RELATION BETWEEN PARTICLES SIZE OF RAW MATERIALS AND PROPERTIES OF MULLITE–ZrO$_2$ COMPOSITES PREPARED BY REACTION-SINTERING

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In this investigation, the mullite–zirconia composites were prepared by reaction-sintering of alumina and zircon powder. Besides, the slip casting method was employed for fabrication of these composites and different times of milling process were used for reducing the particles size of raw materials. Then, the effect of raw materials particles size on the properties of these composites was investigated. The physical properties, fracture toughness, flexural strength, phase composition and microstructure of these composites after firing at 1600°C were studied. The results showed that the milling time and then, particles size of raw materials have a great effect on the phase composition and properties of mullite–zirconia composites. The formation of tetragonal-zirconia is favored by reducing of particle size which, leads to increasing of the fracture toughness and flexural strength of these composites.

INTRODUCTION

The extensive use of mullite–zirconia composites is due to the fact that the zirconia dispersion in the mullite matrix improves the thermo-mechanical properties, leading to toughness by transformation and microcracking. Therefore, mullite–zirconia composites are materials with important technological applications due to their good properties such as toughness, chemical stability, high-creep resistance and good thermal shock resistance. In practice, they are employed in the glass industry and where a high chemical and corrosion stabilities are required [1-6]. For this reason, several researchers have been worked on the zirconia–mullite system and different processing routes to prepare mullite-zirconia composites have been reported [2]. The reaction-sintering of zircon and alumina is a well-established method for producing mullite–zirconia ceramics. Without sintering aids or stabilizing oxides, the densification is achieved at 1450-1500°C and the complete mullitization occurs at temperatures near 1600°C [3, 7, 8]. Generally, slip casting is considered as a successful method to improve density and microstructure of the body so that this technique is applied in the fabrication process of many composites and refractories [4]. Besides, in order to ensure good mechanical properties, slip casting is used as a conventional method to obtain fine and homogeneous microstructures free of agglomerates and packing variations in the green composites [8]. This processing route has other several well-known advantages like low cost and the possibility of obtaining complex shapes that are impossible by other traditional or advanced ceramic processing routes. On the other hand, the studies have shown that particles size distribution of raw materials is important factor which can affect the rheological character of the slip and then, the final properties of composites. To achieve improvements in the properties of these composites, the particles size of raw materials must be controlled. The milling process is generally used to control of the raw materials particles size which can improve the resulting properties of the green and sintered material. Generally, with decreasing of raw materials particles size the density tends to increase. Therefore, very fine powders must be chosen to improve sinterability of these composites. Hence, the high solid concentrations of fine and colloidal particles are needed for slip casting [9, 10]. In this study the mullite-zirconia composites are prepared by slip casting of concentrated aqueous suspensions and the effect of the raw materials particles size on the properties of these composites is investigated. For this reason, different times of milling are used for reducing size of raw materials and then, physical properties, fracture toughness, phase composition and microstructure of these composites after firing at 1600°C are studied.

EXPERIMENTAL

Raw materials and composition

Starting powders were commercially available alumina (α-Al_2O_3, HTM 10 Fiberona Co., India) and zircon ($ZrSiO_4$, Mahlwerke Kreutz, Mikron, Germany) with average size particles 2.6 and 6.5 μm respectively. Table 1 shows the chemical composition of these starting materials given by the producers.

Table 1. Chemical composition of the raw materials.

Oxides	Raw material	
	Zircon	Alumina
SiO_2	34	0.02
Fe_2O_3	0.1	0.02
Al_2O_3	0.01	99.60
ZrO_2	64	–
TiO_2	0.15	–
Na_2O	0.01	0.15
L.O.I.	–	0.11

The mullite-zirconia composites were prepared from a mixture of 54.5 wt. % zircon and 45.5 wt. % alumina with respect to the stoichiometric ratio. The stoichiometric alumina to zircon weight ratio used corresponds to the stoichiometric α-Al_2O_3/$ZrSiO_4$ mole ratio that forms mullite and zirconia after complete conversion at high temperature. The aqueous slips were prepared with 65 wt. % powder, 35 wt. % H_2O and different contents of deflocculant (Dolapix CE64, Zschimmers and Schwartz), with regard to the size distribution of slip particles at pH 9.1-9.2.

