



The Effect of Zircon on Long-Time Corrosion Resistance of Alumina

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ABSTRACT

Corrosion resistance of zircon reinforced alumina refractories has been carried out through the static crucible test. The corrosion measurements, the depth of penetration of the molten steel and the microstructure of the refractories were evaluated after soaking for 150 h at the temperature of 1480 °C. Results showed that the corrosion resistance of alumina was increased by adding 20 wt% of zircon and it was decreased with further increasing of zircon. Also, the sample containing 20 wt% of zircon, which was sintered at the temperature of 1650 °C, was obtained the minimum porosity. Microstructural features of this composite showed the needle-like mullite grains and the high amount of zirconia particles which may be responsible for providing the corrosion resistance to the melt penetration.

1. INTRODUCTION

Development of tailoring advanced composites has a rapid growth over the last decades, which aims to reduce the energy consumption through the use of bricks with longer lifetime. Improved performances are in the terms of higher operating temperatures, thermal shock resistance, mechanical properties, inexpensive raw materials, extreme resistance to the corrosion and creep [1, 2]. The successful use of ceramics to solve materials problems means tolerating severely corrosive conditions at high temperatures that have a wide range of applications [3].

Zirconia-mullite and alumina-zirconia composites are structural ceramics which have better properties than matrix materials (alumina or mullite) [4].

The incorporation of zircon ($ZrSiO_4$) in alumina composites as a corrosion resistance phase by molten glass is commonly reported [5]. Biswas and his coworker [6] reported that zirconia-mullite composites have better corrosion resistance, strength and toughness in compared to mullite and these composites are important ceramic materials that have been specially used in glass furnaces. Also, high strength, toughness, wear and thermal-shock resistance of alumina-zirconia composites have been reported [6, 7]. These composites are employed in the industries with the high level of corrosion [7]. Many researches have studied the reaction

sintering and final properties of alumina composites containing zirconia and mullite [8-10]. According to the effect of different phase relationship on the lifetime, the optimal performance of Al_2O_3 - ZrO_2 - SiO_2 composites is obtained in the appropriate crystalline and glass phase relationship [11].

Although, several studies have investigated the effect of zircon on the performance of alumina-mullite-zirconia (AMZ) composites, the corrosion resistance of AMZ composites and zircon content relationship is not sufficiently known. In fact, the effect of phase composition on the corrosion behavior of AMZ composites is rarely discussed in detail. Therefore, the present work focuses on the corrosion resistance of the composites prepared by the reaction sintering of alumina and zircon. As the technological properties of refractories can be significantly affected by their composition, different sintering temperatures were chosen for evaluating the considerable compositional variability. Composites were obtained by reaction sintering of the different amount of alumina and zircon without any additives. The effect of zircon addition (up to 55 wt%) on the corrosion resistance of alumina during the long-time service at the high temperatures were investigated.

2. EXPERIMENTAL PROCEDURES

Samples were prepared with different amount of alumina (MF25, Silkem, 45 μm) and zircon (Zircobit, Bitossi, 45 μm). Tables 1 and 2 show the chemical composition of the commercially raw materials and

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sample code, respectively. Zircon was added to alumina about 20, 35 and 55 wt%. Raw materials were wet ball milled for 12 h in alumina cups by using 0.5 wt% of Dolapix CE64 as the control process agent (CPA). Cylinder samples with the diameter of 65 mm and the height of 70 mm were pressed at 250 MPa. Samples were sintered at 1550 °C, 1600 °C and 1650 °C for 3 h. Apparent porosity was determined according to ASTM-D20. Phase composition and microstructure of the sintered composites were determined by X-ray diffraction (XRD, Philips PW3710) and scanning electron microscopy (SEM, ZIESS), respectively. Corrosion test was performed by using SPK steel at the temperature of 1480 °C for 150 h. Enlarged photographs of the polished surfaces of perforated blocks were used for corrosion evaluation.

TABLE 1. Chemical composition of commercially raw materials (wt%)

Material	Alumina	Zircon
Al ₂ O ₃	99.20	0.5
ZrO ₂	-	64
SiO ₂	0.03	33.5
HfO ₂	-	0.4
TiO ₂	-	0.19
Fe ₂ O ₃	0.03	0.07
Na ₂ O	0.4	-
L.O.I	0.15	0.3

TABLE 2. Composite codes (wt%)

Composite codes	AZ0	AZ20	AZ35	AZ55
Al ₂ O ₃	100	80	65	45
ZrSiO ₄	0	20	35	55

3. RESULTS AND DISCUSSION

3.1. XRD

It is well known that the final properties of refractories greatly depend on their phase composition. Fig. 1 shows the final phases of the sintered composites at the temperature of 1650 °C. The only crystalline phase of AZ0 sample is alumina and increasing the temperature had no effect on the formation of new phases. In the other samples, alumina, monoclinic zirconia and mullite were detected as the final phases and the peaks of zircon were not observed.

