

# Impact of Magnesia Grain Size on the In Situ Spinel Formation in $\text{Al}_2\text{O}_3$ -MgO-C Refractories

A. Baghaei, H. H. Boroujeni, M. Naeemi

In order to evaluate the effect of magnesia grain size on spinel formation process, four compositions with different dead burned magnesia grain sizes along with fused alumina and graphite were prepared. After pressing, samples were tempered at 220 °C and coked under reducing atmosphere at 1600 °C. Permanent Linear Change (PLC) and physical properties including Bulk Density (BD) and Apparent Porosity (AP) were measured. Phase analyses were investigated by X-Ray Diffraction (XRD) technique and flexural strength of samples at 1400 °C in Ar atmosphere were determined by HMOR test. In addition, the samples were coked once again under coke bed at 1600 °C in order to assess the spinel formation process. The results of the PLC have shown that the use of finer magnesia grain sizes in the composition would increase the available surface area for spinel formation reaction. In fact, the PLC value of the sample M4 was +4 % while this value for other samples M3, M2 and M1 was +3,27, +2,44 and +2,36 %, respectively. Moreover, spinel formation decreased by the increase of magnesia grain size to a certain level. Regarding the results of second coking process, although some unreacted magnesia were characterised by XRD in sample M1, only negligible expansion were recorded for samples which could be due to the formation of spinel phase in the magnesia and alumina interface acting as an ion diffusion barrier. Flexural strength of samples at 1400 °C increased by using finer fractions of magnesia in samples because of the formation of spinel phase in the matrix as a ceramic bond which has been revealed by SEM/EDS investigations.

## 1 Introduction

The application of alumina-magnesia-carbon (AMC) bricks has been limited to the impact area and melting zone of steel ladles

Ali Baghaei, Homeyra Heydari Boroujeni,  
Mehdi Naeemi  
Mehrgodaz Refractories Company  
Sefid-Dasht  
Chaharmahal & Bakhtiari 88751-16655  
Iran

Corresponding author: Ali Baghaei  
E-mail: a.baghaei88@yahoo.com

Keywords: alumina-magnesia-carbon,  
spinel, grain size, carbon containing  
refractories

Received: 02.11.2017

Accepted: 15.01.2018

owing to the chemical attacks of slag in the slag zone. AMC bricks appeared as an alternative to MgO-C and  $\text{Al}_2\text{O}_3$ -C refractories, and their main advantage is the reduction of joint wear due to controlled residual expansion by in situ spinel  $\text{MgAl}_2\text{O}_4$  formation [1]. Mukhopadhyay et al. reported that MgO- $\text{Al}_2\text{O}_3$  spinel readily forms above 1050 °C in the AMC bricks, and the maximum spinel formation takes place around 1600 °C.

From an analysis of the microstructure, it was observed that the rate of spinel formation and associated volume expansion was highly dependent on the reactivity and particle size of Magnesia [2]. Spinel formation and following expansion of the brick helps to reduce the wear in the joints. This reaction also leads to the formation of micro cracks because of the differences in thermal expansion coefficients between spinel phase and its reactants resulting in slag penetration. For this reason, there is a ne-

cessity to use optimum content of magnesia in the bricks composition [3].

In situ formed  $\text{MgAl}_2\text{O}_4$  are almost present at interfaces between particles of MgO and  $\text{Al}_2\text{O}_3$ . Spinel layer, indeed, is created on the surfaces of MgO grains. After formation of initial spinel layers, subsequent growth or thickening of the in situ spinel becomes much more difficult due to indirect contact of the reactants, MgO and  $\text{Al}_2\text{O}_3$ , through slightly impenetrable spinel layer.

Thus, so as to complete the reaction, a complex counter diffusion process is required in which  $\text{Mg}^{2+}$  ions diffuse away from, and  $\text{Al}^{3+}$  ions diffuse toward the MgO- $\text{MgAl}_2\text{O}_4$  interface and vice versa for the  $\text{MgAl}_2\text{O}_4$ - $\text{Al}_2\text{O}_3$  interface. From the reactions which are shown in Fig. 1, it can be understood that the formed spinel phase at the alumina side is three times much more than the magnesia side [4].

