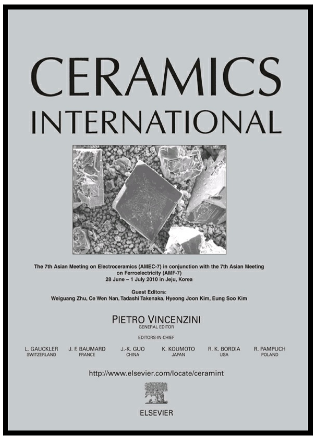

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Microstructural and Diametral Tensile Strength Evaluation of the Zirconia-Mullite Composite

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Abstract

The purpose of the current research was to investigate the effect of duration of the mechanical activation process of starting materials on Vickers micro-hardness and diametral tensile strength of zirconia- mullite composites. Zirconia- mullite composites with 1:1 molar ratio were fabricated by sintering of the mechanically activated kaolinite, gibbsite, and zircon powder mixture as inexpensive and convenient starting materials. Results of dynamic light scattering analysis showed that the mean particle size of the starting powders was reduced from 2.5 µm to 80 nm after 72 h of the mechanical activation process. X-ray diffraction analysis showed that zirconia and mullite were crystallized after 2 h thermal treatment at 1550 °C. Based on the semi-quantification results of X-ray diffraction patterns, increasing the duration of the milling process from 6 to 72 h had a positive effect on improving the amount of tetragonal zirconia in the final matrix. Scanning electron microscopy results revealed a fine and homogeneous distribution of zirconia particles in the mullite matrix after 72 h of the mechanical activation process. Increasing the duration of milling process from 6 h to 72 h had a remarkable effect in increasing the diametral tensile strength values from 30 to 220 MPa. Vickers micro-hardness values were also enhanced considerably from 7.30 to 11.12 GPa by increasing the milling time.

Keywords: Zirconia – Mullite Composites, Diametral Tensile Strength, Mechanical Activation

1. Introduction

Modern and fast sintering methods such as spark plasma, microwave or flash sintering have been widely used for the fabrication of the structural ceramic bodies. However, these techniques are usually expensive and require advanced equipment [1,2]. Traditional fabrication techniques based on the reaction or direct sintering method could not be easily considered as alternatives to these highly efficient and fast sintering process, however, traditional techniques are inexpensive, simple, and available [3]. Microstructural and mechanical properties of final products which have been fabricated by reaction sintering methods could be improved by compromising between their crystallization and sintering processes. However, crystallization of high-temperature phases which are usually responsible for developed mechanical properties requires successive dissociation and transformation of the starting materials which generally occur at relatively elevated temperatures. Application of different pre-heating processes such as mechanical or chemical activation of the mixture of the starting materials can reduce the high temperatures needed for decomposition or dissociation of precursors. Furthermore, these steps can improve the sintering process as well as the reactions speeds by the particle size reduction and homogeneity improvement [4,5].

Mullite containing ceramics have been developed over the past decades due to their improved toughness and chemical resistance in the harsh environments. Among different mullite composites, mullite-zirconia bodies have attracted considerable attention due to their improved toughness, creep resistance, and chemical stability [6–10]. Various starting materials and fabrication methods have been used to form these ceramics, which among them conventional sintering of minerals such as zircon, alumina, and kaolinite is an inexpensive and convenient way to obtain the above-mentioned composite [11–14]. Previously published results showed that mechanical activation of the mixture of zircon with the different source of Al^{3+} and Si^{4+} had a direct impact on the reduction of the crystallization temperatures of mullite and zirconia [15,16]. According to Ashrafi and Emadi *et al*. [4,17], mechanical activation of zircon and alumina mixture for 60 h led to the complete dissociation of zircon structure and resulted in the formation of an amorphous phase. Their results illustrated that the development of mullite-zirconia composite occurred after 4 h of heat treatment at 1400 °C in the samples which were milled for 40 h. Khor *et al*. [18], showed that the crystalline structure of alumina and zircon mixture disappeared after 100 h of the mechanical activation process. According to their results, mullite formation temperature decreased from 1550 ℃ to 1420 ℃ by increasing the duration of milling process from 5 h to 40 h, respectively. Based on our knowledge, there is no published result on the effect of the different time duration of milling process on the mechanical properties of zirconia-mullite composites. However, it is rational to assume that the optimum duration of the mechanical activation process has a direct impact on increasing the degree of crystallinity and decreasing the particle size. Accordingly, it is expected that mechanical properties of final bodies could also enhance by exerting the mechanical activation process on the mixture of starting raw materials. The mechanical strength of mullite-zirconia composites is usually evaluated by compression or flexural strength tests [2,19]. DTS is a method for mechanical evaluation of brittle materials which has a very simple sample preparation. This method could be a suitable test method for comparative studies. In this test, a cylindrical disk is compressed along its diameter and, as a result, the tensile stresses at the center of the disk are developed. The fracture occurs in the specimen when the stresses reach the critical value. Based on our knowledge, DTS has never been used for the mechanical evaluation of zirconia- mullite composites [20–22].

In the present work, zirconia-mullite composites were fabricated by sintering of the gibbsite, zircon, and kaolinite mixture. Since kaolinite could improve the sintering process by the aid of developing a glassy phase, a small amount of this mineral was used as the source of alumina and silica for the first time [23,24]. Different duration of the mechanical activation process was performed to investigate the effect of the mechanical activation on the progress of crystallization in the gibbsite-zircon-kaolinite mixture, during thermal heat treatment at 1250-1550°C. DTS and Vickers micro-hardness tests were used to evaluate the effect of phase evolution on the mechanical properties of samples which were previously mechanically activated for different time durations, which, to the best of our knowledge, is the first time approach to evaluating mechanical properties of such composites. Finally, scanning electron microscopy (SEM) was used to complete studies of microstructural changes of composites.

2. Experimental methods

2.1. Materials and samples preparation

Kaolinite (55 wt. %, the mean particle size of 3µm), zircon (26 wt. %, the mean particle size of 0.5µm), and gibbsite (19 wt. %, the mean particle size of 2µm) were used as starting materials. Their mixture was prepared based on **eq.1**. The detailed chemical compositions of starting raw materials were characterized by X-ray fluorescence (XRF) spectrometer and obtained results were shown in **table 1**.

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

Mechanical activation (MA) process was conducted by dry-milling of prepared mixtures for 6, 12, 24, and 72 h in a planetary ball mill by milling speed of 720 rpm. Zirconia milling media with the ball mean diameter of about 15mm and ball to powder ratio of 10:1 by weight was used for the MA process. Cylindrical samples of 10 mm diameter were prepared by pressing activated powders under 300 bar pressure. All cylindrical samples were heated to 600 ℃ by the heating rate of 5 ℃/min, held for 2 h at this temperature, heated to the maximum temperature in the range of 1250 ℃ - 1550 ℃ by the rate of 10 ℃⁄min, held for another 2 h at the maximum temperature and furnace cooled subsequently.

2.2. Microstructural evaluation

X-ray fluorescence (XRF) spectrometer (Philips PW 1480 Germany) was employed to characterize the chemical composition of raw materials. Particle size distribution (PSA) of raw powders, as well as mechanically activated powders, was examined by Cordnouan Technologies, France. Phase transformations during the milling process and after heat treatment was investigated by X-ray diffraction (XRD) using Cu Kα radiation (step size 0.01º, time per step 1s) by GNR Explorer - Italy. The quantity of crystalline phases and crystallite sizes of detected phases were calculated and semi-quantified by the Rietveld method. The major chemical bands of the samples were recognized by the fourier transform infrared (FT-IR) by Thermo Nicolet AVATAR 370- USA. The microstructure of the as-mixed powders and sintered bodies were studied by scanning electron microscopy (SEM) by Zeiss LEO - 1450vp Germany. Bulk density and apparent porosity of the samples which were heat-treated at 1550 °C were calculated based on the Archimedes principles.

2.3.Mechanical properties evaluation

The mechanical strength of the samples was evaluated by the diametral tensile strength test (Zwick Z250 Germany) at room temperature. 12 disks were loaded by the rate of 1 mm/min for each sample. The maximum load (P) was extracted from the load vs. displacement curve, and the mechanical strength was calculated using **eq.2** in which D and t were the diameter and thickness of the disk, respectively [22].

$\sigma = 2P / \pi D t$ **(eq.2)**

Vickers micro-hardness (Buhueler USA) were evaluated by exerting the load of 1000 g for 30 seconds on the polished surface of heat-treated samples. Average of 10 indents was reported as the hardness of each sample.

2.4.Statistical calculation

The results of mechanical tests were statistically evaluated using the Two-way ANOVA model. Statistical significance was considered at probability values of $p < 0.05$ (*$p < 0.05$, **$p < 0.01$, ***$p < 0.001$, and ****$p < 0.0001$) (GraphPad Prism 7.03 La Jolla, CA 92037, USA).

