

MATRIX DESIGN FOR IMPROVED SPINEL FORMATION IN HIGH ALUMINA REFRACTORY MONOLITHICS THAT IS ADJUSTED TO THE SERVICE CONDITIONS

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ABSTRACT

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. 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 enable a goal oriented strengthening of the 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 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 and the particle size distribution seem 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. But the grain size of spinel and its distribution is essential, too. This is proved by electronic microscopy examinations. Overall these results will provide very valuable information for an intelligent matrix design for an improved spinel formation adjusted to service conditions.

Keywords: refractory castable, spinel forming, matrix design

INTRODUCTION

Refractory linings are necessary for many industrial processes, e.g. production of iron and steel, glass, cement, ceramics, energy generation, etc., and are exposed to severe working conditions. Thermal cycling and the corrosive attack by basic slags is a harsh environment for steel ladle refractories. Spinel containing castables linings have been used in secondary steelmaking vessels due to their outstanding chemical and thermo-mechanical properties [1][2]. The addition of spinel in high alumina refractory castables can be carried out in two different ways: as pre-formed raw material or by the in-situ matrix reaction by Al₂O₃ and MgO at temperatures above 1100 °C [3].

Preformed spinel is added to alumina castables for two major purposes: To increase the slag resistance and to improve the thermo-mechanical properties. The spinel containing castables show less penetration and less corrosion when compared to the pure alumina mixtures [4]. The optimal spinel content is in the range of 15 to 30 wt.-%. Preferred is a content between 20 and 25 wt.-%. If the amount of spinel is too small, it results in a higher corrosion rate whereas, if the amount is too high, this leads to high penetration because the spinel does not react with the infiltrating slag. In comparison to stoichiometric spinel, Alumina rich spinels provide several advantages [3][5][6][7]. An important aspect is the

grain size distribution of spinel. Spinel must be added predominantly to the fine fraction of the castable formulation to attain the best penetration resistance based on industrial experience over the past 20 years. A spinel containing matrix improves the corrosion behaviour of a castable independently, whether the spinel has been added as such to the matrix, or it developed in-situ due to the reaction of alumina with added fine magnesia. Two important aspects for improved corrosion resistance are the total amount of spinel and its distribution with respect to particle size [8].

When forming spinel by an in-situ matrix reaction, the attained spinel is finer and better dispersed in the matrix, which leads to a higher corrosion rate [3][9]. The formation of spinel is followed by a volumetric expansion, resulting in better thermo-mechanical performance, which is a consequence of the compressive thermal stresses generated and the activation of {111}-slip planes. On the other hand, a not well designed spinel expansion could lead to microcracking and lower slag penetration resistance [10]. The in-situ spinel formation expansive behaviour is commonly attributed to the density differences between the reactants and the product (MgO 3.58 g/cm³, Al₂O₃ 3.98g/cm³ and MgAl₂O₄ 3.60 g/cm³). It leads to a volumetric expansion close to 8 % and a linear one of 2.6 % for a stoichiometric alumina-magnesia mixture [11][12]. The formulation of spinel forming alumina-magnesia castables requires different approaches. The use of magnesia as one of the reactants for the spinel formation in castables often causes difficulties like poor flow due to different surface charge or quick setting due to magnesia hydration. Furthermore, the volume expansion caused by the hydration may lead to cracking during the drying step, which is critical when producing pre-cast shapes. The volume expansion of in-situ formed spinel needs to be controlled. Too high expansion leads to mechanical stresses and thus spalling of the lining [13]. By adding pre-formed spinel particles, the inherent chemical benefits related to this phase can be attained at temperatures below 1100 °C and the hydrated problems are inhibited as no free MgO is added to the composition [14]. These compositions also present good volumetric stability as no in-situ spinel formation takes place, which makes them a suitable option in some applications where only small expansion is acceptable [15]. The main drawback of this option is the higher cost of pre-formed sintered or fused spinels. Considering these aspects, the objective of this work is to investigate an alternative way to form in-situ spinels in high-alumina castables by adding different Mg-delivering precursors to the castables formulations. Furthermore, the spinel formation kinetics is investigated.

