

# IMPACT OF CALCIUM MAGNESIUM ALUMINATE ON LIQUID PHASE FORMATION AND HIGH-TEMPERATURE BEHAVIOUR OF MgO-CMA-C LADLE REFRACTORIES

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## ABSTRACT

In a ladle furnace, MgO-C bricks have to withstand high temperatures, thermal shock, and aggressive melts. Industrial applications in numerous steel plants have shown that the addition of calcium magnesium aluminate (CMA) increases the corrosion and penetration resistance of MgO-C ladle bricks by forming a protective slag coating on top of the hot face. However, there is concern that the addition of CMA promotes the formation of liquid phases lowering the high-temperature properties of the bricks. Hence, thermochemical equilibrium calculations using FactSage software were applied to describe the phase development in the range of 1,200 to 1,700 °C. By determining HMOR and RuL of MgO-CMA-C, the calculated portion of the liquid phase in the microstructure was linked with high-temperature properties.

## INTRODUCTION

Refractories based on magnesium oxide and carbon (MgO-C) are the dominating lining materials in steelmaking and refining plants, where they have to withstand high temperatures in the range of 1,600 °C to 1,750 °C, thermal shock, and aggressive steel/slag systems<sup>1</sup>. Also, alumina-magnesia-carbon (AMC) and magnesia-alumina-carbon (MAC) bricks are used for the metal line, impact region, and bottom for integrated steel ladles as well as in converters<sup>2</sup>. AMC and MAC bricks use the in-situ formation of secondary magnesia-alumina (MA) spinel during ladle

operation at temperatures above 1,000 °C followed by an expansive reaction that goes along with a tremendously increased strength by closing joints and densifying the brick structure, prevention of metal and slag infiltration as well as improved corrosion resistance<sup>2-4</sup>.

A new type of spinel and carbon-containing bricks are MgO-CMA-C refractories, which contain coarse- or fine-grained spinel-rich calcium magnesium aluminate to increase corrosion resistance. Industrial trial tests with MgO-C bricks containing CMA were carried out by Pagliosa et al.<sup>2</sup> in the metal line of a 205 t ladle and by Wöhrmeyer et al.<sup>5</sup> in a 130 t, 120 t, and 70 t ladle in different steel shops, respectively. These tests revealed a significant increase of the corrosion and penetration resistance, less wear in the joints, a more homogeneous wear profile, and especially the formation of a protective slag layer on top of the hot face of the bricks. The formation of the protective slag layer is traced to the addition of calcium magnesium aluminate, which increases the alumina and lime content of the infiltrating slag leading to a reduced reactivity<sup>6</sup>.

Based on the Al<sub>2</sub>O<sub>3</sub>-CaO-MgO phase diagram, it is assumed that the addition of CMA to MgO-C also results in the in-situ formation of a small amount of highly viscous liquid phase besides the stable MgO phase at operating temperature, which may reduce the decarburization and slag penetration. Hence, thermodynamic calculations have been

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performed to verify the formation of liquid phases and to identify the composition as a function of temperature. Furthermore, the influence of CMA on the thermomechanical properties of MgO-CMA-C bricks with different graded MgO raw materials have been investigated.

## EXPERIMENTAL

### *Thermodynamic calculations*

Thermochemical equilibrium calculations have been performed to determine the formation, transformation, and melting of phases of the MgO-CMA-C refractories at high temperatures. Therefore, the software package FactSage, V.7.1, with the databases FToxid and FACTPS was used. FACTPS is a pure substance database. FToxid consists of two sections: FToxid53Base.cdb for evaluated and optimized solid and liquid compounds, and FToxid53Soln.sda, which contains evaluated/optimized oxide solutions. FactSage calculations were performed at a composition of 95 Ma.% MgO (98- and 95-grade, respectively, RHI Magnesita, Vienna, Austria) and 5 Ma.% CMA (MagArmour -200 mesh, Imerys, Paris, France, in the following MagA). The overall chemical compositions of the MgO-CMA bricks as input data for FactSage calculations are given in table I.

