

FORMATION OF HEXA-ALUMINATE SOLID SOLUTION PHASES IN SPINEL CONTAINING CASTABLES – MINERALOGICAL INVESTIGATIONS IN THE SYSTEM $\text{CaO-Al}_2\text{O}_3\text{-MgO}$

Sebastian Klaus*, Andreas Buhr
Almatis GmbH, Frankfurt, Germany

Marius Bauer
Almatis GmbH, Ludwigshafen, Germany

Matthias Göbbels
GeoZentrum Nordbayern, Erlangen, Germany

Jerry Dutton
Stourbridge, United Kingdom

4

ABSTRACT

MgAl_2O_4 spinel has been used in the refractory industry for many years and is well known to improve the thermal stability of alumina based refractory materials. Refractory products in demanding application conditions such as purging plugs or impact pads show increased thermo-mechanical stability and high erosion resistance when spinel is included.

This research describes the formation of ternary hexa-aluminate phases CAM I ($\text{C}_2\text{M}_2\text{A}_{14}$) and CAM II (CM_2A_8) at elevated temperatures between 1400°C and 1700°C. Mineralogical investigations of refractory castables prove CAM phases grow into sintered alumina grains resulting in an interlocking of matrix and aggregate compounds. The resulting microstructure contributes to improved hot strength properties, especially thermo-mechanical resistance. Further on, white fused alumina aggregates show a weaker reaction with the surrounding matrix which leads to less potential for interlocking.

INTRODUCTION

High alumina castables based on calcium aluminate binder have CaO with an excess of Al_2O_3 in their matrix composition. During firing or in application this leads to calcium hexaaluminate (CA_6 , $\text{CaAl}_{12}\text{O}_{19}$) formation, a mineral called hibonite, which has a high melting point of 1860°C.

MgAl_2O_4 spinel is incorporated in refractories to increase the high temperature durability in high demanding applications such as purging plugs or impact pads. Spinel based high-alumina castables follow the ternary system $\text{CaO-Al}_2\text{O}_3\text{-MgO}$.

It was shown by Goebbels et al. [1] that at elevated temperatures of 1650°C ternary phases are formed which follow the conjugation between spinel and hibonite. As indicated in Fig. 1, hibonite_{ss} forms a solid solution at 1650°C and can incorporate up to 2.5 mol% of magnesia ($\text{CaMg}_x\text{Al}_{12-x}\text{O}_{19}$ with $0 \leq x \leq 0.18$). As magnesia content increases, the hexa-aluminate phases CAM I_{ss} ($\text{Ca}_2\text{Mg}_{2-3y}\text{Al}_{28+2y}\text{O}_{46}$ with $0 \leq y \leq 0.30$) and CAM-II_{ss} ($\text{CaMg}_z\text{Al}_{16+2z}\text{O}_{27}$ with $0 \leq z \leq 0.20$) are formed. Because the end links of each solid solution series conjugate (indicated as dashed line) it is suggested that CAM I and CAM II are combinations of single spinel and hibonite structure parts.

Recent investigations have shown that CAM-phases are formed in fired spinel based high alumina refractory castables [2]. Due to their platy hexagonal habitus they interlock the aggregate grains with their surrounding matrix resulting in improved hot bending strength.

Investigations with the sintered refractory aggregate BSA 96 revealed that CAM-phases can already be present at 1400°C[3]. Foreign oxides such as TiO_2 or SiO_2 seem to lower the stability temperature of the ternary CAM-phases.

This paper focuses on the formation of CAM-phases and their phase development in association with other calcium aluminate phases for mixtures of pure oxides and castables based on commercially available raw materials.

EXPERIMENTAL

The synthesis of the synthetic mixtures shown in Tab. 1 was performed in several distinct steps. The pure oxides were de-carbonized at 1000°C for 24h and homogenised in a disk mill. The homogenised powders were then densified in a hydrostatic press at approximately 60 bar to ensure effective sintering and material diffusion. The location of both mixtures Low-MgO (I) and High-MgO (II) is shown in the three phase diagram in Fig. 1.

