

Effects of the variations in milling time and sintering temperature on the production of mullite-ZrO₂ composites

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Based on reactive sintering technology, mullite-ZrO₂ composites were fabricated. A powder mixture of 64% wt ZrSiO₄, 18.5% wt Al and 17.5% wt Al₂O₃ was attrition milled for different times (0.5, 3, 6, 12 and 24 h). Precursor powder was cold isostatic pressed at 400 MPa and heat-treated in air at 1450, 1500, 1550 and 1580°C for 2 h. During firing Al oxidizes to Al₂O₃ completely, and ZrSiO₄ dissociation allows the production of mullite with finely dispersed ZrO₂. XRD analysis shows that increases in the milling time and sintering temperature favors densification and mullitization. The influence of both milling time and sintering temperature upon the phases evolution, microstructural development and final mechanical properties, as well as the processing details are discussed in this study.

Key words: Milling, Time, Sintering, Temperature, Mullite-ZrO₂.

Introduction

Mullite is the basic component of the majority of aluminosilicates, and recently its physical properties such as: creep resistance, low dielectric constant, high melting point, etc., have made it a potential candidate for different advanced applications [1]. However, mullite ceramics are difficult to obtain as dense materials [2], in addition they present low quality mechanical properties. In order to increase their properties some authors have developed different processing techniques in order to obtain a ceramic-matrix mullite base with fine ZrO₂ particles well distributed [3-5]. Mullite-ZrO₂ ceramics can be prepared by different methods [6] such as: (1) Sinterization of mullite and ZrO₂, (2) Reactive sinterization of Al₂O₃ and ZrSiO₄ and (3) Reactive sinterization of Al₂O₃, SiO₂ and ZrO₂.

In this work composites of mullite-ZrO₂ are prepared by oxidation and reaction sintering using mixtures of Al, Al₂O₃ and ZrSiO₄, in order to complete reactions 1 and 2 as a function of milling time and sintering temperature.



Experimentation

A powder mixture of 64% wt ZrSiO₄ (~1 μm, Kreuts, Germany), 17.5% wt Al₂O₃ (~0.2 μm, Taimei Chemical

Co. LTD, Japan) and 18.5% wt Al (~5 μm, Analytica, Mexico), was milled in an attritor mill in the presence of isopropyl alcohol and air, using 3 mm diameter zirconia balls. After milling, cylindrical samples were made by cold isostatic pressing at 400 MPa. Then samples were fired following a heating cycle as we were looking for Al oxidation and mullite-ZrO₂ composite formation. Sintering temperatures were: 1450°C, 1500°C, 1550°C and 1580°C, whereas, the sintering time was constant and fixed at 2 h. Phases and the microstructures of sintered composites were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Dimensional and weight changes of samples were evaluated by a thermal analyzer. Specific surface area (Se) was measured by a BET method. Flexural strength was measured in 3 points, Young's modulus by ultrasonic techniques and fracture toughness (K_{IC}) was determined by using Nihara's equation [7] using an indentation techniques.

Results and Discussion

Specific surface area

Table 1 shows powder-specific surface area (Se) values as a function of milling time. Se is bigger with an increase in milling time, which means that milling favors a particle size reduction. However, if γ-Al₂O₃ is formed by Al oxidation as has been suggested by Wu *et al.* [8] in this kind of system, increments in Se can occur, because this oxide is characterized by possessing high specific surface area [9].

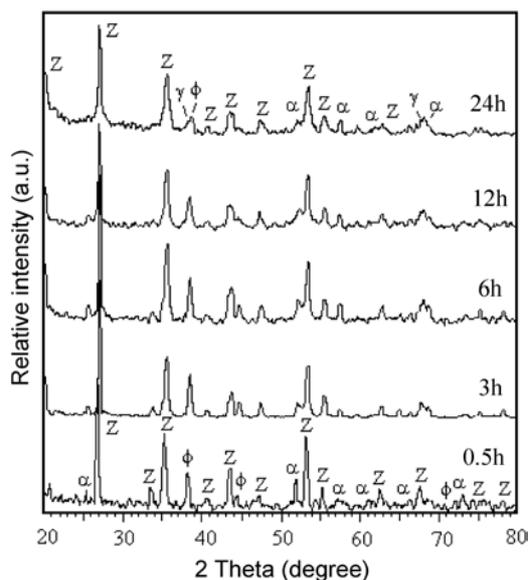
X-ray diffraction

Powder X-ray diffraction patterns are shown in Fig.

