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Effect of mechanical activation and microwave heating on synthesis and sintering of nano-structured mullite

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ABSTRACT

Nano-structured mullite was produced from the microwave heating of a mixture of clay and alumina activated mechanically in a planetary ball mill for 30, 50 and 70 h. XRD results showed after 30 h milling time, clay disappeared and alumina and quartz appeared as the only crystalline phases. The maximum specific surface area was 34.92 m^2/g for the sample activated mechanically for 30 h. The mullitization was completed for powders milled for 30 and 50 h and heated for 30 min (equal to 1376 °C) in a microwave oven. The maximum density and flexural strength values were measured for samples milled for 30 and 50 h, respectively, and sintered for 30 min. The flexural strength values of these samples were 3 and 4.7 times of the strength value of the sample milled for 2 h and sintered at the same conditions.

1. Introduction

Mullite is a promising ceramic with the high temperature applications due to its low thermal expansion, high creep resistance and good thermal shock behaviour and also with good chemical, mechanical and electrical properties [1–5]. Many works have reported the use of kaolin as a key material for synthesis of mullite ceramics [6–8]. The formation of mullite from kaolinite undergoes a series of reactions. During heating process, it lost its physical bound water at low temperatures decomposed to amorphous metakaolin at higher temperatures and finally transforms to mullite.

It has been demonstrated that the mechano-activation process achieved with high-energy mills may enhance the reactivity of solid particles [9–11]. Mechanical activation of oxides and mixed oxides using a high-energy mill is a relevant technique to reduce particle size and increase defects in the crystalline lattices [12]. This method also reduces the phase transformation temperatures and enhances the chemical reactions [13]. The formation of defects enhances densification through the creation of the more diffusion paths. Temuujin et al. [14] reported that when hydroxides or hydrous starting materials are subjected to mechanical treatment, the mixture becomes more homogeneous due to the formation of Si–O–Al bonds, and its behaviour on subsequent thermal treatment resembles that of precursor gels obtained via solution chemistry. The temperature of mullite formation was found about 1200 °C, and the increased reactivity of the ground powders was related to the formation of Si–O–Al bonds rather than decreased particle size resulting from grinding. In another work these authors [15] reported the thermal treatment of precursors prepared by mechanochemical activation from gibbsite and silica gel led to the crystallization of mullite at ≈1200 °C via a spinel phase, while precursors prepared from α-Al_2O_3 and silica gel or gibbsite and fused silica formed mullite at about 1400 °C by solid state reaction between α-Al_2O_3 and cristobalite.

The role of mechanical activation of alumina and silica powders in solid state processing of nano-structured mullite ($3Al_2O_3{\cdot}2SiO_2$) phase has been investigated [16]. The results showed that milling in a conventional ball mill although decreases mullite formation temperature by 200 °C, but does not considerably change mullite phase morphology. Use of a planetary ball mill and milling for 40 h showed to be much more effective in activating the oxide precursors, and mullitization temperature was reduced to below 900 °C and whisker like mullite was formed after sintering at 1450 °C. The mullitization behaviour of the mixture of SiO_2 and Al_2O_3 in the presence of transition metal oxides ($FeO_{1.5}$, CoO and NiO) activated by a high-energy ball milling process was investigated [17]. The mullitization temperature was found about 1200 °C which was 100 °C lower than that required by the conventional process. In another work [18], the stoichiometric mullite was prepared using attrition milling by the decomposition of kyanite (Al_2SiO_5) and its reaction with α-alumina. The complete mullite formation occurred

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Table 1
Chemical composition of clay and alumina.

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	L.O.I.
Clay	39.22	48.46	0.2	0.2	0.5	0.3	1.1	–	9.9
Alumina	98.7	0.07	0.035	0.015	0.04	–	–	0.43	0.7

after firing at only 1350 °C/1 h. Dense mullite ceramic (3.03 g/cm^3) was obtained after firing at 1600 °C for 12 h.

Microwave energy has been extensively used for synthesis and sintering of ceramic materials [19–21]. The most important reasons of using microwave energy over conventional processing are fast and volumetric heating, high heating rates, limited grain growth and forming more uniform grain sizes throughout the ceramic body. Mullitization and densification of ($3Al_2O_3 + 2SiO_2$) powder compacts were found to be accelerated using a microwave furnace in comparison to conventional heating [22]. According to recent work [23] it was found that mullitization behaviour of a mixture of clay and alumina was completed in the compacted powders after 20 min heating in a microwave furnace. The higher density was obtained to a lower temperature by microwave heating rather than conventional heating. The microwave process led to a reduction of 120 °C in sintering temperature for a given value of density.