In AZ55 sample at the temperature of 1550 °C (not shown here), zircon was dissociated and the small amount (about 15%) of zircon was detected. By increasing the temperature of sintering (1600 °C and 1650 °C) the more amount of zircon was dissociated and its peaks were disappeared.

Table 3 shows the dissociation percentage of zircon as a function of temperature. As temperature had the negligible effect on the phase composition of all

sintering samples, only the XRD patterns of sintered samples at 1650 °C have been shown (Fig. 1).

TABLE 3. The dissociation percentage of zircon

Temperature	AZ0	AZ20	AZ35	AZ55
1550 °C	-	100	100	85
1600 °C	-	100	100	100
1650 °C	-	100	100	100

Phase composition of prepared composites is schematically shown in Fig. 2 which has been roughly estimated by the semi-quantitative analysis. The fraction of each phase can be identified by comparing the diffraction peak intensity of the same phase to the intensity of other phases. The uncertainty associated with the reported amounts is about 3%. The amount of alumina was considered 100% in AZ0 composite and after sintering it was decreased ranging from 70% to 0% in other composites. By increasing the content of zircon in the sintered samples at the temperature of 1650 °C, the contents of mullite and zirconia were increased from 0 to 20, 27 and 63%, and from 0 to 10, 19 and 37%, respectively.

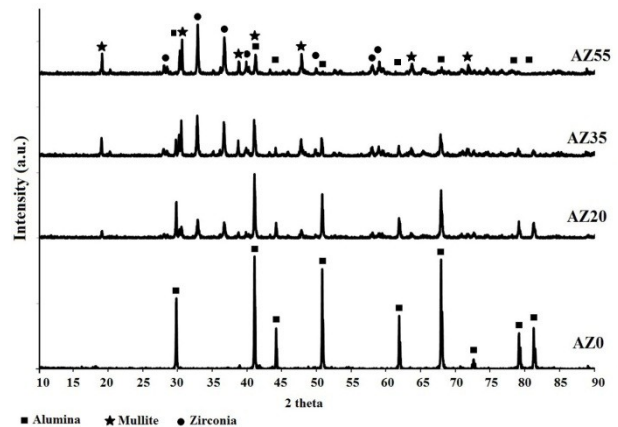


Figure 1. XRD patterns of different samples at the temperature of 1650 °C

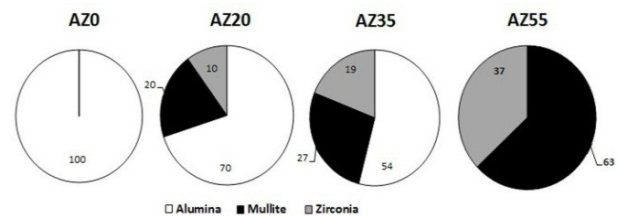


Figure 2. Phase composition of sintered composites sintered at 1650 °C

3.2. Porosity

Table 4 indicates that increasing the temperature of sintering and the amount of zircon to 20 wt% decreases the porosity of samples. The dissociation of zircon

caused the formation of a glassy phase and it may improve the densification through the liquid phase sintering [7]. Furthermore, the dispersion of zirconia grains will be increased the grain boundary cohesion, since the energy of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ grain boundaries is smaller than $\text{Al}_2\text{O}_3\text{-Al}_2\text{O}_3$ grain boundaries [12]. By increasing the amount of zircon (AZ35 and AZ55), the porosity was increased slowly. The increment of porosity can be attributed to the decomposition of zircon and the formation of mullite phase which has less density than alumina [13].

As shown in Table 4, the apparent porosity approximately is decreased by increasing the temperature of sintering and the content of zircon. The latter one has been attributed to the filling of

interparticle void space by the fine zircon particles [5]. Decomposition of zircon is a complex process which depends on the temperature. The samples were prepared three times separately and, every test was repeated three times. The results are the same as the results of the table 3. The porosity of AZ20 sample is lower than other samples and it is related to the more complete decomposition and more perfect reaction sintering between alumina and zircon which results in a full densification. There is a competition between “reaction sintering” and “densification” in these samples and the amount of zircon has an effect on it. The optimum percentage of zircon should be determined by the porosity test. Table 4 represents the total porosity of the AMZ composites that are about 30%.

