Journal of
Ceramic Science
and Technology

J. Ceram. Sci. Technol., **13** [1] 9-14 (2022)
DOI: 10.4416/JCST2021-00009
available online at: http://www.ceramic-science.com

Study on the Effect of MgO Addition on the Physical, Mechanical and Thermal Properties of Alumina-Zirconia-Carbon Refractories

M. Abolfazli[1], M. Hossein Paydar*[1]

[1]Department of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, Iran

received May 31, 2021; received in revised form October 12, 2021; accepted October 13, 2021

Abstract

In this study, the effect of magnesium oxide addition (0 – 10 wt%) on the microstructure, mechanical properties, corrosion and oxidation resistance of alumina-graphite refractory bodies containing 20 wt% zirconia was investigated. Samples were fabricated by mixing raw materials with phenolic resin as a binder. The powder mixtures were isostatically pressed at 850 bar and sintered at 1 400 °C for 8 h under reducing atmosphere. The results showed that the presence of MgO reduces the bulk density, which causes more slag penetration and thus reduces corrosion resistance. Also, evaluation of the mechanical properties reveals that with increasing magnesium content, the flexural strength and compressive strength of the samples decrease. Furthermore, it has been proved that positive permanent linear change owing to spinel formation leads to a reduction in thermal shock resistance.

Keywords: Alumina-carbon composite, refractory, stopper, microstructure, mechanical properties, magnesia

I. Introduction

Refractories are one of the most important industrial materials. Growth in all metallurgical and high-temperature industries depends on these materials. Refractories are mainly made of various oxide materials with low evaporation rate and high temperature stability. Enhancement of the properties and performance of refractories may be achieved by means of combination with carbon as a high-temperature-resistance material [1–2]. These advanced refractories include oxides of nonferrous and carbon such as ZrO_2-C, MgO-C and Al_2O_3-C and are mainly used in the steel industry [3]. One of the most important applications of this type of refractories is in fabrication of stoppers based on Al_2O_3-C, where it is necessary to use a material with a high modulus of rupture, high cold crushing strength, low thermal expansion coefficient, high thermal conductivity, high thermal shock resistance, and slag and molten metal resistance. Despite the aforementioned advantages of using alumina-carbon refractories, they have several problems. The most important issue is carbon oxidation at high temperatures, which increases their residual porosity and thus reduces their strength and corrosion resistance [4]. Another problem is erosion (chemical and physical) owing to the penetration of molten metal or slag into the pores caused by dissolution of alumina by slag or oxidation of carbon by iron oxide in slag and ambient gas. The last problem is direct wear with the flow of liquid iron and thermal or mechanical impacts. These problems may be alleviated by using antioxidants that play an important role in reducing carbon oxidation [5]. Another solution is to prepare composite refractories using other oxides with a high melting point. Accordingly, refractories containing other oxides such as magnesia /graphite [6] and zirconia /graphite [7], etc. have been developed.

Liu Qing-cai and his coworkers [8] studied the corrosion resistance and microstructure of Al_2O_3-C-based refractories. They evaluated the performance of the refractories by submerging them in a quasi-steady state as well as in a rotating state. They deduced that the addition of carbon and zirconia reduced the corrosion rate of Al_2O_3-C-based refractories. In other research, Resende and his coworkers [9] investigated the properties of alumina-magnesia-graphite refractories with resin bonds. Their results revealed that this new class of refractories demonstrates excellent chemical and thermodynamic stability as well as thermal and mechanical properties. Khoshkalam and Faghihi-Sani [10] evaluated the effects of uniaxial and cold isostatic pressing on the mechanical properties of alumina-zirconia-magnesia spinel composite with different compositions and sintered at temperatures in the range of 1 500 – 1 650 °C. They showed that the composites produced by means of cold isostatic pressing have better mechanical properties at a lower sintering temperature. Rand and his coworkers investigated the role of carbon and graphite in composite refractories. They emphasized that the main reason for the use of carbon is not wettability but its ability to modify the thermal shock properties of the composite owing to its unique thermal and mechanical properties [11]. Bakr and Wahsh [1] proved that MgO has a positive effect on refractoriness, apparent porosity and thermal shock resistance of alumina-zirconia-based refractories. Klewski *et al.* [12] studied the effect of different alumina sources with different grain size on the final properties of AMC bricks. Babakhanova and Aripova [13] changed the

---

* Corresponding author: paaydar@shirazu.ac.ir

Table 1: Formulation of samples in wt%.

