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Improved high temperature thermal shock resistance of high alumina refractory monolithics thanks to *in-situ* spinel formation in a smart matrix

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Abstract

In all discontinuous thermal processes, refractory linings are exposed to thermo-mechanical stress that is often responsible for premature wear. This is especially significant for monolithic refractory materials that are typically still in the 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 and a sintered layer or zone is subsequently only formed at the hot face of the monolithic lining. Further away from the hot face, the monolithic lining remains in an unfinished state. In this weak area, the material consists therefore of an unfinished ceramic structure. Especially a zone beneath the sintered one is critical, because in this zone the thermo-mechanical impact is still high. Thermo-mechanically induced spalling is typically initiated in this zone. A smart matrix design including the particle size distribution and the spinel precursor materials allows to adjust the formation velocity and the appearance of spinel in dependence of the temperature. Distinct amounts of low temperature spinel strengthen the weak zone in the lining. Dead burned magnesia (MgO) and a raw magnesite ($MgCO_3$) were implemented in different amounts into cement-containing and cement-free concretes. The influence on physical properties like cold modulus of rupture CMoR, the yield of spinel formed and the ductility during heat treatment were investigated. Generally speaking, 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 the presence of impurities of the alumina fines impact the spinel formation. By adding the spinel precursors to high alumina concretes, the CMoR is influenced. In comparison to $MgCO_3$, MgO seems to be more efficient in promoting the formation of spinel. For an improvement of the thermal shock behaviour, not only the amount of spinel but also the fineness and its distribution play a decisive role. Overall, this information provides a valuable indication for an intelligent matrix design for improved spinel formation adjusted to service conditions.

Keywords: Refractory castable, Spinel forming, Matrix design

POLEPSZONA WYSOKOTEMPERATUROWA ODPORNOŚĆ NA WSTRZĄS CIEPLNY WYSOKOKORUNDOWYCH MONOLITÓW OGNIOTRWAŁYCH DZIĘKI TWORZENIU SIĘ IN-SITU SPINELU W INTELIGENTNEJ OSNOWIE

We wszystkich nieciągłych procesach cieplnych wyłożenia ogniotrwałe wystawiane są na działanie naprężenia cieplno-mechanicznego, które często odpowiedzialne jest za przedwczesne zużycie. Jest to szczególnie warte odnotowania w przypadku monolitycznych materiałów ogniotrwałych, które są w sposób typowy stabilne w stanie surowym przed pierwszym ogrzaniem. Już dawno temu spinel został zidentyfikowany jak ważny czynnik pozwalający uniknąć zniszczenia materiału spowodowanego przez naprężenie cieplne. Znaczące polepszenie pokazują w szczególności ogniotrwałe monolity wysokokorundowe wytwarzające spinel. Jednak podczas użytkowania monolityczne wyłożenia wystawiane są na działanie gradientu temperatur i w wyniku tego warstwa lub strefa spieczona jest tylko tworzona na gorącej stronie monolitycznego wyłożenia. Daleko dalej od strony gorącej monolityczne wyłożenie pozostaje w stanie niedokończonym. W tym słabym obszarze dlatego, materiał składa się z niedokończonej struktury ceramicznej. Szczególnie krytyczna jest strefa tuż pod strefą spieczoną ponieważ w tej strefie szczególnie mocne jest uderzenie termo-mechaniczne. Łuszczenie wywołane termo-mechanicznie jest typowo inicjowane w tej strefie. Projekt inteligentnej osnowy obejmujący rozkład wielkości cząstek i materiały prekursorów spinelu pozwala dostosować szybkość tworzenia i pojawiania się spinelu w zależności od temperatury. Wyraźne ilości niskotemperaturowego spinelu zwiększają wytrzymałość wspomnianej słabej strefy wyłożenia. Magnezja palona (MgO) i magnezyt ($MgCO_3$) zostały dodane w różnych ilościach do betonów cementowych i bezcementowych. Zbadano wpływ właściwości fizycznych takich jak wytrzymałość na zginanie na zimno CMoR, uzysk utworzonego spinelu i plastyczność podczas obróbki cieplnej. Ogólnie mówiąc, im wyższa temperatura wypalania i drobniejsze cząstki, tym wydajniejszy jest proces tworzenia spinelu. Jednakże stan zaglomerowania, rozkład wielkości cząstek i obecność zanieczyszczeń w drobno zmielonym korundzie oddziałują na proces powstawania spinelu. Dodanie prekursora spinelowego do betonu wysokokorundowego oddziaływało na wartości CMoR. MgO wydaje się bardziej wydajny w promowaniu powstawania spinelu w porównaniu z $MgCO_3$. Nie tylko ilość spinelu ale również drobnoziarnistość i rozkład wielkości cząstek odgrywają decydującą rolę w przypadku poprawy odporności na wstrząs cieplny. Ogólnie informacja ta dostarcza wartościowej wskazówki do projektowania inteligentnej osnowy poprawienia warunków tworzenia spinelu dostosowanych do warunków użytkowania.