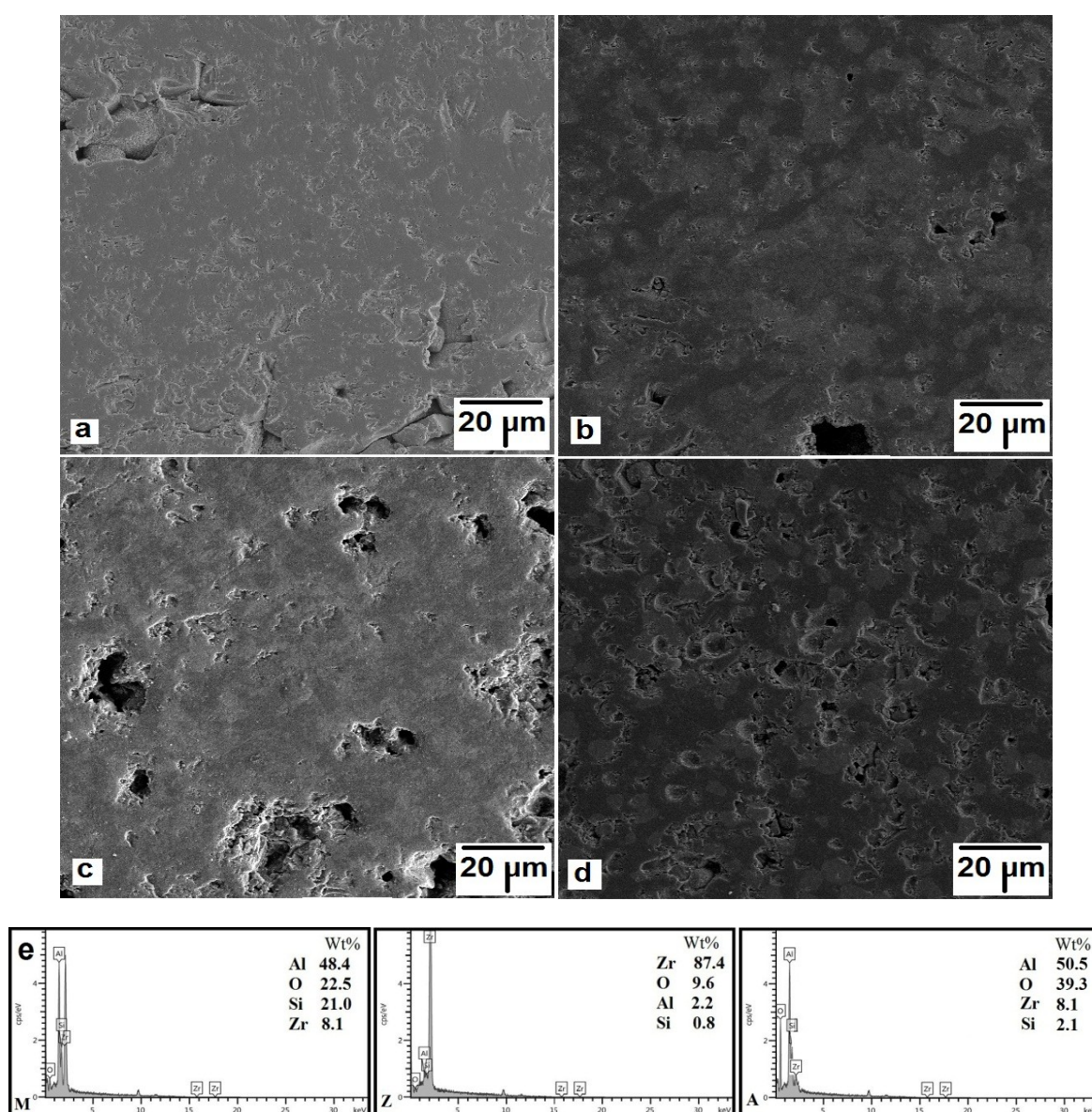


Figure 3. SEM image of the prepared samples at 1650°C (a) AZ0, (b) AZ20, (c) AZ35, (d) AZ55 and (e) EDS results of points M (mullite), Z (zirconia) and A (alumina)