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Table 1. Powder specific surface area with their equivalent size, as a function of milling time

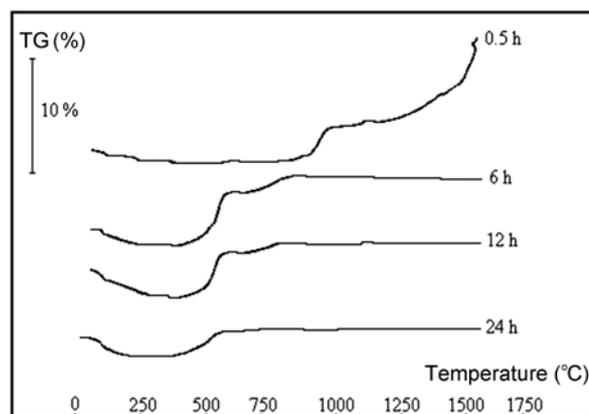
Milling time (h)	Se (m ² g ⁻¹)	Total weight gain (%)	Al oxidized during milling (%)	Al oxidized during heating treatment (%)
0.5	2.9	13.3	*	71.75
3	14.29	-	-	-
6	16.46	8.34	48.74	51.26
12	21.71	6.7	58.82	41.18
24	52.96	3.42	79.02	20.98

**Fig. 1.** X-ray diffraction patterns of powder milled at different times. Z: ZrSiO₄, α : α -Al₂O₃, ϕ : Al, γ : γ -Al₂O₃.

1. For the powder milled for 0.5 h it is possible to observe characteristic peaks of the three mixture components; ZrSiO₄ (Z), α -Al₂O₃ (α) and Al (ϕ). With increments of milling time, the intensity of ZrSiO₄ peaks decrease and become narrower, Al₂O₃ peaks decrease in intensity, whereas, Al peaks have almost disappeared at 24 h. At the same time, in the patterns corresponding to 12 and 24 h two new small peaks at $2\theta=37.5^\circ$ and 67.2° are observed and these peaks have been indexed as γ -Al₂O₃ (γ). The appearance of this γ -Al₂O₃ is due to Al oxidation at long milling times and are in part responsible for the Se increments.

Termogravimetry

Sample's weight changes as a function of heating cycle are presented in Fig. 2. For the powder milled for 0.5 h, the weight gain is developed in two stages. The first one begins at 815°C and occurs faster, with a weight gain of 7%. The second stage begins at 1100°C and this stage does not finish during the heating cycle which follows for this sample. Even when this sample was removed from the furnace, some small Al particles over its surface were observed. The oxidation behavior for samples milled for 6, 12 and 24 h are different

**Fig. 2.** Weight change of samples prepared with powder milled for different times as a function of heating cycle.

compared with the sample 0.5 h, but similar among them. For samples milled for 6 and 12 h the oxidation stage is very similar, because from room temperature to 300°C the organic species evaporation which had been adsorbed during milling produces a weight loss in the sample [10], but from 387°C to 575°C rapid weight gain occurs, followed by a slower weight gain that finishes at 800°C. The behaviour of the 24 h sample differs a little considering the beginning and ending of each stage. Here, weight loss occurs between room temperature and 265°C, whereas, weight gain begins at 347°C and is faster until 547°C, continuing slowly above this temperature and finishes at 711°C. Al oxidation is responsible for all the weight gain of the samples. During the Al oxidation solid-gas reactions occur at lower temperatures than 575°C and liquid-gas reactions at temperatures above 575°C. However, it is interesting to note that Al oxidizes faster when it stays as a solid because its melting point is 660°C. Weight gain for samples milled for 0.5, 6, 12 and 24 h was 13.3%, 8.4%, 6.7% and 3.42% respectively. Also, it is important to observe that with the increments of milling time, less Al is oxidized during the heating cycle, this is due to the Al oxidation during milling.