This paper reports the effect of mechanical activation of alumina and clay in a high-energy mill on the synthesis and sintering of mullite subjected to microwave heating process. The investigation is focused on the phase development, density and porosity, microstructure changes and flexural strength development after milling of precursor powders for different times sintered in a microwave furnace.

2. Experimental procedures

Table 1 reports the chemical composition of used clay (d_{90} = 3.51 μm) and alumina (d_{90} = 7.2 μm). The mixing of clay and alumina powders was carried out using an ordinary ball mill with alumina balls for 2 h. The mechanical activation of mixed powders was carried out using a laboratory high-energy planetary ball mill. The ball to powder mass ratio was 15:1. The milling was started at a grinding speed of 270 rpm and lasted up to 30, 50 and 70 h. Since the friction between alumina balls during milling raises the alumina content, the weight loss of alumina balls was measured before and after milling for different times. For S30, S50 and S70 samples, the weight loss of alumina balls was 8.2, 21.3 and 16.5 g, respectively. These alumina weights were considered in the final alumina amounts needed for the formation of mullite in different samples. Since the amount of added clay was held constant for all samples (11.6 g), then the extra silica amount (4.5 and 2.6 g for S50 and S70, respectively, from MERCK) was added in order of complete transfer of extra alumina into mullite phase. The milled powders were subjected to wet chemical analysis and the results are shown in Table 2. The milled powders for 2 h (ordinary ball mill), and 30, 50 and 70 h (planetary ball mill) were pressed at 255 MPa in a steel die with 10 mm diameter and denoted as S2, S30, S50 and S70, respectively. The heat treatment of pressed samples was carried out using microwave oven (2.45 GHz and 900 W) in air for 5, 10, 15, 20, 30 and 60 min. The used assemble for microwave heating was described elsewhere [23]. The flexural strength of sintered samples was measured using Instron 1923 on 40 mm × 3 mm × 3 mm rectangular samples. At least five samples were tested. The phase evaluation in the milled powders before and after heating was investigated by means of X-ray diffraction method (Siemens, D500 system) using Cu Kα radiation working with 30 kV accelerating voltage, a 25 mA current and 2° 2θ/min. Alumina and quartz formation progresses in the milled powders were determined by considering the intensity ratio of $I_t/(I_t + I_{Si})$ peaks, where 'I_t' is the integrated intensity of alumina (0 1 2) or quartz (1 0 1) and 'I_{Si}' is the integrated intensity of silicon (1 1 1) as a reference. The X-ray results were examined three times and error of the intensity measurements was established to be ±3.4%. The surface morphology was investigated with Cambridge-360 scanning electron microscope on powder and etched samples. The milled powders were subjected to thermal analysis using simultaneous TG/DTA (Model: 320).

Table 2
Alumina and silica amount (wt%) in milled powders.

Milling time (h)	Al_2O_3	SiO_2
30	72.3	27.7
50	71.5	28.5
70	71.1	28.9

3. Results and discussion

3.1. Milled powders before heating

Fig. 1 shows the morphology of the mixture of alumina and clay powders milled for different times. XRD patterns of milled powder