3. Results and Discussions

3.1. Phase Evaluation

Figure 1.A (a - e) showed XRD patterns of the as-mixed mixture of gibbsite-zircon-kaolinite and mechanically activated ones after 6, 12, 24, and 72 h, respectively. **Figures 1.B** and **C** represented higher magnifications of **figure 1.A** at 2θ = 25 - 28º and 2θ = 34 - 37º, respectively. Characteristic XRD peaks of gibbsite (ref. code. 007-0324), zircon (ref. code. 01-075-0785), and alumina (ref. code. 01-075-0785) were identified in **graph (a)** of **figure 1.A**. Comparing **graphs (a)** and **(b)** revealed that after 6 h of mechanical activation process, XRD peaks of gibbsite at 2θ = 18.32º were removed from represented patterns and the only detectable crystalline phases in all four mechanically activated samples (**graphs b-e**) were alumina (ref. code. 01-075-0785) and zircon (ref. code. 01-083-1383). **Graph (c)** indicated that increasing the duration of milling process from 6 h to 12 h, enhanced the intensity of zircon XRD peaks at 2θ = 27.19º and 35.76º. However, based on the **graph (d)**, developing the duration of mechanical activation to 24 h, resulted in the partial broadening of mentioned peaks and decreased their intensity. Finally, according to the **graph (e)** developing milling time to 72 h led to more broadening of the XRD

peaks. These findings which were shown with higher magnifications in **figures 1.B** and **C** could be due to the decrease in the particle size and the degree of crystallinity of the mixed powders as a result of the increase in the duration of milling time. The average particle size of the samples which was mechanically activated for 6, 24, and 72 h were represented in **table 2**. It demonstrated that after 72 h of the mechanical activation process, the average particle size decreased from the micron scale to the nanoscale. Due to the shear stresses and consecutive impacts which were applied to the powder during high energy milling, plastic and elastic strains were created, and temperature increased locally. As a result, in the early stages of mechanical activation, the degree of crystallinity was developed (**figures 1.A, graphs c** and **d**). However, development of the mechanical forces by increasing in the time of milling process and the creation of high enough temperature in the milling container resulted in the progressive fracture of powder particles and elimination of structural water as well. So that, the specific surface area of particles increased continually. The observed decrease in the intensity of XRD results of 72 h mechanical activated samples (**figure 1.A, graph e**) could be related to the mentioned decline in the particle size. Besides, the prolonged mechanical activation process for 72 h could develop the dissociation process of zircon and increase the amount of amorphous phase [4,25] and as a result decrease the intensity of XRD peaks of **figure 1.A, graph e,** in comparison to the other graphs of this figure. Based on XRD and PSA results, 72 h mechanically activated powders were selected for further heat and crystallization investigations. **Figure 2.A** showed the XRD patterns of 72 h milled samples heat-treated at different temperatures. **Figure 2.B** illustrated the XRD results of activated samples for different time durations which were heat-treated at 1550 ℃. Comparing **graphs (a)** and **(b)** of **figure 2.A** revealed that zircon which had been partially dissociated during the mechanical activation process re-associated again after heat treatment at 1250 ℃. Based on **figure 2.A** alumina (ref. code. 01-075-0785) and zircon (ref. code. 01-083-1383) were the main crystalline phases in samples which were heat-treated at 1250 ℃ (**graph (b)**) and 1350 ℃ (**graph (c)**). It seems that the fine particle size of powders provided the required driving force for the reassociation process and growth of zircon up to 1450 ℃. Increasing the heat treatment temperature up to 1450 ℃ (**graph (d)**) led to the appearance of weak peaks of mullite (ref. code. 015-0776) at 2θ = 26.35º and 16.81º. Finally, by conducting heat treatment at 1550 ℃ (**graph (e)**) sharp peaks of mullite (ref. code. 015-0776), tetragonal zirconia (t-ZrO_2, ref. code. 050-1089) and monoclinic zirconia (m- ZrO_2, ref. code. 037-1484) appeared in the samples. XRD results showed that raising the sintering temperature to 1450 ℃, led to the crystallization of primary nucleates of mullite. These results also indicated that great amounts of zircon and alumina remained in the system at 1450 ℃. **Table 3** represented the results of semi-quantification of XRD patterns. Based on this table, 4 wt. % mullite and m-ZrO_2 were crystallized in the 72 h mechanically activated mixtures which heat-treated at 1450 ℃. Published results showed that mechanical activation of alumina and zircon mixture could lead to the crystallization of zirconia-mullite composites at 1450 ℃ [17,18]. Nevertheless, it seems that mullitization in the mixture of gibbsite-zircon-kaolinite needed longer soaking times or higher sintering temperatures. **Graph (e)** of **figure 2.A** indicated that formation of the zirconia-mullite composite progressed at 1550 ℃ and zirconia existed in both monoclinic and tetragonal phases in the final samples. According to **table 3**, raising the temperature to 1550 ℃ improved the amount of mullite and zirconia to 78 wt. % and 17 wt. %, respectively. The effect of milling time on the progress of phase evolution was studied on the samples which were mechanically activated for different times and further heat-treated at 1550 ℃ and obtained results were reported in **figure 2.B**. The sharp peaks of mullite (ref. code. 015-0776), tetragonal zirconia (ref. code. 050-1089) and monoclinic zirconia (ref. code. 037-1484) and a weak peak of alumina at 2θ = 43.46º were seen in all four samples (**graphs a-d**). It was shown that increasing the duration of milling process from 6 to 72 h, weakened the peak of m-ZrO_2 at 2θ = 28.56º and concurrently developed the t-ZrO_2 peak at 2θ = 30.38º. Results of the semi-quantification of XRD pattern for 6, 12, 24, and 72 h milled samples which were heat-treated at 1550 ℃ for 2 h, were represented in **table 3**, as well. These results illustrated that by increasing the milling time from 6 to 24 h, the weight percentage of mullite rose from 64 wt. % to 88 wt. %, respectively. When milling time reached 72 h, the amount of mullite reduced slightly to 78 wt. %. These results could be evidenced that the mechanical activation for more than 24 h was rolled against the mullite crystallization, although it had an effective role in the maintenance of the t-ZrO_2 phase. Furthermore, the weight percentage of t-ZrO_2 changed from 4 wt. % in 6 h milled sample to 10 wt. % in 72 h milled sample, and this increment could be indicated from peaks sharpening in XRD patterns, as well. Crystallite sizes of detected phases were calculated by Scherrer equation and represented in **table 4**. According to this table, by increasing the time duration of mechanical activation process from 6 to 72 h, the crystallite size of t-ZrO_2 and mullite changed from 133 to 50 nm and from 79 to 63 nm, respectively. XRD patterns of **figure 2.B** (**graphs a-d**) and calculated results of **table 4,** both implied that the amount of t-ZrO_2 was enhanced by increasing the milling time. The long-term mechanical activation process improved the homogeneity of the dispersed zirconia phase in the matrix, and these particles could not easily associate together and grow excessively. Hence, the critical size required for tetragonal to m-ZrO_2 transformation was not achieved and the amount of t-ZrO_2 developed in the system [26]. Based on the XRD patterns shown in **figure 2.B**, we can conclude that the samples mechanically activated for different time durations followed by heat sintering at 1550 ℃ can be considered as the final composites since there was not any observable difference in their XRD results. **Table 5** represented the effect of the duration of the milling process on the bulk density and apparent porosity of composite samples which were heat-treated at 1550°C. As these results shown the increase in the duration of the mechanical activation process from 6 to 72 h changed the bulk density and apparent porosity from 3.16 gr/cm^3 to 3.51 gr/cm^3 and from 12 % to 4%, respectively.

The changes in the chemical structure of the mechanically activated and heat-treated powders were studied by IR spectroscopy. Structural bonds of starting materials were also evaluated. FT-IR results of raw materials and their characteristic bands were displayed in **figure 3** and **table 6**, respectively. FT-IR results of mechanically activated and heat-treated powders were also shown in **figure 4** and **table 7**, respectively. As **graphs (a-c)** of **figure 4.A** implied increasing milling time from 6 to 72 h did not change the FT-IR spectra of mechanically activated powders. Comparing **figures 3** and **4.A** showed that characteristic and sharp bands of Si-O at 542 cm^{-1}, 943 cm^{-1}, 1033 cm^{-1}, and 1103 cm^{-1} which were related to kaolinite, were removed or broadened by conducting or prolonging the duration of the mechanical activation process [27–29]. However bands of zircon at 437 cm^{-1}, 612 cm^{-1}, and 899 cm^{-1} still existed [30]. Furthermore, hydroxyl bonds of gibbsite were removed by mechanical activation [27,31]. The movement, broadening, and elimination of bands, could demonstrate to the increase in the amount of the amorphous phase in the mixtures. FT-IR bands of heat-treated powders at 1250 □- 1450 □ which were represented in **graphs (a-c)** of **figure 4.B** indicated that increasing the sintering temperature lowered the intensity of characteristic bands. Alumina and zircon bands were observed in all graphs of this figure [31,32]. As **graph (d)** of **figure 4.B** represented the band at 596 cm^{-1} indicated the formation of t-ZrO_2 in the system [33]. The bands at 572 cm^{-1}, 735 cm^{-1}, and 828 cm^{-1} which did not appear at lower temperatures illustrated the formation of mullite in the system. Bands at 735 cm^{-1} and 828 cm^{-1} were related to the formation of AlO_4 structural groups, as well [34].

