

# New Insight on Developing MgO–SiO<sub>2</sub>–H<sub>2</sub>O Gel Bonded MgO Castables

Hong Peng, Bjørn Myhre

It is well known that brucite forms during MgO hydration and this causes volume expansion and subsequent cracking – a phenomenon commonly called “slaking”. Although much research on lab-scale small prisms has demonstrated that the interaction between MgO and SiO<sub>2</sub> prevents slaking, the mechanism of MgO hydration has not been well understood. Hence, magnesia castables have not been widely used. To overcome problems related to slaking, a new specialty product, SioxX-Mag, has recently been developed for cement-free MgO castables based on MgO–SiO<sub>2</sub>–H<sub>2</sub>O bond. Samples from larger, dried blocks were characterized by XRD. Using SioxX-Mag in combination with microsilica, cracking caused by brucite formation is suppressed. The results demonstrate that the dosage of microsilica and the type of dispersant play essential roles in the crack formation in large specimens. Furthermore, the compatibility of SioxX-Mag with different types of MgO aggregates, medium to high-grade dead burned magnesia and olivine, has been evaluated. High-performance, self-flowing MgO–SiO<sub>2</sub>–H<sub>2</sub>O gel bonded MgO castables have been developed, exhibiting good workability and setting behavior while hot-properties are maintained.

## 1 Introduction

Basic refractory castables play an essential role in state-of-the-art steel-making. Nevertheless magnesia castables are not widely used due to brucite formation (Mg(OH)<sub>2</sub>) during MgO hydration [1]. Brucite has negative impact both during i) placing; ii) curing and iii) drying-out [2–3]. During placing the hydration reduces working time and induces rapid flow-decay; during curing it causes volume expansion and subsequent cracking, a phenomenon commonly called “slaking”. During the dry-out stage brucite will dehydrate at 400–600 °C which will increase the porosity, and subsequently reduce the mechanical strength.

Earlier research has demonstrated that the interaction between MgO and SiO<sub>2</sub> prevents slaking [4–7]. Already in 1989, *Elkem* start-

ed work on a new binder system for basic castables based on the reaction between MgO fines, microsilica (SiO<sub>2</sub>) and water. This bond system was first applied to magnesia, silicon nitride and magnesia-carbon castables. It required low water addition (5,0–5,5 %) and provided adequate mechanical properties. An important observation was that no slaking occurred at 6 % microsilica addition. Microsilica has been reported as one of the most effective anti-hydration agents. It also plays an essential role in the setting and hardening process and improves mechanical properties, at both ambient and high-temperature. At room temperature, microsilica contributes to the bond formation by interaction with MgO fines and hinders the MgO hydration. At intermediate temperatures (above 800 °C), the MgO–SiO<sub>2</sub> bond normally transforms to

forsterite. Forsterite has a melting point of 1810 °C and should provide a good bond in the system.

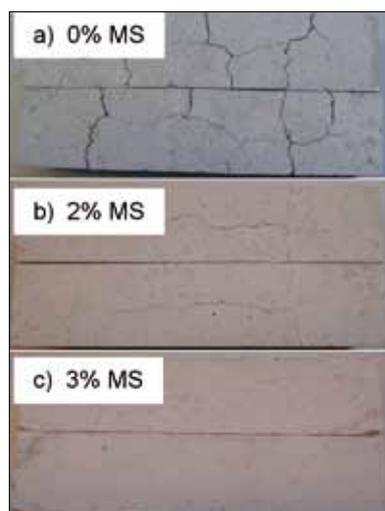
The hydration of magnesia and dehydration of brucite have been thoroughly studied during the last decade [8–13]. The parameters affecting the hydration of MgO castables can be summarized as follows: i) particle size, reactivity and ratio of CaO/SiO<sub>2</sub> of MgO raw materials, especially MgO fines; ii) additives, such as dispersants/water-reducing agents, retarders and/or accelerators, contributing to slow down and/or control the speed of the chemical reaction between MgO and water, i.e. minimizing the brucite formation; iii) microsilica fines; iv) dry-out profile; and v) water addition. Various technologies have been reported to inhibit and/or ultimately avoid the brucite formation by including microsilica as anti-hydration agent, fibres as drying agent to accelerate water evaporation, and optimization of additives and water addition to minimize water available for brucite formation after placing.