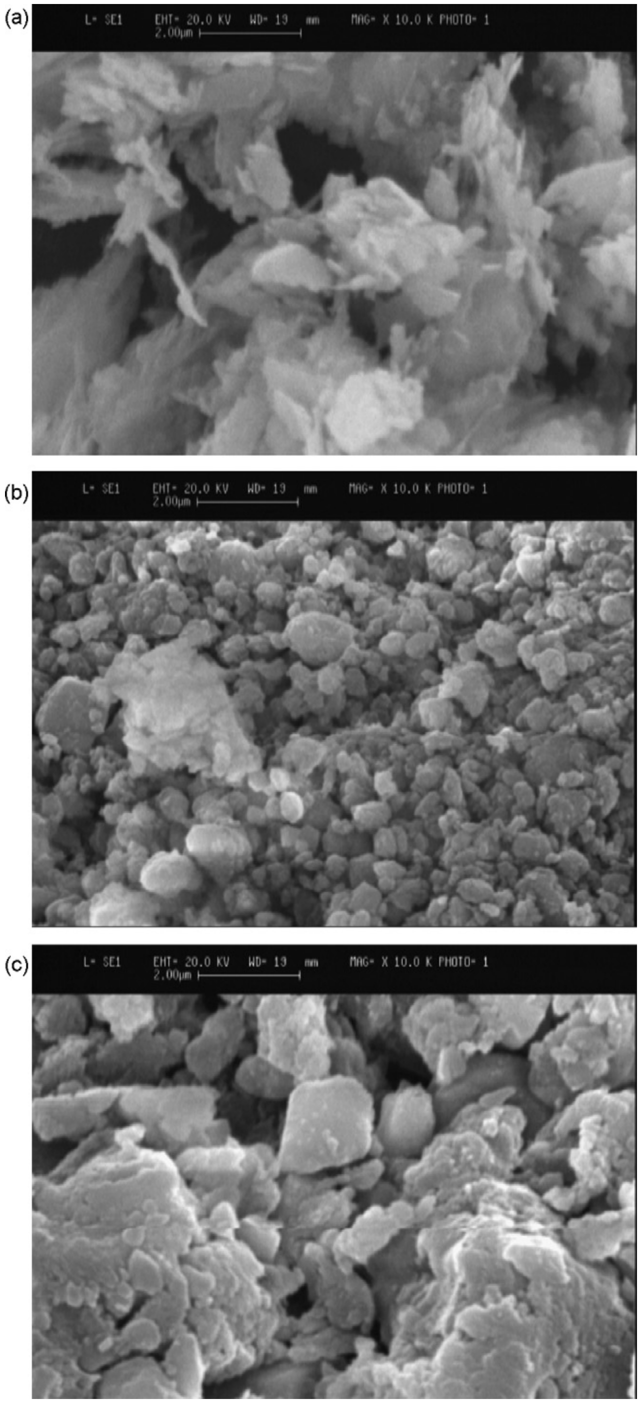

Fig. 1. SEM micrographs of powders milled for (a) 2 h, (b) 30 h and (c) 50 h.

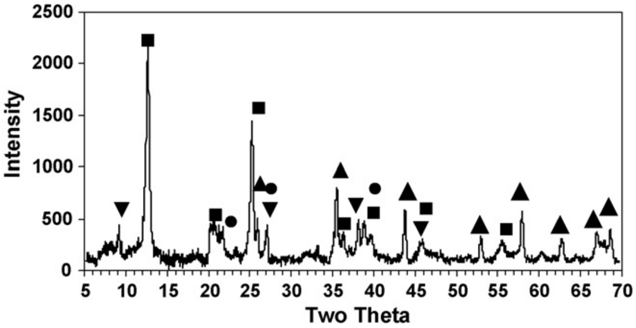

Fig. 2. XRD pattern of powder milled for 2 h in an ordinary ball mill (▲: α-alumina; ▼: muscovite; ●: quartz; ■: kaolinite).

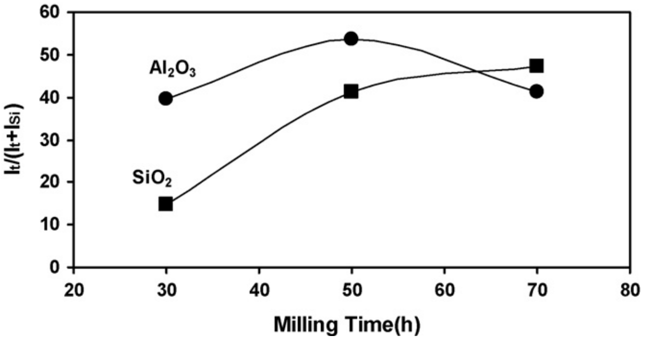

Fig. 4. Evaluation of alumina and quartz phases in milled powders ('I_t' is the integrated intensity of alumina or quartz peaks and 'I_{Si}' is the integrated intensity of silicon peak).