Sample	Tubular alumina	Brown fused alumina	White fused alumina	Fused silica	Coarse-grained graphite	Zirconia	Magnesia	Si	Phenolic resin	
									Powder	Liquid
3	3	5	0	10	20	10	10	10	25	1
3	3	5	5	10	20	10	10	10	25	2
3	3	5	10	10	20	10	10	10	25	3

corundum, talc and graphite amount and showed that the maximum slag strength is related to the composition with the lowest porosity.

Mukhopadhyay *et al.* [14] discussed the effect of MgO grain size and found that the spinelizarion reaction and permanent linear change of the refractories are directly related to the total surface area of magnesia.

Magnesia is used in a wide variety of applications owing to its special properties such as high thermal and low electrical conductivity [15]. In the present study, the effect of using MgO in the range of 0 to 10 wt% on the chemical, physical and mechanical properties of Al_2O_3-zirconia-C refractories is investigated.

II. Experimental Procedure

The chemical composition of the alumina-carbon refractory composite containing magnesia is shown in Table 1. As can be seen, all samples are made of three types of alumina (tubular, white fused and brown fused alumina), fused silica, coarse-grained graphite (specification is illustrated in Table 2), zirconia, silicon and phenolic resin.

All the raw materials used in this study were metallurgical grade. A particle size analyzer and scanning electron microscopy were used to determine the physical properties of the raw materials.

Table 2: Coarse-grained graphite specification.

Fixed carbon (wt%)	Ash (wt%)	Volatile (wt%)	Moisture (wt%)	Particle size (μm)
Min 95	Min 4.00	Max 1.50	Max 0.50	(50 wt%) 100 – 200 (50 wt%) 200 – 350

According to the chemical composition, all materials were wet-milled in a planetary ball mill for 7 h using absolute ethanol as a dispersant. The mixed powders were then passed through 60 mesh sieves to obtain a uniform granulated powder. After being dried, the mixed powders were poured into a latex mold and were vacuumed. Ultimately, the powders were isostatically pressed with the application of 850 bar pressure and sintered at 1 400 °C for 8 h.

Bulk density, modulus of rupture, thermal shock resistance, thermal expansion coefficient, permanent linear changes and oxidation resistance were measured according to ASTMC-138, ASTMC-133, ASTMC-1171, ASTMC-531, ASTMC-113, ASTMC-863 standards, respectively.

III. Results and Discussions

The particle size distribution of the raw materials is presented in Table 3. As can be seen, all materials except alumina are smaller than 100 microns and the average particle size is about 10 microns.

The SEM image of the graphite powder is displayed in Fig. 1. As shown, the graphite particles are flaky and irregular, the particles are almost uniformly distributed, and the average of particle size is estimated at about 150 micrometers.

Table 3: Size and size distribution characteristics of the used raw ceramic materials.

Material	D_{10} μm	D_{50} μm	D_{90} μm
Tabular alumina	0.726	6.968	42.374
Brown fused alumina	38.319	126.927	246.672
White fused alumina	0.996	13.205	62.939
Magnesia	1.037	13.973	67.681
Zirconia	0.544	2.605	7.293
Fused silica	1.363	24.208	99.051