As a matter of fact, the studies on hydration of MgO are mostly focused on “MgO containing” castables, such as spinel-magnesia castables with cement [8–13]. Little work has been done on MgO cement-free castables. Still, suitable dispersants and binder system which provide good placing proper-

Hong Peng  
Bjørn Myhre  
Elkem Silicon Materials  
Kristiansand  
Norway

Corresponding author: Hong Peng  
E-mail: hong.peng@elkem.no

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**Fig. 1** Lab-scale prisms (40 mm × 40 mm × 160 mm) of cement-free MgO castables with different amount of microsilica (MS) after drying at 110 °C for 24 h. At 3 % microsilica all samples are crack-free [15]

ties, setting behaviour and anti-hydration of MgO, are lacking.

Moreover, most of the results mentioned above are based on lab results, and few studies on real-size MgO castable have been reported [2].

At ALAFAR 2012, *Hong, et al.* [14] presented preliminary results using a new product, SioxX-Mag prototype, designed to promote the bond system MgO–SiO<sub>2</sub>–H<sub>2</sub>O for cement-free MgO castables. Since then, the effect of additives and/or microsilica on slaking, flow and the setting mechanism has been further investigated. It has been demonstrated that microsilica addition has a strong influence on flow, setting and slaking in cement-free MgO castables [15].

As seen in Fig. 1, 3 % microsilica effectively suppressed cracking, while at lower dosage cracking was easily recognizable. With sub-micron alumina alone (Fig. 1a) cracking was very pronounced. This indicates that microsilica is an efficient anti-hydration agent, while alumina does not give protection against slaking.

This paper is focused on new insights on developing pure MgO castables using MgO–SiO<sub>2</sub>–H<sub>2</sub>O as binder system. The objectives are: i) to understand the effect of dispersants and microsilica on hydration of MgO in large samples, ii) to introduce a speciality product, SioxX-Mag, purposely designed for magnesia castables to overcome the problem related to slaking and to de-

velop crack-free MgO castables, and iii) to evaluate the compatibility of SioxX-Mag with different magnesia aggregates. The results demonstrate that sufficient microsilica in combination with optimum dispersants are the key factors in obtaining crack-free large magnesia castable samples. High-performance basic refractory castables with different types of MgO aggregates were developed using SioxX-Mag and microsilica.

## 2 Experimental

### 2.1 Composition design

Tab. 1 presents the compositions of the magnesia castables using MgO–SiO<sub>2</sub>–H<sub>2</sub>O as binder system. The particle size distributions (PSD) were calculated using the EMMA program [16]. In the present study, the q-value of all compositions is 0,25, with the exception of the synthetic DBM-C at 0,24. The following raw materials were used: synthetic dead-burned MgO (Nedmag 99, labelled Synthetic DBM), dead-burned MgO 97 (China, DBM 97), dead-burned MgO P94 (Russia, DBM P94), olivine (*Vanguard*, Norway) and microsilica (Elkem 971U). The dispersant was SioxX-Mag. For comparison, the castable containing Synthetic DBM aggregates was tested, also using a different additive, denominated Disp. A. The dosage level of each dispersant was optimized. Water addition was kept at approximately 5,5 % for all mixes.

### 2.2 Sample preparation and characterization

The dry components were mixed using a Hobart mixer for 4 min at 60RPM; water was added, and the castable was wet-mixed for an additional 4 min.