EXPERIMENTAL SETUP

In previous experiments, different spinel precursors were investigated. Mg-delivering compounds (spinel precursors) were chosen according to their ability to form spinel. In matrix formulations, especially the amount of spinel formed was considered. Highly reactive and dead-burned materials with different particle sizes in different concentrations were tested. The amount of spinel formed after sintering at 1400 °C for 4 h was measured by XRD after grinding. The workability of the pre-selected precursors during the mixing process and the formation rate of spinel, two precursors were determinants for the subsequent steps. Poor flow or quick setting properties caused by magnesia

Table 1. Composition of cement containing high-alumina castable

Castable	MCA_MS0_M0	MCA_MS0.5_M4 (Nedmag)	MCA_MS0.5_M8 (Nedmag)	MCA_MS0_M4 (magnesite)	MCA_MS0_M8 (magnesite)
Tabular alumina					
1.0-3.0 mm	25	25	25	25	25
0.5-1.0 mm	21	21	21	21	21
0.2-0.6 mm	11	11	11	11	11
0.0-0.2 mm	12	12	12	12	12
0.0-0.045 mm	9	4	1	5	1
Calcined alumina	10	10	10	10	10
Reactive alumina	7	7	7	7	7
Microsilica (MS)	0	0.5	0.5	0	0
CA cement	5	5	5	5	5
Nedmag	0	4	8	0	0
Magnesite	0	0	0	4	8

hydration was also investigated by Braulio et al. [13] in further investigations. For this work sintered magnesium oxide (Nedmag DIN70; Nedmag Industries Mining & Manufacturing B.V, Nederland) and a raw magnesite ($MgCO_3$; Magnesia GmbH, Germany) were chosen for further investigation.

Furthermore, the spinel formation kinetics was investigated more into deep. Here the focus was laid on the different type of alumina raw-materials (Almatis GmbH, Germany). Coarse particle fractions have no sufficient reactivity to form spinel because of their low specific surface area. Hence only matrix compounds ($d \leq 45 \mu m$) were contemplated.

The alumina powders were mixed in stoichiometric proportions of spinel (71.67 % Al_2O_3 28.33 % MgO) with Nedmag DIN70. The powders were granulated water-free in an intensive mixer (type EL01, EIRICH). Dilatometric investigations on pressed granulates at 1200 °C with a dwell-time of 2 h were executed to determine the expansion and sintering behaviour.

The investigated Mg-delivering precursors Nedmag DIN70 and $MgCO_3$ were implemented in concretes and replace a part of the matrix. 4 and 8 wt % of precursors were added to the mixtures. The basis for each composition is a high alumina concrete with a defined grain size distribution containing 5 wt.-% of cement. The water content was set to 5.2 wt.-% in the reference material and was adjusted to comparable workability when Mg-precursors were added (Table 1). The concretes were mixed in an intensive mixer (type R05, EIRICH). The material was dry mixed for 1 minute and further 5 minutes after water addition. Format D prisms according to ISO 1927 (160 x 40 x 40 mm) were casted thereafter. The setting and curing were carried out under constant ambient conditions in a climatic cabinet for 48 h (20 °C; 95 %rh). Thereafter the samples were dried at 110 °C for 24 h followed by sintering at 1400 °C for 4 h. Cold Modulus of Rupture and the open porosity in sintered state were measured. The spinel yield after the sintering process was quantified by Rietveld analysis after grinding.

The wedge splitting test was executed supplementary for all formulations listed in Table 1. These measurements were executed at Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany. For this purpose cubic test pieces (100 x 100 x 75 mm³) were prepared in which a starter notch and two guide notches are included. A large groove is machined into the the upper face of the test pieces to mount the mechanism that transmits the load from a wedge onto the test piece. During a test, the vertical force F_M applied by a press originates two horizontal forces F_H by means of a prismatic wedge and the load transmission pieces. The two horizontal forces cause the sample to split. The main advantage of the method is to promote stable propagation of cracks on a large fracture area (circa 65 mm x 65 mm) that is representative of the typical coarse grain structure of refractory products. Micrographs

obtained by scanning electron microscopy (SEM) give useful information about the formation process of the in-situ formed spinel [16].

RESULTS AND DISCUSSION

Results of dilatometric measurements with subsequent Rietveld analysis can be summarized as follows. In all samples the spinel yield obtained at a sintering temperature of 1200 °C was determined with 8 %. As envisaged in Fig. 1, the expansion behaviour of CTC20 and CTC22 is almost identical. Samples prepared with CT3000SG show lower expansion over the whole dwell-time. The smaller particle size distribution of CT3000SG (Fig. 2) and thus the higher specific surface area leads to a higher sinter reactivity and therefore to a higher shrinkage during sintering at 1200 °C.