With the percentage weight change during the heat treatment, Al oxidation was determined during this stage, and the difference with respect to the initial Al content before milling, Al oxidized during the milling stage was estimated. The result of these calculations are also reported in Table 1, where it is evident that high Al quantities are oxidized during milling, mainly when the powder is milled for more than 6 h. In the sample milled for 0.5 h, almost 28% of the initial Al stays without oxidation after the heating cycle.

Influence of milling time on phase evolution

X-ray diffraction patterns of samples sintered at 1550°C for 2 h as a function of milling time are shown in Fig. 3. In the pattern of the sample made with powder milled for 0.5 h it is possible to observe intense peaks of ZrSiO₄, α -Al₂O₃ and Al, whereas phases

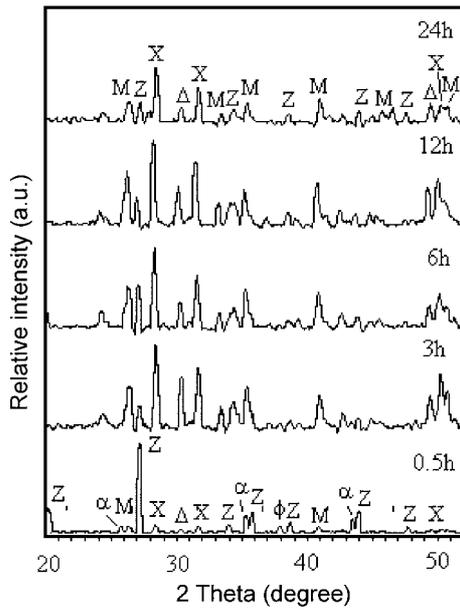


Fig. 3. X-ray diffraction patterns of samples sintered at 1550°C for 2 h as a function of milling time. Z: ZrSiO₄, M: mullite, X: m-ZrO₂, Δ: t-ZrO₂, α: α-Al₂O₃.

corresponding to mullite and ZrO₂ only appear in small quantities. Al peaks disappear completely in samples prepared with powder milled for more than 3 h. In this case, intensity peaks of ZrSiO₄ decrease with the milling time increments, and as a consequence the mixture of monoclinic ZrO₂ (m-ZrO₂) and tetragonal ZrO₂ (t-ZrO₂) increases proportionally. The mullitization reaction is more complete in the 24 h sample, since α-Al₂O₃ almost has disappeared, whereas ZrSiO₂ is present only to a small extent, and mullite and a mixture of m-ZrO₂ and t-ZrO are more evident.

Influence of heating temperature on phase evolution

X-ray diffraction patterns of samples milled for 12 h

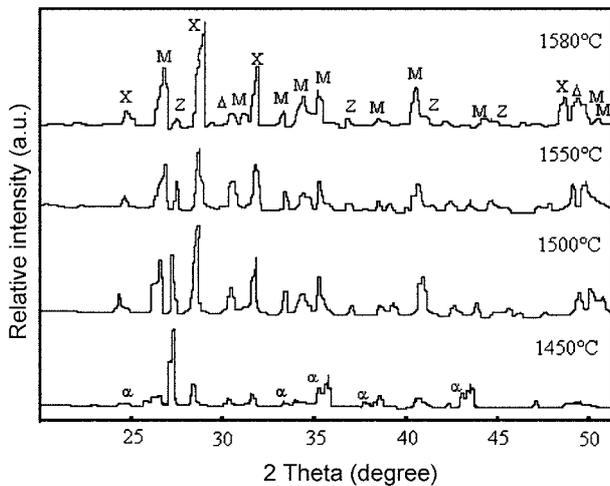


Fig. 4. X-ray diffraction patterns of milled samples for different sintering times at 1550°C for 2 h. Z: ZrSiO₄, M: mullite, X: m-ZrO₂, Δ: t-ZrO₂, α: α-Al₂O₃, φ: Al.