Self-flow and vibration-flow of the fresh mix were measured using the flow-cone described in ASTM C230 (height of 50 mm, not the more recent cone of 80 mm described in EN 1402-4:2003). The self-flow value is the percent increase of the diameter of the fresh mix measured 90 s after removing the cone.

The material was then cast into 25 mm × 25 mm × 150 mm moulds for Hot Modulus of Rupture (HMoR) measurements. The moulds were kept at 20 °C at >90 % RH for 24 h before de-moulding, then dried at 110 °C for 24 h. All lab-scale small prisms were crack-free.

**Tab. 1** Composition of microsilica-gel bonded MgO castables

[mass-%]		Synthetic DBM			Other Aggregates		
		A	B	C	DBM97	DBM P94	Olivine
Synthetic DBM	5–3 mm	12	12	10			
	3–1 mm	24	24	35			
	1–0 mm	27	27	20			
	100 mesh	10	10	6	5		4
	325 mesh	21	21	20	21		21
DBM97	2–4 mm				21		
	1–2 mm				25		
	0–1 mm				21		
DBM P94	3–5 mm					12	
	1–3 mm					25	
	0–1 mm					29	
	100 mesh					10	
	325 mesh					17	
Olivine	2–6 mm						17
	1–3 mm						15
	180–500 µm						20
	63–125 µm						4
	710–1400 µm						12
Microsilica	Elkem971U	6	6	8	7	7	7
Additives		Disp. A	SioxX-Mag				

The castables labelled Synthetic DBM-A, B and C were cast into larger moulds with dimensions: i) 300 mm × 300 mm × 300 mm (~70 kg) and ii) 300 mm × 300 mm × 150 mm (~35 kg). They were de-moulded after one day and air-cured at ambient temperature for another two days before the dry-out started. The following dry-out profile was used [2]: i) 5 °C/min from room temperature to 80 °C, ii) 5 h at 80 °C, iii) 5 °C/min from 80 to 150 °C, and iv) 12 h at 150 °C. Afterwards, the oven was turned off and left to cool.

The dried large samples were photographed and samples from the core were taken for characterization. An X-ray diffractometer (XRD, x'Pert Pro, Philips/NL) employing CuK $\alpha$  radiation was applied for the mineralogical phase analysis. A Scanning Electronic Microscope (SEM, Quanta 400, FEI Company/US) equipped with Energy Dispersive Spectroscopy (EDS, Noran 623M-3SUT, Thermo Electron Corporation/JP) was used for examination of the microstructure on the polished surface of the samples.