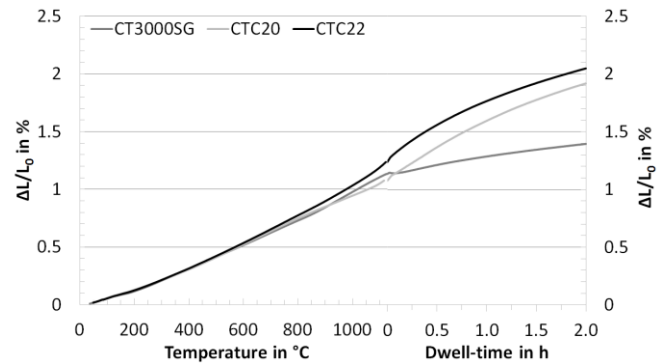


Fig. 1. Thermal behaviour of pressed granulates of stoichiometric mixtures of CTC20, CTC22 and CT3000SG with Nedmag DIN70 at 1200 °C. The results were obtained by means of a modified dilatometer measurement where 1200 °C were held for further 2 hours.

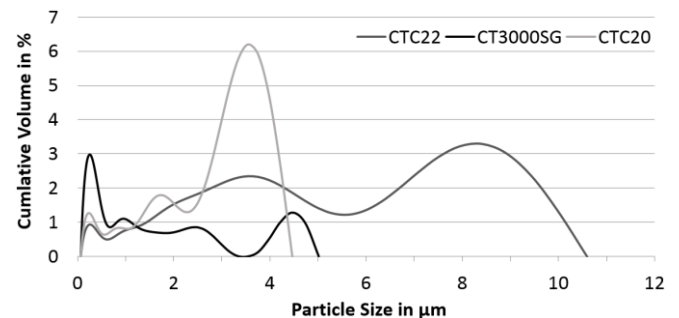


Fig. 2. Particle size distribution of alumina-powders CTC20, CTC22 and CT3000SG

It is assumed that the higher sinterability compensates the expected expansion when 8 wt.-% spinel is formed. Similar results were reported by Braulio et al. [17]. Therefore it appears reasonable to choose the alumina precursor by its sinter activity, because the shrinkage caused by sintering compensates the volume gain when spinel is formed.

In a further step the Mg-precursors Nedmag DIN70 and $MgCO_3$ were implemented in a tabular alumina based refractory LC-castable containing 5 wt.-% CAC as envisaged in Table 1. With increasing amount of Nedmag DIN70 or $MgCO_3$, CMoR decreases systematically (Fig. 3).

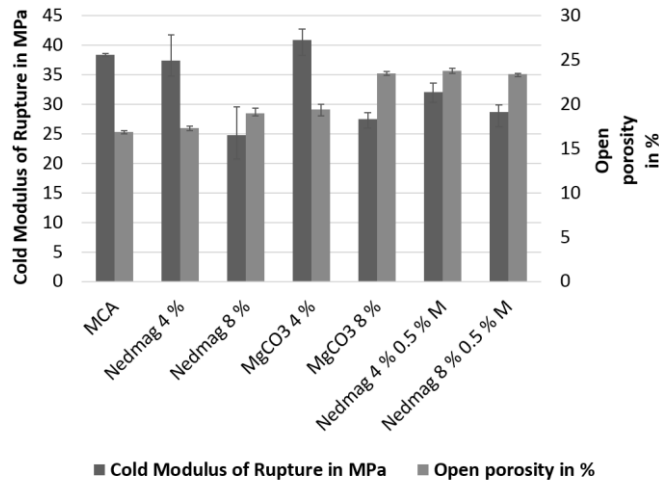


Fig. 3. Cold modulus of rupture and open porosity of cement containing high-alumina concretes with different additions of Nedmag DIN70 und $MgCO_3$ sintered at 1400 °C for 4 h (M = Microsilica)

The highest values for open porosity derived from mixture with 8 % $MgCO_3$ can be explained with a higher water demand that is necessary to disperse the formulation for a sufficient workability. If 8 wt.-% Nedmag DIN70 is added CMoR decreases more pronounced than in case of the addition of $MgCO_3$. The test pieces

even show macrocracks, that lead to reduced mechanical strength due to the brucite formation. This can be avoided if 0.5 wt.-% microsilica is added to the formulations that are prepared with Nedmag DIN70. Microsilica is assumed to impede the formation of brucite that leads to a volume expansion of 53 vol.-% [18]. According to Sako et al. [19], the lower open porosity of the mixtures with microsilica is evoked by the higher flowability and thus densification.