This mechanism, often called the Wagner mechanism, indicated inverse cation diffu-

sion through the spinel layer. This mechanism completely avoids the need for anion transport through the spinel layer through the starting oxides or through the gas phase. The basic assumption in this mechanism including:

- The reaction layer is dense and does not contain non equilibrium defect such as dislocation or grain boundaries.
- Interface reactions are fast in comparison with ion transport through the spinel.
- Diffusing species are coupled only by the requirements of local equilibrium and electro-neutrality, and otherwise move independently.

Thermodynamic equilibrium exists at phase boundaries [6].

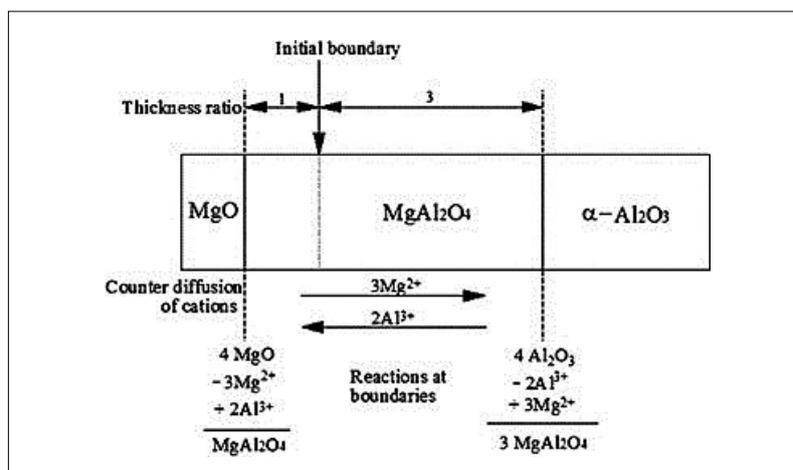
In this study, in order to understand the role of magnesia grain size on the spinel  $MgAl_2O_4$  formation process and functional properties of AMC refractories, different samples were prepared with different magnesia grain sizes, fused alumina and graphite.

## 2 Experimental

Two sets of four compositions with different grain sizes of magnesia with certain codes (Tab. 1), along with fused alumina, graphite, novolac resin and special additives were prepared. After mixing in a laboratory intensive mixer, mixtures aged for 24 h. Then, bar type samples (25 mm × 25 mm × 150 mm) were pressed at 150 MPa followed by tempering at 220 °C for 12 h. All samples were heat treated under coke-bed at 1600 °C for 4 h. Afterward, physical properties including Apparent Porosity (AP) as well as Bulk Density (BD), Hot Modulus of Rupture at 1400 °C (HMOR; HRY-05QP/CN) and permanent linear change (PLC) were measured. Furthermore, phase analysis was determined by X-ray diffraction analysis (XRD; X'Pert PRO MPD PANalytical Company) technique. In terms of spinel formation process investigation, samples were fired under coke bed at 1600 °C for second time. After that, Permanent Linear Changes (PLC) of samples were determined, and phase analysis was evaluated by XRD analysis while the microstructures of samples were investigated by scanning electron microscope (FESEM, MIRA3, TESCAN).

## 3 Results and discussion

As can be seen in (Tab. 2), AP and BD of almost all samples after tempering were the



**Fig. 1** Formation of spinel layer between alumina and magnesia [5]

same. Nevertheless, these figures after coking at 1600 °C experienced much differences where the highest AP and the lowest BD were related to sample (M4) while the lowest AP and the highest BD were recorded for sample (M2). Drawing a comparison between the BD and AP results of samples revealed that using both fine and extra coarse fractions of magnesia grain sizes in samples lead to increase the AP and reduce the BD. In fact, the thermal expansion coefficient of magnesia at elevated temperatures is more than its value for alumina and especially carbon of the matrix [7]. For this reason, in the course of firing, magnesia has more thermal expansion than the other components which cause compression stresses on the matrix of AMC refractories. These stress-

es can be concentrated by the increase of magnesia grain size.