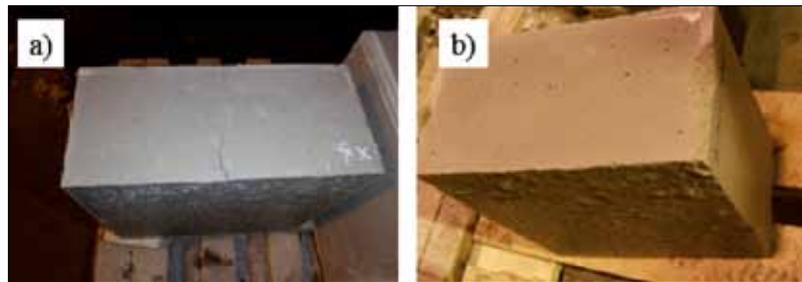
### 3 Results and discussion

#### 3.1 Hydration behaviour

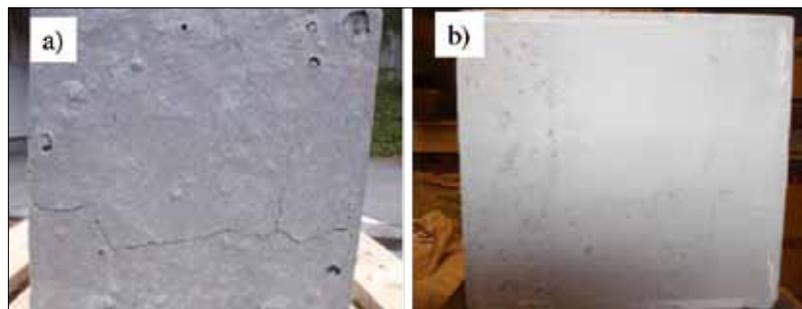
In previous work [15] we reported that crack-free lab-scale samples were made at microsilica dosage above 3 % and that MgO castables containing 6 % microsilica without alumina outperform others in terms of hot properties. Hence, in this work we use MgO castables with 6 % microsilica as benchmark (Tab. 1). Larger blocks of synthetic DBM-A, B, and C were made. When de-moulded after 1 day, all blocks were perfect, no cracks were observed.

Fig. 2 shows that perfect blocks of DBM-B (and C) were made, while small cracks were observed on the DBM-A. In order to check how the thickness affects the cracking, blocks with doubled thickness (300 mm) of castable DBM-B and DBM-C were made (Fig. 3). DBM-C with 8 % microsilica did not crack, while DBM-B with 6 % microsilica had small cracks.

As illustrated in Fig. 2 – 3, the type of dispersants, the amount of microsilica, and the thickness of the samples seem to have strong impact on the hydration of MgO and subsequent cracking of the dried castable. For larger blocks the dimensions, the dry-out profile, and how the additives affect the



**Fig. 2** Blocks (300 mm × 300 mm × 150 mm) after dry-out: a) DBM-A, and b) DBM-B; DBM-C looked similar to DBM-B



**Fig. 3** Blocks (300 mm × 300 mm × 300 mm) after dry-out: a) DBM-B with 6 % microsilica, and b) DBM-C with 8 % microsilica

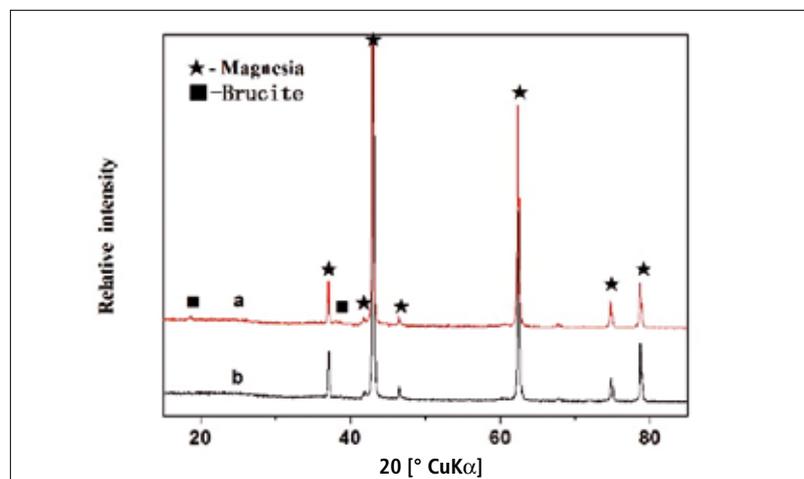
dry-out process have to be taken into account.

In order to understand the MgO hydration mechanism, samples were taken from the blocks of DBM-B and DBM-C (Fig. 3). XRD characterization was carried out and Fig. 4 presents the XRD patterns. The DBM-B samples contain mainly periclase (MgO) and small amounts of brucite. In DBM-C, only periclase is observed and no brucite phases could be detected. In both samples, no magnesia silicate hydrate (M–S–H) could be detected, indicating that the M–S–H has poor crystallinity. The major difference in