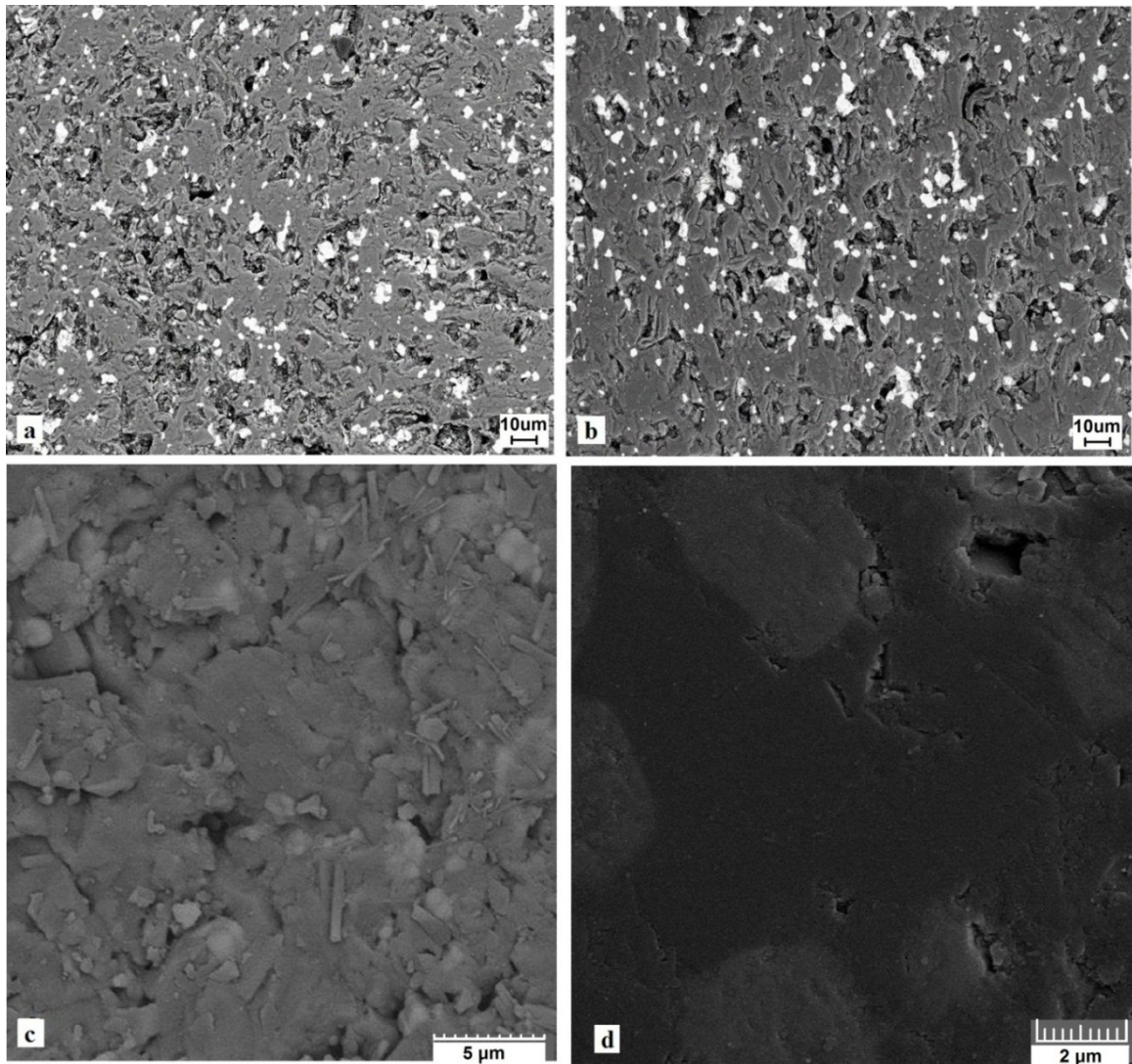


Figure 4. SEM images of AZ20 sample (a) 1600 °C, (b) 1650 °C and (c, d) 1650 °C at the higher magnifications (at 5.00kx and 10.0kx magnifications, respectively)

TABLE 4. The percentage of porosity of the sintered samples at the different temperatures

Sample Code	1550 °C	1600 °C	1650 °C
AZ0	32	30	26
AZ20	28	22	12
AZ35	26	25	20
AZ55	27	24	22

3.3. Microstructure and line scanning

Fig. 3 shows the SEM image of the prepared AMZ samples at the temperature of 1650 °C. AZ0 sample contained alumina and the other samples contained mullite and zirconia grains surrounded by corundum grains as the matrix.