Preparation of samples

The starting powder mixes were ground and homogenized in a laboratory planetary mill for 1, 2, 3, 4 and 5 h, using corundum balls as the grinding bodies. Subsequently, prepared slips were cast in plaster molds. The size distribution of slip particles was analyzed by a laser particle diameter analyzer (Honeywell Microtrac X-100) after each milling. Generally, the changes in slip particles size distribution have a direct effect on the rheological character of the slip [10]. Therefore, slip cast bars were consolidated in a plaster mold from the optimal slip condition for each composition such as deflocculant content. The prismatic bars 7.5 mm × 7.5 mm × 50 mm were produced from well dispersed suspensions by slip casting in a plaster molds. Dried probes were fired in an electric furnace with a heating rate of 10°C/min up to 1600°C for 5 h.

Test methods

The fired samples were tested for bulk density (B.D) and apparent porosity (A.P). The flexural strength at room temperature was measured on the fired rectangular bars by three-point bending method using an Instron-1185 universal testing machine. For correct Weibull statistical analysis the standards require at least 30 specimens to be tested. However, because of exploratory nature of this study, such quantities of normalized bending bars were not available. Here, only five samples of each material were tested to obtain the average strength and standard deviation and the results were used as a representative estimate of the strength properties. Crystalline phases present in fired bodies were determined by X-ray diffraction (Philips 3020, Cu Kα radiation and Ni filter at 40 kV and 20 mA). Quantitative phase analysis was performed following the Rietveld method using the software package X'Pert Highscore Plus. Here, tetragonal zirconia (t-ZrO_2) in association with monoclinic zirconia (m-ZrO_2) and mullite are expected phases to be developed after sintering. The t-ZrO_2 fraction content is determined on the sintered surfaces from the ratio of XRD integrated peak intensity of t-ZrO_2 (111) to m-ZrO_2 (111) and m-ZrO_2 (111) following Garvie and Nicholson's equation [11-13]. The microstructures of green and fired composites were studied by scanning electron microscopy (Cambridge S-360 SEM at 10-20 kV) on fracture surfaces. Vickers hardness (H) was measured by microhardness tester (SHIMADZU, HSV-20) using the equation (1):

$$H = 1.854 \, P/d^2 \qquad (1)$$

where P is the applied load (5 kg) and d the average diagonal length of the indentation (mm). The microhardness tester was also used to measure the fracture toughness (K_{IC}) using the equation (2) [8, 14 and 15]:

$$K_{IC} = 0.016 \, (E/H)^{1/2} (P/C^{3/2}) \qquad (2)$$

where E is the Young's modulus (GPa), H the Vickers hardness (GPa), P the indentation load (N), C the crack length (m) from the centre of the indentation impression to the crack tip. The Young's modulus of sintered samples was measured by sonic method [16].

RESULTS AND DISCUSSION

Variation in the particles size of the milled slips

The median particles size of raw materials, d_{50}, as a function of the milling time is shown in Figure 1. The reduction in particles size is very apparent during the initial time, e.g., after 3 h of milling, the size is reduced to 1.1 μm. This shows that the fragmentation of particles is the dominant phenomenon in the early stage. However, after 3 h of milling, as shown in Figure 1, the rate of particle size reduction tends to decline. This indicates that the alternate and/or concurrent actions of fragmentation and agglomeration are caused by milling. A further increase in milling time (> 4 h) is less effective, which is probably due to agglomeration of particles or high strength of particles.
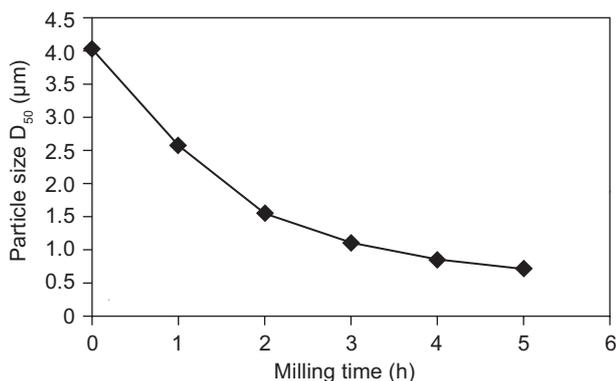
Figure 1. Median particles size after the various milling times.