During cooling down to ambient temperatures, magnesia grains experience greater shrinkage in comparison to the matrix and regarding the spinel formation at high temperatures, based on Kirkendall effect, a great portion of  $Mg^{2+}$  ions migrate to the alumina lattice which reduce the size of magnesia grains so that the gaps between magnesia grains and the matrix (Fig. 2) were created and the apparent porosity was increased [4, 8].

However, increasing the specific surface area of magnesia in sample M4, resulting in additional available surfaces for spinel formation reaction which can be proven by taking the figures of PLC (Tab. 2) into ac-

**Tab. 1** Composition of samples with different fractions of magnesia

Code	M1 [%]	M2 [%]	M3 [%]	M4 [%]
Magnesia	10	10	10	10
Fused alumina	81,5	81,5	81,5	81,5
Natural flake graphite	7	7	7	7
Novolac resin + hexa.	+3	+3	+3	+3
Additives	+1,5	+1,5	+1,5	+1,5
Grain size of magnesia	1–3,35 mm	0–1 mm	<45 μm + 0–1 mm	<45 μm

**Tab. 2** Properties of samples with different fraction of magnesia.

Sample Code	Tempered (220 °C)		Coked (1600 °C)		Average of Primary PLC [%]
	BD [g/cm <sup>3</sup> ]	AP [%]	BD [g/cm <sup>3</sup> ]	AP [%]	
M1	3,30	7,43	3,00	16,58	+2,36
M2	3,31	7,65	3,04	15,57	+2,44
M3	3,32	7,84	3,02	16,32	+3,27
M4	3,31	7,98	2,97	17,05	+4,00



**Fig. 2** Digital micrograph of the surface of sample M1

**Tab. 3** PLC values of samples after secondary coking process

Sample Code	Average of Secondary PLC [%]
M1	+0,11
M2	+0,06
M3	+0,16
M4	-0,02

count followed by enhancement of apparent porosity and decrease of bulk density after coking at 1600 °C. As expected, PLC values of samples increased from sample M1 to M4 which is owing to the further spinel formation by reducing the size of magnesia in AMC samples.

Properties of samples with different magnesia grain sizes are shown in (Tab. 2).

Spinel formation reaction begins from the surface of magnesia grains and propagates to the interior sites. In M1 and M2, PLC values are close to each other because of the formation of spinel layer at the interface of magnesia and alumina with a dif-

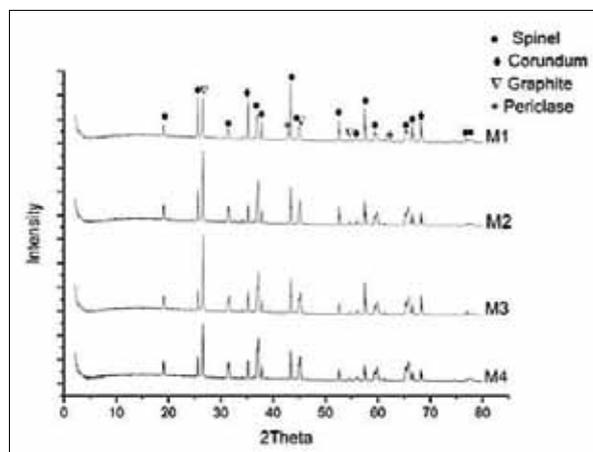
ferent diffusion coefficient that acted as an ion diffusion barrier and introducing a pinning effect resulting in hindering the cation counter diffusion through the interfaces [8]. In this way, spinel formation rate gradually decreased. X-ray diffraction patterns of M1 to 4 samples after first coking at 1600 °C are shown in Fig. 3.