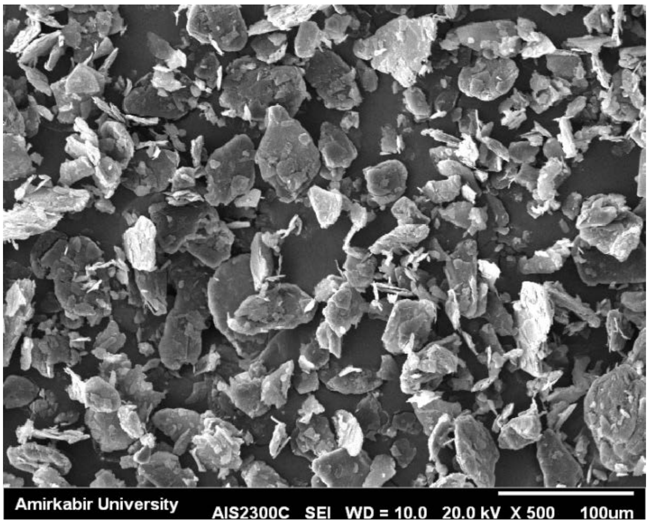

Fig. 1: SEM image of coarse-grained flaky graphite.

The effect of MgO addition on the physical properties of the fabricated refractory composites is shown in Fig. 2 and is also reported in Table 4. As can be seen, addition of MgO led to a decrease in the bulk density, MOR, CRS and TSR of the composite. The presence of magnesia increases the grain size of zirconia [1], which can reduce the bulk density of the samples, subsequently leading to a decrease in the MOR, CRS and TSR of the composite. The modulus of rupture and other physical properties depend on the grain size, grain shape, apparent porosity, nature and amount of phases in the sintered body, which are mainly influenced by the chemical composition [16].

The grain size of samples that do not contain magnesia is smaller and, as a result, their cold crushing strength and modulus of rupture is higher [1]. In addition, although magnesia has good thermal conductivity, its high coefficient of linear thermal expansion reduces shock resistance.

