Advanced Ceramics Progress

Research Article

Journal Homepage: www.acerp.ir

Crystallization Behavior and Mechanical Properties of In-situ Alumina-Zirconia Composite Bodies

Pooneh Barfi Sistani, Sahar Mollazadeh Beidokhti*, Alireza Kiani-Rashid

Department of Materials Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Iran

PAPER INFO

Paper history:

Received 18 May 2019
Accepted in revised form 22 June 2019

Keywords:

Amorphous aluminosilicate phase
Magnesia
Alumina-zirconia composites

ABSTRACT

In-situ alumina-zirconia composite bodies were fabricated by heat treatment of gibbsite-zircon-kaolinite mixture at 1450ºC. The current research investigated crystallization behavior and mechanical properties of the mentioned mixture in the presence of 5 wt.% MgO as an additive. X-ray diffraction (XRD) results showed that alumina, zirconia, and magnesium aluminosilicate were crystallized during the heat treatment at 1250-1550ºC. It was expected that mullite and zirconia were crystallized as the final phases; however, the addition of 5 wt.% of MgO changed the behavior of the mentioned mixture during the heat treatment at 1250-1550ºC. Energy diffractive X-Ray spectroscopy (EDS) reported that after heat treatment at 1450ºC, an Al^{3+}-rich aluminosilicate phase was formed as the matrix of the composite. Crystallization of alumina and zirconia and the existence of the amorphous aluminosilicate phase formed a composite with appropriate hardness and mechanical strength. The diametral tensile strength and Vickers microhardness values of the final composite were 130±7 MPa and 7.49 ± 1.2 GPa, respectively.

1. INTRODUCTION

Among the wide variety of zirconia toughened ceramics, zirconia-mullite composite obtained more attention due to its valuable creep resistance, chemical stability, and hardness [1–3]. Reaction sintering of zircon and alumina, direct sintering of mullite and zirconia, and exerting chemical routes can be considered as the most popular techniques which are used for fabrication of the zirconia-mullite ceramics [4–6]. Among these methods, reaction sintering of mechanically activated powders in the presence of oxide additives is a simple production technique of ceramic composites [7–9]. Oxide additives are utilized in zirconia-mullite composites for three purposes: 1) acceleration of mullitization, 2) facilitation of sintering and densification process, and 3) retention of tetragonal zirconia phase [4,10,11]. TiO_2, MgO, CeO_2, and CaO are oxides which utilized to obtain these purposes in the alumina-zircon mixtures [10,12]. Among these oxides, MgO influenced the final composite properties by improving the densification process [13]. According to Chandra et al. [10], the addition of 2.5 – 10 wt. % MgO to the zircon-alumina mixture led to the formation of spinel and mullite phases at 1450ºC. However, mullite and zirconia were the only crystalline phases at 1550ºC.

Previous work of authors [14] has investigated the behavior of the gibbsite-zircon-kaolinite mixture during the mechanical activation process and subsequent heat treatment. Results illustrated that by heat treatment of samples at 1550ºC, after 72h of the mechanical activation process, the zirconia-mullite composite was formed successfully. The results showed that increasing the milling time has a direct effect on improving the homogeneity, morphology, and mechanical properties, as well.

In the present research, for the first time, the effect of MgO addition on the behavior of the gibbsite-zircon-kaolinite mixture was studied. It was assumed that using MgO decreases the formation temperature of the mullite-zirconia composite and enhances the sintering behavior. Besides, since MgO is known as a stabilizer oxide of tetragonal zirconia ($t\text{-}ZrO_2$) phase, it was expected that this phase could remain after the high-temperature thermal process. Based on the prior research, the time 72h was selected for mechanical

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* *Corresponding author:, E-mail: Mollazadeh.b@um.ac.ir (S. Mollazadeh)*

activation process in this investigation. The microstructural and mechanical properties of the final product were evaluated and compared to the additive-free zirconia-mullite composites.