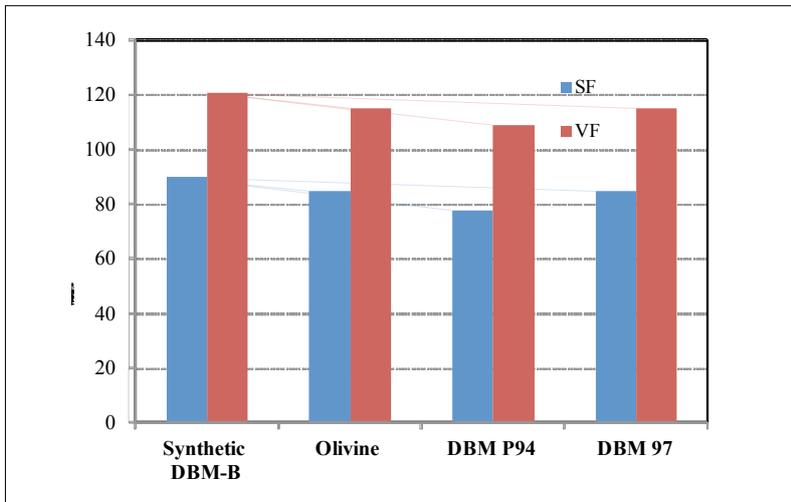
composition of DBM-B and C is the microsilica content; 6 % and 8 % respectively.

It is therefore believed that a higher dosage of microsilica in MgO castables is an effective way to prevent and/or slow-down brucite formation during the curing and drying process. When 6 % microsilica is used, the MgO hydration is obviously reduced to a greater extent, and this results in crack-free lab-scale prisms as the water evaporates relatively fast.

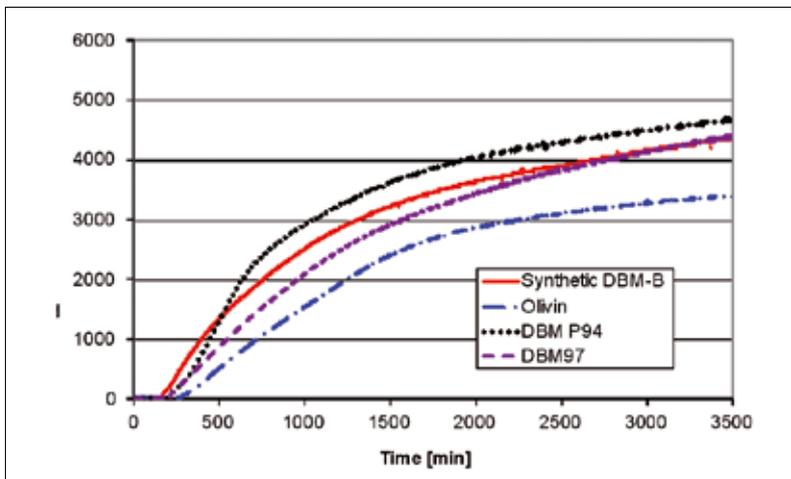
However, when larger blocks are made, cracks may be generated during the dry-out process (Fig. 2 and 3).



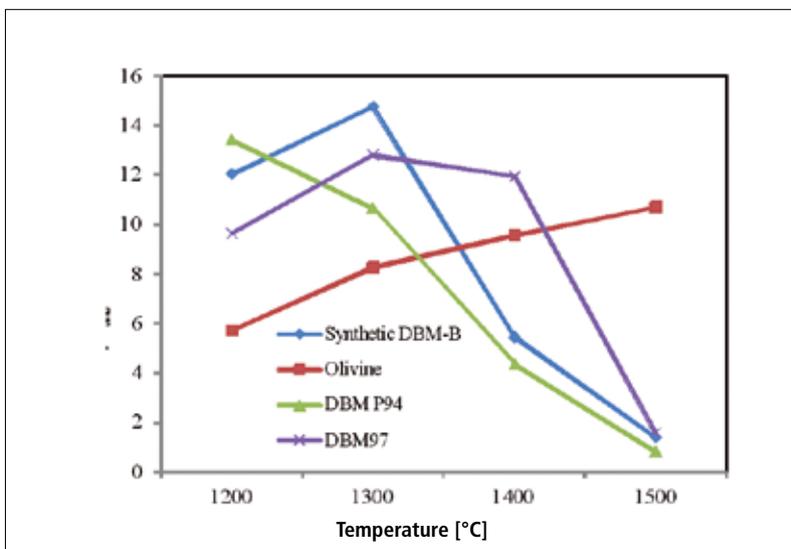
**Fig. 4** XRD patterns of: a) DBM-B, and b) DBM-C samples