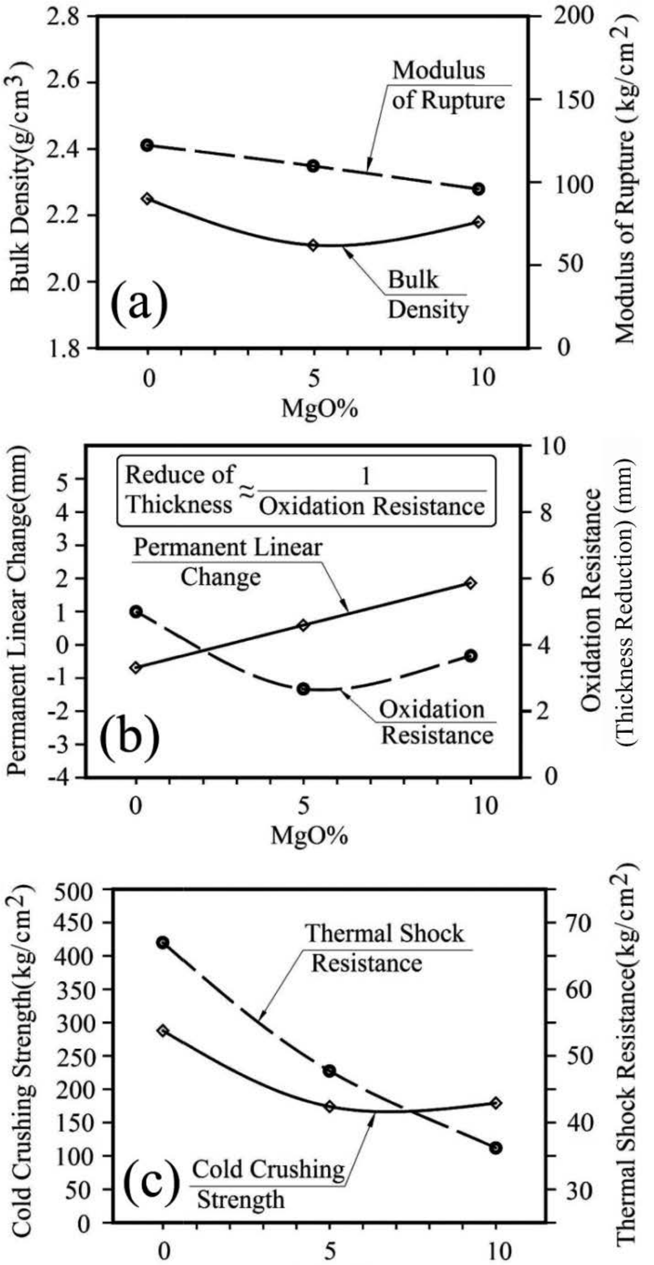

Fig. 2: (a) Bulk density and modulus of rupture, (b) Permanent linear changes and oxidation resistance (c) Cold crushing strength, and thermal shock resistance.

As shown in Fig. 2b, the permanent linear change of a magnesium-free sample is negative, meaning that the sample shrinks during sintering. The addition of magnesia causes $MgAl_2O_4$ spinel formation, which results in positive permanent linear changes.

The effect of magnesia on the oxidation resistance of the fabricated refractories is also shown in Fig. 2b. As can be seen, the sample containing 5 wt% magnesia has the least reduction in thickness and therefore the highest oxidation resistance. In fact, the oxidation of carbon-carbon bonds depends on the texture, grain size distribution, purity and chemical composition of the raw material, as well as on the amount of residual porosity and pore size distribution. Using alumina as a basic raw material in fabrication of C-alumina refractories leads to higher oxidation of graphite. The presence of alumina in alumina-carbon refractories accelerates the oxidation of graphite. Al^{3+} ions in alumina act as an electron acceptor against C^{4+} and weaken the C-C bond, thus increasing graphite oxidation. On the other hand, ZrO_2 and MgO are electron donors that prevent oxidation by stabilizing the electron distribution of the graphite structure [16]. Therefore, oxidation resistance can be expected to improve with the addition of magnesia. However, it is observed that adding more than 5 wt% of magnesia reduces the oxidation resistance, which is due to the increase in residual porosity. The large amount of porosity in the samples leads to the irreversible expansion of graphite at high temperatures, which can affect the oxidation resistance.

The effect of MgO addition on the thermal expansion of alumina-carbon refractories is shown in Fig. 3 and the values of thermal expansion coefficient are presented in Table 5.

As can be seen, for the sample without MgO, at about 1 100 °C, a significant change in the slope of the expansion diagram versus temperature (from positive to negative values) is observed, which changes again to a positive value when the temperature is increased up to 1 200 °C.

Table 4: Bulk density, cold crushing strength, modulus of rupture, thermal shock resistance, permeant linear changes and oxidation resistance.

Properties	0 % MgO	5 % MgO	10 % MgO
Bulk density (g/cm³)	2.25	2.10	2.15
Cold crushing strength (kg/cm²)	287.95	174.7	182.02
Modulus of rupture (kg/cm²)	109.72	122.21	72.69
Thermal shock resistance (kg/cm²)	67.05	47.75	36.2
Permanent linear changes (mm)	-0.69	0.59	1.86
Oxidation resistance (thickness reduction (mm))	5	2.6	3.6

Table 5: Thermal expansion coefficient (×10^{-6}) values of Al_2O_3-C refractories containing MgO.

Temperature (°C)	0 wt% MgO	5 wt% MgO	10 wt% MgO
145	3.57	2.74	3.71
500	4.59	4.50	5.93
800	5.92	5.79	7.98
900	6.20	6.05	8.09
1 000	4.19	4.01	7.60
1 125	-1.10	2.47	2.56
1 200	4.51	3.12	5.86