2. EXPERIMNTAL METHODS

2.1 Starting Materials and Processing

Gibbsite (~2µm, ~99.5 % purity), zircon (~ 0.5µm, ~95% purity) and kaolinite (~ 3µm, ~95% purity) were employed from industrial mineral sources to prepare a zirconia-mullite composite. The chemical composition of the used raw materials was given in Table 1. 55.52wt.% gibbsite, 26.09 wt.% zircon and 18.38wt.% kaolinite were mixed based on Equation 1 which was used for acquirement the zirconia-mullite composite by 1:1 molar ratio [14]. 5.00 wt.% MgO was added as an additive to the mentioned system.

$$10Al(OH)_3 + 2ZrSiO_4 + Al_2O_3.2SiO_2.2H_2O \rightarrow 2ZrO_2 + 2(3Al_2O_3.2SiO_2) + 17H_2O \quad (1)$$

The mixture of raw materials was dry milled in a planetary ball mill for 6-72h at ambient conditions. Zirconia vials and balls were employed to carry out the mechanical activation process. The ball to powder weight ratio and the rotation speed were 10:1 and 720 rpm, respectively. The samples were uniaxially pressed under the pressure of 300 bar in the form of disks having a 10mm diameter. Prepared samples were heat treated from room temperature to 600ºC by the rate of 5ºC/min, holding for 2h at this temperature; then the temperature was increased to the maximum temperature (1250 – 1550ºC) by the rate of 10 ºC/min holding for 2h in the maximum temperature, as well, and finally cooled in the furnace.

TABLE 1. The chemical composition of raw materials

Materials	Gibbsite	Zircon	Kaolinite
Al_2O_3	89.55	1.89	38.87
SiO_2	0.09	36.75	45.18
ZrO_2	0.00	58.63	0.00
Na_2O	0.17	0.26	0.07
MgO	0.17	0.36	0.50
CaO	0.04	0.21	0.01
Fe_2O_3	0.03	0.24	1.13
K_2O	0.01	0.00	2.21
Cl	0.01	0.00	0.00
P_2O_5	0.00	0.30	0.06
TiO_2	0.00	0.19	0.08
CuO	0.00	0.65	0.00
MnO	0.00	0.00	0.03
LOI	9.92	0.38	11.72

2.2 Microstructural Studies

After the mechanical activation process, particle size distribution was examined by dynamic light scattering (Cordnouan Technologies, France). Phase development was studied by X-Ray diffraction (GNR Explorer, Italy) using Cu Kα radiation (step size 0.01º, time per step 1s). Differential thermal analysis (Netzsch Geratebau, Germany) was used to study the phase development of the mixture from room temperature to 1100ºC by the rate of 10ºC/min at ambient pressure. The microstructure and fracture surface of the sintered sample was studied by scanning electron microscopy (SEM) (Zeiss LEO - 1450vp Germany) using backscatter mode. Also, the chemical composition of the matrix was characterized using energy dispersive spectroscopy (EDS).

2.3 Mechanical Properties Evaluation

Diametral tensile strength was employed for mechanical strength evaluation and comparative studies. Three samples of each code were tested by the rate of 1 mm/min. The maximum force was extracted from the force vs displacement curve, and the strength of the samples was calculated based on Equation 2. *P*, *t*, and *D* were maximum load, thickness, and diameter of the sample, respectively.

$$\sigma=2P/\pi Dt \quad (2)$$

Vickers microhardness of samples was evaluated by applying the loading force of 1000 g for 30 seconds on the prepared surface of the final samples. Average of 12 indents were reported as the mean Vickers microhardness of samples.

3. RESULTS AND DISSCUSSION

3.1 Phase Development

XRD patterns of mixtures after 6, 12, 24, and 72h of the MA process are shown in Figure 1 (graphs (a-d)), respectively. These graphs represent that by increasing the milling time from 6 to 24h, no significant changes could be detected in the peak position. However, peaks were broadened after 72h of mechanical activation. The broadening of observed peak could be the result of particle size decreasing and increasing the amorphous phase, as well. Results of DLS after 72h of the MA process showed that the particle size reduced to 220 ± 106 nm which depicted that the partic le size was approximately 140nm larger than that of the additive-free sample (80 nm). Comparing these results with previous ones [14] also indicates that unlike additive-free mixture, in the MgO containing one the gibbsite peaks at $2\theta=18.28^{\circ}$ retained even after 24 h of the MA process. This is while the gibbsite structure was entirely disappeared by 6h of MA in the additive-free mixture. The most significant peaks of zircon, alumina, and gibbsite are revealed in Figures 1 (B), (C), and (D), respectively. These figures indicate the peaks intensity reduction and peaks broadening accurately. Results of DLS after different durations of the MA process are displayed in Table 2, as well.

