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Seeded Sol–Gel Derived Alumina–Zirconia Composites

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Abstract: The effect of α-alumina seed particles on the densification and microstructure development of the sol–gel derived alumina–zirconia composites has been studied. The alumina–zirconia sols have been prepared from two different alumina sols (polymer and particulate) and two different types of zirconia particles. Addition of the seed particles decreases the θ to α-alumina transformation temperature by more than 100°C and changes its mechanism, resulting in a homogeneous and very fine scale composite microstructure. The α-alumina seed particles do not have the same efficiency on the polymer and particulate alumina matrix transformation. Besides, it has been shown that densification, the homogeneity of the zirconia particles distribution and the temperature of the martensitic tetragonal to monoclinic zirconia transformation are determined by the nature and the size of the original zirconia particles.

1 INTRODUCTION

Zirconia-toughened alumina (ZTA) is a desirable material for engineering applications, because of its high hardness, high wear resistance and high toughness. In ZTA, the fracture toughness of alumina is significantly increased by utilizing the martensitic tetragonal (t) to monoclinic (m) phase transformation of zirconia particles dispersed in the alumina matrix.[1–4] Such an increase was usually attributed to the stress induced phase transformation and microcracks formation, which enable additional energy dissipation at crack tips.[4–6] The magnitude of toughening is completely dependent on the alumina–zirconia composite microstructure (ZrO_2 volume fraction, its size, the distribution and amount of t/m ZrO_2).[2–5]

The homogeneous microstructure with well dispersed zirconia particles is the most important requirement for the best mechanical properties of ZTA and could easily be achieved by sol–gel processing.[7–12] However, in the sol–gel processing of the alumina–zirconia composites there are still many unresolved problems. One set of them concerns the control of the microstructure development of the alumina matrix, which is determined by the existence of many metastable alumina phases before the stable one (α-alumina) is formed. The final θ to α-alumina transformation (controlled by nucleation) is characterised by the formation of open porosity, which results in low density and a coarse nonuniform matrix grain structure. This microstructure development could be avoided with the addition of certain seed particles to the starting sol.[7,13] The seeding of the α-alumina transformation, according to Messing,[7,13] has a dramatic effect on the θ to α-alumina transformation temperature, microstructure development and densification. The other set of problems refers to the zirconia particles, i.e. particle size, distribution and crystalline structure.[3,5,11] It has been shown[7,8,12] that the distribution of zirconia particles in sol–gel derived alumina–zirconia composites could be intra- and intergranular. The intergranular distribution of zirconia particles (favourable for the toughening) could be easily achieved with the seeding, but the control of processing parameters, (zirconia concentration, original alumina/zirconia size ratio, dopant type and level, etc.) are also very important.[5,11,14] In addition, for the sol–gel processing of alumina–zirconia composites a coupled interaction between alumina and zirconia should also be taken into consideration.[12,15]

The aim of this study is to determine the influence of α-alumina seed particles, added into two different alumina matrices (polymer and particulate), on the densification and microstructure development of the alumina–zirconia composites. Also, two different types of zirconia particles were introduced into the alumina matrix, because we believe that, besides the type of seed particles[16,17] and the alumina matrix, the type of original zirconia particles may also determine the phase transformation and microstructure development in the composite.

The phase transformation and microstructure changes in the alumina–zirconia composites, after heating, were observed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and density measurements.

2 EXPERIMENTAL

The starting alumina–zirconia composite sols, with 20 wt% ZrO_2 on the oxide basis, were obtained by mixing separately prepared alumina and zirconia sols. Two different aqueous alumina sols, a polymer and a particulate one, were prepared: the first by hydrolysis of aluminium-sec–butoxide, Al^sBu, after Yoldas[18] under acidic conditions; and the second by dispersing 20 wt% boehmite powder* in distilled water with nitric acid at pH = 3, at room temperature.

The polymer matrix composite sol, denoted by 3.1-B, was prepared by mixing the polymer alumina sol and acidic zirconia sol prepared by hydrolysis of zirconium-*n*-propoxide, Zr^nPr, dissolved in anhydrous ethanol, under acidic condition at ambient temperature (alkoxide, water, acid and ethanol molar ratio was 1 : 6 : 1 : 15).