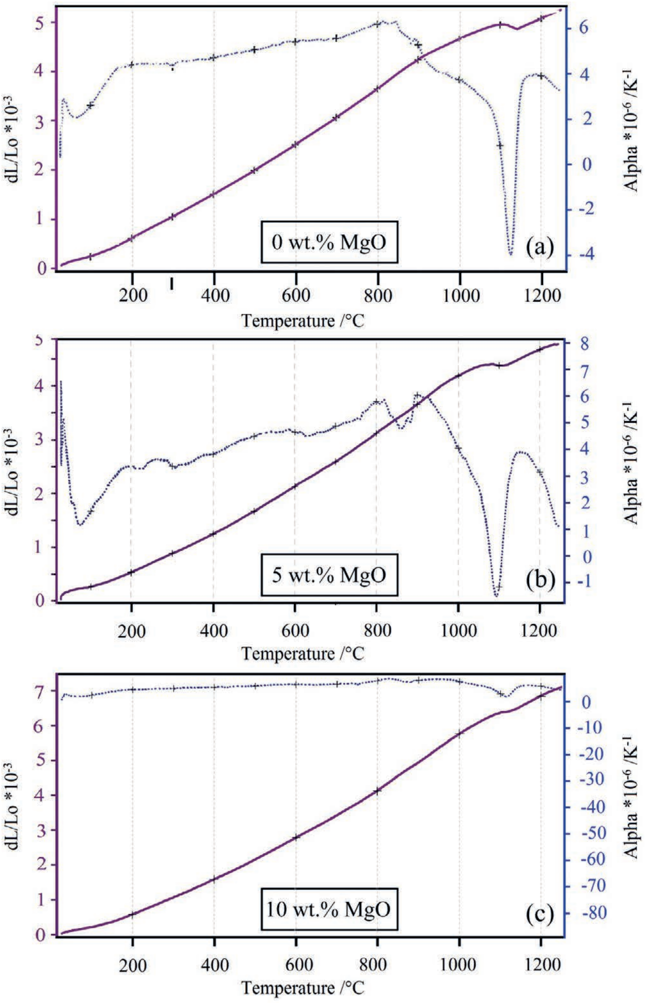

Fig. 3: Thermal expansion of the alumina-carbon refractories containing (a) 0, (b) 5 and (c) 10 wt% magnesia.

For the sample containing 5 wt% MgO, almost the same trend (with less intensity) can be observed, but in the sample containing 10 wt% MgO, no significant change in the slope was recorded. The change in the slope is probably due to zirconia phase transformation from monoclinic to tetragonal, which is expected to occur in the temperature range of 1 100 to 1 200 °C. For the sample containing 10 wt% magnesia, according to the XRD pattern (Fig. 4), zirconium silicate (zircon) and cordierite phases are formed and as a result no change in the slope is observed. Based on the thermal expansion coefficient data presented in Table 5, the sample containing 10 wt% MgO, in the temperature range of 100 to 1 200 °C, has the highest TEC values.

The X-ray diffraction pattern of the samples is presented in Fig. 4. As can be seen, for the sample containing 0 wt% MgO, only peaks related to the raw materials are observable and it seems that no significant reaction has occurred. In the sample containing 5 wt% magnesium, compared with the magnesia-free sample, the peaks related to cristobalite are eliminated and there are peaks of ZrO_2 (zirconia), $ZrSiO_4$ (zirconium silicate), $MgAl_2O_4$ (spinel) and $Mg_2Al_4Si_5O_{18}$ (cordierite), which indicates that some reactions have occurred in the sample. Finally, in the sample containing 10 wt% magnesia, the reactions are completed, and no peaks associated with the raw materials except alumina can be detected. All reactions occurred in the solid-state sintering process. The formation of cordierite as the most important compound in the SiO_2-MgO-Al_2O_3 ternary system, due to its desirable properties such as low TEC, high refractive index, high chemical resistance, low dielectric coefficient and high thermal shock resistance, can affect the properties of the samples [17–19]. The properties of refractories containing cordierite phase are expected to be significantly improved.