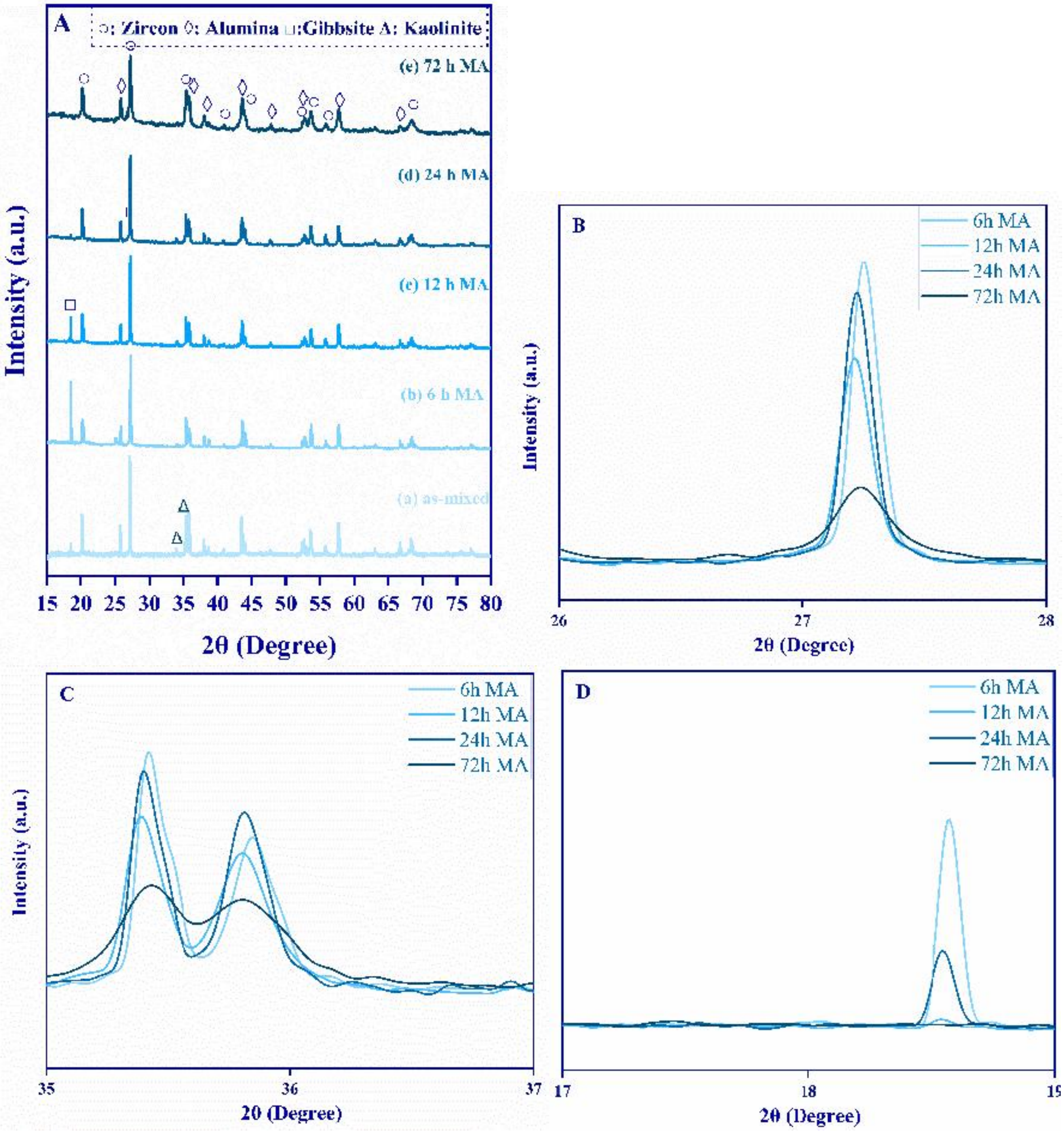

Figure 1. A) The XRD patterns of mechanically activated samples for 6, 12, 24, and 72h before heat treatment ; **B)** Higher magnification of zircon peaks in the range of 26-28°; **C)** Higher magnification of zircon and alumina peaks in the range of 35-37°; **D)** Higher magnification of gibbsite peak in the range of 17-19°