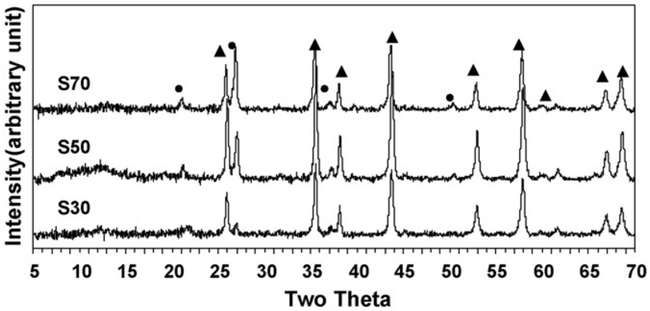

Fig. 3. XRD patterns of S30, S50 and S70 powders milled in a planetary mill before heating (▲: alumina; ●: quartz).

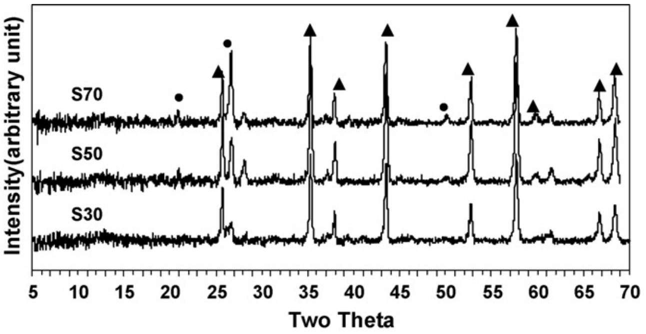

Fig. 5. XRD patterns of S30, S50 and S70 powders heated for 15 min (from room temperature to 1052 °C) (▲: alumina; ●: quartz).

for 2 h (Fig. 2) indicate the major peaks of kaolinite and the minor peaks of alumina, quartz and muscovite which are the only crystalline phases. The kaolinite and muscovite peaks disappeared after 30 h milling (Fig. 3) indicating the decomposition of the kaolinite and muscovite crystalline phases and their transformation into an amorphous phase. Alumina and quartz were the only crystalline phases even after a long milling time of 70 h.

The specific surface area of powders milled for different times is shown in Table 3. As observed with milling of mixed powders from 2 to 30 h, the specific surface area values increased from 23.3 to 34.9 m^2/g. For sample milled for over 30 h, the specific surface area values decreased and reached down 15.6 m^2/g after 70 h milling. The possible reason for the reduction of specific surface area values with the increase of milling times could be attributed to the formation of agglomerates after milling (Fig. 1c). The mean particle size of milled powders calculated from BET data is summarized in Table 3. From these data it can be concluded that by increasing milling time from 2 to 30 h, the mean size of particles reduces which can be attributed to the increase of surface area and powder density values. By increasing milling time over 30 h, the mean particle size increased as a result of decreasing the surface area in spite of the increase of powder density. A reason for the increase of powder density with milling time could be explained with observing the XRD curves taken from the milled powders (Figs. 2 and 3) and the existence of alumina and quartz after milling (Fig. 4). The existence of alumina and quartz as the only crystalline phases increases the powder density in S30 sample (Fig. 3), while S2 sample which contains kaolinite as the major phase (Fig. 2) has a lower density. As Table 3 exhibits, the powder density increases in S50 sample in comparison with S30 sample attributed to more alumina and quartz phases (Fig. 4). The decrease of powder density for S70 sample in comparison with S50 sample (Table 3) can be ascribed to the less alumina content in the former sample (Fig. 4).

3.2. *Milled powders after heating*

The milled powders were pressed and heated at different temperatures. It was found that samples heated at 700 °C (5 min heating in microwave furnace) contained alumina and quartz as the only crystalline phases. As Fig. 5 reveals, the height of alumina peaks decreased after increasing the heating time to 15 min (from room temperature to 1052 °C). The weak peaks of mullite phase appeared in S30 sample (Fig. 6) after heating for 20 min (from room temperature to 1176 °C). Mullite was the only crystalline phase in S30 and S50 samples after heating for 30 min (from room temperature to 1376 °C); in the mean-time the sharp peaks of alumina phase were still remained in S70 sample (Fig. 7). The advanced formation of mullite in S30 sample in comparison with S50 and S70 sam-

Table 3
Particle size distribution of milled powders before heating and physical and mechanical properties of sintered samples vs. milling time.