The microstructures of green composites which prepared by use of unmilled and 5 h milled slips are shown in Figure 2 and 3. It could be seen that the agglomerates are broken by milling and a reduction in particles size is observed. However, the milling time was not long enough to break all the agglomerates and all the large particles. On the other hand, the investigation

Figure 2. SEM photomicrograph of green composite prepared by use of unmilled slip.
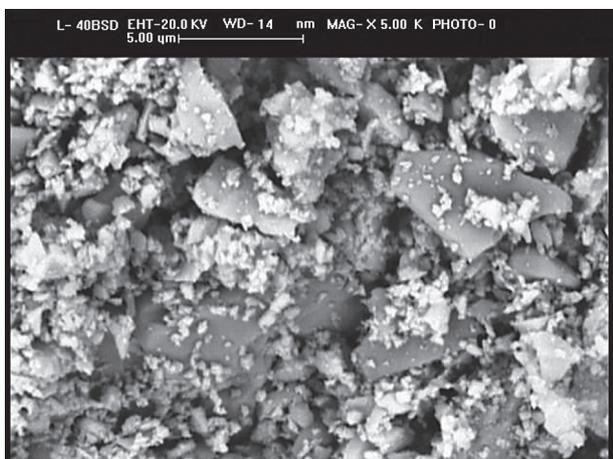

Figure 3. SEM photomicrograph of green composite prepared by use of 5 h milled slip.

of microstructures shows that with increasing of milling time, the mean diameter of particles is decreased but agglomerates of fine particles are formed. Palaniandy et al. [17] reported that the agglomeration of particles is a major factor when the raw materials particles are ground to less than 10 μm, especially with particles having a high surface energy.

Relation between the particles size of the milled slips and physical properties

The relation between milling time of slip and physical properties of fired mullite-zirconia composite such as; B.D and A.P is shown in Figure 4.
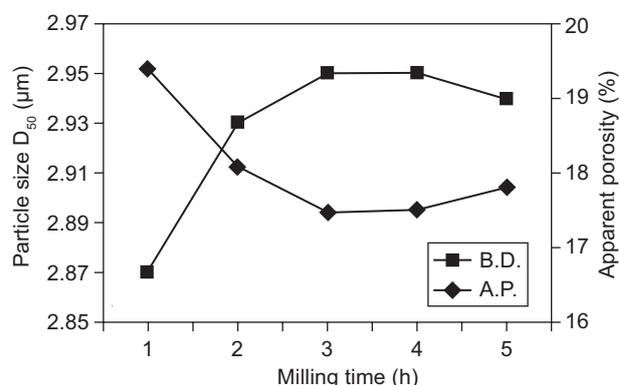

Figure 4. The effect of milling time on the B.D and A.P of mullite-zirconia composite after firing.

The results show that increasing of milling time and decreasing of raw materials particles size at early stage of milling leads to decreasing of A.P and then, increasing of B.D. On the other hand, A.P is increased with further milling which, leads to decreasing of B.D. With respect to microstructure investigations, this behavior at early stage of milling can be attributed to the better ability of finer particles to fill the voids between coarser particles and then, better compaction of particles. But, agglomerations of fine particles can be formed with further time of milling which, leads to increasing of pores between particles. Therefore, total densification of the fired compacts was not possible because of the agglomeration of the particles and low green density.

Relation between the particles size of the milled slips and phase composition

The XRD results of fired mullite-zirconia composites prepared with slips which milled at different times are shown in Figure 5.