The particulate matrix composite sols, denoted by 3.1-A and 3.2-A, were prepared by mixing the particulate alumina sol with two different types of zirconia sols. These zirconia sols have a hypothesized difference in zirconia particle size and probably nature, after our previous experimental experience.[11,15] In the first composite, denoted by 3.1-A, the same zirconia sol as in the polymer matrix composite 3.1-B was used, whereas in the second, denoted by 3.2-A, the zirconia sol was prepared under the same condiitons as in the 3.1-B and 3.1-A samples, only the alkoxide, water, acid and ethanol molar ratio was 1 : 1 : 0 : 45.

In addition, half of each sol mixture was seeded with α-alumina seed particle† (5 wt% of α-Al_2O_3 on the α-alumina basis). The seed particles were added in the form of dispersion, which was prepared by dispersing (ultrasonically) α-alumina particles in distilled water with nitric acid. In the sample notation, the subscript 'o' stands for unseeded and 'c' for seeded composites.

Resulting sols were gelled by heating at 70°C. The composite gels were aged at room temperature, dried in air for a few days, up to 120°C, and heated, first at 600°C for 1 h, then at 1100°C (or 1150°C) for 1 h and finally up to 1500°C for 1 h.

The bulk density of the dried and heat treated gels was measured by the Archimedes' method (the porous samples were coated by paraffin). X-ray diffraction data were obtained with a diffractometer using Ni-filtered CuK_α radiation. The ratio of t/m ZrO_2 was determined using the integrated intensity of the tetragonal (111) and monoclinic (111) and $(11\bar{1})$ peaks. Microstructure development and grain size were analyzed from SEM micrographs of fractured surfaces and from polished and thermally etched surfaces, using the SEM JEOL 035.

3 RESULTS AND DISCUSSION

3.1 Evidence of the various types of composite gels

The gel characteristics and macroscopic observations of the unseeded and seeded polymer (3.1-B) and particulate (3.1-A and 3.2-A) matrix gels are presented in Table 1 and Fig. 1. The polymer matrix gels have lower solid concentration at the gel point than the particulate matrix gels (Table 1). For this reason, considerable shrinkage and pronounced cracking exist in the polymer matrix gels. The amount of liquid, in the gel after drying, is higher for the polymer matrix composites too (Table 1). Dried composite gels are opaque except the 3.1-B_o one, which is translucent. Nontransparency for the seeded gels is caused by the presence of the α-alumina seed particles. All dried composite gels have a more or less crystalline boehmite-like structure but without any traces of zirconia phases, according to the XRD results.[15] Seeded gels exhibit a somewhat higher density than unseeded (Table 1), but similar microstructures (Fig. 1). The dried 3.2-A gels have the lowest density and a relatively coarse particulate microstructure,

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* Advanced Ceramic H-3500, Union Carbide, Cleveland, OH, USA.

† Ceralox HPA 0·5, Condea Chemie, Brusbuettel, Germany.

Table 1. Gel characteristics

Sample notation	Solid concentration at gel point [wt%]	Mass of dried gel related to the theoretical mass	Density [g/cm^3]	Macroscopic observation
3.1-B$_0$	4·9	1·33	2·29	Translucent
3.1-B$_c$	5·6	1·31	2·44	Opaque
3.1-A$_0$	11·2	1·08	1·94	Opaque
3.1-A$_c$	11·5	1·09	1·97	Opaque
3.2-A$_0$	14·7	1·04	1·62	Opaque
3.2-A$_c$	15·2	1·04	1·70	Opaque

where it is possible to distinguish zirconia particles from alumina particles (Fig. 1c). However, in the microstructure of the dried 3.1-A gels it is not possible to distinguish between two phases (alumina and zirconia) (Fig. 1b). In contrast the polymer matrix dried gels, 3.1-B, have somewhat higher density and a more diffuse microstructure (Fig. 1a).

These results only confirm our assumption about the presence of different composite gel microstructure used in our investigation, i.e. different original microstructures of the composite matrix (3.1-B and 3.1-A) and zirconia particles (3.1-A and 3.2-A).

3.2 The phase transformation and microstructure development after heating

The X-ray diffraction spectra for the unseeded and seeded composite samples are presented in Fig. 2. As can be seen in the unseeded composite sample the transformation of θ to α-alumina begins at a relatively high temperature, i.e. at about 1170°C for the polymer (3.1-B$_0$) and at about 1150°C for both the particulate matrix composites (3.1-A$_0$ and 3.2-A$_0$). According to our previous study,[15] where a detailed analysis of the phase transformations in these unseeded samples was made, the relatively high θ to α-alumina transformation temperature was related to the mutual interaction between alumina and zirconia.