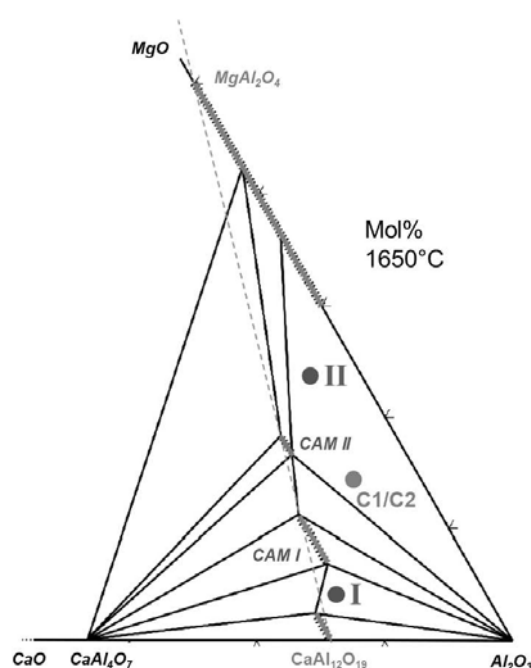


Fig. 1: Part of phase diagram $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ at 1650°C including CAM I and CAM II phases. Modified after [1].

Tab. 1: Oxide composition of synthetic admixtures.

Mix, wt.-%	Supplier	I Low-MgO	II High-MgO
Al ₂ O ₃	Almatis GmbH	92.4	86.6
MgO	Merck	1.6	10.3
CaO	CaCO ₃ , Alfa Aesar	6.0	3.1

Refractory castables based on Tabular alumina T60/T64 (C1) and white fused alumina (WFA) (C2) were prepared in addition to the synthetic raw mixtures. As shown in Tab. 2 the castables contain 12 wt.% pre-formed spinel AR 78, which is a sintered spinel with a phase composition of 100% alumina-rich non-stoichiometric spinel. The test bars were pre-sintered at 1000°C and cylindrical shaped samples were drilled and extracted.

The chemical composition of the fine fraction with particle size <0.5 mm is shown in Fig. 1 (C1/C2).

All samples were sintered at temperatures ranging from 1400°C to 1600°C for defined periods of time. For temperatures up to 1600°C a chamber furnace (Nabertherm LHT 08/18 and LTC 08/16) with a temperature variation of ±30°C was used. In addition, the synthetic mixtures were investigated at 1700°C in a tube furnace (Eurotherm 2408) with a much lower temperature variation of ±3°C.

Tab. 2: Composition of investigated refractory castables based on Tabular Alumina and white fused alumina.

Castable C1 / C2		Wt.-%
T60/T64 (C1) / WFA (C2)	3-6 mm	20
	1-3 mm	20
	0.5-1 mm	14
	0-0.5 mm	15
Spinel AR 78	0-0.045 mm	5
	0-0.020 mm	7
Alumina	CTC 30	13
Cement	CA-14 M	6
Dry mix		100%
Dispersing Aluminas	ADS 3	0.5
	ADW 1	0.5
Water	H ₂ O	4.3

A microprobe from JEOL (JXA-8200) was used for BSE images and WDX measurements. The X-ray diffraction patterns were measured with a D5000 and D8 from Bruker and evaluated with the Rietveld method using TOPAS. The structures for Rietveld refinement of CAM I and CAM II were based on Iyi et al. [4].

RESULTS AND DISCUSSION

Microstructure development of synthetic mixtures

The microstructure for both synthetic mixtures sintered at 1400°C for 14 days is shown in Fig. 2. In principle, the microstructure can be divided into dark grey phases and secondary bright grey plate phases. Pores are visible as black areas. The phases within one grey scale cannot be distinguished because of their similar atomic weight. The bright plate phase is formed during the sintering process and consists of hibonite and CAM I. The phase CAM II

was not present at such low sinter temperatures. MgAl₂O₄ spinel and corundum are visible as the dark grey phases.