TABLE 2. Particle size of samples after different durations of the mechanical activation process

Samples	6h MA	12h MA	24h MA	72h MA
Average of particle size	6 ± 1.3 µm	8 ± 1.6 µm	4 ± 2.5 µm	220 ± 106 nm

Results of the differential thermal analysis (DTA) of samples after 6 and 72h of the MA process are shown in Figure 2 (a) and (b), respectively. Results of these graphs demonstrate the positive effect of the MA process on improving the crystallization process of phases, accurately. The endothermic peak at 300ºC showed the loss of the structural water related to the kaolinite and gibbsite structures [15]. The observed endothermic peak at 500-600ºC could be related to the derived Al_2O_3 polymorph from dehydration of gibbsite [15]. The observed exothermic peak at 900°C, which is more intensive in graph b, indicated the reassociation of zircon phase which was partially dissociated after 6h of milling. The observed intensive peak in graph b could indicate that the zircon phase had dissociated more entirely in the related sample as a result of the MA process. Consequently, more complete dissociation of the zircon results in more recrystallization of this phase [7]. Furthermore, there is a broad peak at the range of 600-800°C in 6h milled sample and 400-800°C in 72h milled sample which is related to the formation of an amorphous aluminosilicate phase from the kaolinite-gibbsite mixture. These results indicate that as a result of the mechanical activation process, Si-O-Si bands were broken, and new Si-O-Al bands were formed [16].

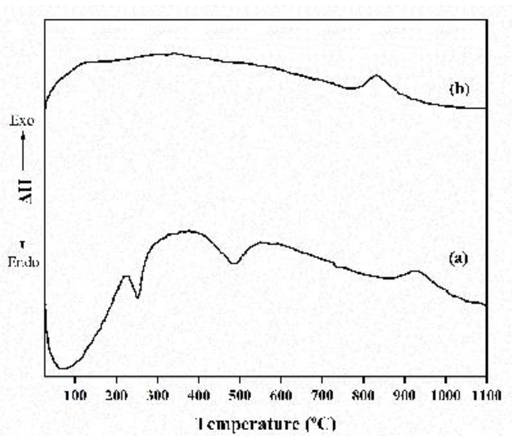

Figure 2. DTA results of 6 and 72h mechanically activated samples from room temperature to 1100°C; a) 6h mechanically activated mixture, b) 72h mechanically activated mixture

Considering the results of Figure 1, Figure 2, and the previous study [14], the 72h mechanically activated sample was selected for further crystallization studies. Figure 3 shows the XRD results of samples after heat treatment at 1250, 1350, 1450 and 1550ºC. As Figure 3 graph (a) shows, alumina (2θ=35.4) and zircon (2θ=27.2) were the only detected phases in the system after heat treatment at 1250ºC. This graph indicated that the peaks of these two phases, which were partially broadened after 72h of the MA process, were intensified again after heat treatment at 1250ºC. Raising the heat treatment temperature to 1350ºC (Figure 3 graph (b)) changed crystallization behavior in the MgO containing mixture comparing to the none-additive samples. A magnesium aluminosilicate phase with the formula of $MgAl_2Si_3O_{10}$ was formed in this sample. Figure 3 graph (c) represented that by increasing the temperature up to 1450ºC, the monoclinic and tetragonal zirconia peaks existed at 2θ=28.6° and 2θ=30.4°, respectively, which is an indication of the dissociation of the zircon in the system. Only a weak peak of zircon at 2θ=27.19° still remained. The XRD results indicated that although the zircon phase was dissociated, the resulted silica did not associate in mullitization reaction. Previously reported research by Chandra *et al.* [10] recommended MgO as an appropriate additive in the formation of the zirconia-mullite composite. Nevertheless, in the gibbsite-zircon-kaolinite mixture, despite its positive influence in zircon dissociation, this oxide prevented the mullite formation. Partially sharp peaks of alumina (2θ=35.4) and $MgAl_2Si_3O_{10}$ (2θ=25.7) were still observed in the XRD pattern after heat treatment at 1450ºC, as well. Additionally, it should be noted that silica polymorphs were not crystallized. Considering no crystalline silica-containing phase, it is possible that the matrix contains an amorphous aluminosilicate phase. Results of the XRD of none-additive samples at the same conditions [14] showed weak peaks of mullite, while sharp peaks of zircon still remained in the structure. Increasing the temperature up to 1550ºC (Figure 3 graph (d)) did not lead to the formation of mullite; however, the transformation of the tetragonal to the monoclinic zirconia phase was completed as a result of the mentioned temperature development. Besides, the increased intensity of the XRD peaks of the alumina phase at 2θ=35.4º by raising the temperature from 1450ºC to 1550ºC showed that the aluminosilicate matrix might be altered to a silicate one through the crystallization of corundum phase.

