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Y(E)-doped tetragonal zirconia polycrystalline solid electrolyte

Part 2 *Microstructure and mechanical properties*

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Polycrystalline dense zirconia containing 100% metastable tetragonal phase was obtained by alloying zirconia with 2 to 3 mol% Y_2O_3 (Er_2O_3). A critical temperature, approximately 1400° C, for full densification (100% theoretical density) was found, and above that a sudden density decrease in all sintered bodies took place. The fracture toughness (K_{IC}) was found to be strongly dependent on the grain size, and a critical grain size (0.29 μm in Y-TZP and 0.38 μm in Er-TZP) existed beyond which a steep K_{IC} decrease was produced. Phase composition and microstructural development seem to influence such mechanical behaviour.

1. Introduction

In Part 1 [1] of this series of papers a study was made of the different processing parameters leading to the obtention of an optimized powder with both a good sinterability and better sintering behaviour. From the point of view of its applicability as a high-temperature solid electrolyte, some of the more important requirements are, among others, phase stability and mechanical behaviour under the working conditions, and both of these are closely related to microstructure of the powder. In Part 2 we place particular emphasis on those parameters controlling the microstructure of the sintered bodies (fundamentally density and grain size) which, to a great extent, contribute to a homogeneous and small crack size distribution and, thus to a high fracture toughness. On the other hand, a factor of primary importance is the amount of retained tetragonal zirconia which, being the toughening agent, is decisive in obtaining a tough material via a transformation toughening process. In this sense Gupta *et al.* [2, 3] established that the retention of tetragonal zirconia solid solution, depending on the kind of solute and matrix, occurs when the grain size was below a critical size of 320 nm. Above that critical size the transformation to monoclinic should be possible during the cooling at room temperature. Lange [4–8] and Lange and Claussen [9] reported that although the grain size is a very important factor in controlling the amount of tetragonal phase retained, however the influence of additives in decreasing the chemical free energy (ΔG) of the system is another parameter to take into account. Therefore, the critical grain size could also be affected by both the kind and amount of additive. In the case of MgO the critical grain size was estimated to be 200 nm [10], and 190 nm for CaO [11]. Our experience on TZP ceramics showed that the retention of the tetragonal phase cannot be supported by the critical grain size being the only limiting parameter to take into account. In our opinion, and assuming both a deagglomerated powder and an ideal distribution of the solute in the matrix, the retention degree of the tetragonal phase in a single-phase TZP constraining matrix could be determined by the following conditions: (a) sintered density, (b) grain size, (c) amount of additive, (d) temperature, and (e) grain dihedral angle (for a non-uniform microstructure).

The purpose of the study reported here, the second of a series of papers, was to ascertain the best conditions for retaining the tetragonal phase during the cooling at room temperature in ZrO_2 alloyed separately with two-different additives, Y_2O_3 and Er_2O_3. The influence of temperature and additive amount on the critical grain size and, at the same time, on the fracture toughness of the sintered bodies was also a goal of this investigation.

2. Experimental procedure

Sintering experiments on isopresed (250 MPa) Y(Er)-doped tetragonal zirconia powders, as prepared elsewhere [1], were carried out in air at temperatures between 1200 and 1600° C and for times of 1 to 6 h. After sintering, densities were measured by the water displacement method. Phase identification was made using an X-ray diffractometer. Quantitative analysis of the phases present, monoclinic and tetragonal or cubic zirconia, was carried out by measuring the relative intensity of the (1 1 1) and $(1\,1\,\bar{1})$ diffraction peaks. In the case of cubic zirconia phase the relative intensity of (3 1 1) and (4 0 0) diffraction peaks were measured. In both cases a goniometer speed of 1/8 deg min^{-1} was used. Critical stress intensity factor (K_{IC}), which is a measure of the fracture toughness was determined on polished samples by an indentation technique with the Vickers indentor. In all cases the load of the indentor was kept constant at 200 N. Taking into account the hardness measurements, an

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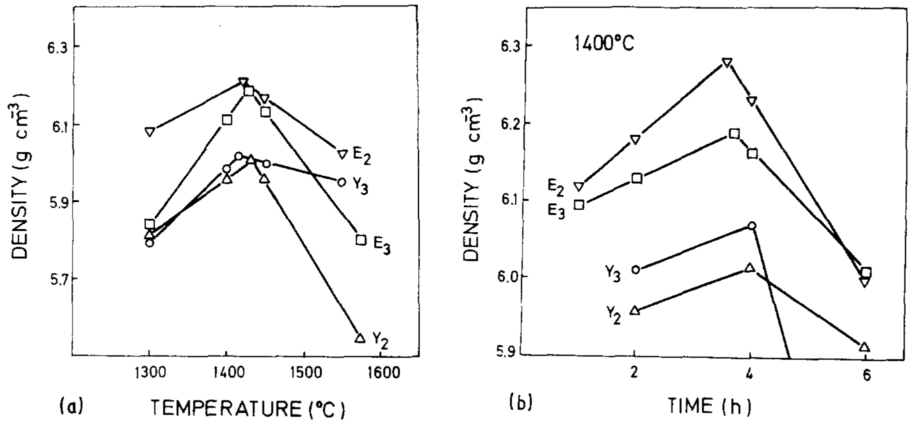

Figure 1 Densification evolution against (a) sintering temperature and (b) sintering time.

indentation crack length, C, and the indentation impression radius, a, the value of K_{IC} for each composition was calculated using the calibration curve reported by Evans and Charles [12]. Three or more measurements were made for each sample.