Mullite grains were detected hard and fairly dark gray grains were distinguished as mullite. Furthermore, this

figure reveals a homogenous dispersion of reinforcement phases throughout the alumina matrix. The closed pores are observed in the microstructure of all samples. Increasing level of porosity can be observed from Figs. 3a to 3d that it means porosity of AZ55 sample is more than others. The distribution of pores size was not identified precisely in the prepared AMZ composites. However, the high amount of zircon which results in higher porosity and larger pore size can be decreased the corrosion resistance and increased the depth of penetration. Decreasing the corrosion resistance is due to the larger surface area exposed to the melt. The extensive dispersion and growth of mullite grains were more apparent in AZ55 sample.

Fig. 4 shows the SEM images of AZ20 sample at the temperatures of 1600 °C and 1650 °C at different magnification. In this figure, light grains which represent zirconia phase, are more detectable. Low

porosity is observed at the higher temperature. Porous materials with high porosity and large size of pores had poor corrosion resistance, due to the larger surface area exposed to the melt.

Furthermore, the needle-like mullite grains were more observed in AZ20 sample which had a dense microstructure and low porosity (Fig. 4c). Glassy phase was not detected in the microstructure of samples (Fig. 4d)

Fig. 5 shows the results of line scan test for a part of AZ20 sample which had been cut for the evaluation of penetrating of molten SPK. The graphs show that the concentrations of SPK elements (Fe, Si, Cr and Mn) have been decreased through the depth of AZ20 sample. It means that there are not any melt penetrations in the other regions of the test body.