Results of Figure 3 illustrated that MgO addition could decrease the dissociation temperature of zircon. However, this addition not only could not play a decisive role in mullitization reaction but also had a suppressive role. In many studies, MgO was added to zircon-alumina as a sintering aid for zirconia-mullite composite, and its role had been constructive [17]. The published results showed that MgO could also have a positive role in the kaolinite-alumina mixture. Based on Hao *et al.*, MgO accelerated the mullitization and promoted the needle-like mullite formation [18]. Despite all reports, while these three raw materials combine together, MgO addition does not show its positive role anymore. It seems that in the case of this study, MgO could not be suggested as a proper additive for zirconia-mullite composite formation. It is believed that the simultaneous presence of kaolinite and MgO in this specific mixture could be the reason for the observed phenomenon. Kaolinite, itself could form a liquid phase during high temperature-processes in the ceramics body. On the other side, the published results disclosed that MgO could form a transitory liquid phase in Al_2O_3-SiO_2 systems. Finally, the existence of both of these phases could reduce the viscosity excessively and embed the mullitization reaction [19]. Consequently, the final composite was an alumina-zirconia composite with a probable amorphous aluminosilicate matrix. Decreasing the amount of MgO additive to less than 5 wt.% could aid to the two-sided role of MgO, which were the acceleration of zircon dissociation and also mullitization.

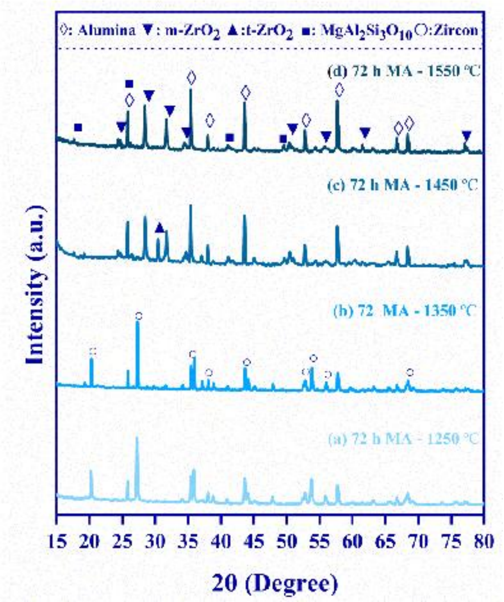

Figure 3. XRD patterns of 72h mechanically activated samples after heat treatment at 1250, 1350, 1450, and 1550ºC

In order to study the effect of the MA process on the phase transformation of the starting mixture, different durations of the MA process were considered, as well. Figure 4 shows the XRD results of samples which were heat treated at 1550ºC after milling for different times. These results designated that the shorter MA process did not lead to the formation of mullite in these bodies. Like the sample 72h MA-1550ºC, in the shorter time duration of the MA process, the alumina, zirconia, and $MgAl_2Si_3O_{10}$ were the only crystalline phases in these samples. Hence, it could be concluded that the obtained result was not connected to the duration of the MA process, and it is directly related to the combination of raw materials.

3.2. Mechanical Properties

Figure 5(A) shows the diametral tensile strength of the bodies after heat treatment at 1250, 1350, 1450, and 1550ºC. These results showed that by increasing the temperature from 1250 to 1450ºC, the fracture strength was improved from 38±5 MPa to 130±7 MPa. Further temperature increasing up to 1550ºC reduced fracture strength to 45±13 MPa. The increasing of the fracture strength could be the result of the existence of two high strength phases of alumina and zirconia. Afterward, by increasing the temperature up to 1550ºC, as it was discussed, (section 3.1) amorphous silicate phase formed and as a result, the fracture strength decreased. Besides, completion of monoclinic to tetragonal transformation might reduce the diametral tensile strength. Furthermore, Figure 5(B) indicates that the Vickers microhardness of samples reached 10.42±0.76 GPa after heat treatment at 1350ºC. It is increased to 7.49±1.2 GPa by raising the temperature up to 1450ºC. The observed decrease in the Vickers microhardness values could be related to the presence of amorphous silica and dissociation of the zircon to zirconia phase which has lower hardness values. According to the microstructural and mechanical properties results, it could be concluded that the heat treatment temperature of 1450ºC is the optimum heat treatment temperature in this study.