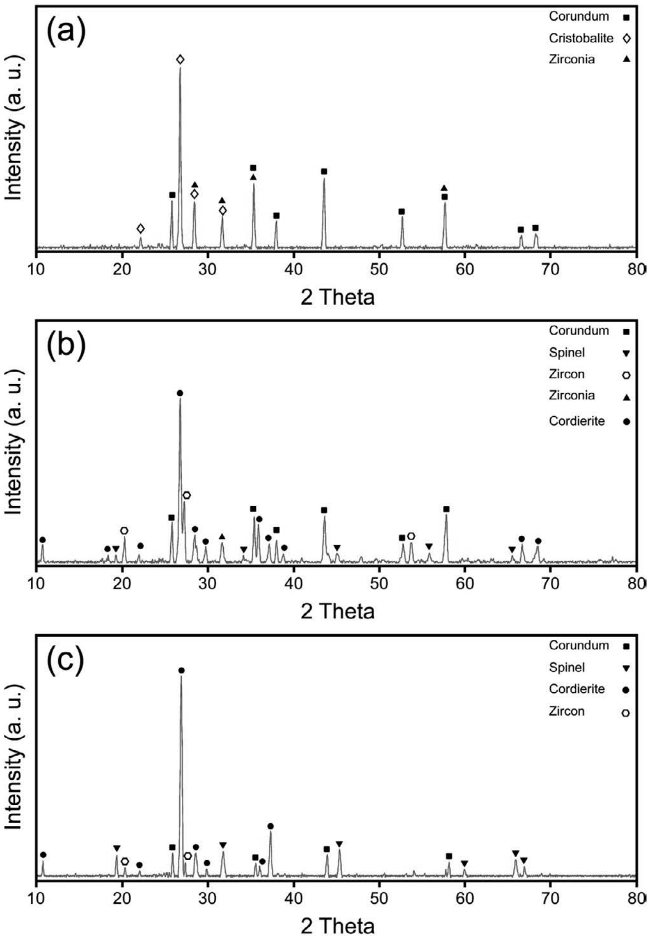

Fig. 4: X-ray diffraction of the samples containing (a) 0, (b) 5 and (c) 10 wt% magnesia.

Fig. 5 shows the surface of samples containing 0, 5 and 10 wt% magnesia before and after corrosion by the molten