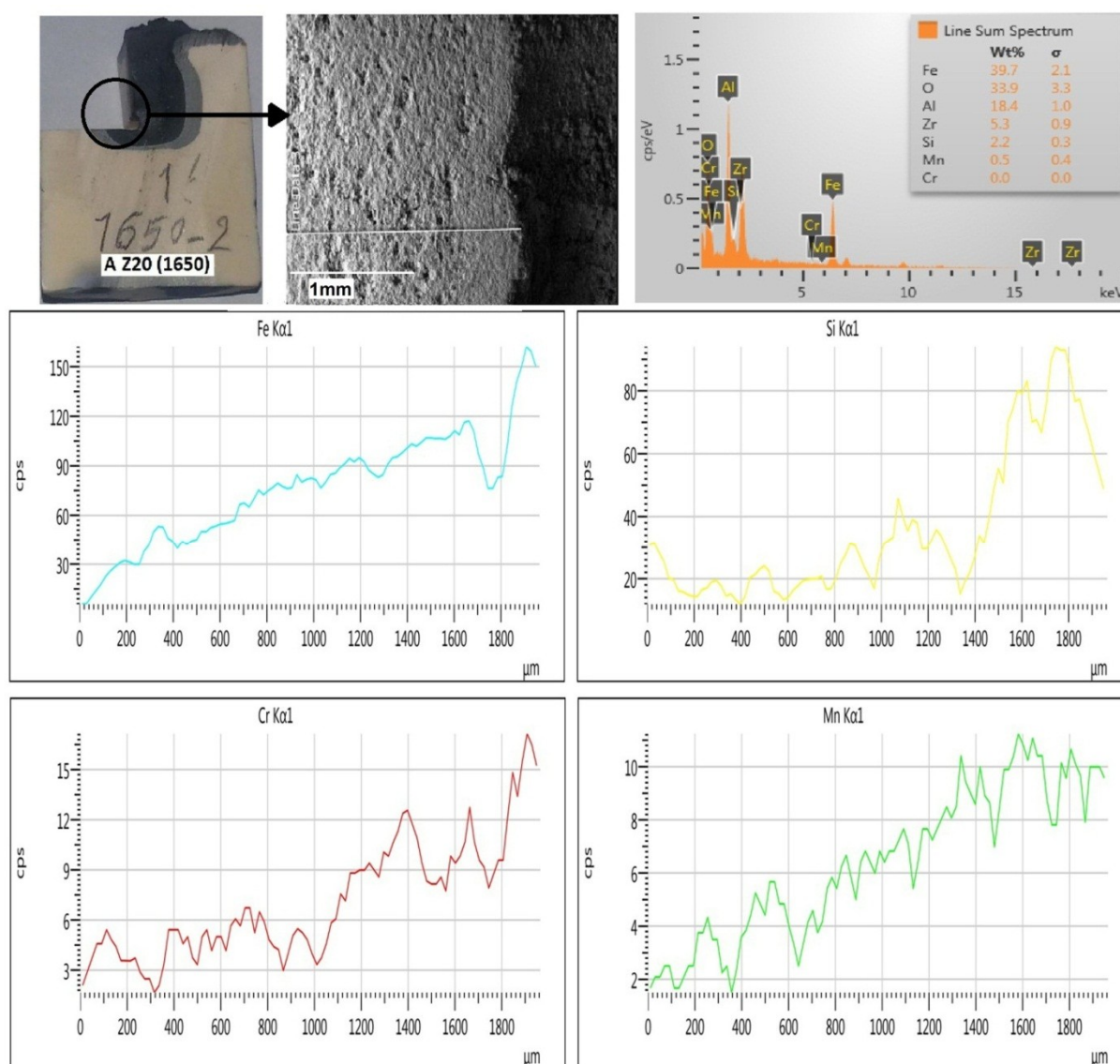


Figure 5. Line scan test of AZ20 sample

3.4. Corrosion resistance

Corrosion resistance depends on the amount of glassy phase and its chemical composition. Corrosion resistance of the prepared composites has been shown in Fig. 6 and 7. The corrosion of sintered alumina at 1550 °C was about 14% which was decreased to 7% for the sintered sample at the temperature of 1650 °C. The

corrosion resistance and melt penetration of all samples were decreased by increasing the temperature of sintering. This is due to the increasing of densification and formation of more mullite and zirconia phases. The lowest porosity was obtained by the sintered samples at 1650 °C and the corrosion resistance of them was significantly improved.

The percentage of corrosion and the depth of penetration were minimized by adding 20 wt% of zircon due to the lowest value of porosity. The amount of porosity and wetting capability of slag determined the reactivity and solubility of a matrix phase [14].

Nevertheless, the penetration is minimized by decreasing the porosity, dissolution is more important than penetration in refractories [3]. Therefore, the depth of penetration is reduced by increasing the temperature from 1550 °C to 1650 °C and decreasing the porosity.