With respect to these results, the mullite phase exists in addition to monoclinic zirconia (m-ZrO₂) and tetragonal zirconia (t-ZrO₂) phases at all compositions. Besides, some zircon and alumina phases as raw materials are presented. Generally, zircon (ZrSiO₄) is dissociated

in the solid state and is converted to ZrO_2 and amorphous SiO_2 which, SiO_2 reacts with Al_2O_3 to yield mullite. The presence of alumina and zircon in the composition after firing indicates that the complete reaction is not occurred. Besides, the results show that the content of remaining raw materials in the composite is decreased with increasing of milling time. Therefore, the increasing of milling time leads to complete the reaction-sintering and then, increasing of mullite and zirconia contents. Thus, use of the raw materials with smaller particles size is necessary for completion of reaction-sintering. On the other hand, the results reveal that the content of $t-ZrO_2$ is considerably enhanced with increasing of milling time which, the highest amount of this phase is seen after 2 h milling. Therefore, it can be conclude that the content of formed phases in these composites depends on milling time and then, the particle size of raw materials. The amount of the formed phases after firing in the mullite-zirconia compositions was determined by quantitative XRD analysis. The results are plotted in Figure 6 as a function of milling time.

The results of Figure 4 show that with increasing of milling time and then, the decreasing of raw materials particles size the mullite content is increased. With
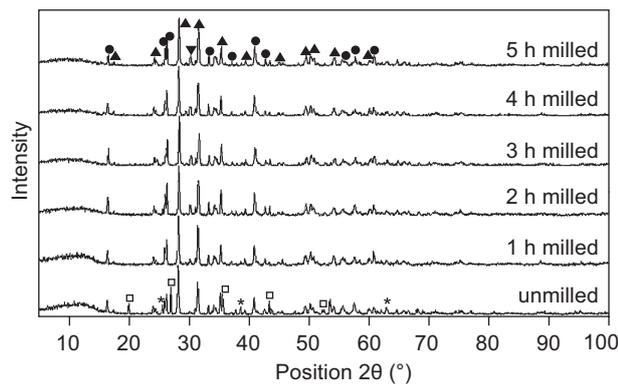

Figure 5. The XRD results of fired mullite-zirconia composites prepared with milled slips at different times (● - Mullite, ▲ - m-Zirconia, ▼ - t-Zirconia, □ - Zircon, ∗ - Corundum).
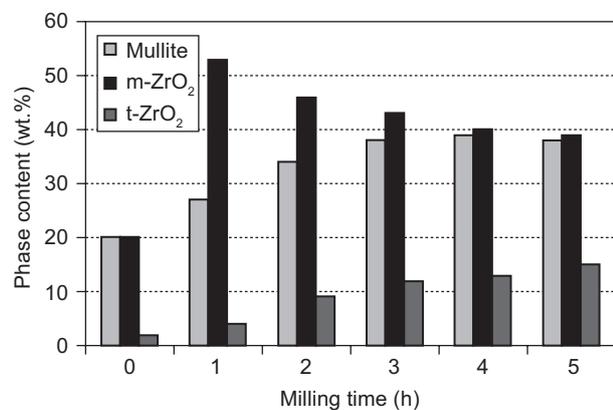

Figure 6. The relation between milling time and the formed phases in the fired mullite-zirconia composites.

increasing of milling time, the higher decomposition of the zircon particles occurs and then, the higher zirconia phase forms. Besides, reducing of particles size with increasing of milling time leads to increasing of particles surface area and number of grain boundaries which, in turn enhance reaction between particles. Hence, higher reaction and solid phase sintering take place which, lead to higher content of mullite phase. From Figure 4, it can be observed that considerable amount of metastable $t-ZrO_2$ is formed with increasing of milling time. Simultaneously, the content of $m-ZrO_2$ is decreased with increasing of $t-ZrO_2$ content. Generally, it is known that monoclinic zirconia undertakes a martensitic transformation to tetragonal form over 1100°C on the heating cycle, reverting around 900°C in the cooling cycle. This reversibility depends on several conditions which, the particle size also can influences on this transformation [18]. Particles smaller than a critical size (approx. 0.3–0.5 μm) do not go through the reverse transformation and remain in a meta-stable tetragonal form at room temperature due to constraint force of the rigid mullite matrix. It is also noted that milling of starting powder promotes crystallization of mullite and $t-ZrO_2$ in ceramic material [19 and 20]. However, the part of $t-ZrO_2$ can not transform into stable monoclinic form due to their smaller particles size.