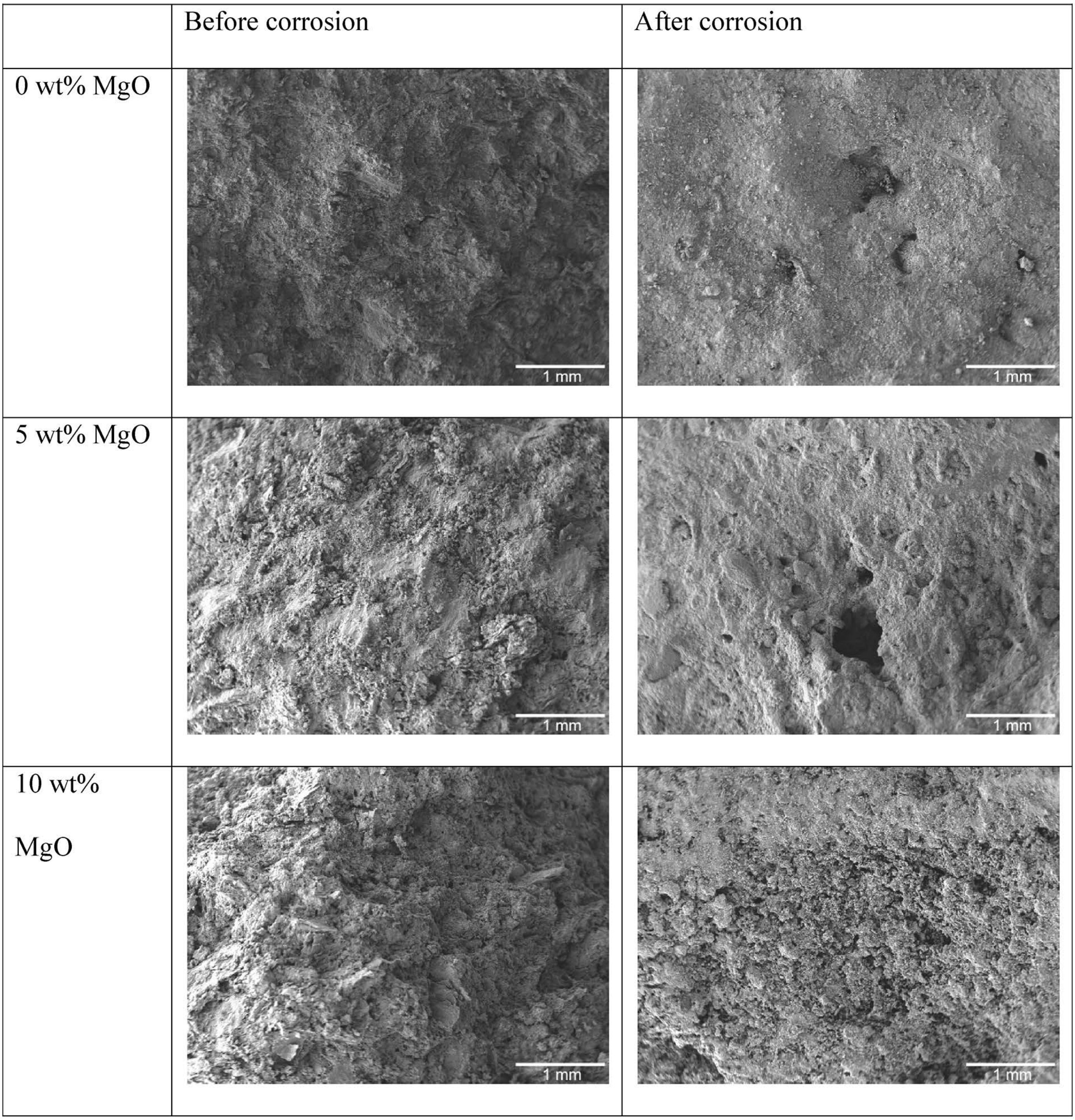

Fig. 5: Surface of samples containing 0, 5 and 10 wt% magnesia before and after corrosion. See table 1.

metal at 1 600 °C. As can be seen, the microstructure integrity of the sample containing 0 wt% MgO is higher than other samples, which is consistent with the density results. Images show some pitting on the eroded surface, indicating the corrosion process. As can be seen, as the amount of magnesium increases, so does the corrosion, which is likely due to the lower density and greater penetration of the melt.

IV. Conclusions

Alumina-carbon refractory composites containing zirconia were prepared and the effect of magnesium addition on their physical, chemical and mechanical properties was investigated. The results showed that the addition of magnesia reduces the bulk density, cold crushing strength, modulus of rupture, and thermal shock resistance. It also causes expansion during the sintering process and shows positive permeant linear change. The sample containing 10 % MgO had the highest thermal expansion coefficient and the lowest corrosion resistance. The results also showed that oxidation resistance was improved with the addition of 5 wt% magnesia.

Acknowledgment

This research is supported by Shiraz University, which is gratefully acknowledged.

References

1 Bakr, I.M., Wahsh, M.M.S.: Fabrication and characterization of multi-phase ceramic composites based on zircon-alumina-magnesia mixtures, *Mat. & Des.*, **35**, 99 – 105, (2012).

2 Garbers-Craig, A.M.: Presidential address: how cool are refractory materials?, *J. S. Afr. Inst. Min. Metall.*, **108**, [9], 491 – 506, (2008).

3 Ruffaldi A.: State of the art and recent development of carbon bonded refractory materials. Paper presented at: TICR 2004., Proceedings of the Tehran International Conference on Refractories, Tehran-Iran, 2004.

4 Khanna, R., Sahajwalla, V., Rodgers, B., McCarthy, F.: Dissolution of carbon from alumina-carbon mixtures into liquid iron: influence of carbonaceous materials, *Metall. & Mat. Trans. B*, **37**, [4], 623 – 632, (2006).