On the other side (Fig. 2), in all seeded alumina–zirconia composite samples the α-alumina already appears at temperatures up to 1050°C and the total conversion to α-alumina occurs at a temperature somewhat lower than 1100°C. It is evident that seeding of the alumina–zirconia composites with α-alumina particles decreases the θ to α-alumina transformation temperature by more than 100°C in respect to the unseeded samples.

It is interesting to note that in the seeded composite samples the partial t → m zirconia phase transformation also occurs at lower temperature, relative to the unseeded samples. Thus, in the seeded composites (Fig. 2), already at 1100°C, the portion of the monoclinic zirconia is relatively high (12%, 19% and 78% for the 3.1-B$_c$, 3.1-A$_c$ and 3.2-A$_c$ composite samples, respectively), whereas at the same temperature monoclinic zirconia still does not become evident in the unseeded, 3.1-B$_0$ and 3.1-A$_0$ samples (Fig. 2). In the unseeded composites, after the α-alumina formation, the portion of monoclinic zirconia increases, indicating that the formation of the α-alumina alters the mutual stability of the tetragonal zirconia and the transitional aluminas, which exist in the sol–gel derived composites at these temperatures,[15] and enable a faster growth of the zirconia particles.

The typical microstructures of the unseeded and seeded composites heated at 1200°C are presented in Fig. 3. In general, after full transformation to α-alumina, the unseeded composite samples developed the characteristic vermicular alumina matrix structure, as a result of rapid uncontrolled growth of the transformed alumina (Fig. 3a). Although it is difficult to distinguish very small zirconia from alumina particles, it seems that zirconia particles

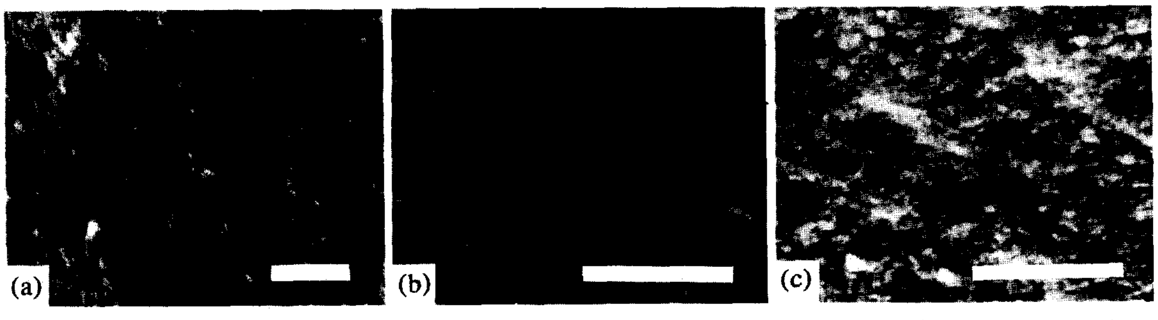

Fig. 1. SEM micrographs of the alumina–zirconia composite gels: (a) 3.1-B, (b) 3.1-A and (c) 3.2-A (bar = 1 μm).