Phase analysis after coking has shown that the main peak in sample M1 is Corundum phase. Meanwhile, decreasing the magnesia grain sizes (from M1 to M4) resulted in lower intensity of corundum phase and higher intensity of spinel phase that is due to higher spinel formation in M4 sample in comparison to M1. In addition, related peaks of periclase phase were distinguished in M1 that is because of incomplete spinel formation reaction which was explained extensively in previous section. Furthermore, using smaller magnesia grain size in the composition resulted in elimination of the peaks of periclase phase and enhancement of spinel peaks which is a concise proof of previous statements. XRD patterns of sam-

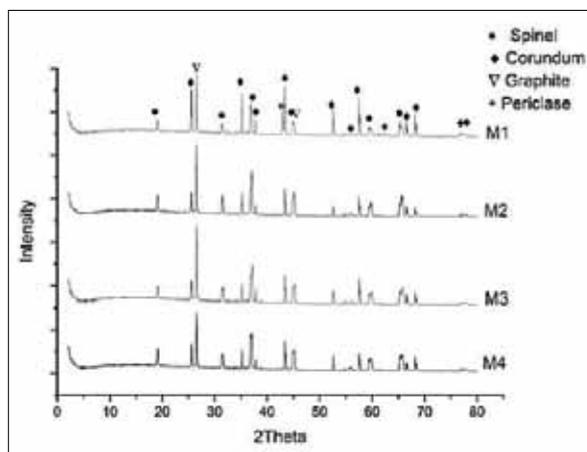
ples after second coking at 1600 °C are shown in Fig. 4.

Although the peaks of periclase phase after re-coking at 1600 °C was distinguished in M1 sample, changing the intensity of spinel phase peaks in this sample and specifically the spinel formation was negligible. In fact, Mg<sup>2+</sup> and Al<sup>3+</sup> cations counter diffusion through the interfacial spinel layer were insufficient for completing the spinel formation reaction while the use of finer magnesia fractions in M2 and M3 samples resulted in the completion of spinel formation reaction during re-coking. Also, regarding the accuracy level of XRD technique, the related periclase peaks in both XRD patterns (Fig. 3–4) were not revealed in M2, M3 and M4 samples, but the PLC figures after re-coking which is presented in (Tab. 3) confirmed that a very low spinel formation during re-coking was happened in M2 and M3 samples and the spinel formation reaction was completed in M4 sample during first coking. SEM micrographs of samples are shown in Figs. 5–8.

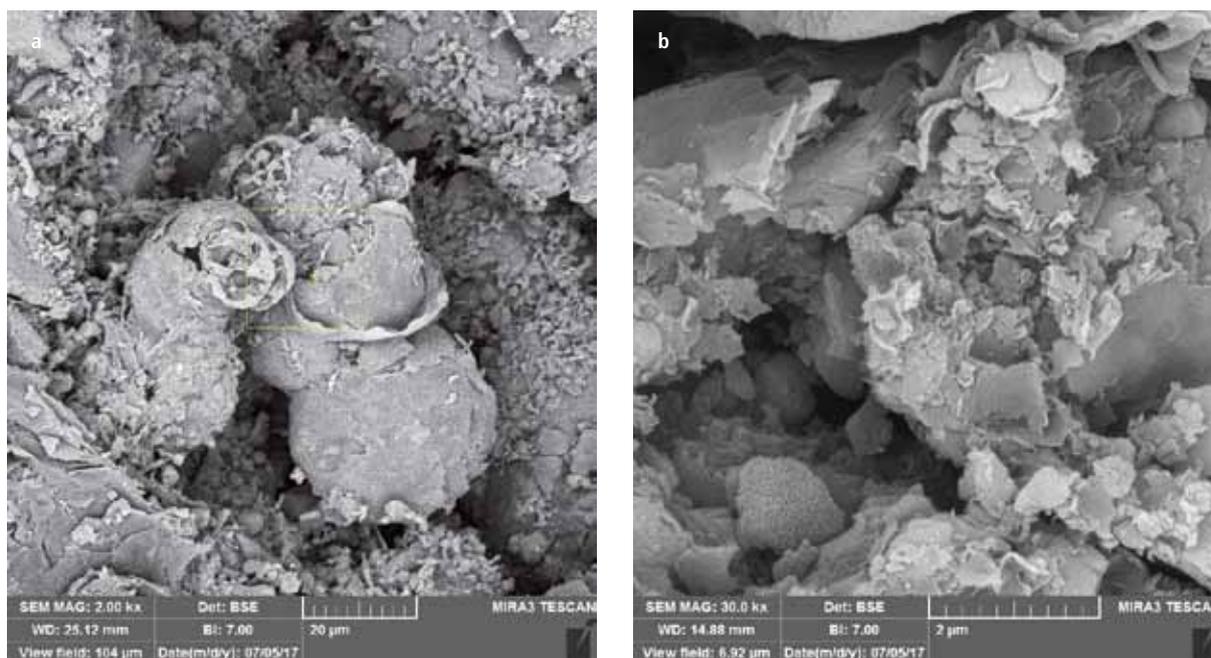
As can be seen in Fig. 5, distributed bonds were created by the reaction of anti-oxidants and carbon of the matrix (Fig. 5 a) while carbonaceous bonds were distinguished as the main bonding phase in the microstructure (Fig. 5 b). Regarding the Fig. 6, it has been shown that the carbonaceous bonding was existed in the microstructure of sample M2. In the microstructure of sample M3 (Fig. 7), major amount of carbonaceous and negligible amount of spinel bonds were characterised. Presence of major spinel bonds in the microstructure of sample M4 was revealed in SEM micrographs of Fig. 8.