Milling time (h)	Particle size (μm) (d_{BET})	Powder density (g/cm^3)	Specific surface area (m^2/g)	Sintering temperature (°C)	Bulk density (g/cm^3)	Porosity (%)	Flexural strength (MPa)
2	0.087	2.96 ± 0.002	23.3	1376	1.64	48.07	37.4 ± 10.9
30	0.054	3.16 ± 0.002	34.9	1376	2.82	10.41	114.6 ± 3.5
50	0.107	3.37 ± 0.001	16.5	1376	2.79	10.40	176.8 ± 2.2
70	0.119	3.22 ± 0.001	15.6	1483	2.43	17.75	89.8 ± 4.7

The d_{BET} results from nitrogen adsorption.

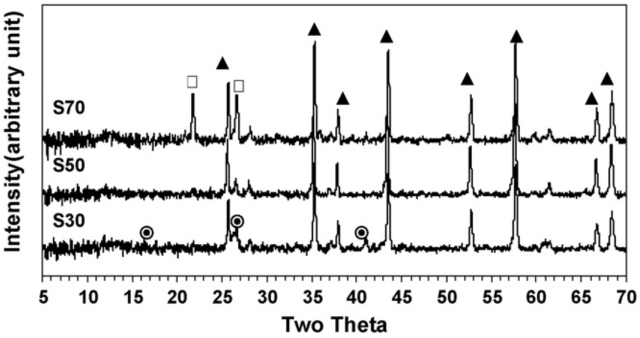

Fig. 6. XRD patterns of S30, S50 and S70 powders heated for 20 min (from room temperature to 1176 °C) (▲: alumina; ⦿ : mullite; ♦: cristobalite).

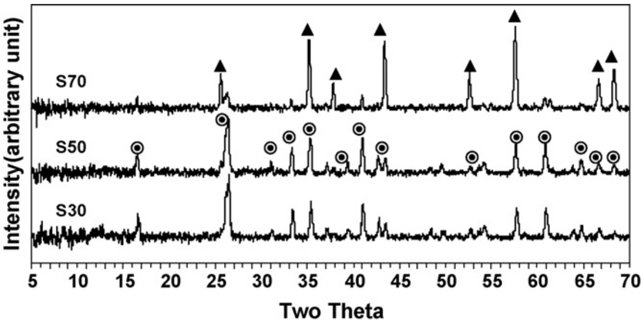

Fig. 7. XRD patterns of S30, S50 and S70 powders heated for 30 min (from room temperature to 1376 °C) (▲: alumina; ⦿ : mullite).

ples can be attributed to the higher specific surface area of this powder (Table 3). From above results it can be concluded that the mullitization of the mixture of alumina and clay activated mechanically and heated in microwave furnace can be completed at a low temperature and short heating time.

DTA curves of milled powders (Fig. 8) reveal the shift of exothermic peak from 998.5 to 988 °C corresponds to the formation of mullite phase in S2 and S30 samples, respectively. This exothermic peak became broader by increasing the milling time over 30 h. The sharp endothermic peak at 517 °C corresponds to the elimination of molecular water of clay can be only detected in the S2 sample. By increasing the milling time to 30 h and over, the endothermic peak was not detected as a result of the decomposition of clay during milling, as X-ray patterns of milled powders (Fig. 3) confirm. The density and porosity measurements were carried out on samples sintered between 1376 and 1483 °C (Table 3). From these data it appears that the least and most values of density belong to S2 and S30 samples, respectively. By increasing the heating time from 30 to 70 min, the density and porosity values increased and decreased, respectively (Table 3). SEM image of S30 sample sintered at 1376 °C (Fig. 9a) shows almost the equiaxed nano-grains of mullite. At the same heating conditions, the sharp growth of mullite grains was observed for S50 sample (Fig. 9b) which may be attributed to the growth of agglomerated particles in initial milled powders as specific surface area value (Table 3) and SEM micrograph (Fig. 1c) of this powder confirm.