**Fig. 5** Self-flow (SF) and vibration-flow (VF) of magnesia castables with different types of aggregates



**Fig. 6** Setting and hardening process of magnesia castables with SiOX-Mag and different aggregates



**Fig. 7** Hot Modulus of Rupture (HMoR) as a function of test temperature and aggregate type

In larger blocks, the contact time with water at the core is longer than in small samples and the hydration of MgO at the centre is accelerated due to high vapour pressure and availability of water locally.

By using SiOX-Mag and 6 % microsilica, crack-free blocks with a thickness of 150 mm have been made. If more thickness is needed, adding more microsilica seems to be an alternative. The mechanism of how dispersants, drying agent and drying profile affect the MgO hydration in large samples is not well understood yet. Further investigations are ongoing and will be reported in the future.

### 3.2 Workability of MgO castables

The performance of SiOX-Mag in magnesia castables with different types of MgO aggregates has been evaluated (Tab. 1). The self- and vibration-flow are summarized in Fig. 5.

Self-flow around 80 % and vibration-flow of 110–120 % are achieved, no matter the quality and type of MgO aggregates, as long as the q-value remains constant, in these mixes at 0,25, and high quality microsilica is used. The water addition is kept constant at 15,3 vol.-%. It is clearly demonstrated that self-flowing MgO castables can be made with SiOX-Mag, high quality microsilica and different aggregates.

As gel-bonded MgO castables do not give good temperature readings using the exotherm curves, the propagation of ultrasonic waves through the castable was used to monitor the setting and hardening process. Fig. 6 shows the ultrasonic velocity development for castables with the different aggregates. Obviously the type of aggregates has some impact on the setting and hardening, probably due to the impurity level and the reactivity of the aggregates. The working time with SiOX-Mag is kept between 2 and 5 h for all castables. The olivine is less reactive than the synthetic DBM when in contact with water, thus the microsilica-gel bonded olivine castable provides longer working time (some 5 h) than that of the synthetic DBM castables (some 3 h).

### 3.3 Hot-properties of MgO castables

HMoR is plotted as a function of test temperature in Fig. 7. For DBM-B and DBM 97, the development of HMoR is similar and

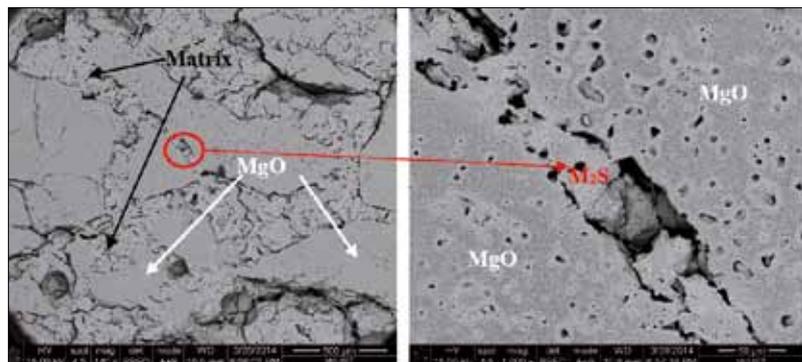
reaches a maximum value at 1300 °C. For DBM94, HMoR is continuously decreasing from 1200 towards 1500 °C. For olivine the development is completely different since HMoR increases dramatically from approximately 6 to 11 MPa from 1200 to 1500 °C. At 1500 °C, the olivine castable is 6 times stronger than the mix with DBM97 and 12 times stronger than the one with DPB94. The difference in HMoR is probably attributed to the degree of sintering between the MgO matrix and the MgO/olivine aggregates involving different phase transformations/formation during firing. For DBM aggregates no visual sintering is observed; while for olivine, obvious sintering between the aggregates and matrix is observed in the samples fired at 1400 and 1500 °C. Scanning Electron Microscopy (SEM) analysis of the samples was carried out, as shown in Fig. 8.

