as a reference material, and the minimum relative standard deviation (MRSD) method based on least squares criterion principle was used to determine the analysis results. Data statistics and results analysis show that the most possible mullite structure of samples could be determined by using the MRSD method, and meanwhile, this method can also improve the accuracy of measured glass content to that of chemical method.

**P10) THE EFFECTS OF B2O3 CONTENT ON THE PROPERTIES OF ALUMINA-MAGNESIA DRY RAMMING MATERIALS**

Song, Y.(1); Zhu, H.(1); Deng, C.(1); Ding, S.(1);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China

The paper explored the effect of appropriate number of B2O3 on the properties of alumina-magnesia dry ramming materials through analysis of its phases, morphology of the samples fired at a high temperature with different amounts of B2O3. Different sizes of corundum, \( \alpha\text{-Al}_2\text{O}_3 \) powder and fused magnesia were used as raw materials, boron oxide as binding agent and a hand-ramming molding method to keep its shape. The test results of the samples fired at 1600 °C for 3h showed that the most appropriate amount of B2O3 addition was 1.5wt%, at this condition, the Al2O3 and MgO reacted with each other to generate a great amount of aluminum-magnesium spinel with the size ranging from 3μm to 15μm. Some of the alumina-magnesia spinel were closely combined together for sintering and crystallization, and the ones of small size showed a more regular shape.

**P11) SYNTHESIS OF \( \alpha\text{-SI}_3\text{N}_4 \) POWDER BY MOLTEN SALT CATALYTIC NITRIDATION**

Chai, Z.(1); Ding, J.(1); Deng, C.(1); Zhu, H.(1); Yu, C.(1); Kan, X.(1);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China
In this paper, it was intended that reducing the cost of Si3N4 powder according to the application prospect of Si3N4 ceramic. Using Fe micro powder as catalyst, the α-Si3N4 powder was prepared by molten salt catalytic nitridation in the NaCl-NaF molten salt media. The effects of nitridation temperatures and the content of catalyst on nitridation of Si powder were investigated. Moreover, the composition and microstructure of samples were characterized by XRD, XPS, SEM and TEM. The results showed that addition of 2 wt% Fe powder, the nitridation of Si powder was completed after 5 h nitridation at 1250 °C in the NaCl-NaF eutectic salts. The crystal morphologies of as-prepared α-Si3N4 were in the presentation of anomalous and short rod in the samples.

**P12) SYNTHESIS AND CHARACTERIZATION AL2OC–SIC COMPOSITES BY CARBOTHERMAL REDUCTION**

Chen, K.(1); Yu, C.(1); Zhu, H.(1); Deng, C.(1); Ding, J.(1);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China

Al2OC–SiC composites were synthesized using a mixture of α–alumina, silica, carbon black and magnesium oxide as the starting materials. The effects of heating temperature and MgO addition on Al2OC–SiC composites formation were investigated. The results showed that Al4O4C formed as intermediate product when the batch mixture was heated in argon atmosphere, and MgO addition accelerated the synthesis reaction for Al2OC–SiC composites. The synthesized powders consisted of plate-like Al2OC and whisker-like SiC. The oxidation characteristics of Al2OC–SiC composites was measured by TG method.

**P13) STRENGTHENING AND TOUGHENING OF MULLITE-SILICON CARBIDE MATERIALS FOR CDQ**

Zhang, M.(1); Ni, K.(1); Gu, H.(1); Li, H.(2); Shao, Z.(2);
(1): The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, Hubei, China (2): Furnace Roof sealing Engineering Co.Ltd. of Yixing City, Yixing, Jiangshu, China

Coke dry quenching (CDQ) is an advanced technology because of the advantages of saving energy and environmentally friendly, but the damage of CDQ furnace ramp pillar seriously affected the safe operation and production efficiency in the CDQ. Therefore, the development of a durable refractory for CDQ furnace ramp pillar is of great significance. The CDQ furnace ramp pillar need withstand great bending stress and thermal stress, but the strength and thermal shock resistance of current mullite-silicon carbide material is poor. In this paper, the toughening effect of the in-situ generated AlN whiskers on mullite-SiC materials were studied and examined. The results show adding the metal aluminum powder into the mullite-SiC materials, the strength and thermal shock resistance of materials increase obviously, especially at the amount of 6wt%. The hexagonal AlN phase formed in materials added with metal aluminium after nitriding at 850°C, and the in-situ AlN whiskers with a length of 2mm~10mm, a diameter of
5nm~100nm generated after nitriding at 1000°C. A network structure of AlN whiskers formed in the matrix material, improved the toughness through whiskers pull out and whiskers federation. The flexural strength of the sample at 1000°C was improved from 9.6MPa to 39.6MPa. Reducing the particle size of metal aluminium powder can promote the generating of AlN whiskers.

**P14) EVALUATING HIGH-TEMPERATURE CORROSION OF SIC REFRACTORIES BY COAL SLAG USING IMPROVED EXPERIMENTAL METHOD**

Zhao, S.(1); Li, H.(1); Cai, B.(1); Sun, H.(1); Wang, G.(1);
(1): State Key Laboratory of Advanced Refractories, Sinosteel Luoyang Institute of Refractories Research Co., Ltd., Luoyang, China

**Abstract:** SiC refractories are currently utilized as lining material for water-cooled gasifier at a service temperature lower than 1300oC. Very few researches have been reported on the corrosion of SiC materials at even higher temperature. Furthermore, the standard test method for rotary slag testing of refractory materials can not simulate the real gasification atmosphere, which may lead to inaccuracy of evaluation results. In this paper, corrosion behavior of SSiC and Si3N4-SiC refractories by coal slag was investigated at 1500oC under reducing atmosphere using improved rotary slag testing method. Moreover, interactions between refractory materials and molten slag were also predicted by thermodynamic calculations using modified model under the same conditions. The results showed that SSiC and Si3N4-SiC refractories presented the similar stability and corrosion behavior under simulated gasification conditions. The porous materials showed small amounts of slag infiltration but obvious oxidation reactions. SiC reacted with FeO to form Si-Fe-C alloy on the surface of the corroded materials. Meanwhile, SiO2 phase was also formed by oxidation of SiC in the experimental atmosphere and then dissolved into molten slag eventually. The thermodynamic calculation results matched well to the experimental observations.
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