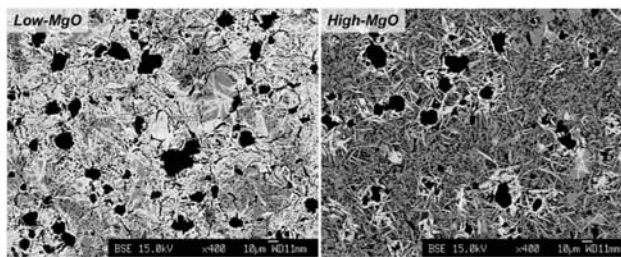


Fig. 2: BSE images of synthetic mixtures Low-MgO and High-MgO sintered at 1400°C for 14d.

The qualitative phase content is shown in Tab. 3. The main phases in the mixture with low MgO are corundum and hibonite. Spinel is present, but to lesser extent. On the contrary, the high MgO content in mixture High-MgO leads to a very dominant spinel development.

Tab. 3: Qualitative phase content of synthetic mixtures sintered at 1400°C for 14d.

1400°C, 14d	Low-MgO	High-MgO
Corundum (dark)	++	++
Spinel (dark)	+	+++
Hibonite (bright)	++	+
CAM I (bright)	+	+
CAM II (bright)	-	-

With a temperature of 1600°C and an annealing time of 3 days the secondary phases increase in size and grow into the dark grey phases (Fig. 3). For mixture Low-MgO all spinel is consumed with the formation of CAM I. The qualitative phase content shows a clear coexistence of spinel and CAM I for the mixture High-MgO (Tab. 4). Also CAM II is initially visible at this temperature.

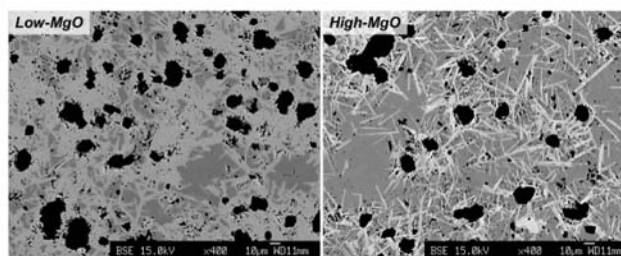


Fig. 3: BSE images of synthetic mixtures Low-MgO and High-MgO sintered at 1600°C for 3d.

Tab. 4: Qualitative phase content of synthetic mixtures sintered at 1600°C for 3d.

1600°C, 3d	Low-MgO	High-MgO
Corundum (dark)	+	+
Spinel (dark)	-	+++
Hibonite (bright)	+	-
CAM I (bright)	+++	+++
CAM II (bright)	-	+

The microstructures sintered in a tube furnace for 3 days at 1700°C are shown in Fig. 4. The bright phases dominate the microstructure, especially for the mixture with low MgO content. The associated phases CAM I, hibonite and corundum fit with the ternary phase diagram as presented in Fig. 1.

For the mixture with high MgO content, corundum and hibonite are consumed during the formation of the main phases spinel and CAM II. The bright crystals are larger in size when compared with the mixture with low MgO content. Interestingly, the theoretical phase association suggests at 1650°C the presence of corundum, CAM II and spinel. However, spinel can incorporate increasing amounts of Al₂O₃ at elevated temperatures. If there is no excess of alumina it will be incorporated into spinel until all corundum is consumed. In 1995 Iyi et al. [4] presented investigations at elevated temperatures of 1800°C showing a shift of CAM stability due to solid solution of spinel, CAM I and CAM II.

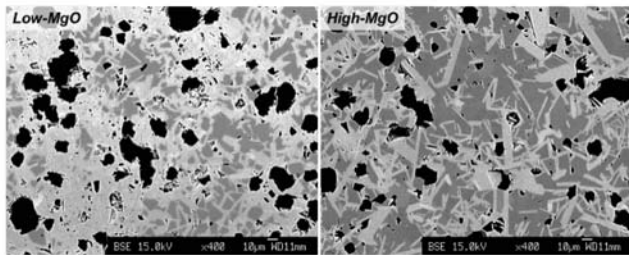


Fig. 4: BSE images of synthetic mixtures Low-MgO and High-MgO sintered at 1700°C for 3d.