Table I. Chemical composition of 95 Ma.% MgO (98- and 95 grade) and 5 Ma.% CMA -200 mesh (MagA) bricks

Component (Ma.%)	MgO95-5CMA	MgO98-5CMA
MgO	90.86	93.10
CaO	2.77	1.54
Al <sub>2</sub> O <sub>3</sub>	3.86	3.90
SiO <sub>2</sub>	1.70	1.02
Fe <sub>2</sub> O <sub>3</sub>	0.71	0.53
P <sub>2</sub> O <sub>5</sub>	0.10	-

A wavelength-dispersive spectrometer (Bruker AXS GmbH, Billerica, USA) was used to ascertain the chemical composition of the

raw materials by XRF (X-ray fluorescence analysis). Only the main and minor compounds, and the main trace elements (Fe<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>) were taken into account. Carbon was also not added to the batch since it would oxidize. All calculations were performed under oxidizing conditions. The oxygen partial pressure was fixed to 0.21 bar (fixed activity option in FactSage). The high-temperature phase development was measured from 1,200 °C to 1,700 °C in 20 K steps.

### *Determination of thermomechanical properties of MgO-CMA-C*

The raw materials used for the preparation of the MgO-CMA-C sample bodies were MgO with a purity of 95 and 98 %, respectively (both RHI Magnesita, Vienna, Austria), and MagA powder (-200 mesh, Imerys, Paris, France) in a range of 2.5 to 7.5 Ma.%. Table II shows the composition of the samples. MgO was used with varied fractions up to 4 mm particle size and the carbon content was adjusted to 2.2 Ma.%, whereby graphite and carbon black were added in equal parts.

As the first mixing step, the coarse MgO fractions were premixed for 3 min. Afterwards, the liquid resin 9308-FL (Hexion, Duisburg, Germany) was added and mixed for another 2 min. As the last step in the mixing process, fine MgO, MagA -200 mesh, graphite NFL, carbon black Thermaxx N991 (Luvomaxx, Hamburg, Germany), powder resin 0235 DP and hexamethylenetetramine (both Hexion, Duisburg, Germany) as hardener were added and mixed for another 5 min.

After completing the mixing process of all batches, bar-shaped samples (25 mm x 25 mm x 150 mm) and cylinders with 50 mm height and 50 mm diameter were pressed with a uniaxial press (RUCKS engine building GmbH, Germany) with an applied pressure of 120 MPa. Thermal treatment was applied to the samples after pressing by hardening in a three steps schedule with a maximum temperature of 180 °C. Afterwards, the samples were

carbonized in SiC retorts filled with petrol coke for 5 h at a temperature of 1,400 °C to provide a reducing atmosphere.

The Hot Modulus of Rupture (HMOR) was determined on bar-shaped sample bodies under argon atmosphere based on DIN EN 993-7 with an apparatus from Netzsch, Germany. The final temperature of the HMOR was 1,400 °C with a heating rate of 10 K·min<sup>-1</sup> and a dwell time of 30 min was applied for a homogenous temperature distribution before the HMOR test.

Table II. Composition of the samples containing MgO 98- and MgO 95-grade, respectively

Raw material (Ma.%)	MgO 95/98 -CMA 2.5	MgO 95/98 -CMA 5.0	MgO 95/98 -CMA 7.5
MgO 2-4 mm	17.0		
MgO 1-2 mm	24.7		
MgO 0-1 mm	34.3		
MgO powder	19.3	16.8	14.3
CMA (MagA)	2.5	5.0	7.5
Graphite	1.1		
Carbon black	1.1		
Powder resin	1.5		
Liquid resin	1.5		
Hardener	0.3		

The refractoriness under load (RuL) was measured according to EN 993-8 under air atmosphere at a sample composed of 100 % MagA, 100 % MgO 98-grade, and sample MgO98-CMA5.0 without carbon, respectively.

## RESULTS AND DISCUSSION

### *Thermodynamic calculations of liquid phase formation*

The thermodynamic calculations of the MgO95-CMA and MgO98-CMA batches referring to the weight of 100 g are depicted in Fig. 1. At 1,200 °C, MgO 95-grade with 5 Ma.% MagA contains solid metal oxides (mainly MgO, minor Fe<sub>2</sub>O<sub>3</sub>), spinels (mainly MgAl<sub>2</sub>O<sub>4</sub>, minor Al<sub>3</sub>O<sub>4</sub>, Mg<sub>3</sub>O<sub>4</sub>, and FeAl<sub>2</sub>O<sub>4</sub>), calcium magnesium silicates (mainly Ca<sub>7</sub>Mg(SiO<sub>4</sub>) and Ca<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub>), and other silicates (CaSiO<sub>4</sub>). The phosphorus is bonded in Ca<sub>7</sub>P<sub>2</sub>Si<sub>2</sub>O<sub>16</sub> (1,200 °C) and Ca<sub>3</sub>P<sub>2</sub>O<sub>8</sub> (from 1,220 °C).