3.2. Mechanical Properties

The variation of the diametral tensile strength and Vickers micro-hardness of samples as a function of heat treatment temperature were shown in **figures 5.A** and **B**, respectively. DTS and hardness values of samples which were mechanically activated for different milling time durations and heat-treated at 1550 ℃ were also represented **in figures 5.C** and **D**, respectively. Although XRD patterns of samples which were heated at 1250 ℃ and 1350 ℃ showed relatively the same results, **figure 5.A** indicated that DTS values changed significantly from 30 ± 19 MPa to 143 ± 22 MPa (****$p < 0.0001$) by increasing the temperature of heat treatment from 1250 ℃ to 1350 ℃, respectively. The observed change in DTS values of samples which were heat-treated at 1450 ℃ was not significant in comparison with samples which were heated at 1350 ℃. Although the crystallization of the mullite and zirconia started at 1450 °C, incomplete crystallization of these phases at this temperature (**figure 2.A, graph (d)**) could be the reason to the non-significant change in DTS values of heat-treated samples 1350 °C and 1450 °C. However, a more detailed study is required to clarify the exact reasons for these observations. Finally, heat treatment at 1550 ℃ for 2 h, increased the DTS values significantly to 220 ± 30 MPa (****$p < 0.0001$). Completion of the sintering reaction as a result of higher temperature and the formation of mullite and zirconia as high strength ceramic phases could be the main reasons for the intensive and significant increase in the mechanical strength of samples which were heat-treated at 1550 ℃ [2]. As results of **figure 5.B** showed when temperature increased from 1250 ℃ to 1550 ℃, micro-hardness values improved significantly from 0.83 ± 0.30 GPa to 11.12 ± 1.80 GPa (****$p < 0.0001$), as well. While the hardness values of zircon and alumina are higher than those of zirconia and mullite, increasing the heat treatment temperature and the resultant decline in the amount of zircon and alumina (**figure 2.A**), did not decrease the hardness of samples. The observed improvements in hardness values could be the result of more homogeneity and crystallization of remained amorphous phases [1]. **Figures 5.C** and **D** showed the DTS values and Vickers micro-hardness of samples which were mechanically activated for 6, 12, 24, and 72 h and heat-treated at 1550 ℃, respectively. Based on these figures, the DTS of samples increased significantly by increasing the milling time (****$p < 0.0001$). Although XRD patterns of these samples did not show any major differences in the type of developed crystalline phases, mechanical properties showed an ascending trend for both mechanical strength and micro-hardness values as a result of increasing the milling time. The intensive increase of mechanical strength from 27 ± 12 MPa for 6 h milled sample to 220 ± 30 MPa for 72 h mechanical activated ones which were both heat-treated at 1550 ℃ demonstrates the very well progress of sintering reaction as a result of prolongation of the mechanical activation process which we believe favored the reduction of the particle size distribution. As semi-quantification of XRD results in **table 3** showed, improvement in the amount of t-ZrO_2 phase to 10 wt. % could also be responsible for the observed improvement in the mechanical strength values. Strengthening of the interfaces which further discussed in SEM micrographs and reduction of the porosity percentage based on the results of **table 5** could enhance the DTS values of mentioned samples, as well. Low sinterability is one of the major weaknesses of mullite bodies which could be enhanced by the addition of zirconia and resulting formation of zirconia-mullite composites [35]. Therefore, a partial decrease in mullite content from 88 wt. % to 78 wt. % by prolonging the milling time and presence of an amorphous phase could lead to better sintering of this ceramic body and improve its mechanical strength. Micro-hardness results indicated that the bulk hardness also had ascending progress from 7.30 ± 1.08 GPa to 11.12 ± 1.80 GPa by increasing the milling time from 6 h to 72 h. Considering mechanical properties evaluations, 72 h mechanical activation process of starting mixtures seems to be essential, and this process could improve the mechanical properties of the final heat-treated composites. It is worth to mention here that the hardness values of the final zirconia-mullite composites with 1:1 molar ratio was comparable to the previously published result on the composite with a 2:1 molar ratio of zirconia-mullite [4]. By considering the lower amount of zirconia in the present work, the enhancement of the hardness values could be the sign of more homogeneous distribution of the crystalline phases. However, for a thorough interpretation of hardness values obtained in this research as well as those of other research, comprehensive investigation of porosity and particles size of zirconia-mullite composites are required.

3.3. SEM Studies:

The backscattered SEM micrographs of heat-treated samples at 1250, 1350, 1450 and 1550 ℃ after 72 h of the mechanical activation process were displayed in **figures 6 (a-h)**, respectively.

Figures 6 (a-f) indicated that the microstructure of samples changed gradually and transformed to more homogeneous ones when the temperature increased from 1250 ℃ to 1450 ℃. **Figures 6 (g** and **h)** illustrated the homogeneous crystallization and distribution of the zirconia phase in the alumino-silicate matrix at 1550 ℃. The SEM micrographs approved the ascending results of the mechanical strength which were shown in **figure 5.A**. The presence of cracks and in-homogeneities which were marked in **figures 6 (b)** and **(d)**, indicated that the sintering did not occur at 1250 ℃ and 1350 ℃. By increasing the temperature to 1450 ℃, according to **figure 6 (f)**, a more homogeneous distribution of crystalline phases in the matrix was achieved which improved the mechanical strength. Finally, the formation of a homogeneous composite at 1550 ℃ (**figures 6 (g)** and **(h)**), enhanced the mechanical strength properties. The fracture surfaces of the samples heated at 1550 ℃ which were previously mechanically activated for different times were also studied by SEM, and the obtained results showed in **figure 7**. Although the XRD patterns of these samples (**figure 2.B**) indicated that increasing the time duration of the milling process did not lead to an intensive increase in XRD peaks of mullite and t-ZrO_2 at $2\theta = 26.35^o$ and 30.38^o, respectively, SEM micrographs illustrated that increasing the milling time had an effective role in distribution and progress of phase transformation. According to SEM images, the requirement of the long-term mechanical activation is inevitable. These images demonstrated the formation of improved interfaces between different phases by increasing the milling time. Although XRD results indicated that after 6 h of mechanical activation zirconia crystallized in heat-treated samples, **figures 7 (a-c)** demonstrated that this phase did not show an appropriate distribution in the alumino-silicate matrix. The weak interfaces between zirconia aggregates and mullite matrix, the large size of zirconia particles, and their inappropriate distribution in the matrix in 6 h activated sample which was represented in **figures 7 (a-c)** altogether confirmed that the formation reaction of the composite was incomplete in these samples. Besides, it was expected that the large difference of thermal expansion coefficient of m-zirconia (6.5×10^{-6} k^{-1}[1]) to that of t-zirconia (10×10^{-6} k^{-1}[1]) and mullite (4.5×10^{-6} k^{-1}[9]) would lead to the formation of micro-cracks which were shown in 6 h milled samples (**figures 7 (a)**-**(c)**). As shown in **figures 7 (d)**-**(i) b**y increasing the milling duration to 12 and 24 h, the size of zirconia aggregates decreased from 10 μ (**figure 7 (c)**) to 5 μ (**figures. 7 (f) and (i)**). Finally, as **figures 7 (j-l)** showed, by raising the milling durations to 72 h, distribution of zirconia particles in the mullite matrix became more homogeneous and their size decreased effectively. As it was mentioned before, SEM micrographs which were shown in **figure 7** could be beneficial for a more accurate discussion on the DTS results. Improvement of the homogeneity and also better distribution of the zirconia phase in the alumino-silicate matrix by increasing the milling time to 72 h, could be the main reasons for the enhanced DTS values of 72 h milled samples. It was also observed that (**figures 7 (j)-(l)**) the zirconia-mullite interfaces which were so weak in 6 h milled sample, became more strong which could be another good reason for the increased mechanical strength values. SEM images alongside mechanical properties evaluations for 72 h mechanically activated samples which were heat-treated at 1550 ℃ approved that an ideal microstructure, more homogeneous distribution of phases and finer particle sizes could be achieved by prolonging the mechanical activation process, although XRD patterns did not reveal any major changes.

4. Conclusion

Zirconia-mullite composites, with 1:1 molar ratio, were fabricated by reaction sintering of gibbsite, zircon, and kaolinite mixture. The effect of mechanical activation duration (6 - 72 h) and heat treatment temperature (1250 ℃ - 1450 ℃) on the progress of the phase transformation in heat-treated composites were studied. The impact of the above-mentioned parameters on the mechanical properties of the final composites was also investigated by evaluation the diametral tensile strength and Vickers micro-hardness. Regardless of the duration of the mechanical activation process, crystallization of zirconia and mullite phases were initiated at 1450 ℃ and about the total of 4 wt. % zirconia and mullite were crystallized at this temperature. After heat treatment at 1550 ℃ for 2 h, zirconia and mullite weight percent increased to 18 wt. % and 78 wt. %, respectively. SEM and XRD results of mixtures approved that increasing the duration of milling process from 6 h to 72 h developed the homogeneity of the final phases and prevented the tetragonal to monoclinic zirconia transformation at 1550 ℃. Diametral tensile stress and Vickers micro-hardness of samples which were mechanically activated for 72 h and heat-treated at 1550 ℃ were 220 ± 30 MPa and 11.12 ± 1.80 GPa, respectively. Although zirconia content as high strength and hard phase was low in the final composites, the obtained results of the micro-hardness test were comparable with obtained hardness values of composites with zirconia to mullite molar ratio equal to 2:1.

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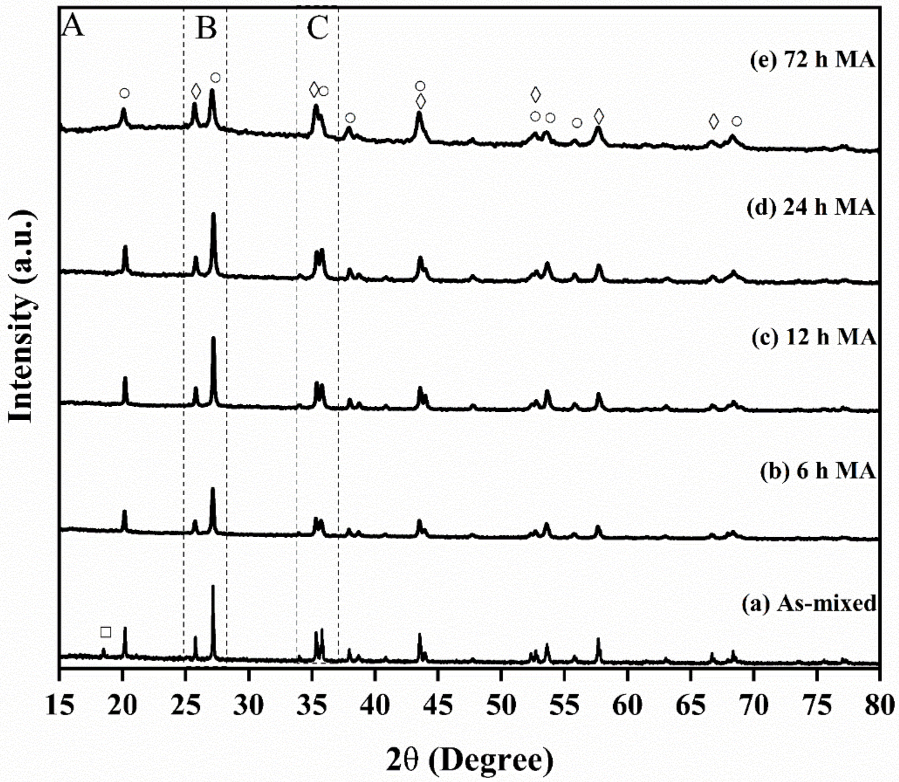
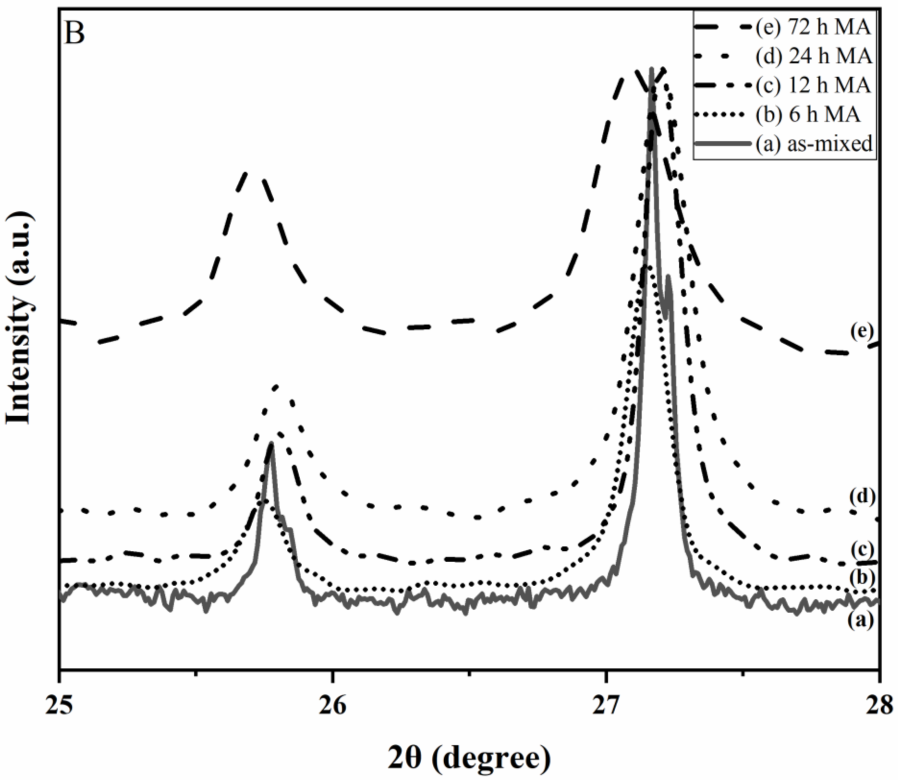