Tab. 5: Qualitative phase content of synthetic mixtures sintered at 1700°C for 3d.

1700°C, 3d	Low-MgO	High-MgO
Corundum (dark)	+	-
Spinel (dark)	-	+++
Hibonite (bright)	+	-
CAM I (bright)	+++	+
CAM II (bright)	-	+++

Microstructure development of refractory castables

Comparison of refractory castables sintered at 1400°C for 14 days is shown in Fig. 5. Castable C1 shows the typical sintered alumina grain with closed micropores embedded in a matrix consisting of spinel fines, alumina fines and calcium hexa-aluminate phases. Similar to the synthetic mixtures, the bright phases are secondary phases formed during the sinter process. The WFA alumina aggregate shows very dense areas but also very porous areas. Although the phase content is very similar (compare Tab. 6), the microstructural development is very different. For castable C1 the secondary phases hibonite and CAM I grow into the sintered aggregates. In contrast, the WFA grains are partly surrounded by secondary phases without growing into the aggregate structure. This phenomena has already been described for AluMagCarbon bricks based on BSA 96, a sintered alternative to brown fused alumina (Klewski et al. [5]).

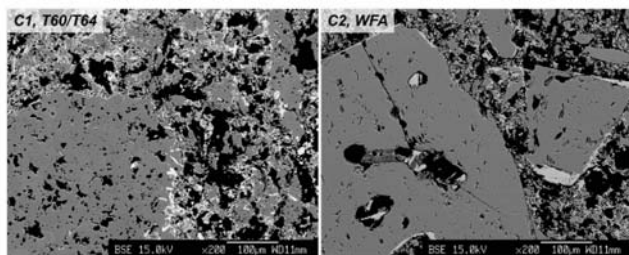


Fig. 5: BSE images of refractory castables C1 and C2 sintered at 1400°C for 14d.

Tab. 6: Qualitative phase content of refractory castables sintered at 1400°C for 14d.

1400°C, 14d	C1, T60/T64	C2, WFA
Corundum (dark)	+++	+++
Spinel (dark)	++	++
Hibonite (bright)	+	+
CAM I (bright)	+	+
CAM II (bright)	-	-

Higher sinter temperature as shown in Fig. 6 results in pronounced growth of secondary phases CAM I and hibonite. Again, the outer layer of the sintered alumina grains is penetrated by CAM phases, whereas the fused grain shows a surface reaction only. It is possible that the CAM phases grow along the crystal boundaries, which are usually weaker and higher in foreign ions. Typically, fused aggregates have larger crystals and therefore less “openings” for crystal penetration.

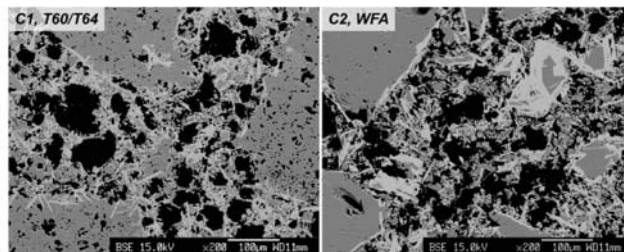


Fig. 6: BSE images of refractory castables C1 and C2 sintered at 1600°C for 7d.

The qualitative phase association is very similar between C1 and C2. Compared to the previously discussed sinter temperature of 1400°C, the phase content of CAM I has increased.

CAM II, which would be expected considering the matrix chemistry as indicated in Fig. 1, is not present.

Tab. 7: Qualitative phase content of refractory castables sintered at 1600°C for 7d.