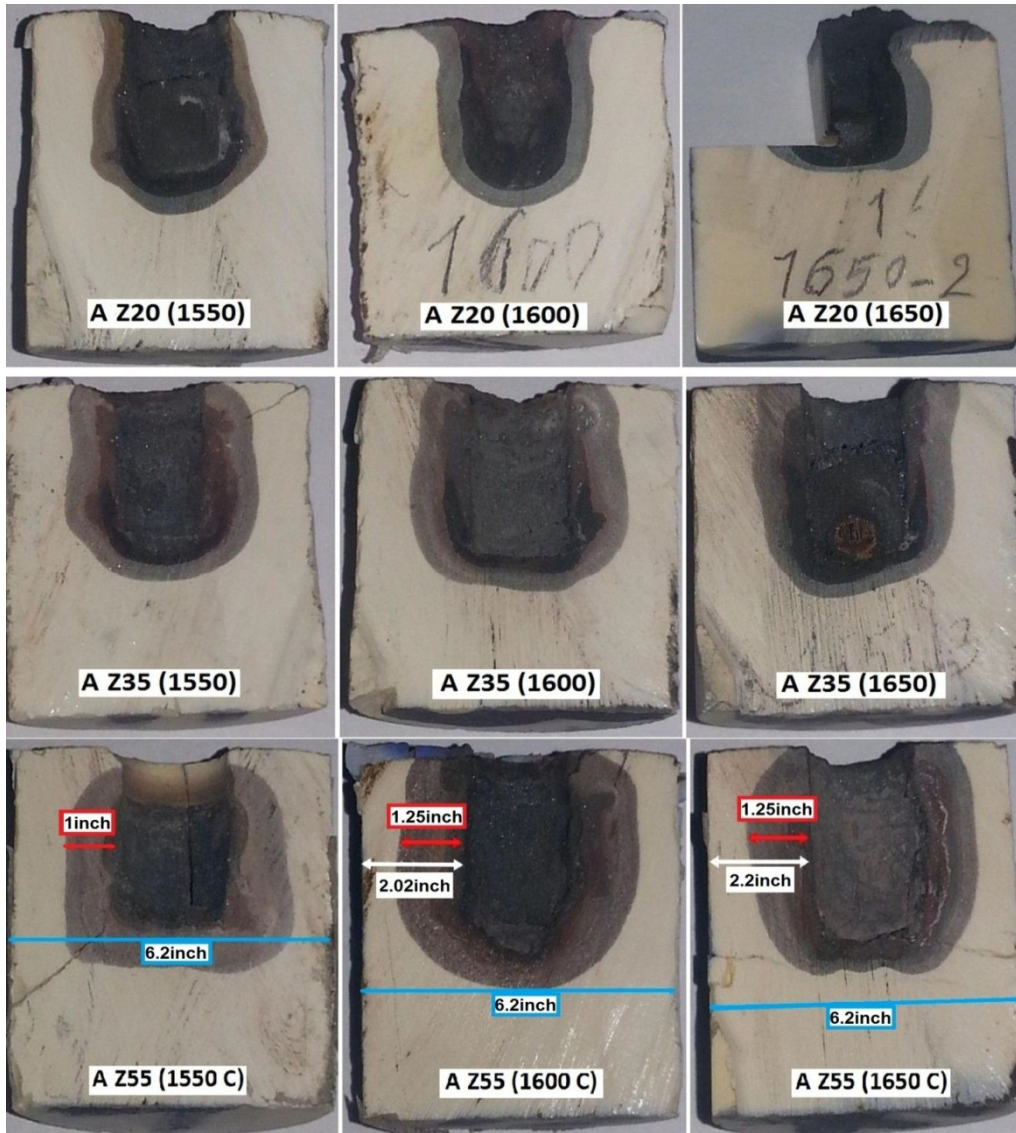


Figure 6. Cup test for the AMZ samples

Sintered AZ35 sample at the temperatures below 1650 °C had slightly higher corrosion compared to AZ20 sample, and the corrosion was reached to the same value by increasing the sintering temperature to 1650 °C. The reaction sintering of alumina and zircon was not completed at 1550 °C and the porosity of sample was high; therefore, it was expected the penetration of the molten steel was overcome. The reaction sintering of alumina and zircon was promoted at the temperature of 1650 °C and phases of mullite and zirconia were detected more in the sample. On the other hand, a lower

porosity of AZ20 sample might lead to the more corrosion resistance at this temperature.

As an overview, it can be observed the corrosion of AZ0 sample is higher than other samples. Therefore, the addition of zircon caused the decreasing the depth of penetration and improving the corrosion resistance of alumina samples.

Fig. 7 shows the penetration of the molten liquid into the refractory which was decreased from 1.4 to 0.5 inches (3.5 mm to 1.25 mm) by increasing the content of zircon to 20 wt%. Aksel [5] observed a similar trend

and a higher depth of penetration for the studied samples (from 4.5 mm to 3 mm). The penetration and corrosion were increased by increasing the porosity of the samples due to the increment of zircon. The porosity of a refractory allows the penetration of a molten liquid and it is considered as a major factor for determining the rate of corrosion [5, 15]. It can be observed that the depth of penetration and amount of the corroded region has a similar trend with the amount of porosity which is indicated the apparent porosity has an important role on the corrosion resistance. Chandra and his coworkers [7] evaluated the corrosion resistance of alumina-zirconia-mullite composite against molten soda-lime-silicate glass and reported the corrosion resistance of these composites was negligible which could be related to the unique microstructural features, which was involved interlocking of mullite crystals, the glassy phase and the most insoluble ZrO_2 crystals.