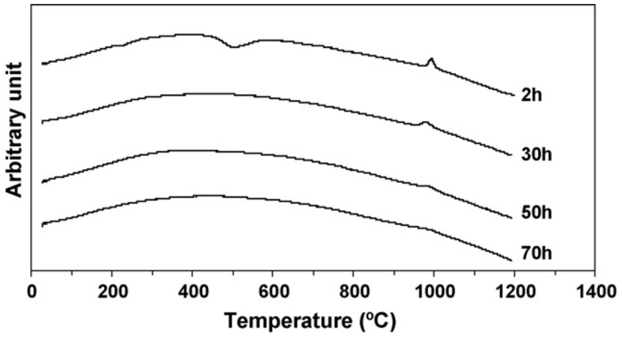

Fig. 8. DTA curves for the powders milled for different times.

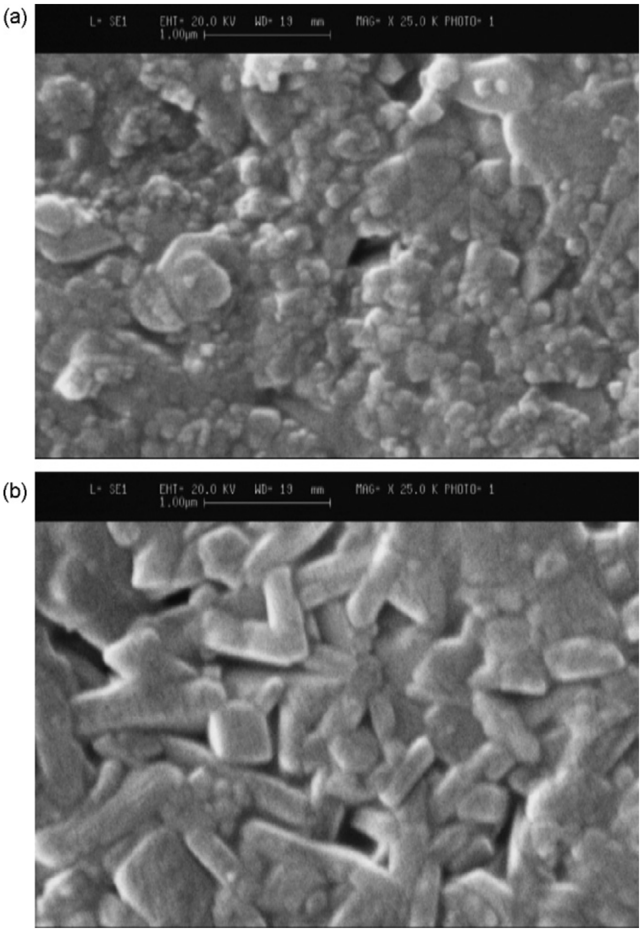

Fig. 9. SEM images of (a) S30 and (b) S50 samples sintered for 30 min (from room temperature to 1376 °C).

The flexural strength measurements of S2, S30 and S50 samples sintered at 1376 °C and S70 sample sintered at 1483 °C (Table 3) reveal that the strength of S2 sample has the least value because of its high porous structure (43% porosity). The strength values increased from S30 to S50 in spit of the similarity of density and porosity values of these samples. The observed behaviour can be explained by considering the microstructure of S30 and S50 samples (Fig. 9a and b). As observed, in S30 sample mullite grains are equiaxed with an average grain size of 78.5 ± 50 nm, while in S50 sample mullite grains have two sizes; one almost equiaxed grains with an average size of 121.3 ± 21.4 nm and another acicular grains with the average width and length sizes of 241 ± 40 nm and 0.85 ± 0.25 μm, respectively. The possible reason for the increase of strength value for S50 sample in comparison with other samples can be attributed to the existence of these elongated mullite grains which are at least in the nanometer size in one dimension.

4. Conclusions

The results of this work indicate that using mechanical activation accompanied by microwave heating of the alumina and clay mixture improves physical and mechanical properties and microstructure of sintered samples under microwave heating conditions.

The decomposition of clay occurred after 30 h milling of alumina and clay mixture and XRD revealed alumina and quartz were the only crystalline phases. By the increase of the milling time from 30 to 70 h, the intensity of quartz peaks increased. The formation of mullite occurred first in sample milled for 30 h and heated for 20 min (from room temperature to 1176 °C). In samples milled for 30 and 50 h, the mullitization was completed after 30 min heating (from room temperature to 1376 °C). Samples milled for 30 h reached to 89% theoretical density and obtained 41.8% higher density than sample milled for 2 h at the same sintering conditions. The samples milled for 30 h and over had higher strength values in comparison with sample milled for 2 h.

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