A
B
C
(e) 72 h MA
(d) 24 h MA
(c) 12 h MA
(b) 6 h MA
(a) As-mixed
○
◊
□
Intensity (a.u.)
2θ (Degree)
15
20
25
30
35
40
45
50
55
60
65
70
75
80


B
(e) 72 h MA
(d) 24 h MA
(c) 12 h MA
(b) 6 h MA
(a) as-mixed
(e)
(d)
(c)
(b)
(a)
Intensity (a.u.)
25
26
27
28
2θ (degree)

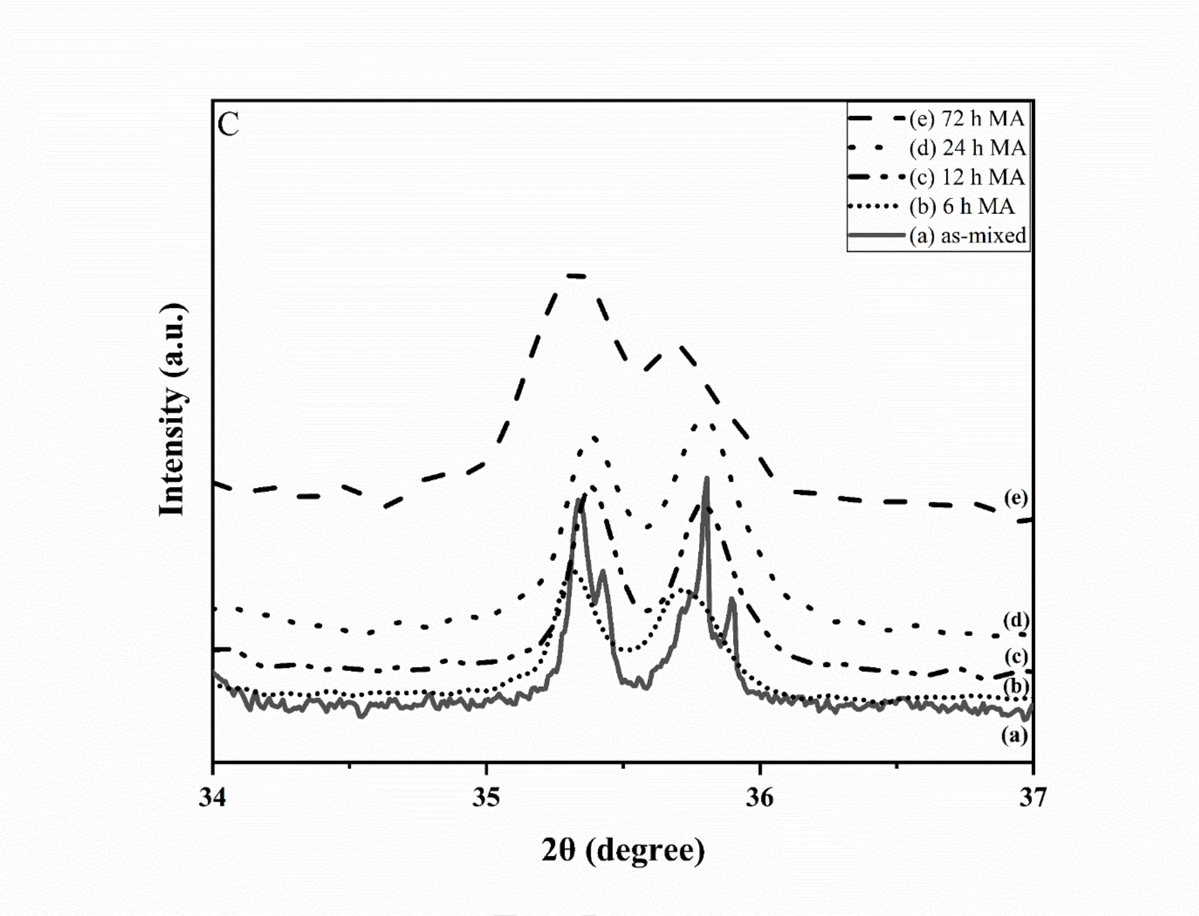
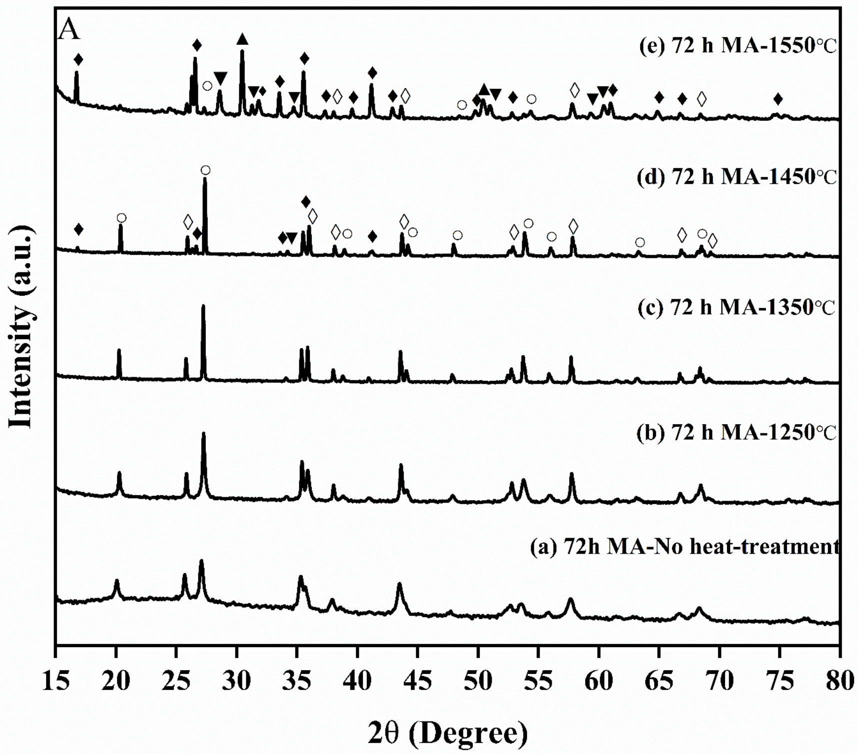


Figure 1. **(A)** XRD patterns of mixture of raw materials without heat treatments after different times of mechanical activation process (MA), (○: zircon, □: gibbsite, ◊: alumina), Higher magnification of figure **(A)** at: **(B)** 2θ = 34 - 37º, **(C)** 2θ =25 - 28º.


A
(e) 72 h MA-1550℃
(d) 72 h MA-1450℃
(c) 72 h MA-1350℃
(b) 72 h MA-1250℃
(a) 72h MA-No heat-treatment
Intensity (a.u.)
2θ (Degree)
15
20
25
30
35
40
45
50
55
60
65
70
75
80

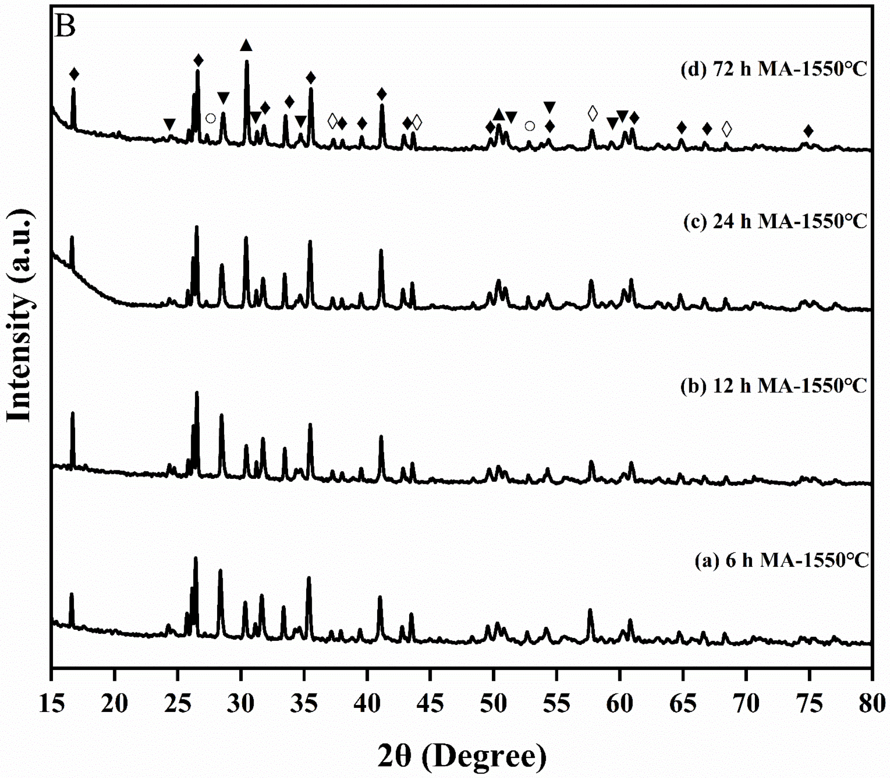


Figure 2. (A) XRD patterns of 72 h mechanically activated (MA) samples heated at different temperatures, **(B)** XRD patterns of samples with different mechanical activation (MA) durations heated at 1550℃ (○: zircon, ◊: alumina, ♦: mullite, ▼: m-ZrO_2, ▲: t-ZrO_2).