and sintered at different temperatures over 2 h are shown in Fig. 4. For the sample sintered at 1450°C mullite formation is observed. However, the intensity of the peaks from this phase show only small quantities of mullite are formed. On the other hand, the intensity of ZrSiO₄ peaks is higher, although decomposition of this material has begun, this being deduced by the presence of m-ZrO₂ and t-ZrO₂ in the sample. In this same pattern, one can observe some small peaks corresponding to α-Al₂O₃. For the pattern of the sample treated at 1500°C it is clear that ZrSiO₄ decomposition and mullite formation have occurred more intensely, however these reactions are not complete. Some quantities of ZrSiO₄ and α-Al₂O₃ remain in the sample. At 1550°C the reactions cited before are still incomplete. However, formation of a mullite and ZrO₂ mixture now is considerable. Also it is possible to observe some diffuse peaks corresponding to ZrSiO₄ and α-Al₂O₃. For the sample treated at 1580°C both reactions have almost been completed, because mullite peaks are very intense, α-Al₂O₃ has disappeared from the sample, whereas ZrSiO₄ is present only as traces and the content of ZrO₂ is higher. For all samples treated at different temperatures, ZrO₂ is predominantly in its monoclinic form.

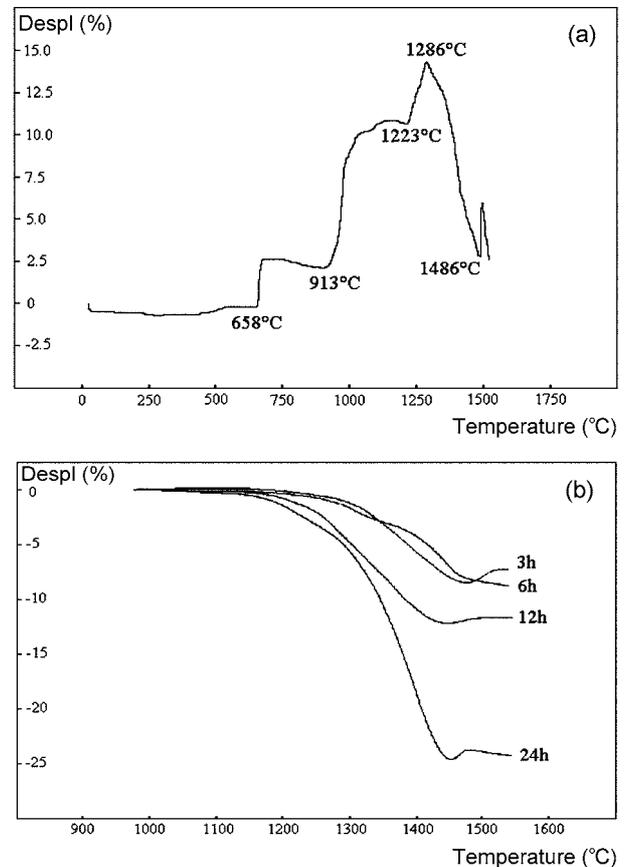


Fig. 5. Dimensional changes for samples compacted at 400 MPa as a function of heating cycle. Sintering temperature 1550°C for 2 h. (a) sample 0.5 h and (b) samples 3, 6, 12 and 24 h.

Dilatometry

A dilatometric curve of the sample milled for 0.5 h is shown in Fig. 5a. In this figure it is an expansion of the sample at 658°C that has been associated with Al melting; at 913°C a new expansion occurs due to Al oxidation, and at 1223°C another expansion in the sample is observed. This last expansion could not be associated with any phenomenon that can occur in the sample during heat treatment. However, it is important to comment here that during a dilatometric test, the sample is placed between two platinum plaques. At the end of the test these plaques were partially melted, likewise some Al drops were present in the sample, causing the plaques to be glued to that sample. Perhaps, expansion at 1223°C is associated with this behavior. At 1486°C mullite formation is reflected as a sintering interruption and the expansion of the sample.