1600°C, 7d	C1, T60/T64	C2, WFA
Corundum (dark)	+++	+++
Spinel (dark)	++	++
Hibonite (bright)	+	+
CAM I (bright)	++	++
CAM II (bright)	-	-

Phase development of synthetic mixtures and EPMA analysis

The phase development for every single sinter step of the synthetic mixtures Low-MgO and High-MgO is presented in Fig. 7. For both mixtures residual clinker phases such as CA or CA₂ are no longer present at 1400°C. Instead, CaO is incorporated in hibonite and CAM I. Spinel is completely consumed for mixture Low-MgO at temperatures above 1400°C. Instead, CAM I is increasing in content up to 65wt% at 1700°C. Corundum and hibonite remain stable as the mixture has reached the equilibrium and the stable phase association. CAM II was not present in Low-MgO under any sinter condition.

The high MgO content for mixture High-MgO leads to intensive spinel formation before 1400°C. Corundum is consumed to provide the needed alumina for spinel formation. Minor amounts of CAM I are formed at 1400°C but considerably increases at temperatures up to 1600°C. At the same time corundum and hibonite are decreasing in content with only minor amounts left

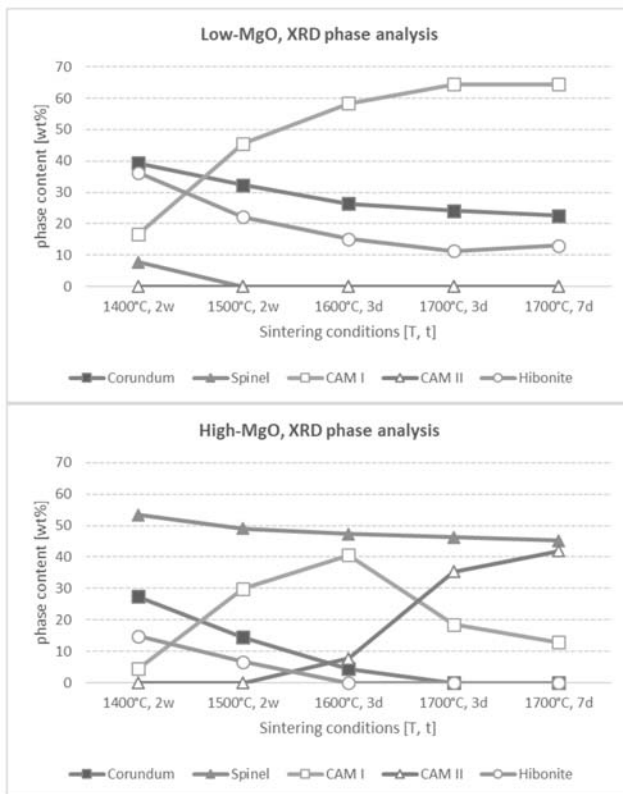


Fig. 7: Quantitative phase analysis of synthetic mixtures Low-MgO and High-MgO.

at 1600°C. Alumina is incorporated in the temperature dependent solid solution field of spinel, which is clearly shown in Fig. 8.

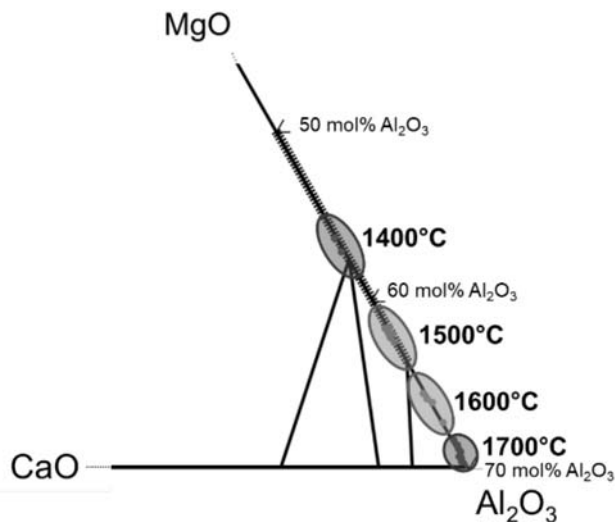


Fig. 8: Spinel part of the ternary phase diagram $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ (1650°C) including WDX measurements of spinel in mixture High-MgO.