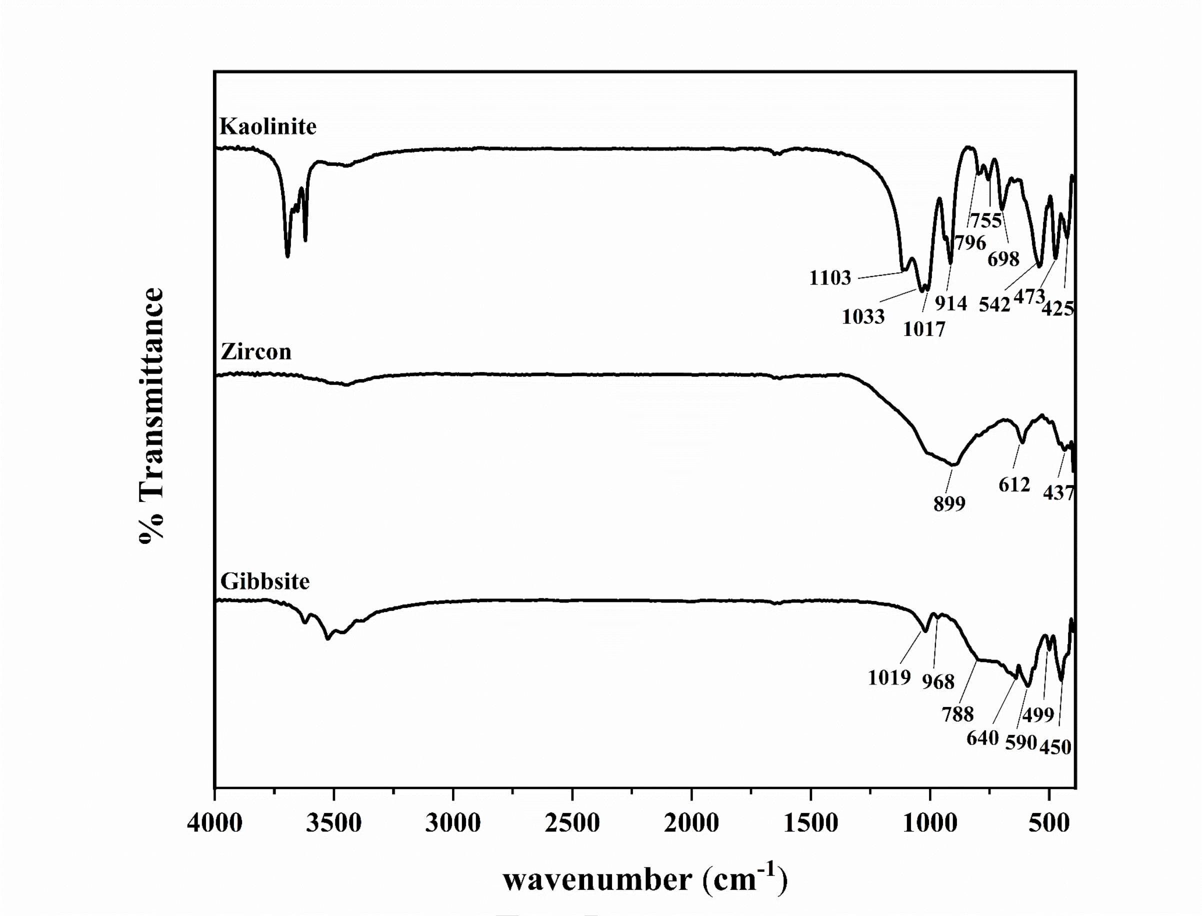


Figure 3. IR spectra of raw materials.