Dilatometric curves for samples milled for 3, 6, 12 and 24 h are shown in Fig. 5b. Curves in this figure are plotted from 1000°C to 1550°C. All samples below 1000°C did not show any dimensional change, including expansion related to Al oxidation. In this figure we see that the start of shrinkage temperature decreases with milling time. The sintering rate is higher in samples milled for 12 and 24 h. The beginning of mullite formation is marked by an expansion or a decrease in the speed of shrinkage for all samples. In this way mullite formation begins at 1480, 1455, 1448 and 1452°C for samples after milling for 3, 6, 12 and 24 h respectively. From these results, it can be seen that at the end of the heating cycle shrinkage is minimal for

samples prepared with powder milled for short times. The total shrinkages were: 7.72%, 9.43%, 13.30% and 25.13% for samples milled for 3, 6, 12 and 24 h respectively.

Influence of milling time on microstructure

The microstructure of samples sintered at 1550°C for 2h, prepared with powder milled for 3, 6, 12 and 24 h are presented in Fig. 6. In all these pictures three different phases are observed; ZrO₂ particles (white) homogeneously dispersed and located at intergranular and intragranular regions in a mullite matrix (dark), also some isolated regions corresponding to ZrSiO₄ are observed (gray). Microstructures made with powders milled for 12 and 24 h generally are the most homogeneous, present less porosity and ZrSiO₄ regions. It is also possible to appreciate equiaxed microstructures where the grain size depends on the sample. In this way the finest microstructure is that prepared with powder milled for the longest times. The microstructure of the sample milled for 3 h presents large amounts of porosity and a large quantity of ZrSiO₄ particles, indicating the low reaction and sintered state of this sample.

The results of phase quantifications and relative density for samples fabricated with powder milled for different times and sintered at 1550°C for 2 h, are shown in Table 2. The Phase content was quantified directly in micrographs by metallographic techniques, for the fraction of t-ZrO₂ and m-ZrO₂, equation 3 was employed [11]. In this table it is observed that increments in milling time favor ZrSiO₄ decomposition,

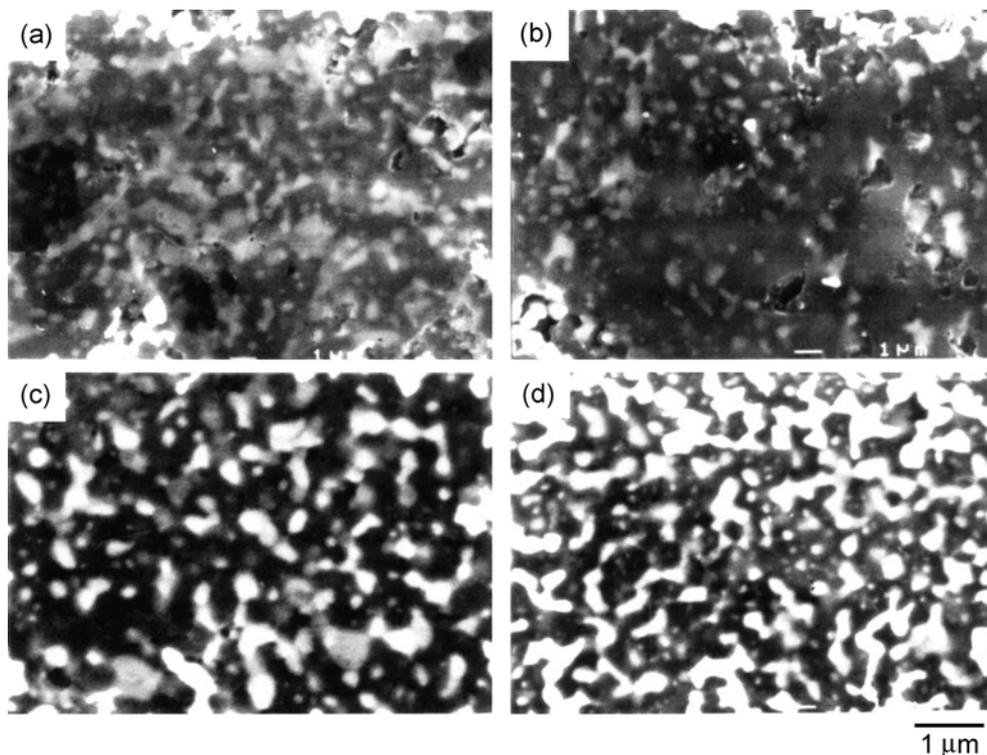


Fig. 6. Microstructure of samples treated at 1550°C, for 2 h as a function of the milling time. (a) 3 h, (b) 6 h, (c) 12 h and (d) 24 h.