5 Rashmi R.R.: Studies on the effect of alumina aggregates on the performances of alumina-carbon refractories. M.Sc. Thesis. Department of ceramic engineering national institute of technology. Rourkela-76008, 2009.

6 Zhu, T., Li, Y., Sang, S.: Heightening mechanical properties and thermal shock resistance of low-carbon magnesia-graphite refractories through the catalytic formation of nanocarbons and ceramic bonding phases, *J. Alloy. Compd.*, **783**, 990 – 1000, (2019).

7 Yagovtsev, A.V., Obabkov, N.V., Kashcheev, I.D.: Study of effect of zirconia-graphite material composition on its properties, *Refract. Ind. Ceram.*, **54**, [5], 388 – 391, (2014).

8 Liu, Q.C., Zheng, H.M., Lu, C.F., Gao, W.: Corrosion resistance of high-alumina graphite based refractories to the smelting reduction melts, *J. Mater. Sci. & Eng.*, **2**, [12], 49 – 53, (2008).

9 Resende, W.S., Stoll, R.M., Justus, S.M., Andrade, R.M., Lono, E., Baldo, J.B., Leite, E.R., Paskocimas, C.A., Soledade, L.E.B., Gomes, J.E., Varela, J.A.: Key feature of alumina/magnesia/graphite refractories for steel ladle lining, *J. Eur. Ceram. Soc.*, **20**, 1419 – 1427, (2000).

10 Khoshkalam, M., Faghihi-Sani, M.A.: An investigation on mechanical properties of alumina-zirconia-magnesia spinel composite ceramics fabricated by gel-casting using solution combustion synthesized powder, *Mater. Sci. & Eng. A.*, **587**, 336 – 343, (2013).

11 Rand, B., Ahmed, A.S., Ramos, V.P.S.: The role of carbon in refractories, *Iran. J. Mat. Sci. & Eng.*, 1, [3], 9 – 15, (2004).

12 Klewski, M., Lucyna, O., Michał, S.: Alumina-magnesia-carbon bricks for steel ladle. In: Proceedings of the Unified International Technical Conference on Refractories (UNITECR 2013). Hoboken, NJ, USA, 2014.

13 Mukhopadhyay, S., Chattopadhyay, A.K., Das, G.C., Maitra, S.: Effect of MgO grain size on thermal expansion behavior of alumina-magnesia-carbon refractory, *Int. J. of Appl. Ceram. Tech.*, **11**, [6], 1012 – 1019, (2014).

14 Babakhanova, Z.A., Aripova, M.K.: Highly refractory alumina-periclase-carbon ceramic materials based on a spinel binder, *Refract. Ind. Ceram.*, **59**, [5], 454 – 458, (2019).

15 Li, J.M., Hu, Y.B.: O_2 atmospheric annealing-tunable defects in ionic oxide MgO nanoribbons, *Appl. Phys. Lett.*, **114**, [20], 203101, (2019).

16 Budnikov, P.P.: The technology of ceramics and refractories. M.I.T. Press, Cambridge, 1964.

17 Kiani, M., Ebadzadeh, T.: Effect of mechanical activation and microwave sintering on crystallization and mechanical strength of cordierite nanograins, *Ceram. Int.*, **41**, 2342 – 2347, (2015).

18 Benito, J.M., Turrillas, X., Cuello, G.J., De Aza, A.H., De Aza, S., Rodríguez, M.A.: Cordierite synthesis. A time-resolved neutron diffraction study, *J. Eur. Ceram. Soc.*, **32**, 371 – 379, (2012).

19 Li, Y., Cheng, X., Zhang, R., Wang, Y., Zhang, H.: Effect of excess MgO on the properties of cordierite ceramic sintered by solid-state method, *Int. J. Appl. Ceram. Tech.*, **12**, 443 – 450, (2015).