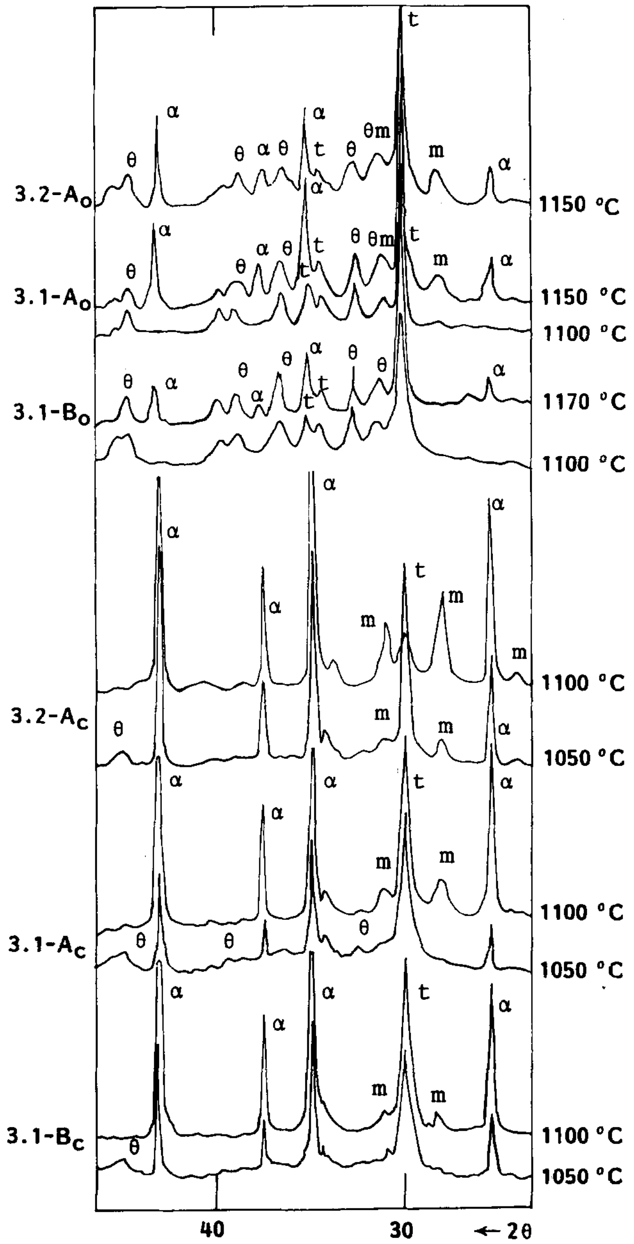

Fig. 2. X-ray diffraction patterns of heat treated unseeded and seeded composites.

were entrapped within a pore channel of this structure. For this reason, they would have little influence on the further microstructure development, which could be expected in the alumina composite containing 20 wt% ZrO_2.[14,19,20] On the other hand, the microstructure of all the heated composites seeded with α-alumina particles is quite different and characterized by discrete α-alumina grains (0·1–0·2 μm) and both zirconia particles and pores distributed between the grains (Fig. 3b). This structure was formed because the seed particles, acting as nuclei for the transformation of θ to α-alumina, successfully controlled the transformation and retained the formation of the vermicular α-alumina structure.

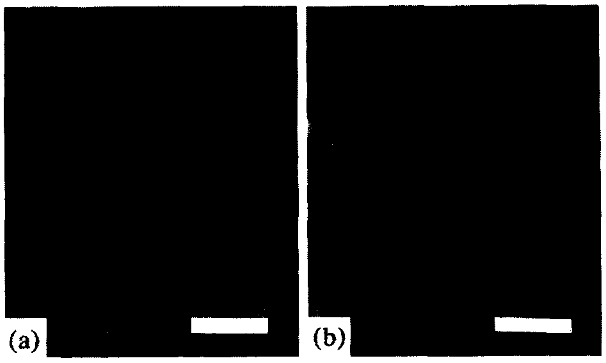

Fig. 3. SEM micrographs of (a) unseeded 3.1-A$_o$ and (b) seeded 3.1-A$_c$ gels heated at 1200°C (bar = 0·5 μm).

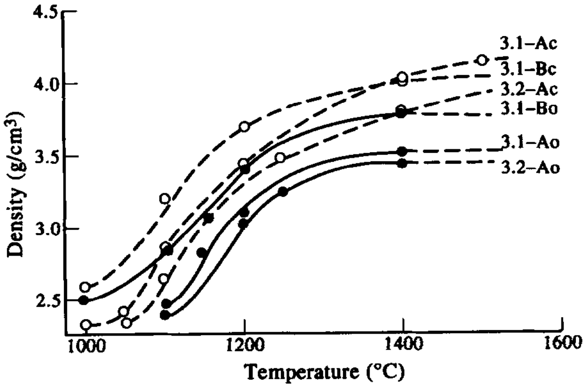

Fig. 4. Density of unseeded and seeded gels as a function of temperature.

Densities of the unseeded and seeded alumina–zirconia composites as a function of temperature are plotted in Fig. 4. The densities of the unseeded composites increase considerably during the θ to α-alumina transformation, but reach only relatively low values at 1400°C (79%, 80% and 88% theoretical density for the 3.2-A$_0$, 3.1-A$_0$ and 3.1-B$_0$ composites, respectively). As can be seen (Fig. 4), for all unseeded samples a plateau was almost reached at 1400°C, indicating that any further increase of the temperature would not effect densification anymore. The typical microstructure of the unseeded composite sintered at 1400°C is shown in Fig. 5. As can be seen (Fig. 5), porosity is very large and intragranularly distributed, which caused low density to be reached at this tempera-

Fig. 5. SEM micrographs of unseeded composite 3.1-A$_o$ gel heated at 1400°C (bar = 1μm).