Mineral phases were measured by XRD. It should be noted that $MgCO_3$ leads to less spinel (due to the decarbonisation) when compared to Nedmag DIN70. Despite this, Nedmag DIN70 seems to be more efficient to promote the spinel formation after firing irrespective of the adding of microsilica (Fig. 4).

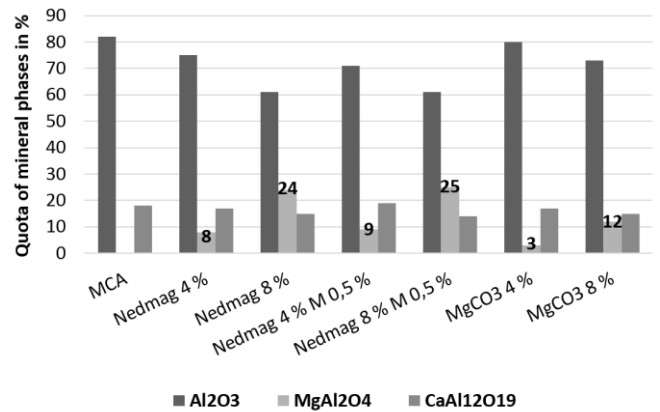


Fig. 4. Spinel yield as a function of different Mg-precursors in high alumina LC-castables that were sintered at 1400 °C for 4 h (M = Microsilica)

Microscopic examinations (Fig. 5) provide valuable informations that help to understand the observed thermomechanical behaviour of the LC-castables. The reference castable without addition of microsilica or spinel precursor (MCA_MS0_M0) displays a straightforward fracture path able to crack large grains (brittle trans-granular fracture). When Nedmag DIN70 and 0.5 % microsilica are added the observed fracture appears much more