The obtained results showed that the mechanical behavior of these samples was extremely different from the behavior of none-additive ones. The increase of the heat treatment temperature from 1250 to 1550ºC persistently improved the studied mechanical properties in the none-additive containing sample. However, in the case of MgO containing sample, the mechanical behavior completely changed. Although the diametral tensile strength of MgO containing samples was comparable with the none-additive ones after heat treatment at 1450ºC (136 MPa), it could not reach to such a high strength of 220 MPa which none-additive mixture was showed after heat treatment at 1550ºC.

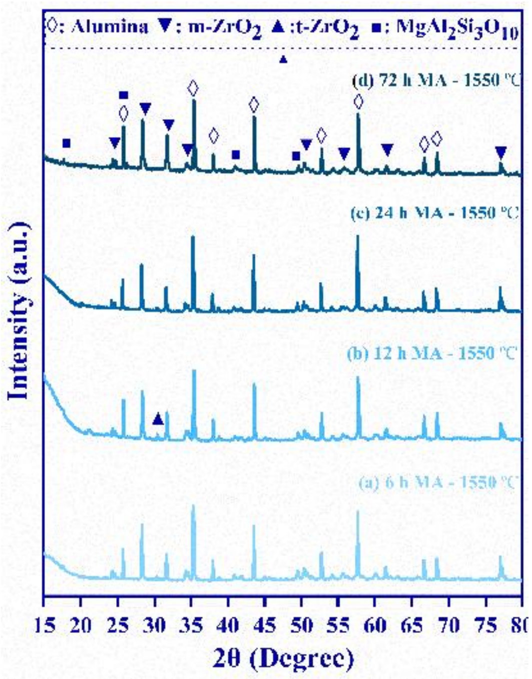

Figure 4. XRD results of 6, 12, 24, and 72h mechanically activated samples heat treated at 1550ºC

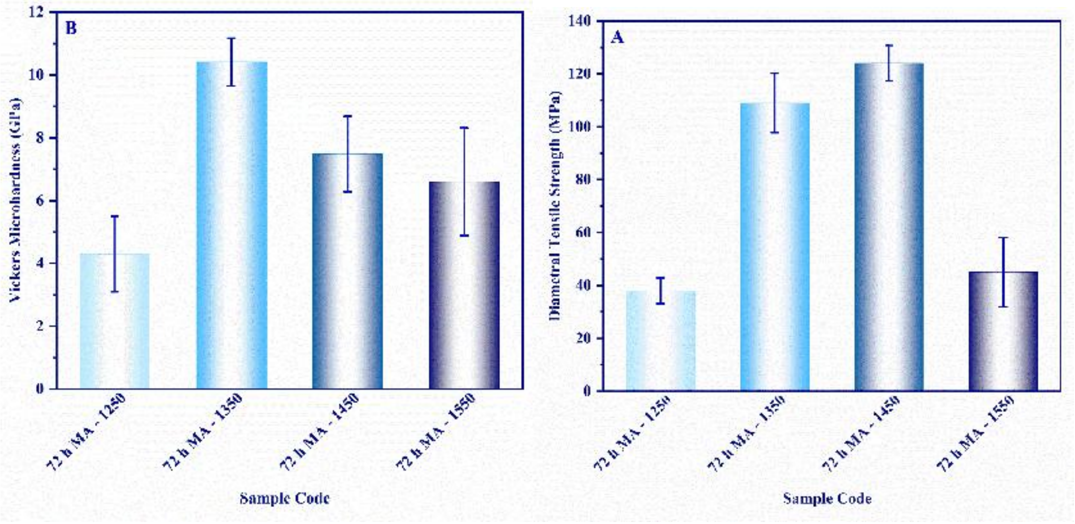

Figure 5. A) Diametral tensile strength and, **B)** Vickers microhardness of composites after 72 h of the MA process and heat treatment at different temperature