With increasing temperature spinel incorporates close to 70 mol% Al_2O_3 at 1700°C. It can be assumed that the excess of MgO is used in further formation of CAM I and CAM II.

CAM I has reached its maximum content at 1600°C and is decreasing as soon as corundum is completely consumed at temperatures >1600°C. The absence of hibonite and corundum seems to trigger the accelerated conversion from CAM I to CAM II. At 1700°C corundum and hibonite are completely consumed and the main phases are CAM II together with an alumina-rich spinel. Residual CAM I exists only as a minor phase.

The EPMA WDX measurements for all investigated temperatures are shown in Fig. 9. The original chemistry for the synthetic mixture High-MgO is represented by the black star. Hibonite, spinel and CAM I were measured in accordance with the expected composition. However, CAM II was measured between CAM I and CAM II, probably because of small crystal size leading to mixed analysis.

The final phase association as obtained with mixture High-MgO suggests that the stable 3-phase fields are shifted at elevated temperatures >1650°C due to the ability of spinel to incorporate additional alumina through increased solid solution.

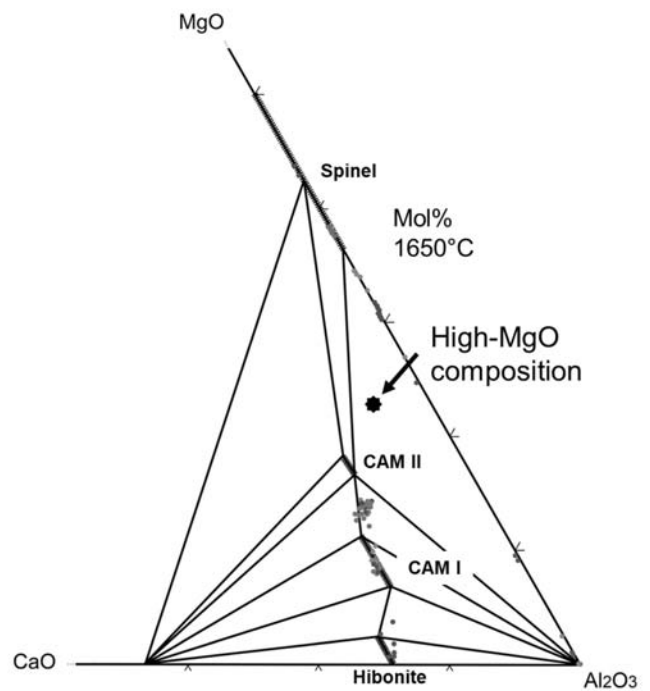


Fig. 9: Ternary phase diagram $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ including WDX measurements for all investigated temperatures.

Phase development of the refractory castable

The quantitative phase development in Fig. 10 clearly shows that even relative low sinter temperatures of 1400°C are enough to form low amounts of CAM I with a typical refractory castable formulation. Corundum is not shown in the diagram but is the phase with highest content anyway, due to the addition of large alumina aggregates.

The hibonite content is decreasing under further formation of CAM I with increasing sinter temperature. Apart from corundum, CAM I is the main phase at the final sinter temperature of 1600°C.

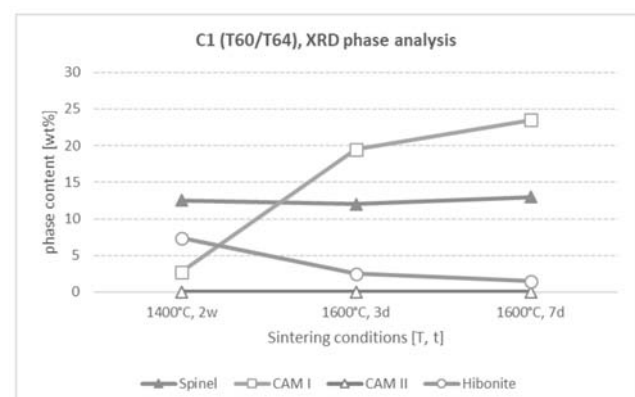


Fig. 10: Quantitative phase analysis for the Tabular alumina based refractory castable C1.