Table 2. Phases quantification of samples sintered at 1550°C for 2 h as a function of milling time

Milling time (h)	ZrSiO ₄ (%)	m-ZrO ₂ (%)	t-ZrO ₂ (%)	Mullite (%)
3	58.93	8.81	2.14	30.12
6	17.28	26.03	6.15	50.54
12	14.09	23.29	6.56	56.06
24	10.97	22.86	7.35	58.82

because its percentage tends to diminish, at the same time at larger milling times larger quantities of mullite and ZrO₂ are formed. The differences between microstructure for samples milled for 12 and 24 h are minimal. With the results of this quantification, theoretical densities were computed considering that the rule of mixtures is satisfied, and with this data and the value of the real density it was possible to compute the percentage of relative density (%ρ_r) reached for each sample. The final percentage of relative density reached for the sample milled for 24 h is larger. Also, in this table we see that densification is better in samples prepared with powder milled for longer times.

% t-ZrO₂=

$$\frac{I[t=\text{ZrO}_2(111)]}{I[t=\text{ZrO}_2(111)]+I[m=\text{ZrO}_2(111)]+I[t=\text{ZrO}_2(\bar{1}\bar{1}\bar{1})]} \quad (3)$$

Where:

I=Integrated area of peaks corresponding to Miller indices, given in the formula and those corresponding to principal peaks of each phase considered.

t-ZrO₂ tetragonal ZrO₂

m-ZrO₂ monoclinic ZrO₂

Influence of heating temperature on microstructure

The microstructure of samples treated for 2 h at different temperatures is shown in Fig. 7. In these pictures it is possible to distinguish that mullite formation (dark phase) does not occur at temperatures as low as 1450°C. At this temperature (Fig. 7a) the microstructure is mainly constituted of ZrO₂ particles (white phase) and a large quantity of ZrSiO₄ (gray phase). At 1500°C (Fig. 7b) is observed a sample with a larger mullite formation, although ZrSiO₄ is still present in large quantities, and at the same temperature ZrO₂ grains have grown. At 1550°C (Fig. 7c) the microstructure consist mainly of a mullite matrix with an homogeneous dispersion of ZrO₂ particles. An important observation here is that a marked growth of the microstructure has occurred between 1500 and 1550°C. Finally, the microstructure of the sample treated at 1580°C is observed in Fig. 7d. Here mullite formation still continues, whereas the ZrSiO₄ phase has almost disappeared, also there is a good dispersion of ZrO₂ in the matrix. General growth of the microstructure occurs in this sample. Some ZrO₂ particles have coalesced forming