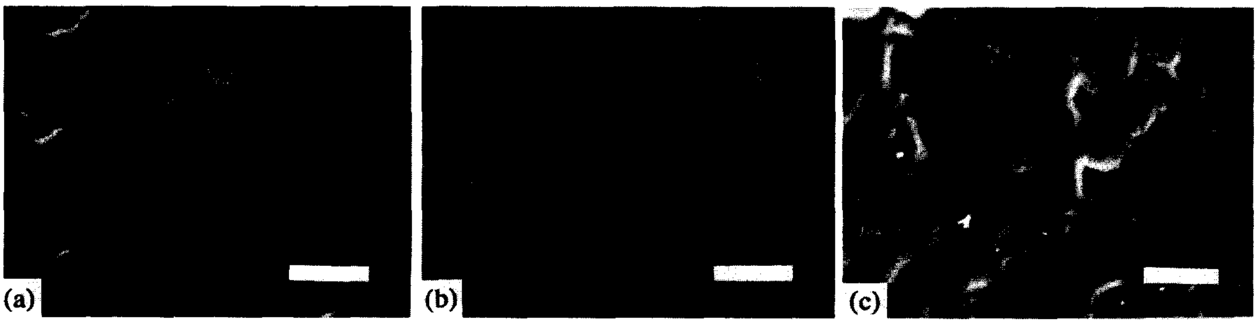

Fig. 6. SEM micrographs of seeded composite gels heated at 1400°C: (a) 3.1-B_c, (b) 3.1-A_c and (c) 3.2-A_c (bar = 0·5 μm).

ture, and could be the reason why this structure could not be densified, even at higher temperatures.

The density of the seeded samples in general is higher relative to the unseeded composite samples. This difference is more evident above 1200°C (Fig. 4) and can be related to the faster densification of the composite with small discrete α-alumina grains and fine zirconia particles and pores between them, than of the composite structure with vermicular matrix and intragranularly distributed zirconia particles.[7] According to the density results of the seeded composites, it is evident that differences between the polymer, 3.1-B_c, and particulate matrix, 3.1-A_c, exist. Although the 3.1-B_c has a higher density than the 3.1-A_c sample below 1300°C, the opposite can be observed at higher temperatures (Fig. 4). One of the reasons for this is a very fine net of cracks in the 3.1-B_c sample (probably already formed in the gel during drying) and the second reason is the microstructure development, which will be explained in the next paragraph. On the other hand, the densification rate of the 3.1-A_c and 3.2-A_c samples are similar (Fig. 4), only the 3.1-A_c sample has a higher density at a given temperature than the 3.2-A_c sample, but it has a higher green density too.

In contrast to the unseeded alumina–zirconia composites (Fig. 5), the seeded samples sintered at 1400°C developed uniformly, for the 3.1-A_c samples almost poreless structure, with submicrometer α-alumina grains and homogeneously distributed small zirconia particles primarily on the three or four grain junctions (Fig. 6). The effect of the different seeded alumina matrices (polymer and particlate) on the microstructure of the alumina–zirconia composite heated at 1400°C can be seen in Figs 6a and 6b. In the polymer matrix composite, 3.1-B_c, abnormal growth of some alumina grains appears (Fig. 6a), whereas the particulate matrix composite, 3.1-A_c, has a more uniform size distribution of alumina grains (Fig. 6b). The appearance of abnormal growth of some alumina grains already at 1400°C (Fig. 6a) and a smaller densification rate of the 3.1-B_c than 3.1-A_c composite samples (Fig. 4) could be related to the less pronounced efficiency of α-alumina seed particles, used in experiments, in the polymer than the particulate matrix alumina–zirconia composite. We believe that smaller α-alumina particles than we used as the seeds, would be more efficient in the case of the polymer matrix composite.