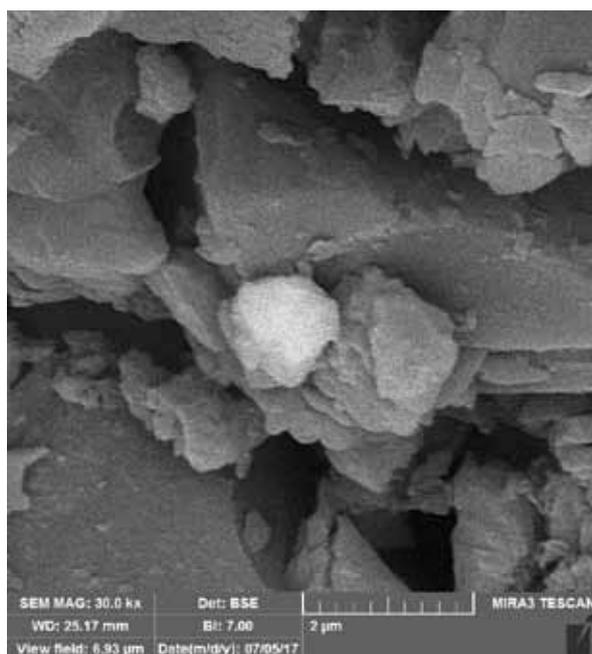
**Fig. 3** X-ray diffraction patterns of samples after primary coking at 1600 °C



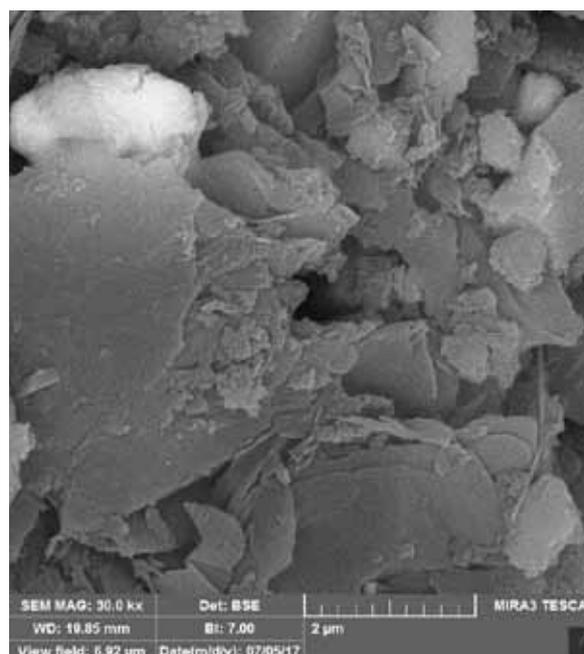
**Fig. 4** X-ray diffraction patterns of samples after secondary coking at 1600 °C