Słowa kluczowe: materiały ogniotrwałe odlewane, powstawanie spinelu, projekt osnowy

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1. 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 Al_2O_3 and MgO at temperatures above 1100°C [3].

Pre-formed 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 best spinel content is in the range of 15 wt.% to 30 wt.%. Preferred is a content between 20 wt.% 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]. 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 [5].

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, 6]. 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 micro-cracking and lower slag penetration resistance [7]. 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, Al_2O_3 3.98g/cm³ and $MgAl_2O_4$ 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 [8]. 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 [9]. 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 [10]. 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 [11]. 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.

2. 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. 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 deeply. 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 ≤ 45 μm) were considered. The alumina powders were mixed in stoichiometric proportions of spinel (71.67% Al_2O_3 and 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 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 or hydratable alumina. The water content was set to 5.2 wt.% (cement) / 6.5 wt.% (hydratable alumina) in the reference material and was adjusted to comparable workability when Mg-precursors were added (Table 1 and 2). 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 mm × 40 mm × 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. The cold modulus of rupture in the sintered state was measured. The spinel yield after the sintering process was quantified by Rietveld analysis after grinding.

Wedge splitting tests were performed on all formulations listed in Table 1. These measurements were executed at Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany. The main advantage of the method is to promote stable propagation of cracks on a large fracture area (circa 65 mm × 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 [12].

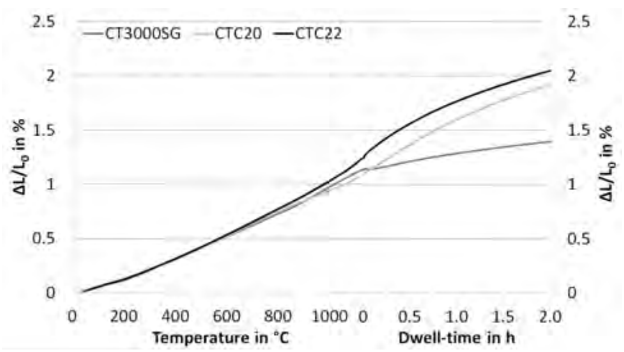

Fig. 1. Thermal behaviour of pressed granulates of stoichiometric mixtures of CTC20, CTC22 and CT3000SG with Nedmag DIN70 at 1200°C. The results were obtained by means of a modified dilatometer measurement where 1200°C were held for further 2 hours.

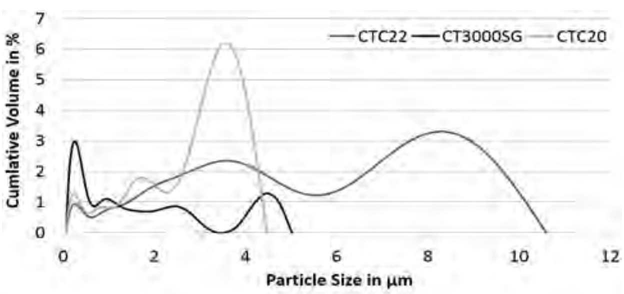

Fig. 2. Particle size distribution of alumina-powders CTC20, CTC22 and CT3000SG.

3. 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 wt.%. 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. 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. [9]. Therefore, it appears reasonable to choose the alumina precursor according to its

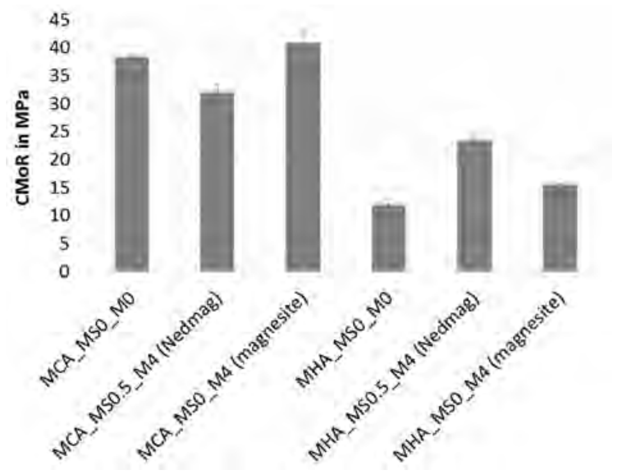

Fig. 3. Cold modulus of rupture of cement containing and cement free high-alumina concretes with different additions of Nedmag DIN70 and magnesite sintered at 1400°C for 4 h (M = Microsilica)

Table 1. Composition of cement containing high alumina castable.