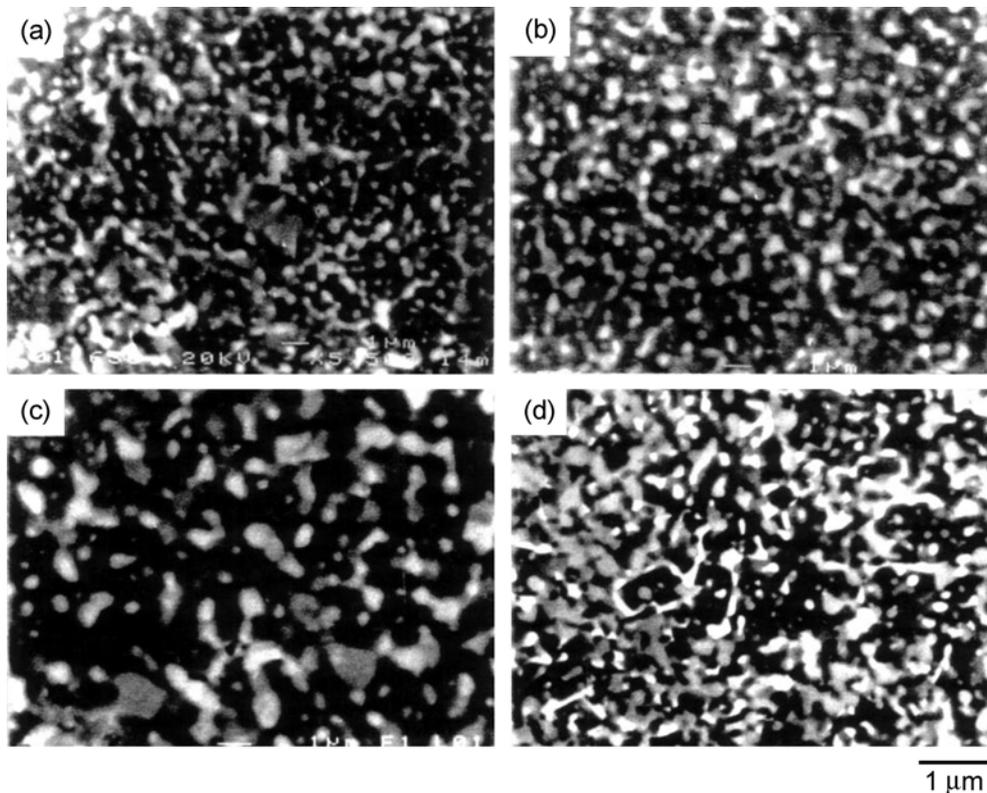


Fig. 7. Microstructure of samples treated at different temperatures during 2 h (samples milled 12 h) (a) 1450°C, (b) 1500°C, (c) 1550°C and (d) 1580°C.

Table 3. Phases quantification of samples sintered at different temperatures for 2 h. (samples prepared with powder milled for 12 h)

Temperature (°C)	ZrSiO ₄ (%)	m-ZrO ₂ (%)	t-ZrO ₂ (%)	Mullite (%)
1450	61.02	16.51	4.0	18.46
1500	28.43	20.86	4.52	46.18
1550	14.09	23.29	6.56	56.06
1580	4.86	25.57	6.81	62.76

Table 4. Mechanical properties data obtained in mullite-ZrO₂ composites, sintered at 1550°C for 2 h

Sample	Hardness (Gpa)	E (Gpa)	K _{IC} (MPa·m ^{1/2})	σ _r (MPa)	ρ _r (%)
6 h	518	91	1.64	276 +/- 60	86.86
12 h	1047	145	2.38	305 +/- 43	92.07

E.- Young's modulus, K_{IC}- toughness, σ_r- flexural strength, ρ_r- relative density.

larger particles and a low porosity is observed in this sample.

Table 3 shows the results of the quantification made in samples milled for 12 h, treated for 2 h at different temperatures. In this table it is observed that with increments in temperature, the ZrSiO₄ content in the sample decreases, and therefore the ZrO₂ content is higher. In the same way mullite formation is encouraged with a temperature increase. So, we can note that with increments in the temperature the reaction for product formation (mullite-ZrO₂) is enhanced.

Mechanical properties

The mechanical property values of composite mullite-ZrO₂ samples fabricated with powders milled for 6 and 12 h and sintered at 1550°C for 2 h, are presented in Table 4. All values of mechanical properties obtained for samples prepared with milled powder for 12 h are better compared with the values of samples milled for 6 h. For the same 12 h milled samples relative density is larger than the relative density of the samples milled for 6 h and this is one of the causes for the difference in mechanical properties. The toughness and strength of pure mullite are 2 MPa·m^{1/2} and 200 MPa respectively [12], in accord with this data, the values presented by the composite prepared with powder milled for 12 h are better and therefore the proposed method for fabricating this type of composite is good. However,

the processing need to be optimized, controlling the quantity of Al oxidized during milling, also reached a density of only 92%, and likewise there is not a total transformation of reactants. We can expect, if it is possible to control all these different situations, then the mechanical properties of the composites can be improved.

Conclusions

1. Increments in milling time and sintering temperature favor densification, reaction progress and mechanical properties of the composites obtained.
2. Mullite formation occurs accompanied by an expansion of the material and in consequence shrinkage is interrupted.
3. Long milling times induces Al oxidation during this stage.
4. If processing conditions are properly controlled an improvement in mechanical properties of composites can be obtained.

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