**Fig. 5** SEM micrographs of sample M1 with different magnifications: a) 2 k ×, b) 30 k ×



**Fig. 6** SEM micrographs of sample M2 with 30 k × magnification



**Fig. 7** SEM micrographs of sample M3 with 30 k × magnification

This can be proven by consideration of EDS analysis into account. In addition, as can be seen in Fig. 8 c, grains and particles were interconnected by well distributed spinel crystals which recognized as ceramic bonds. Generation of these spinel bonds were due to the use of fine magnesia grain size in the composition. These ceramic bonds are ionic and generally have the following properties: high hardness, high temperature strength and chemical inertness [9]. Spinel formation

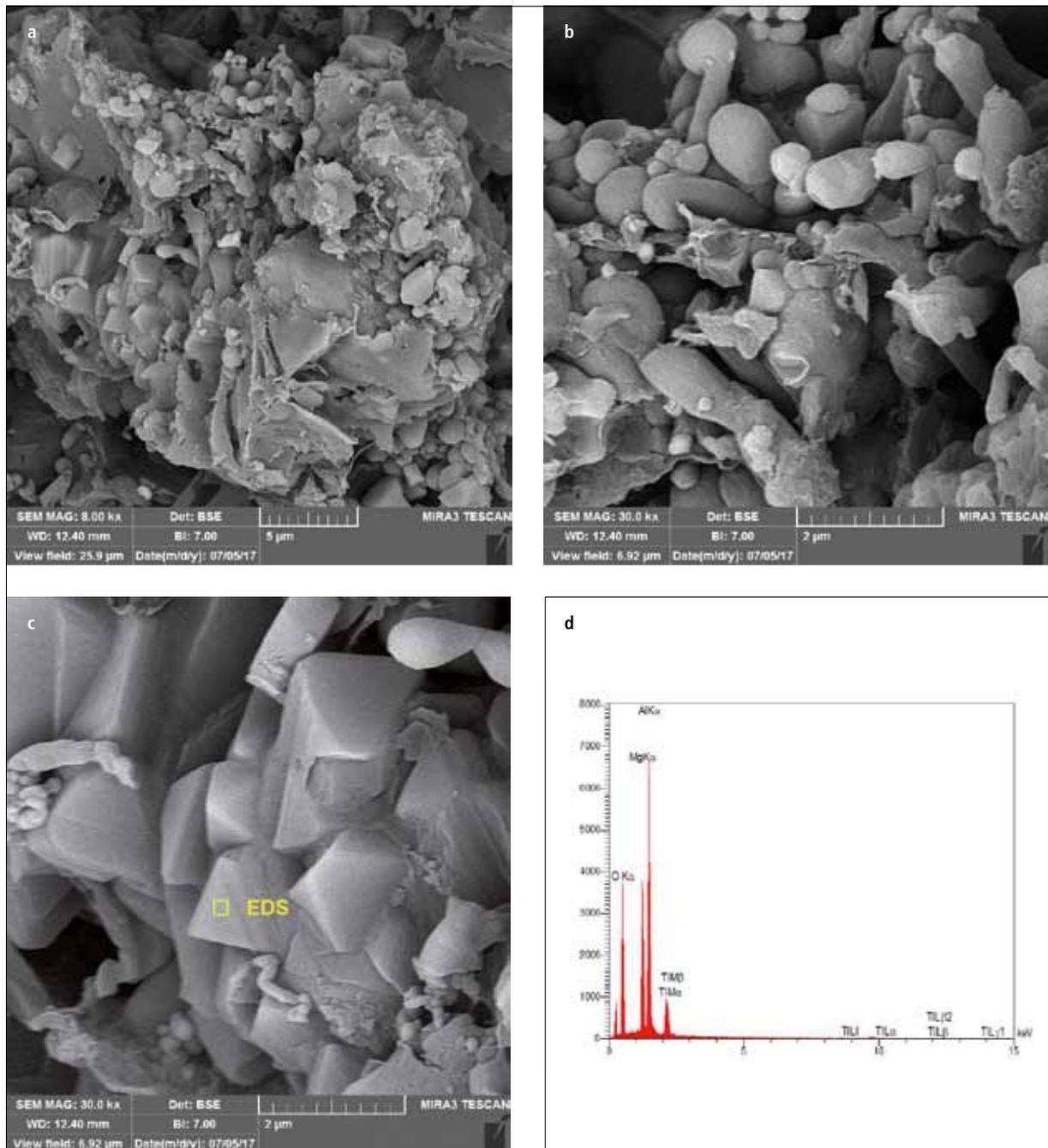
reaction also produces micro-cracks in the matrix because of differences in the thermal expansion coefficient of spinel and alumina and magnesia which favours the toughness of the refractory [10].