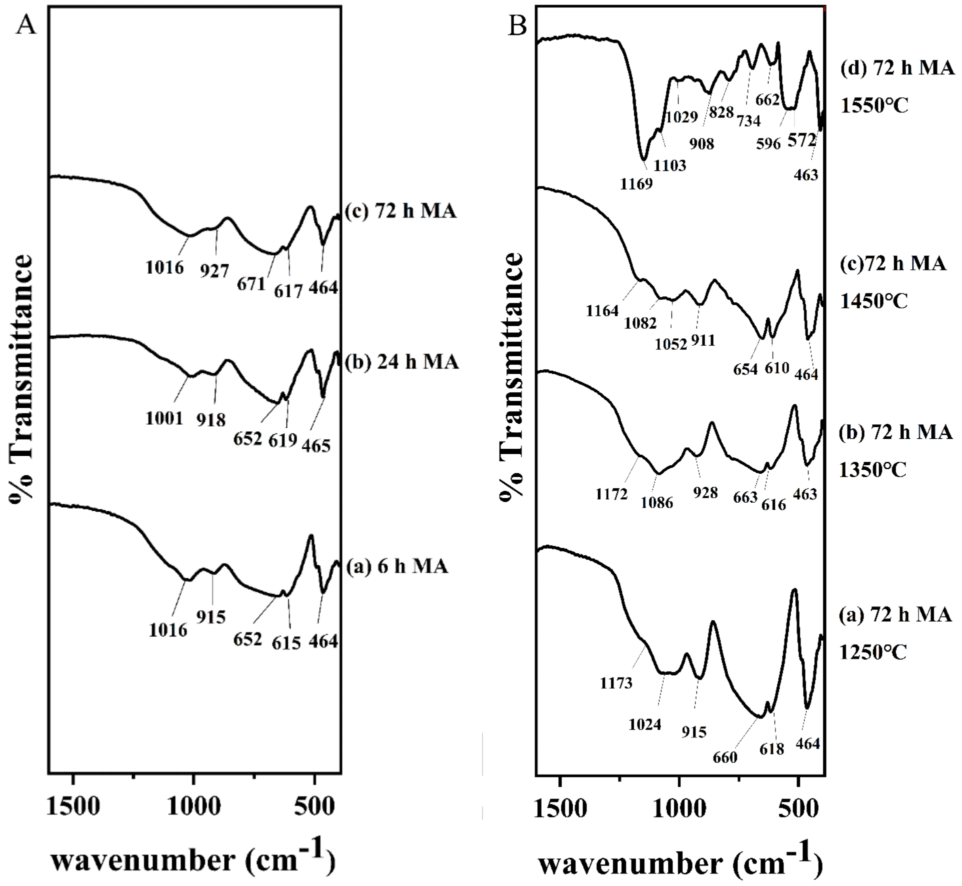
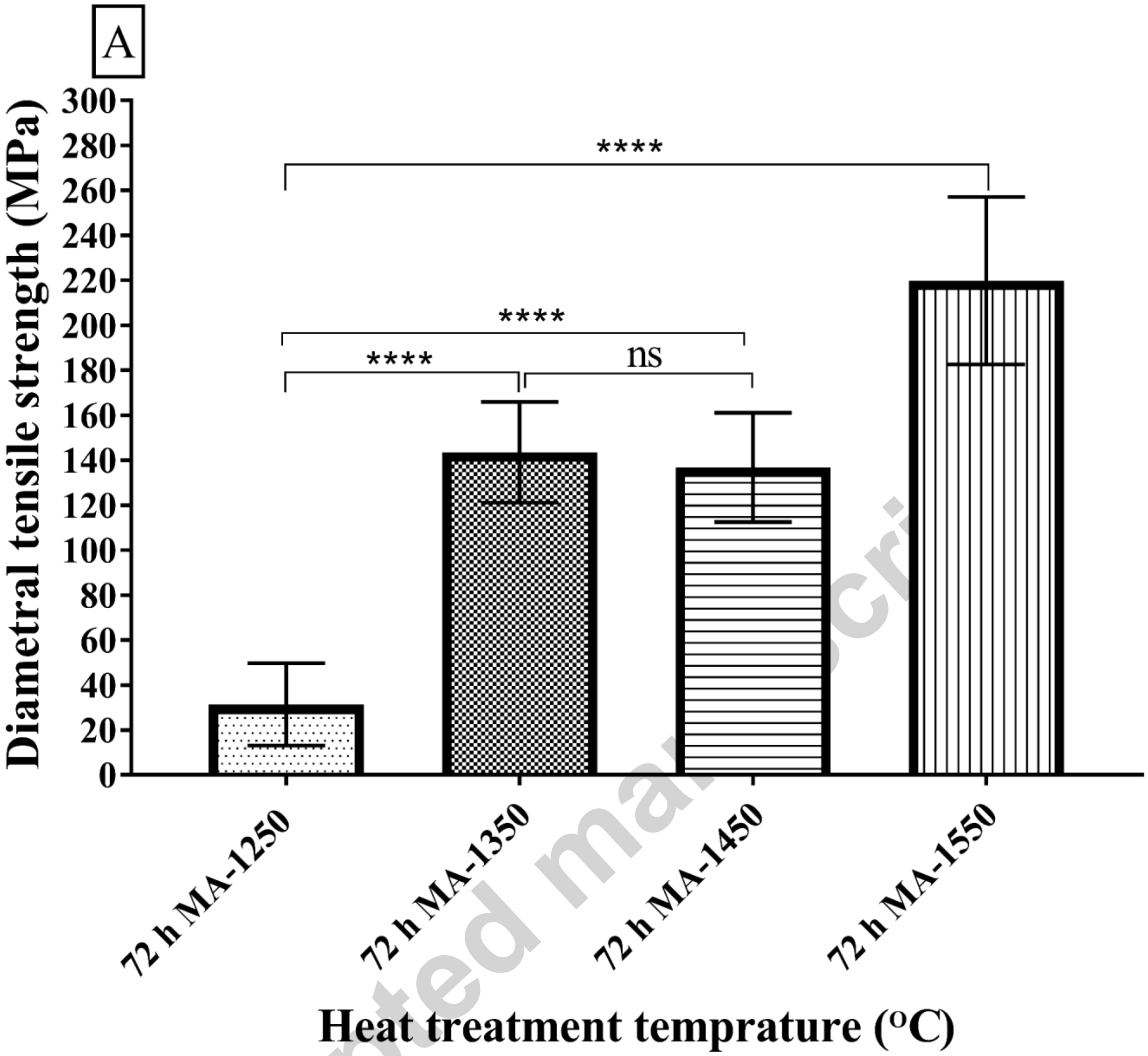
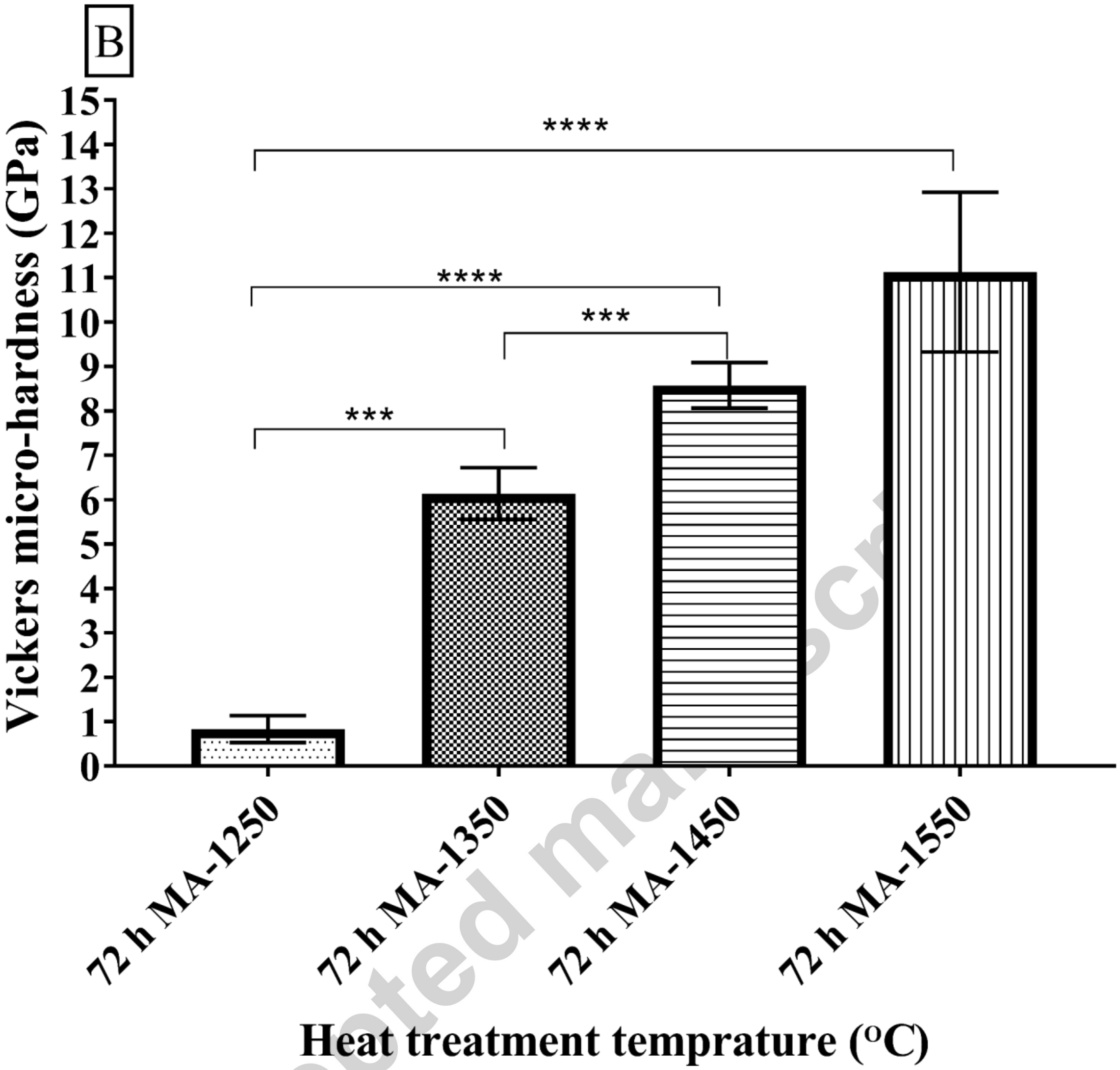
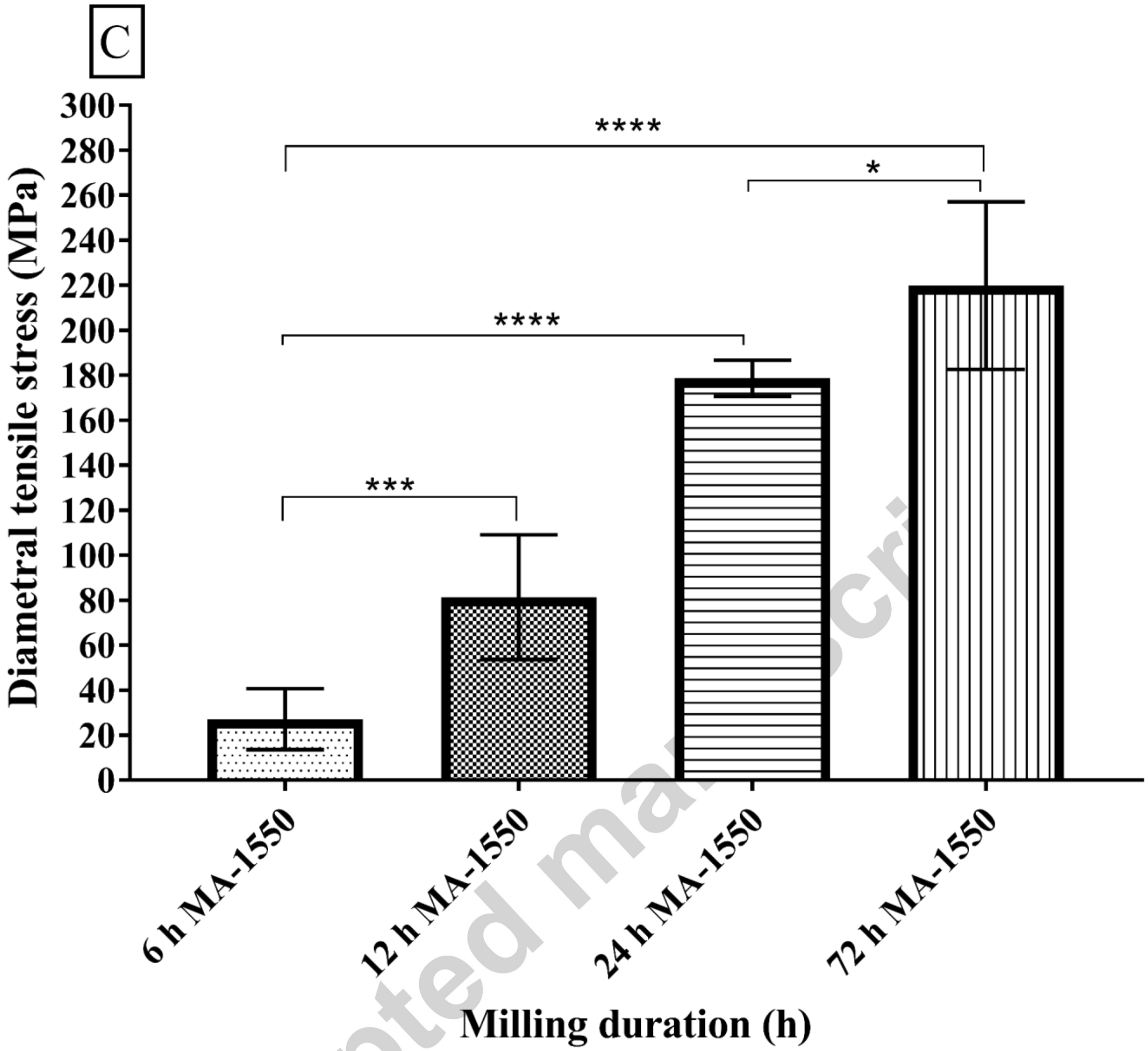


Figure 4. **(A)** FT-IR spectra of mixtures after 6, 24, and 72 h of the mechanical activation process, (**B)** FT-IR spectra of 72 h mechanically activated samples heated at different temperatures.