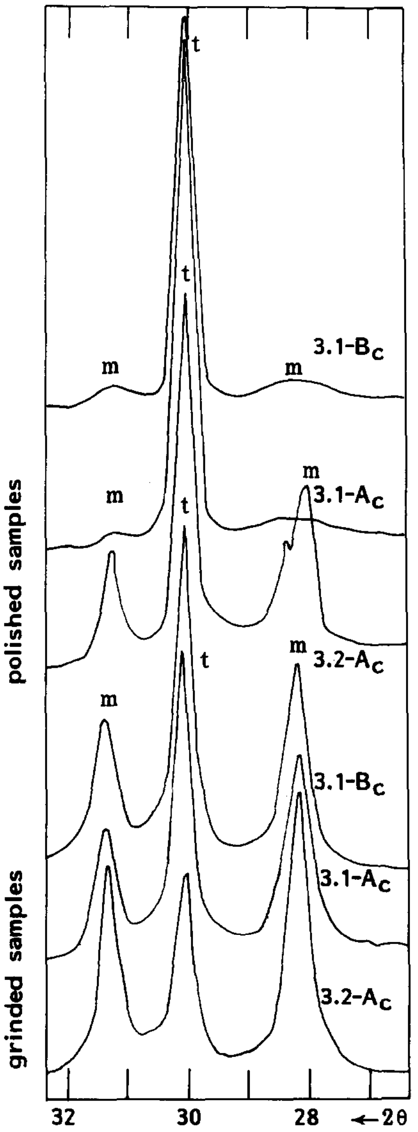

Fig. 7. X-ray diffraction patterns of ground and polished (and annealed) composite samples heated at 1400°C.

In both 3.1-B_c and 3.1-A_c composites, zirconia particles are very small (with average size of ~0·1 μm) and mainly on the grain junctions (Figs 6a and 6b). Although the zirconia particles are very small, the portion of tetragonal phase is relatively low (61 vol% and 53 vol% for the 3.1-B_c and 3.1-A_c sample, respectively) (Fig. 7). In order to check this result, XRD was taken from the polished and annealed composite surface. In Fig. 7, the results of XRD from polished and ground samples were compared. As the portion of tetragonal zirconia is very high for both polished and annealed 3.1-B_c and 3.1-A_c samples, the low portion of tetragonal zirconia in composites after grinding could be explained by the induced tetragonal to monoclinic zirconia phase transformation during the sample preparation for XRD by grinding.

The effect of the different original zirconia particles on the microstructure of the alumina–zirconia composite heated at 1400°C and 1500°C can be seen in Fig. 6 (b and c) and Fig. 8, respectively. The 3.2-A_c sample has larger alumina grains than the 3.1-A_c sample at both temperatures, but also a relatively inhomogeneous structure with a higher amount of porosity. This could be related to the different size and nature of the original zirconia particles. We believe that already in the composite sol the larger zirconia particles, processed under approximately neutral conditions (pH = 5·5), could not be well mixed with the alumina particles. After heating, less homogeneous dispersed zirconia particles in the alumina matrix of the 3.2-A_c sample cause less efficient inhibition of alumina grain growth and results in a coarser microstructure than in the 3.1-A_c composite. In both composite samples, the size of zirconia particles increases with temperature (Figs 6b and 6c and Fig. 8). It is evident that the zirconia particles are larger in the 3.2-A_c than in the 3.1-A_c composite, which explains the higher portion of monoclinic zirconia in the first one (Fig. 7).

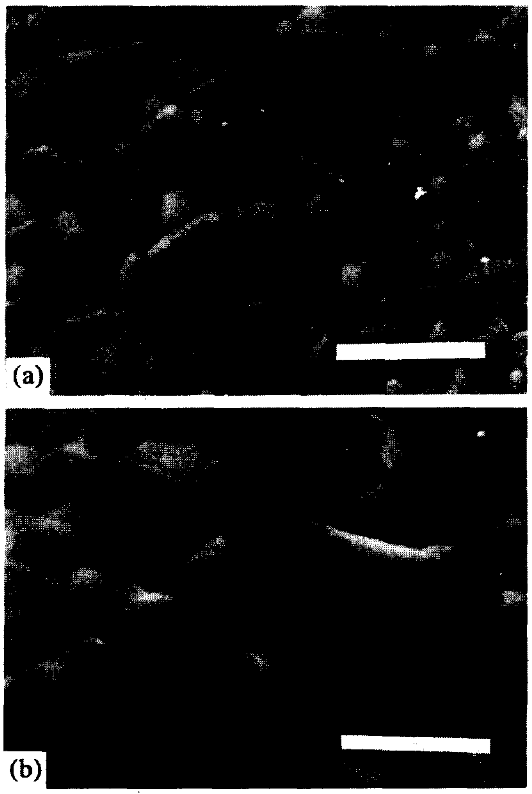

Fig. 8. SEM micrographs of seeded composite gels heated at 1500°C: (a) 3.1-A_c and (b) 3.2-A_c (bar = 1 μm).

4 CONCLUSION

Our experimental results, presented above, give an indication that one must choose the size of α-alumina seed particles and the size and nature of the zirconia particles for the specific alumina matrix, in order to obtain a desirable composite microstructure.

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