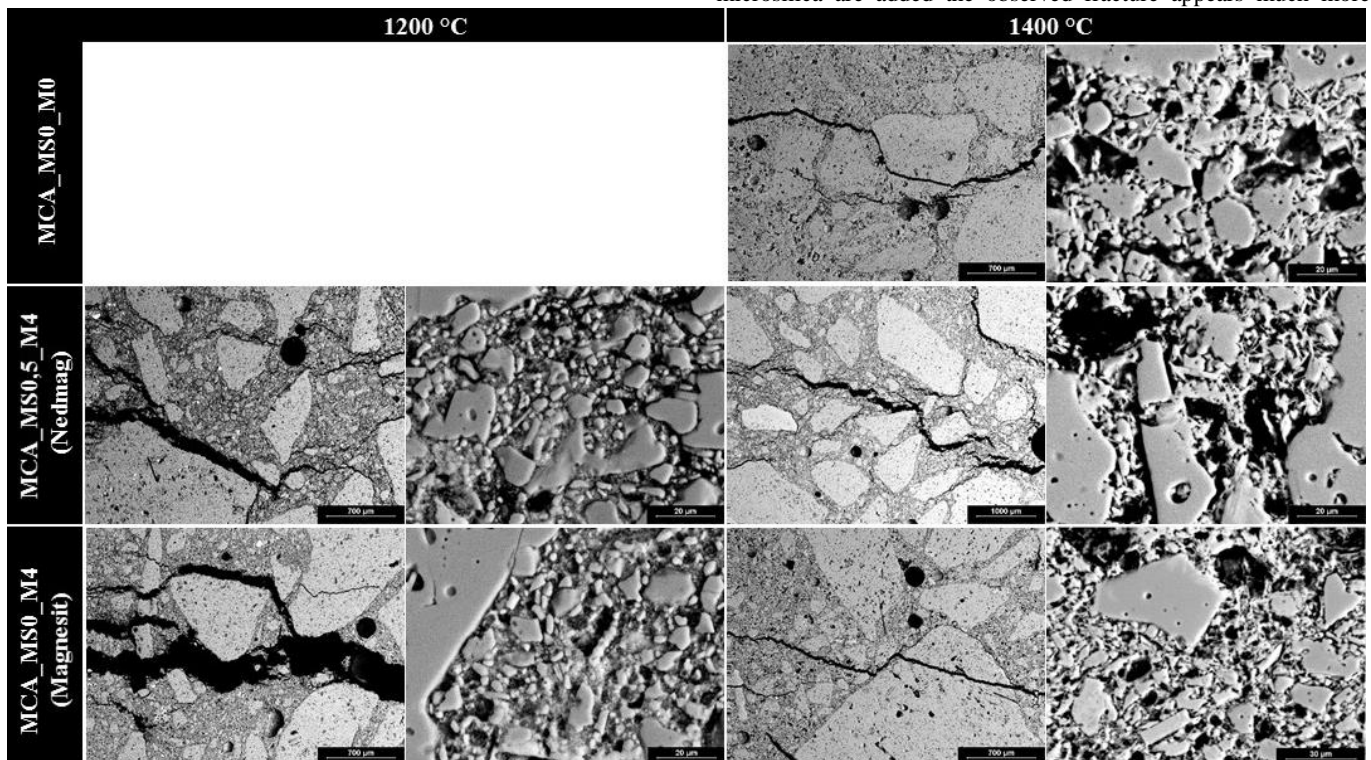


Fig. 5. Microstructural observations (Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany) of the fracture path (30x magnification) and microstructure (1500x magnification) for the reference castable and the castables with 4 % Nedmag DIN70 or magnesite as spinel precursor after wedge splitting tests at 1200 °C and 1400 °C (dwell time 1 hour at the testing temperature) [16]

ductile with no transgranular cracks. Cracks are branching out in the matrix that speaks for a more flexible structure. After soaking at 1400 °C, alumina grains start to interfere with the cement components and forms a liquid phase. The grain shapes get rounded and are covered by a vitreous phase. In further hibonite platelets are extensively formed and some small grains of spinel could be identified.

MgCO₃-containing microsilica-free castables also display extensive cracks branching in the matrix however in contrast to the Nedmag DIN70 containing castable trans-granular cracks occur. This suggested that in this case a stronger matrix/grain bond is still in force even at 1400 °C that improves the flexibility of the material in comparison to the castables where Nedmag is added. As discovered before in the Nedmag DIN70 containing castable, hibonite platelets are present after firing at 1400 °C. Spinel phase, already identified by XRD-measurements, could hardly be identified under the electron microscope. Here the spinel formation only leads to the formation of very small grains because in contrast to the microsilica containing castable no liquid phase is present during the spinel formation. The mass transport is hampered because of the absence of a liquid phase. The grain size of spinel is much smaller and distributed disperse but more homogenous over the matrix. This microstructure leads to a higher strength and structural flexibility as measured with the hot wedge splitting test [16].

CONCLUSION

Dilatometric investigations indicate that the lower the Al₂O₃-particle size, the higher the shrinkage due to sintering. This may compensate the linear expansion due to the spinel formation. When adding the spinel forming additives Nedmag DIN70 and MgCO₃ to a tabular alumina based LC-castable CMoR decreases. If microsilica is added the formation of brucite can be prevented in case of Nedmag DIN70 addition. Generally, it can be stated, that in comparison to MgCO₃, Nedmag DIN70 seems to be more efficient to promote a spinel formation after firing. However, the grain size and distribution of spinel must be considered. The reference LC-castable without microsilica or spinel precursor behaves, as expected, brittle up to at least 1400 °C. The addition of spinel precursor (Nedmag DIN70 or magnesite) leads to extensively improved flexibility of the system at temperatures higher than 1200 °C. This correlates with the formation of spinel that intensifies in this temperature range within the matrix. Crack branching provides more flexibility and avoids rupture of the castable. The ceramic structure obtain an elevated mechanical strength. Addition of microsilica, necessary to avoid the crack formation due to the brucite formation during setting and curing of the castable, leads to a significant strength decrease above 1200 °C. This is due to the formation of a liquid phase that weakens the matrix bonding of the castable. A spinel forming microsilica-free formulation was developed by using magnesite as spinel precursor. Crack free test pieces could be manufactured that display high mechanical stability and structural flexibility up to at least 1400 °C. Crack branching as well as inter-granular cracks can be observed in castables where 4 wt.-% MgCO₃ were added. In this case, the disperse and homogenous distribution of spinel in the matrix obviously improve the strength and structural flexibility of the castable without the formation of a liquid phase. This in further increases the thermal stability even at temperature higher than 1400 °C.

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