A
Diametral tensile strength (MPa)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
****
****
****
ns
72 h MA-1250
72 h MA-1350
72 h MA-1450
72 h MA-1550
Heat treatment temprature (oC)


B
Vickers micro-hardness (GPa)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
****
****
***
***
72 h MA-1250
72 h MA-1350
72 h MA-1450
72 h MA-1550
Heat treatment temprature (°C)


C
Diametral tensile stress (MPa)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
****
*
****
***
6 h MA-1550
12 h MA-1550
24 h MA-1550
72 h MA-1550
Milling duration (h)

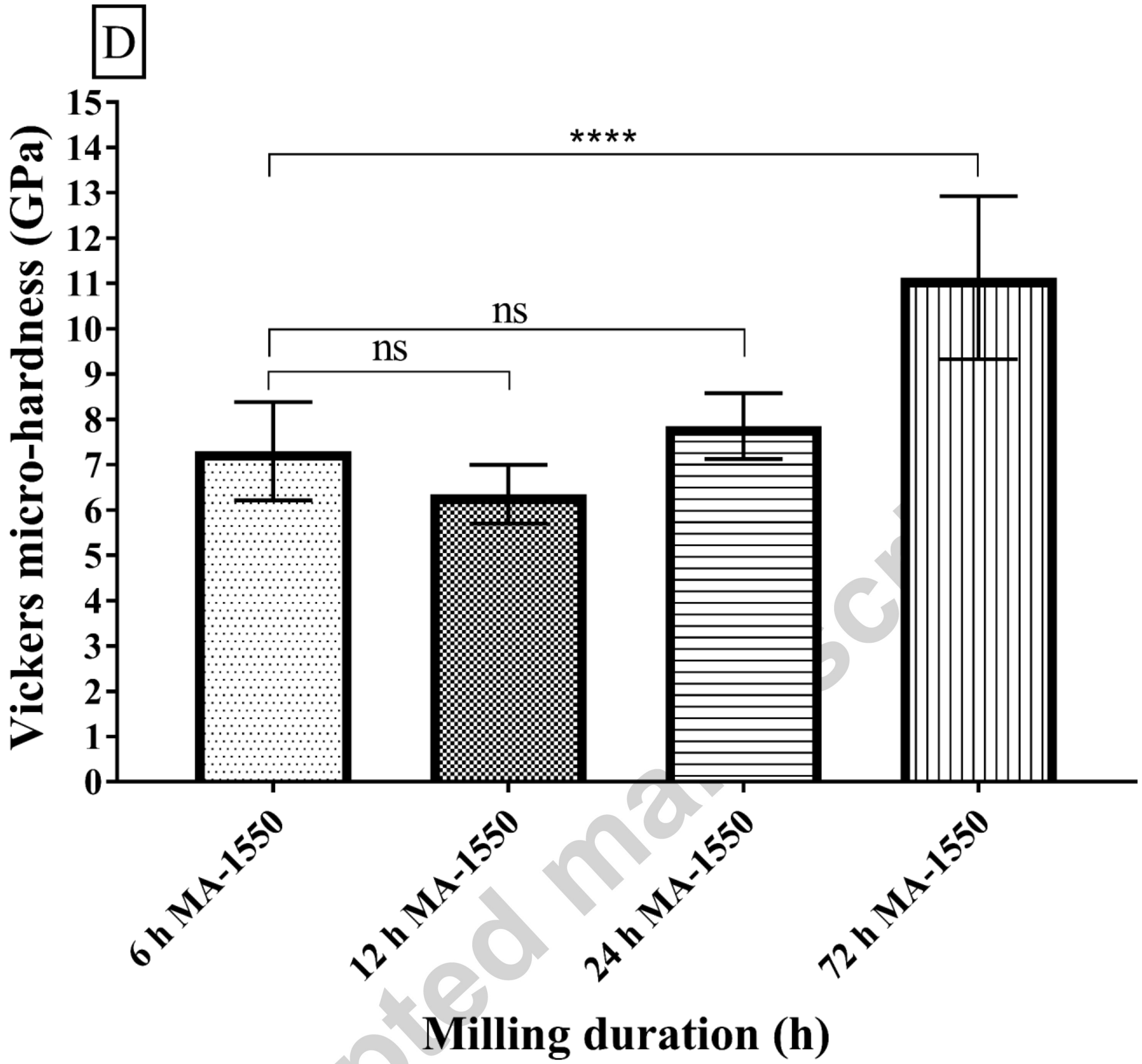


Figure 5. Results of mechanical properties as: (**A)** Diametral tensile strength and (**B)** Vickers micro-hardness of 72 h mechanically activated samples heated at different temperatures, **(C)** Diametral tension strength and (**D)** Vickers micro-hardness of samples heated at 1550℃ and mechanically activated for different time durations (*p < 0.05, **p < 0.01, ***p < 0.001, and ****p < 0.0001, ns = non-significant).

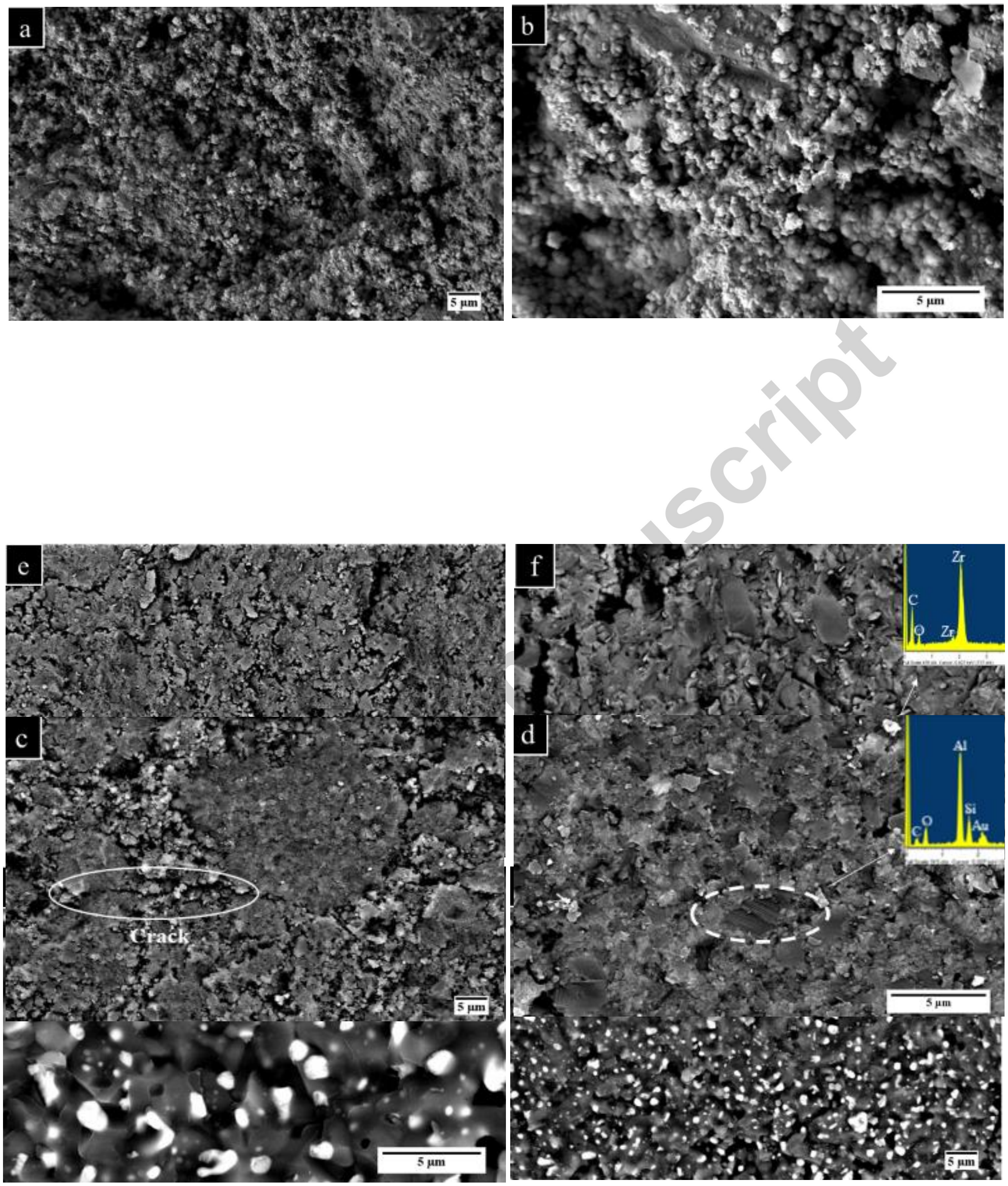
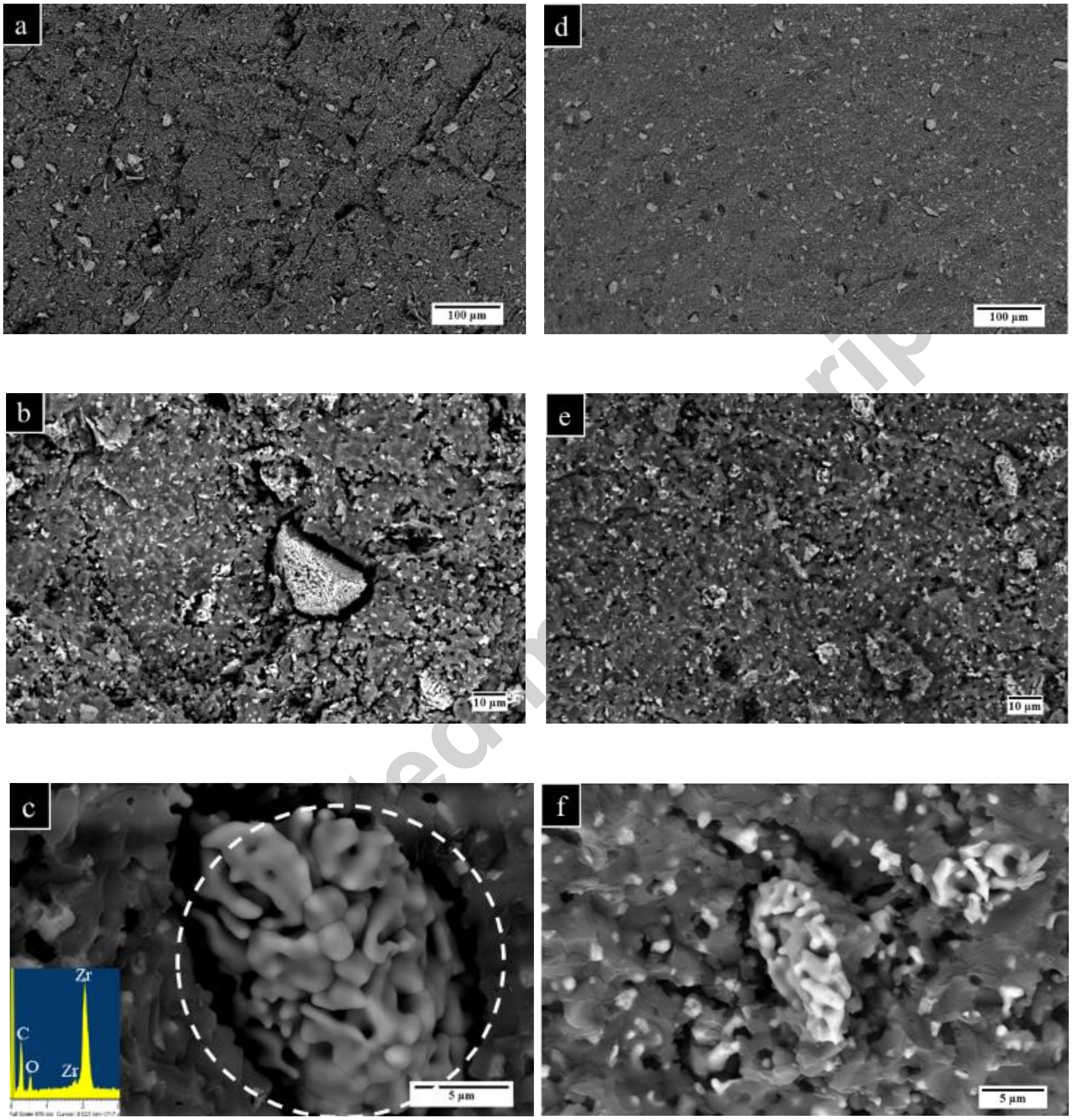