Castable	MCA_MS0_ M0	MCA_MS0.5_ M4 (Nedmag)	MCA_ MS0_M4 (Magnesite)	MHA_MS0_ M0	MHA_MS0.5_ M4 (Nedmag)	MHA_ MS0_M4 (Magnesite)
Tabular alumina						
1.0–3.0 mm	25	25	25	25	25	25
0.5–1.0 mm	21	21	21	21	21	21
0.2–0.6 mm	11	11	11	11	11	11
0.0–0.2 mm	12	12	12	12	12	12
0.0–0.045 mm	9	5	5	9	5	5
Calcined alumina	10	10	10	10	10	10
Reactive alumina	7	7	7	7	7	7
Microsilica (MS)	0	0.5	0	0	0.5	0
CA cement	5	5	5	0	0	0
Hydratable alumina	0	0	0	5	5	5
Nedmag DIN70	0	4	0	0	4	0
Magnesite	0	0	4	0	0	4
Dispersant (PCE)	0.15	0.15	0.15	0.15	0.15	0.15
Water	5.2	5.2	5.2	6.5	6.5	6.5

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 and a cement free castable with 5 wt.% hydratable alumina as envisaged in Table 1. If Nedmag DIN70 is added CMoR decreases and the test pieces even show macro-cracks 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.% [13].

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 (Figs. 4 and 5).

Microscopic examinations (Figs. 4 and 5) provide valuable information that help to understand the observed

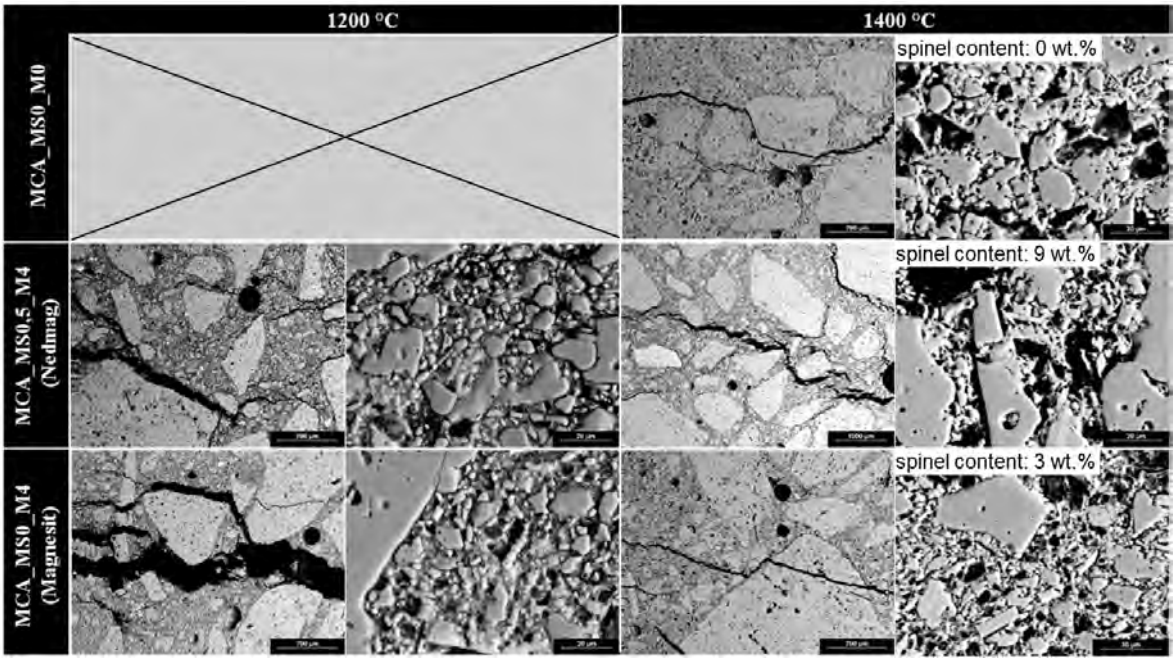

Fig. 4. Microstructural observations (Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany) of the fracture path (30× magnification) and microstructure (1500× magnification) for the cement containing reference castable and the castables with 4% Nedmag DIN70 or magnesite as spinel precursor after wedge splitting tests at 1200 °C and 1400 °C (dwell time 1 hour at the testing temperature) [12].