Results of HMOR test has been indicated in Tab. 4. It can be inferred that the flexural strength of samples at elevated temperatures increased by using finer fractions of magnesia in samples. Indeed, further modulus of rupture in sample M4 is due to the

presence of stronger spinel phase ceramic bonds between alumina grains in the matrix.

**Tab. 4** HMOR values of samples at 1400 °C in Ar atmosphere

Sample Code	Average of HOMR [MPa]
M1	4,5
M2	6,9
M3	7,4
M4	8,2



**Fig. 8** SEM micrographs of sample M4 with different magnifications: a) 8 k x, b) 30 k x, and c) 30 k x, d) EDS analysis of micrograph (8c)

#### 4 Conclusion

Drawing a comparison between the BD and AP results of samples revealed that using both fine and extra coarse fractions of magnesia grain sizes in samples lead to increase the AP and reduce the BD. Apparent porosity increased by different mechanisms in samples. The mechanism of increasing the AP in M2 to M4 samples is the increase of spinel formation followed by elevated PLC

values, but in case of sample M1, it has been related to use of the coarse magnesia grains resulting in generation of gaps between magnesia grains and the matrix. It has been shown by XRD analyses that the formation of spinel layer at the interface of magnesia and alumina with a different diffusion coefficient especially in the coarse grain samples acted as an ion diffusion barrier and introducing a pinning effect resulting in hindering the cation counter diffusion

through the interfaces. Hence, spinel formation reaction rate gradually decreased. Results has been shown that PLC values of samples increased from sample M1 to M4 which is owing to the further spinel formation by reducing the grain size of magnesia in AMC samples. SEM investigations showed the presence of spinel phase as a ceramic bond in fine grain samples which assisted to increase the modulus of rupture at high temperatures.

## Acknowledgement

Authors would like to express their sincere gratitude to the authorities of Mehrgodaz Refractories Company and the personnel of R&D Center for their supports of this research.

## References

- [1] Muñoz, V.; et al.: Chemical wear of  $Al_2O_3$ -MgO-C bricks by air and basic slag. *J. Europ. Ceram. Soc.* **35** (2015) [5] 1621–1635
- [2] Mukhopadhyay, S.; et al.: Effect of MgO Grain size on thermal expansion behavior of alumina-magnesia-carbon refractory. *Int. J. Appl. Ceram. Technol.* **1019** (2013) 1012–1019
- [3] Muñoz, V.; Martinez, A.G.T.: Thermal evolution of  $Al_2O_3$ -MgO-C refractories. *Procedia Mater. Sci.* **1** (2012) 410–417
- [4] Engineering, C.; Sahoo, S.: Study on the effect of the effect of different raw materials sources on spinelization and densification of MgO- $Al_2O_3$  spinel, 2014
- [5] Emmel, M.; et al.: In situ spinel formation in  $Al_2O_3$ -MgO-C filter materials for steel melt filtration. *Ceram. Int. PART B* **40** (2014) [8] 13507–13513
- [6] Armijo, J.S.: The kinetics and mechanism of solid-state spinel formation – A review and critique. *Oxid. Met.* **1** (1969) [1] 2, 171–198
- [7] Routschka, G.; Wuthnow, H.: Pocket manual refractory materials. Design, properties and testing. Essen 2008
- [8] Jin Fan, H.; et al.: Monocrystalline spinel nanotube fabrication based on the Kirkendall effect. *Nat. Mater.* **5** (2008) [8] 627–631, 2006
- [9] Swain, M.V. (Ed.): Structure and properties of ceramics. Weinheim 1994
- [10] Baudin, C.: High temperature mechanical behavior of magnesia-graphite refractories. In: Fundamentals of refractory technology. Westerville, Ohio 2012