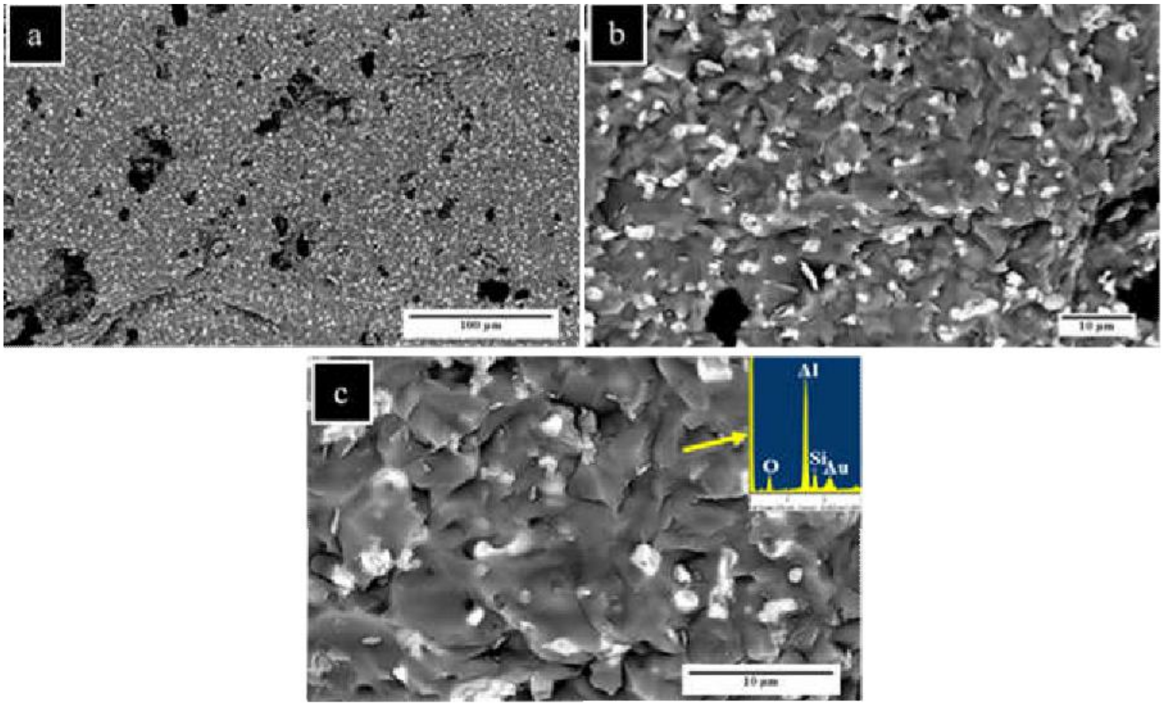

Figure 6. SEM micrographs of the optimum sample at different magnifications (72h mechanically activated and heat treated at 1450ºC), Inset of micrograph c) EDS result of the matrix

3.3. Microstructural Studies

Figure 6 displays the SEM micrographs of the heat treated sample at 1450 °C. EDS report is showed inset additionally. These images showed that zirconia particles were appropriately distributed in the matrix of the composite. A layer of the amorphous phase covered the surface EDS analysis illustrated that this phase is an Al^{3+}-rich aluminosilicate phase.

4. CONCLUSIONS

In this study, the effect of MgO addition on the phase development and mechanical properties of the 72h mechanically activated mixture of gibbsite-zircon-kaolinite was investigated. The results are as follows:

1) MgO could not lead to the crystallization of the mullite and zirconia composites.
2) Final composite was an alumina-zirconia composite dispersed in an aluminosilicate matrix which was obtained by heat treatment of 72h mechanically activated mixture at 1450ºC.
3) The maximum diametral tensile strength of the composite was 130±7 MPa which was obtained after heat treatment at 1450ºC. However, the maximum value of Vickers microhardness was 10.42±0.76 GPa which was acquired by heat treatment at 1350ºC.
4) The EDS of matrix showed that the formed aluminosilicate phase was an Al^{3+}-rich phase which could influence the mechanical properties positively at 1450ºC.

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