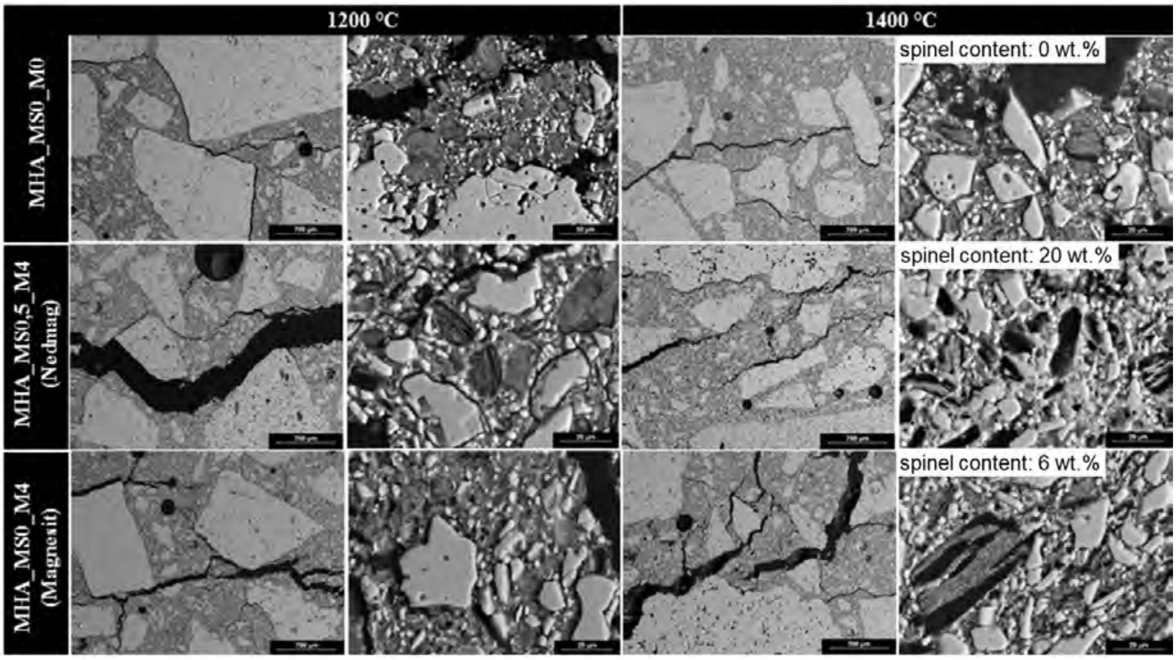

Fig. 5. Microstructural observations (Forschungsgemeinschaft Feuerfest e.V., Höhr-Grenzhausen, Germany) of the fracture path (30× magnification) and microstructure (1500× magnification) for the cement free reference castable and the castables with 4% Nedmag DIN70 or magnesite as spinel precursor after wedge splitting tests at 1200 °C and 1400 °C (dwell time 1 hour at the testing temperature) [12].

thermomechanical behaviour of the castables. The reference LC-castable without addition of microsilica or spinel precursor (Fig. 4) displays a straightforward fracture path able to crack large grains (brittle trans-granular fracture). When Nedmag DIN70 and 0.5% microsilica is added, the observed fracture appears much more ductile with no trans-granular 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. In further hibonite platelets are extensively formed and some small grains of spinel could be identified. $MgCO_3$-containing microsilica-free castables also display extensive cracks branching in the matrix, however, trans-granular cracks occur in contrast to the Nedmag DIN70 containing castable. 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 reference cement free castable (Fig. 5) shows a dried-out structure at 1400°C. When spinel precursors are added the matrix grain boundaries become reinforced and the microstructure behaves more ductile. As can be seen the spinel content is higher when precursors are added and the castables exhibit a better sintering and a higher CMoR what is shown in Fig. 3.

4. Conclusion

Dilatometric investigations indicate that the lower the Al_2O_3-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 magnesite to a tabular alumina based castable, CMoR is influenced. At 1400°C the sintering and CMoR increases by the in-situ spinel formation in comparison to the reference material without the spinel precursor. If microsilica is added the formation of brucite can be prevented in case of the Nedmag DIN70 addition. Generally, it can be stated that in comparison to magnesite, Nedmag DIN70 seems to be more efficient to promote the 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 the 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 obtains an elevated mechanical strength. The 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. When using magnesite as a 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.% magnesite were added. In this case, the disperse and homogenous distribution of spinel in the matrix obviously improves 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. The in-situ spinel formation in the cement free castables provokes a better sintering resulting in a higher CMoR at 1400°C in comparison to the reference castable.

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