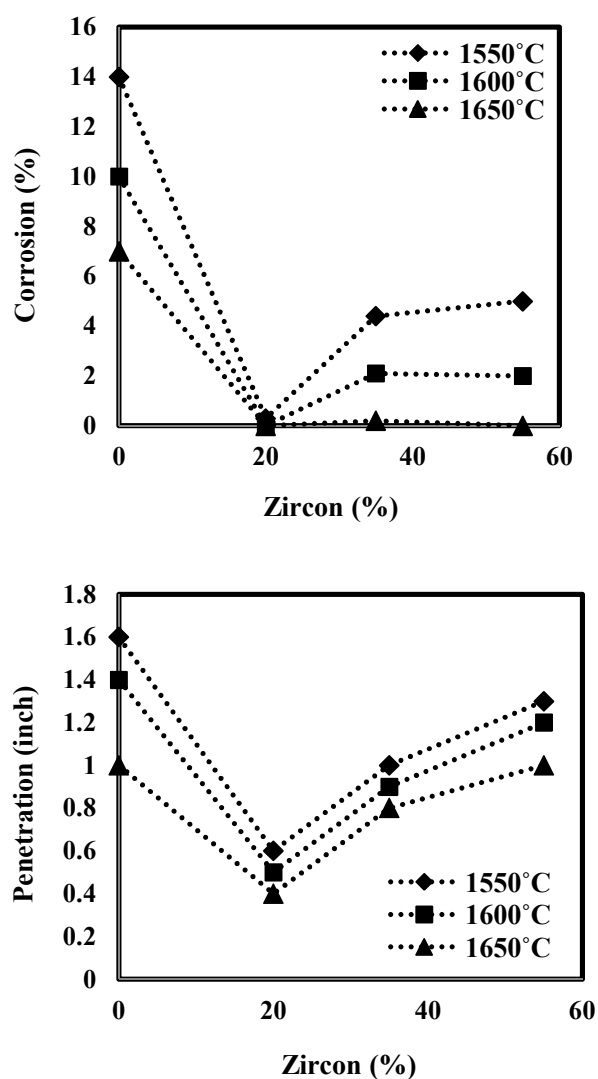


Figure 7. The Corrosion resistance and the depth of penetration for AMZ samples

The corrosion behavior of zirconia-alumina-silica composites against glass melts was investigated, and it was concluded the corrosion was originated by the diffusion of the metal ions of lead glass into the glassy phase of the refractory [15].

Alumina and other coarse particles can be considered as inert fillers in matrix while the bonding matrix phases determine the properties of the refractory [5]. A combination of different mechanisms, such as dissolution, penetration, grain boundary, stress corrosion, oxidation-reduction reactions, desorption and mass transport phenomena are involved in the corrosion [3]. Particle-particle bridges, glass films and pockets at particle-particle contact points are the important areas that determine the properties of composite. Due to the destruction of the bond phase by the liquid glass and the chemical dissolution of phases, corrosion process can be considered as the debonding and physical fragmentation of a refractory [5]. Alumina, mullite and zirconia grains will be attacked relatively slower than the intergranular bonding phase which is the starting point of the reaction with contacting melt.

Interaction of zirconia grains with the advancing molten steel may be increased the viscosity of the liquid phase resulting in the less penetration. It had been reported that [6] molten iron decomposed mullite incongruently to Al_2O_3 and SiO_2 and then reacted with SiO_2 to produce low melting compounds, for e.g. fayalite ($2FeO.SiO_2$) and wustite ($FeO.SiO_2$). Therefore, the composites containing more mullite phase were rapidly corroded by molten iron. Due to the molten iron formed a high melting point compound, for e.g. hercynite ($FeO.Al_2O_3$), by reaction with Al_2O_3 [6], the composites contained more Al_2O_3 that have a slower corrosion rate. Improving the corrosion resistance by increasing the content of alumina had been reported for refractories. It should be mentioned that the slag penetration resistance of high alumina refractories is weak. High corrosion resistance of zirconia had been known that is due to weak wettability by metals and steels [3].

The presence of more than one phase complicates the corrosion process in the composite because of the different solubility of each phase in the slag. Corrodibility of a composite is affected by the nature of each phase in the microstructure (grain size, shape and adjacent porosity level) [16]. The porous bond and/or matrix is initially attacked by the molten phases.

Determining the controlling mechanism of the corrosion or oxidation process is very difficult without considering the processing characteristics and the intrinsic of the raw materials. For porous solids such as refractories, with open porosity and with matrix materials being fine and highly reactive, both dissolution and penetration occur; hence, most slagging situations involve chemical attack of the matrix or low-melting constituent phases, which disrupts the structure

and allows the coarse-grained aggregates to be carried away by the slag movement. When penetration is more important than dissolution, another mechanism of degradation, structural spalling should be considered.

4. CONCLUDING REMARKS

In this work, the different ratio of alumina and zircon, and the temperature of sintering were investigated for determining the optimum composition and sintering conditions to obtain a high corrosion resistance composite. Results indicated that the significant corrosion resistance had been obtained by adding 20 wt% of zircon into alumina based composites. The presence of homogeneous grains of zirconia and mullite in the matrix and the minimal porosity were responsible for the improvement of the corrosion resistance of compounds. This suggested that the zirconia particles in the intergranular voids, as a relatively stable phase, restricted the porosity of the refractory and the rate of penetration of molten glass into the pores. The higher temperature of (1650 °C) caused higher densification and more corrosion resistance in the samples.

5. ACKNOWLEDGMENTS

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