Relation between the particles size of the milled slips and mechanical properties

The fracture toughness and flexural strength of the fired mullite-zirconia composites as a function of milling time are shown in Figure 7.
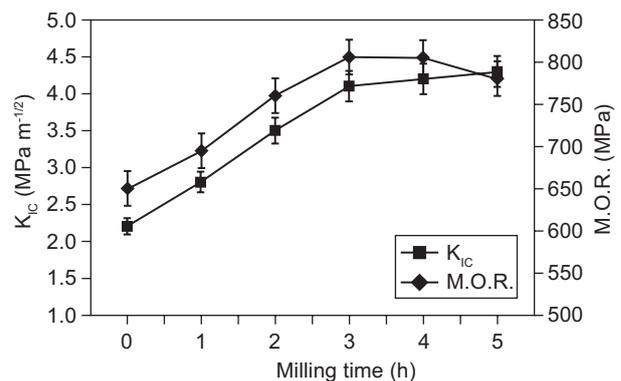

Figure 7. The fracture toughness and flexural strength of the fired mullite-zirconia composites as a function of milling time.

With respect to these results, with increasing of milling time and then, decreasing of raw materials particles size the fracture toughness of the fired mullite-zirconia composite is considerably increased. There are several mechanisms contributing to enhance fracture properties of reaction sintered mullite-ZrO_2 composites prepared from a mixture of alumina and zircon, such as microcracking and transformation toughening.

Generally, the tetragonal to the monoclinic phase transformation is martensitic and it has large volume increase (between 3 and 5 %) due to anisotropic behavior. Therefore, this transformation leads to a change in shape of the transformed crystal, which results in the development of microcracking in the matrix. This transformation can be used for the strengthening of mullite–ZrO₂ composites ("transformation toughening"). This toughening can by due either to the micro-cracking or transformation, depending on the size, amount and solute content of zirconia particles. The retention of t-ZrO₂ at room temperature in mullite matrix has been shown to be advantageous for the increase in strength and fracture toughness. The martensitic transformation of the metastable t-phase to the monoclinic product in the stress field around propagating cracks is the key to the phenomenon of transformation toughening in zirconia based ceramics [21]. With respect to XRD results (Figure 6), the considerable amount of t-ZrO₂ is formed with increasing of milling time. Therefore, the increasing of milling time and then, decreasing of raw materials particles size leads to the increasing of fracture toughness. With respect to these results, decreasing of raw materials particles size at early stage of milling leads to decreasing of mechanical strength. Generally, several factors can affect the strength of ceramic composites, including bonding type, amount of porosity and phases developed during sintering. With respect to physical properties results (Figure 4), with increasing of milling time the A.P of fired composite tends to decrease. Hence, the mechanical strength can increase with decreasing of A.P. On the other hand, A.P is increased with further milling which, leads to decreasing of mechanical strength. Besides, it is known that the change from tetragonal to monoclinic generates microcracks in the microstructure that will negatively affect the flexural strength of the composite [21]. Therefore, with decreasing of this polymorphic change and then, decreasing of monoclinic amount the flexural strength can increase. However, there is a considerable scatter of the strength values.

Generally, the strength of ceramic materials is statistically distributed according to the flaw size distribution in the material. Therefore, brittle fracture depends on the probability of a material to contain a flaw equal to or larger than the critical size for a given applied stress. Also, fracture depends on the stressed area or the volume of the material, since larger areas or volumes increase the probability to present a critical flaw [22]. Therefore, the strength of ceramic composites depends on a wide range of random factors which results in a considerable scatter of the experimental data.

Relation between the particles size of the milled slips and microstructure

The microstructure of fired mullite-zirconia composite prepared with unmilled slip is presented in Figure 8.