Figure 6. SEM micrographs of the fracture surface of 72 h mechanical activated samples heat-treated at: **(a, b)** 1250℃, **(c, d)** 1350℃, **(e, f)** 1450℃, **(g, h)** 1550℃ (two different magnifications were represented for each temperature).


a
100 µm
d
100 µm
b
10 µm
e
10 µm
c
Zr
C
O
Zr
5 µm
f
5 µm

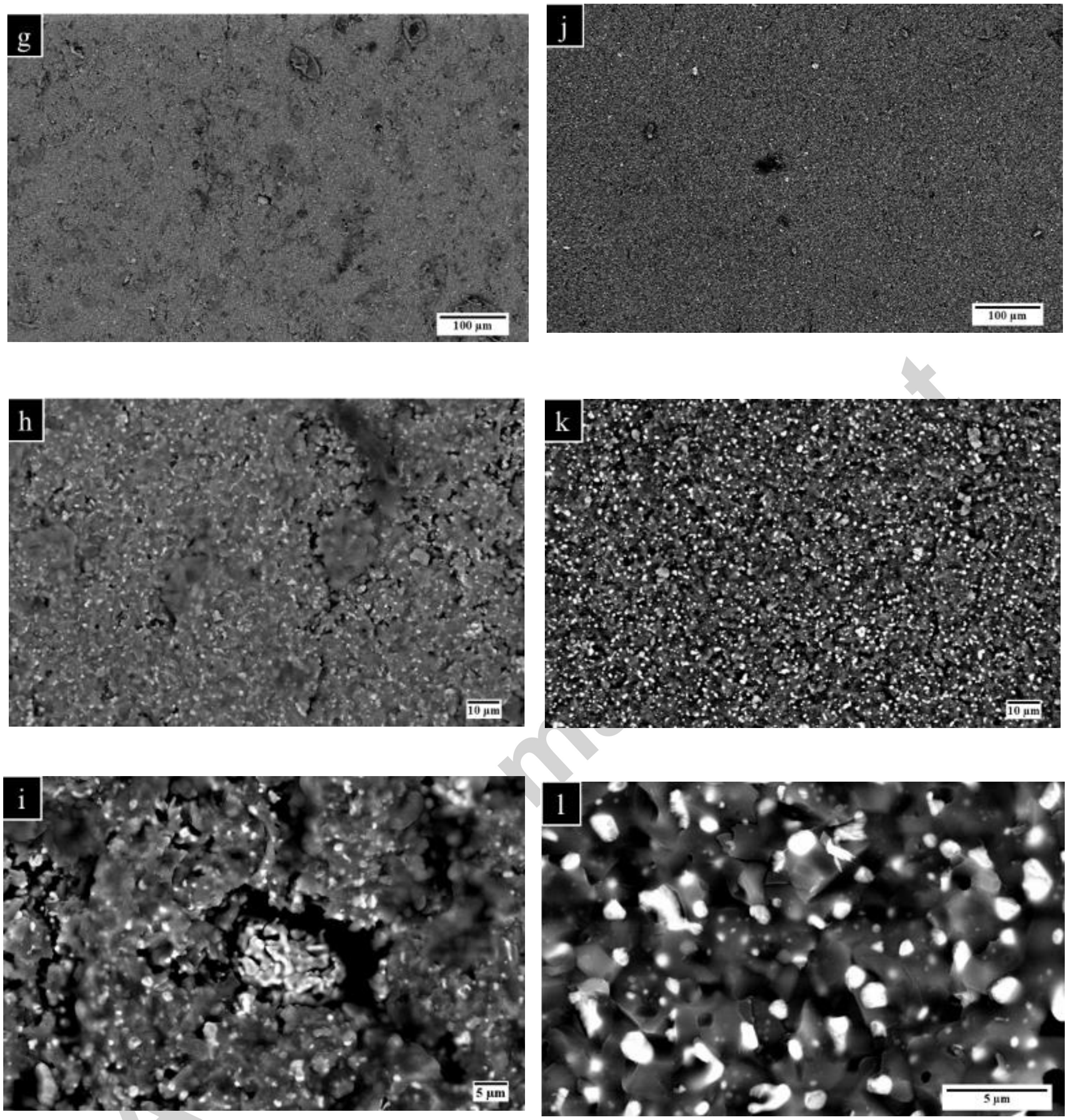


Figure 7. SEM micrographs of samples heated at 1550℃ with different durations of mechanical activation process: **(a, b, c)** 6 h, **(d, e, f)** 12 h, **(g, h, i)** 24 h, **(j, k, l)** 72 h (three different magnifications were represented for each temperature).

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

Table 2. Effect of different times of mechanical activation process on the particle size distribution of the starting materials

Sample	D_{mean}	D_{10}	D_{50}	D_{90}
6 h MA	2.5 ± 0.8 μm	3.3 ± 0.2 μm	7.1 ± 0.3 μm	9.5 ± 0.2 μm
24 h MA	0.4 ± 0.1 μm	0.7 ± 0.4 μm	2.2 ± 1.1 μm	4.6 ± 3.9 μm
72 h MA	80 ± 9.6 nm	120 ± 10 nm	290 ± 10 nm	530 ± 10 nm

Table 3. Effect of heat treatment temperature and the duration of the mechanical activation process on the semi-quantification results of the crystalline phases

Sample	**72 h MA-1250℃**	**72 h MA-1350℃**	**72 h MA-1450℃**	**6 h MA-1550℃**	**12 h MA-1550℃**	**24 h MA-1550℃**	**72 h MA-1550℃**
Mullite	-	-	4 wt. %	64 wt. %	70 wt. %	88 wt. %	78 wt. %
t-ZrO_2	-	-	-	4 wt. %	4 wt. %	8 wt. %	10 wt. %
m-ZrO_2	-	-	4 wt. %	10 wt. %	1 wt. %	2 wt. %	7 wt. %
Al_2O_3	69 wt. %	70 wt. %	67 wt. %	21 wt. %	14 wt. %	1 wt. %	3 wt. %
Zircon	31 wt. %	30 wt. %	25 wt. %	1 wt. %	11 wt. %	1 wt. %	2 wt. %

Table 4. Effect of the duration of the mechanical activation process on the crystallite size of mullite and zirconia phases

Sample	**6 h MA- 1550℃**	**12 h MA- 1550℃**	**24 h MA- 1550℃**	**72 h MA- 1550℃**
Mullite	79 nm	61 nm	72 nm	63 nm
t-ZrO_2	133 nm	59 nm	15 nm	50 nm
m-ZrO_2	54 nm	68 nm	61 nm	38 nm

Table 5. The effect of the duration of the mechanical activation process on the bulk density and apparent porosity of samples heat-treated at 1550 °C

Sample	**6 h MA-1550℃**	**12 h MA- 1550℃**	**24 h MA-1550℃**	**72 h MA-1550℃**
Bulk Density (g/cm^3)	3.16	3.21	3.34	3.41
Apparent Porosity (%)	12	10	6	4

Table 6. FTIR bands of used raw materials

Material	Wavenumber (cm^{-1})	Assignment	Ref
Kaolinite	943	δ (Al-OH)	[28]
	425	δ (Al-O) in AlO_6	[31]
	473	Deformation mode of Si-O-Si in amorphous silica	[31]
	913 , 1017 , 1103	ν (Si-O)	[28]
	542	Si-O-Al	[29]
	698 , 755	Surface hydroxyls	[29]
Zircon	437, 612	δ (Si-O) in SiO_4	[30]
	899	ν (Si-O) in SiO_4	[30]
Gibbsite	968	δ (Al-OH)	[28]
	450 , 590	δ (Al-O) in AlO_6	[31]
	640	ν (Al-O) in AlO_6	[31]
	740	ν (Al-O) in AlO_4	[31]

Table 7. The IR bands of the mechanically activated mixtures and heat-treated samples

Phase	Wavenumber (cm^{-1})	Assignment	Sample	Ref.
Zircon	610 - 618	δ (Si-O) in SiO_4	All samples except 72 h -1550 ℃	[30]
	908 - 928 , 1001 - 1081	ν (Si-O) in SiO_4	All samples	[30]
Alumina	463 - 465, 651 - 671	ν (Al-O) in AlO_6	All samples	[32]
Alumino-silicate	1164 - 1173	ν (Si-O) in SiO_4	Heat-treated samples	[32]
m-ZrO_2	463 , 734	Zr-O	72 h - 1550℃	[33]
t-ZrO_2	596	Zr-O	72 h - 1550℃	[33]
Mullite	735 , 828	(Al-O) in AlO_4	72 h - 1550℃	[34]
	735	Stretching mode of (Si-O-Al)	72 h - 1550℃	[34]
	1103	ν(SiO_4)	72 h - 1550℃	[34]