It can be assumed that hibonite will be completely consumed at temperatures above 1600°C with all residual calcia incorporated into CAM I.

The phase development for the WFA based refractory castable C2 was very comparable to C1. However, the final amount of formed CAM I content was with nearly 20 wt% a bit less.

CONCLUSIONS

This work clearly demonstrated the presence of the ternary hexa-aluminate phases CAM I ($C_2M_2A_{14}$) and CAM II (CM_2A_8) for synthetic mixtures in the system CaO-Al₂O₃-MgO in addition to cement bonded refractory castables.

It is assumed that the formation of CAM phases strongly contribute to the superior hot strength properties of alumina-spinel based refractory castables. For example, Fig. 11 shows the difference in hot modulus of rupture at 1500°C of an alumina-spinel castable when compared to a pure alumina castable.

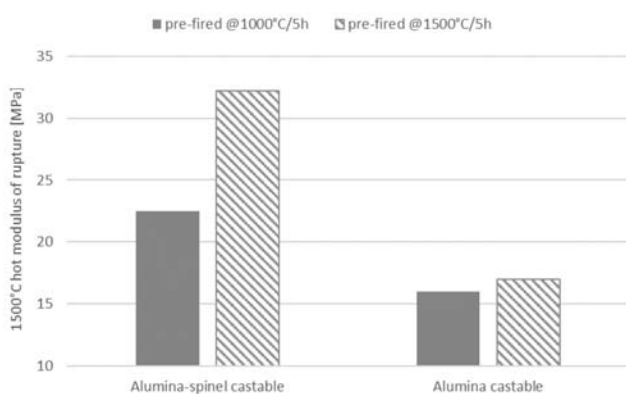


Fig. 11: Hot modulus of rupture measured at 1500°C for an alumina castable and an alumina-spinel castable. Figure drawn after Long et al. [6].

The microstructure investigations show an interlocking of aggregates and their surrounding matrix through formed CAM phases. Tabular alumina, due to its sintered structure, shows a more pronounced interconnection when compared to white fused alumina aggregates.

REFERENCES

- [1] M. Göbbels, E. Woermann and J. Jung, "The Al-rich part of the system CaO-Al₂O₃-MgO Part I. Phase relationships," *Journal of Solid State Chemistry*, vol. 120, pp. 358-363, 1995.
- [2] B. Long, A. Buhr, I.-H. Jung, S. Sin, H. Harmuth and J. Dutton, "Comparison of Cement- and Hydratable Alumina-Bonded Alumina-Spinel Materials for Steel Ladle Purging Plugs," *Refractories Worldforum*, vol. 9, pp. 93-106, 2017.
- [3] M. Schnabel, S. Klaus, A. Buhr, D. Schmidtmeier and J. Dutton, "Five Years after Market Launch – Experiences with BSA 96," *Refractories Worldforum*, vol. 3, pp. 87-92, 2016.
- [4] N. Iyi, M. Göbbels and Y. Matsui, "The Al-Rich Part of the System CaO-Al₂O₃-MgO PART II. Structure Refinement of Two New Magnetoplumbite-Related Phases," *Journal of Solid State Chemistry*, vol. 120, pp. 364-371, 1995.
- [5] M. Klewski, G. Maracha, A. Buhr, M. Schnabel and J. Dutton, "Spinel Formation and Technical Properties of Alumagcarbon Bricks with Different Alumina Aggregates," in *UNITECR2015 – 14th Biennial Worldwide Congress*, 2015.
- [6] B. Long, A. Buhr and G. Xu, "Thermodynamic evaluation and properties of refractory materials for steel ladle purging plugs in the system Al₂O₃-MgO-CaO," *Ceramics International*, vol. 42, pp. 11930-11940, 2016.