As shown, the microstructure of this composite comprises of mullite phase as matrix and dispersed zirconia particles. The bright zirconia grains are somewhat distributed throughout the darker mullite matrix. It is observed that the mullite grains are acicular probably due to a considerable amount of glassy phases present during sintering. The zirconia grains are mainly intergranular. ZrO₂ particles were found to be irregular in size. Besides, there are some clusters of zircon and alumina particles as raw materials which, indicates that the complete decomposition reaction of zircon is not occurred. On the other hand, the high amounts of porosities with large size exist between particles, which indicate that the complete densification process is not occurred. The microstructures of fired mullite-zirconia composites prepared with 2, 3 and 5 h milled slips are shown in Figures 9, 10 and 11.

These Figures show more homogeneous microstructures with a continuous mullite matrix and uniformly dispersed zirconia particles. Besides, the lower amounts of raw materials particles exist which, indicates that the complete reaction between raw materials is occurred. In addition, there are the lower amounts of porosities in
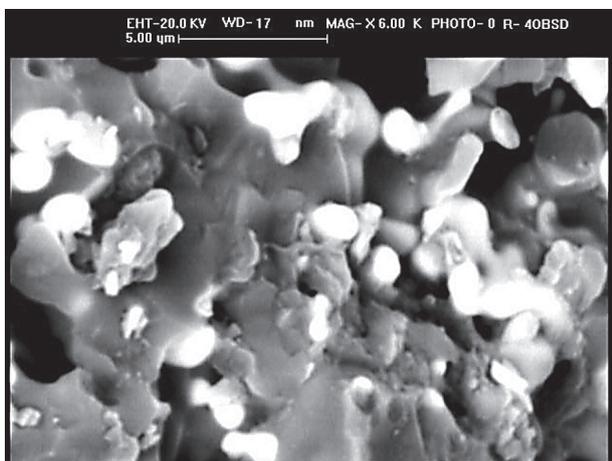

Figure 8. SEM photomicrograph of fired mullite-zirconia composite prepared with unmilled slip.
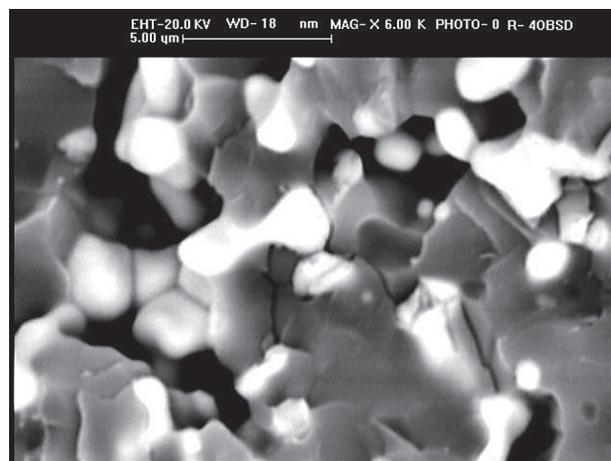

Figure 9. SEM photomicrograph of fired mullite-zirconia composite prepared with 2 h milled slip.

comparison to the samples with a larger particles size (Figure 8). Two types of zirconia grains are present which, one is inter-granular zirconia located between the mullite grains and the other one is intra-granular zirconia
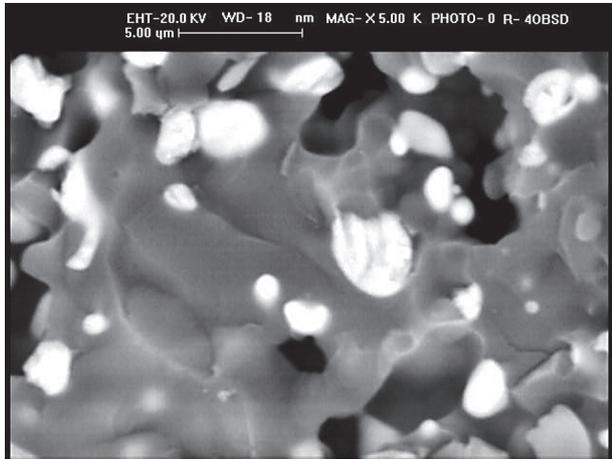