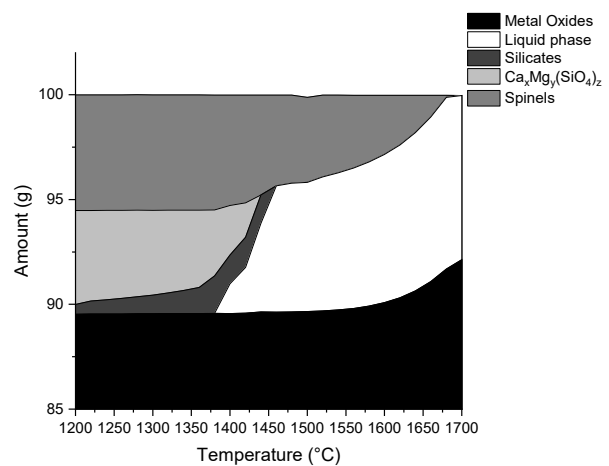


Fig. 1. Development of equilibrium phases in MgO 95-grade with 5 Ma.-% MagA in the temperature range of 1,200 to 1,700 °C

In contrast to the MgO 95-grade raw material, no liquid phase is formed at low temperature and no monticellite is detectable<sup>7</sup>. With increasing temperature, Ca<sub>7</sub>Mg(SiO<sub>4</sub>) decomposes and consequently the amounts of Ca<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub> and silicates, mainly CaSiO<sub>4</sub>, increase. From 1,400 to 1,460 °C solid calcium magnesium silicates (up to 1,440 °C) and the other silicates (up to 1,460 °C) are quickly replaced by a liquid phase in which also small amounts of spinels progressively dissolve. The calculated liquid phase chemistry is composed of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CaO, Fe<sub>x</sub>O<sub>y</sub>, MgO, and P<sub>2</sub>O<sub>5</sub> (in

the case of use of MgO 95-grade). Above 1,460 °C, the spinels content further decreases from approx. 4.3 Ma.% until all spinels convert into the liquid phase at 1,700 °C, leading to a progressive increase of liquid phase to 7.8 Ma.% at 1,700 °C. The amount of MgO (approx. 89.5 Ma.%) is almost stable in the analyzed temperature range.

MgO 98-grade with 5 Ma.% MagA contains solid metal oxides (mainly MgO, minor Fe<sub>2</sub>O<sub>3</sub>), spinels (mainly MgAl<sub>2</sub>O<sub>4</sub>, minor Al<sub>3</sub>O<sub>4</sub>, Mg<sub>3</sub>O<sub>4</sub>, and FeAl<sub>2</sub>O<sub>4</sub>), Ca<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub> as calcium magnesium silicate phase, and other silicates (mainly CaSiO<sub>4</sub>) with constant amounts from 1,200 up to 1,440 °C (Fig. 2). At 1,460 °C, the whole amount of Ca<sub>3</sub>MgSi<sub>2</sub>O<sub>8</sub>, as well as parts of silicates (0.4 Ma.%) and spinels (0.5 Ma.%), form a liquid phase. With increasing temperature, the amount of liquid phase increases from 3.1 Ma.% at 1,460 °C to 4.8 Ma.% at 1,700 °C due to the melting of the silicates above 1,460 °C and decomposition of the spinels from 5.5 Ma.% at 1,440 °C to 0.5 Ma.% at 1,700 °C. The amount of solid metal oxide phases increases significantly from less than 92 Ma.% to close to 95 Ma.%.

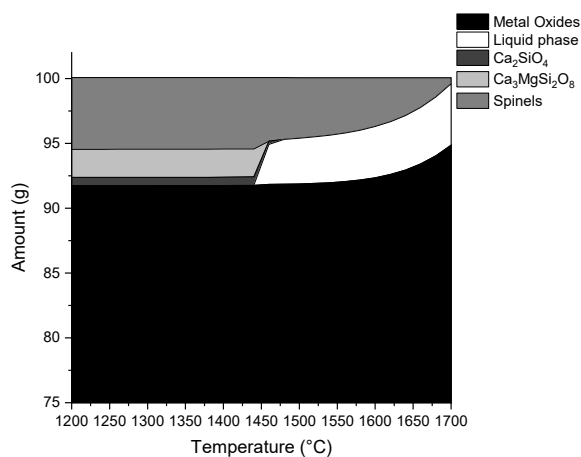


Fig. 2. Development of equilibrium phases in MgO 98-grade with 5 Ma.-% MagA in the temperature range of 1,200 to 1,700 °C