The DBM-B castable sample mainly consists of periclase (MgO) and in the matrix, large amounts of forsterite ( $Mg_2SiO_4$ ) are observed and no microsilica is detected. Furthermore, micro-cracks are observed between the MgO aggregates and the matrix. The presence of micro-cracks probably contributes to the reduced HMoR at 1500 °C. In the olivine castable sample the matrix consists of forsterite and a certain quantity of a ferrous-oxide containing phase (Fig. 8b). The ferrous-oxide containing phase is observed as light grey spots in the matrix. According to EDS characterization, the composition of these spots is Hortonoilite ( $MgO_xFeO_y$ ) $SiO_2$ . Iron from the olivine seems to react with the MgO fines and microsilica in the matrix at high temperatures. The HMoR of the olivine castable increases with increasing test temperatures (Fig. 7) due to sintering between the matrix and aggregates.

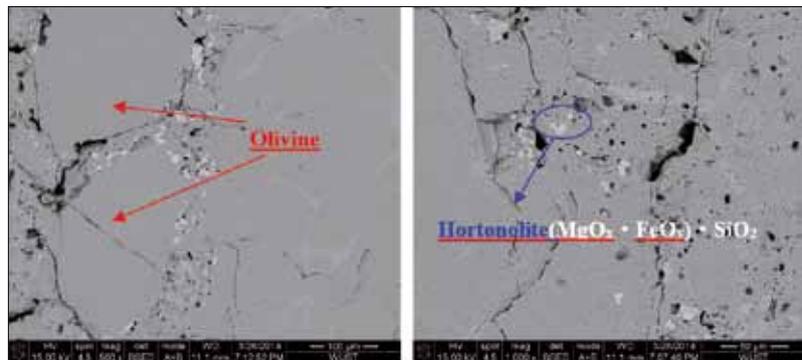
Microsilica reacts with MgO fines to form forsterite at high temperatures, hence no free microsilica particles are detected after firing. It should be emphasized that the relatively high dosage of microsilica has no negative effect on the hot-strength of the tested MgO castables.

#### 4 Conclusions

This study of the hydration of MgO in larger MgO castable blocks, as well as the work on self-flowing MgO castables using different basic aggregates, provide new insight to



a) Synthetic DBM-B



b) Olivine

**Fig. 8** SEM micrographs of MgO castables after HMoR test at 1500 °C:

a) DBM-B, and b) olivine

further develop microsilica gel-bonded MgO castables.

- The mechanism of hydration of MgO in larger MgO castable blocks seems to be different from that in lab-scale specimens. In larger blocks, both microsilica dosage and the type of dispersant affect the MgO hydration and related cracking during the dry-out process. Microsilica in combination with SiOX-Mag seems to be an efficient solution for anti-hydration of MgO.
- XRD characterization confirms that brucite formation can be avoided, provided sufficient microsilica is present. Only trace amounts of brucite were detected at 6 % microsilica, whereas no brucite was found at 8 %. Crack-free larger blocks, 300 mm × 300 mm × 300 mm (~70 kg), were produced.
- Microsilica gel-bonded self-flowing MgO castables using different aggregates, have been developed, exhibiting good placing properties and high hot-strength. The bond system MgO–SiO<sub>2</sub>–H<sub>2</sub>O contains only small amounts of bound water. Once the free water is removed, the castables can be fired at very high heating rates.

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