Figure 10. SEM photomicrograph of fired mullite-zirconia composite prepared with 3 h milled slip.
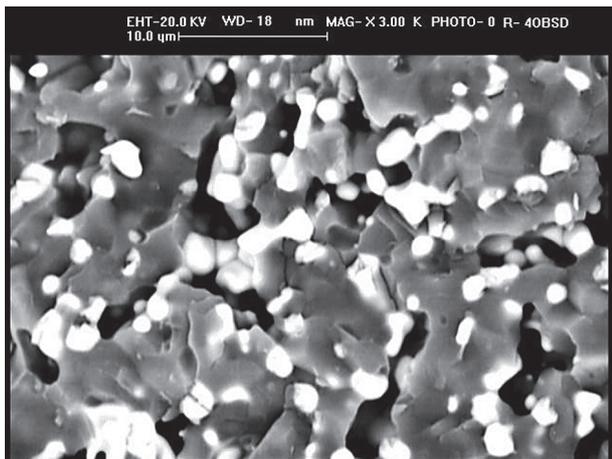

Figure 11. SEM photomicrograph of fired mullite-zirconia composite prepared with 5 h milled slip.
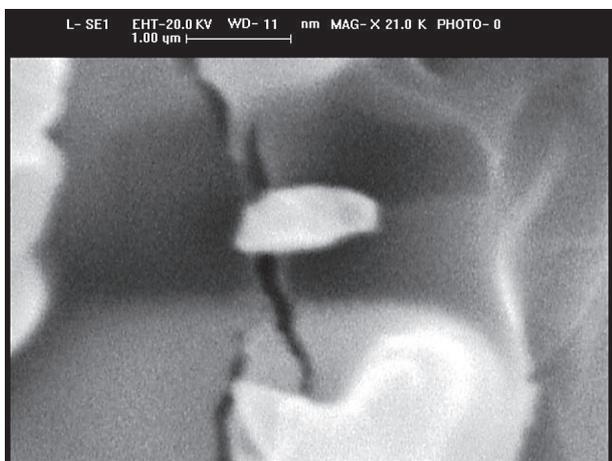

Figure 12. SEM photomicrograph of fired mullite-zirconia composite prepared with 5 h milled slip.

present within mullite matrix. Many researchers [6, 23] are shown that intra-granular particles as spherical shape are tetragonal ZrO_2, while the inter-granular ZrO_2 is mainly monoclinic. Rounded morphology of the ZrO_2 is due to the transient liquid phase. The stabilization of tetragonal zirconia in the composite microstructure is successfully accomplished by the uniform distribution of fine zirconia particles. The other obvious characteristic in these Figures is that there are very fine micro-cracks in the microstructure. It is known that the volume change associated with the ZrO_2 martensitic transformation during the cooling leads to micro-crack formation in the microstructure. Figure 12 shows a higher magnification image of the microstructure which, micro-cracks in the mullite matrix can be seen as a consequence of the ZrO_2 martensitic transformat

These micro-cracks will give their contribution to the improvement of the fracture toughness by micro-cracking toughening mechanism. Besides, microstructural evaluations show that with increasing of milling time the amount of micro-cracks in the microstructure tends to decrease which leads to increase of mechanical strength (Figure 7).

CONCLUSIONS

The mullite-zirconia composites were prepared by reaction-sintering of alumina and zircon powder and then, relation between particles size of raw materials and properties of these composites was investigated. This study confirmed the strong influence that the raw materials particles size exerts on the phase composition, microstructure and then, properties of these composites. The fired mullite-zirconia composites were porous and greater fired density was possible by the milling of the starting powders. According to the results the amount of formed phases in the composition depends on milling time and then, the raw materials particles size. So that, the amount of t-ZrO_2 phase in the composition is enhanced with increasing of milling time. The retention of t-ZrO_2 at room temperature in mullite matrix has advantageous for the increase in strength and fracture toughness. By use of proper milling time and then, proper size of raw materials the maximum amount of mullite phase during reaction-sintering process can be obtained.

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