Fig. 3 gives an overview of the impact of MagA addition on the liquid phase formation in

MgO. The addition of 5 Ma.% MagA to sintered MgO 95-grade retards the liquid phase formation up to the temperature of 1,400 °C. In contrast to MgO 95-grade raw material<sup>7</sup>, an increase of liquid phase portion with increasing temperature is calculated. The thermodynamic calculation assigns the alumina portion of the batch to Al<sub>3</sub>O<sub>4</sub> spinel at low temperatures, but as Al<sub>2</sub>O<sub>3</sub> in the solid metal oxide group and liquid phase at high temperature. However, the occurrence of an Al<sub>3</sub>O<sub>4</sub> spinel, and consequently the increase of liquid phase portion with increasing temperature, was never observed under real conditions. So in the end, the liquid phase portion is increased from 5.3 Ma.% in the MgO 95-grade raw material to 6 Ma.% by adding MagA (data from T = 1,500 °C, plotted as a dotted line). Also in the batch with fused MgO 98-grade, the liquid phase formation is retarded by the addition of 5 Ma.% MagA up to a temperature of 1,460 °C (1,400 °C in MgO 98 raw material<sup>7</sup>) and the amount of liquid phase increases from 2.9 Ma.% to 3.5 Ma.% at 1,480 °C (dotted line).

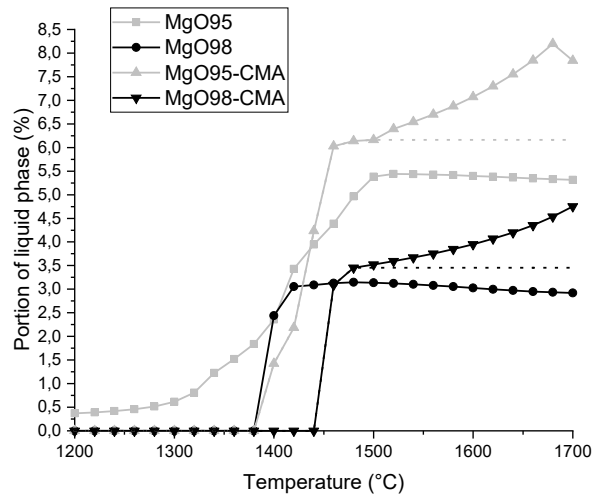


Fig. 3. Influence of the addition of 5 Ma.% MagA on the liquid phase formation in MgO 95- and 98-grade, respectively (dotted plots describe corrected liquid phase portions).

### Thermomechanical properties

Preisker et al. analyzed the influence of MagA on the material properties such as cold crushing strength (CCS), median pore diameter and apparent porosity of carbonized MgO-C bricks<sup>8</sup>. Using MgO 95-grade and fine-grained MagA results in the highest CCS, independent of the amount of added MagA. Also for MgO 98-grade, the use of fine-grained MagA was recommended for higher CCS. Apparent porosity was in the range of 16.8 to 21.3 % and tended to be lower in batches with MgO 98-grade and low portions of fine-grained MagA. For pore size, a vice versa effect was observed: the samples containing MgO 95-grade and high amounts of fine-grained MagA exhibit the lowest pore size of  $d_{50} = 3.9 \mu\text{m}$ . In summary, the change in material properties was not distinctive to recommend a specific grain size or amount of MagA used in MgO-C batches. Also, the thermodynamic calculations revealed a negligible impact of MagA on the liquid phase formation in MgO at high temperatures. Therefore, no significant difference in the high-temperature behavior of samples or products with and without MagA is expected.

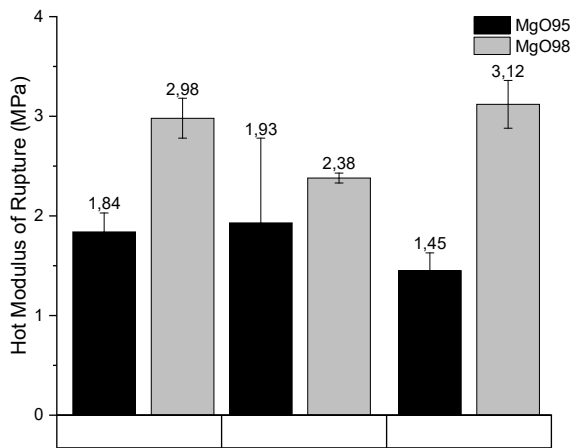


Fig. 4. HMOR of samples containing MgO 98- and 95-grade as well as 2.5, 5.0, and 7.5 Ma.% MagA, respectively

Fig. 4 displays the average HMOR values at 1,400 °C of samples containing MgO 98- and 95-grade, respectively, as well as MagA with

varying MagA content. As expected, the samples containing MgO 98-grade and hence fewer impurities and amount of liquid phase according to the thermodynamic calculations exhibit higher HMOR values compared to the samples containing MgO 95-grade. For MgO 95-grade, sample MgO95-CMA5.0 with 5.0 Ma.% MagA showed the highest HMOR of 1.93 MPa, whereas sample MgO98-CMA7.5 possess the highest measured HMOR of 3.12 MPa. In general, the MagA content showed no distinctive impact on the HMOR. This can be explained by the nearly full decarburization of the samples during the test run, even by constant argon flow, which led to a loss of the binding structure (carbon network). The high standard deviation supports this assumption.

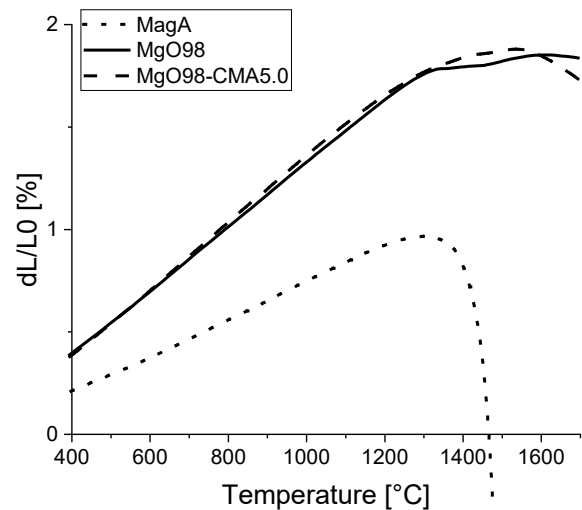


Fig. 5. RuL of samples composed of 100 % MagA, 100 % MgO 98-grade, and sample MgO98-CMA5.0 without carbon, respectively

The high amounts of CA and CA<sub>2</sub> phases next to MgAl<sub>2</sub>O<sub>4</sub> in MagA<sup>9</sup> result in poor refractoriness of the raw material (sample MagA) with a T<sub>05</sub>-value of 1,371 °C (see Fig. 5 and table II). However, the addition of 5 Ma.% of MagA to a MgO-rich batch (sample MgO98-CMA5.0) has no significant negative effect on the RuL, resulting in a high T<sub>05</sub>-value of 1,617 °C, which is comparable to the

refractoriness of high-quality refractories such as mullite bricks and MgO with low iron impurities.

Table II. The temperature of maximum elongation  $T_{d\max}$  and  $T_{05}$  of samples composed of 100 % MagA, 100 % MgO 98-grade, and sample 98MgO-CMA5.0 without carbon, respectively

Sample	$T_{d\max}$ (°C)	$T_{05}$ (°C)
MagA	1,297	1,371
MgO98	1,613	>1,700
98MgO-CMA5.0	1,538	1,617

## CONCLUSIONS

Thermodynamic calculations identified solid metal oxides, spinels, silicates, merwinite, and a liquid phase in MgO with and without the addition of fine-grained calcium magnesium aluminate (MagA). Based on the calculations, the addition of 5 Ma.% fine-grained calcium magnesium aluminate (MagA) to MgO 98-grade retarded the liquid phase formation from 1,400 °C to a temperature of 1,460 °C. The calculated liquid phase was composed of  $\text{Fe}_x\text{O}_y$ ,  $\text{SiO}_2$ , MgO, CaO, and  $\text{Al}_2\text{O}_3$ . Overall, the increase in the liquid phase portion by adding MagA was only marginal with +0.6 Ma.% in MgO 98-grade batches with a total amount of 3.5 Ma.% and +0.7 Ma.% in MgO 95-grade batches with a total amount of 6 Ma.%.

The determination of high-temperature properties of MgO–C with MagA has also proven that there is no negative effect and assist the results of the thermodynamic calculations. Sample MgO98-CMA7.5 with 7.5 Ma.% MagA possess an HMOR of 3.12 MPa at 1,400 °C. Additionally, MgO 98-grade with 5 Ma.% MagA provides a high  $T_{05}$ -value of 1,617 °C, which is comparable to the refractoriness of high-quality refractories.

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