The microstructure of both polished and thermally etched and fracture surfaces of sintered bodies was observed using a scanning electron microscope, and the intercept method [13] for measuring the grain size was used.

3. Results

3.1. Densification of the fabricated bodies

Figs 1a and b show the results of density as a function of temperature and time of sintered bodies. As can be seen, the density increased as the temperature was increased up to 1400° C and then diminished at higher temperatures. A similar phenomenon seems to occur in the variation of density as a function of time at 1400° C, as can be seen in Fig. 1b. These apparently anomalous results could be discussed in the light of information obtained from the phase equilibrium diagrams for the two systems ZrO_2–Y_2O_3 (Er_2O_3) as shown in Fig. 2. According to these phase equilibrium diagrams, the compositions Z3Y and Z3E sintered at 1400° C will be constituted by tetragonal zirconia solid solution as the only phase and by two phases, tetragonal + cubic zirconia solid solutions, above that temperature. In the case of the compositions Z2Y and Z2E, both will be constituted by tetragonal zirconia solid solution as the only phase over the whole sintering temperature range investigated. The phases in the sintered samples, identified by X-ray analysis, were in agreement with those predicted by the phase equilibrium diagrams.

In the case of the Z3Y and Z3E composition, the densification behaviour could be explained if it is taken into account that above 1400° C a new phase, cubic zirconia solid solution, starts to form accordingly the following partitioning reaction:

$$\begin{array}{c}\text{Tetragonal phase (T)} \xrightarrow{>1400^\circ\text{C}} \\ (3\,\text{mol}\,\%\ Y_2O_3)\end{array}$$

$$\begin{array}{cc}\text{Tetragonal phase (T}') + & \text{Cubic phase (C)} \\ (<3\,\text{mol}\,\%\ Y_2O_3) & (>3\,\text{mol}\,\%\ Y_2O_3)\end{array}$$

The formation of the cubic phase (C) takes place with rejection of zirconium at the same time that some of the oxygen is formed. On cooling, the tetragonal phase (T′) could transform to monoclinic phase if the grain size is greater than the critical size for this new tetragonal phase. In such a case the formation of both

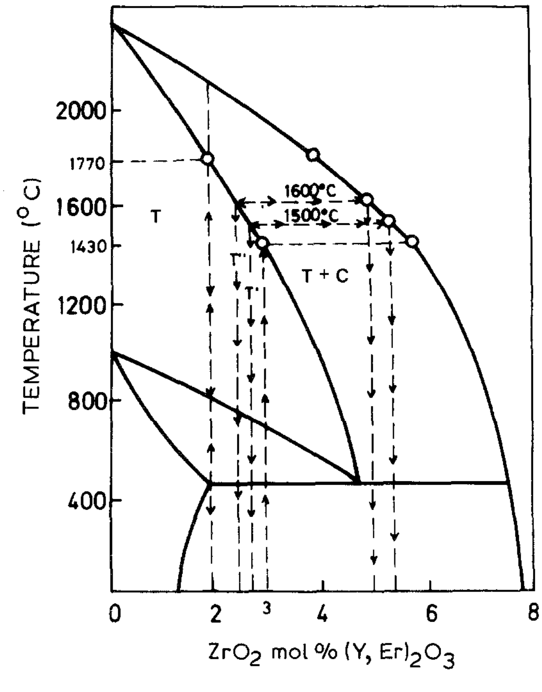

Figure 2 High zirconia rich-region of the phase diagram ZrO_2–$(Y, Er)_2O_3$.

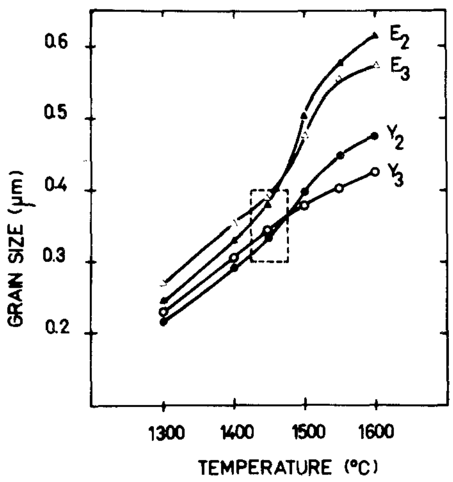

Figure 3 Grain size evolution as a function of sintering temperature of the $(Y, Er)_2O_3$–TZP ceramics.

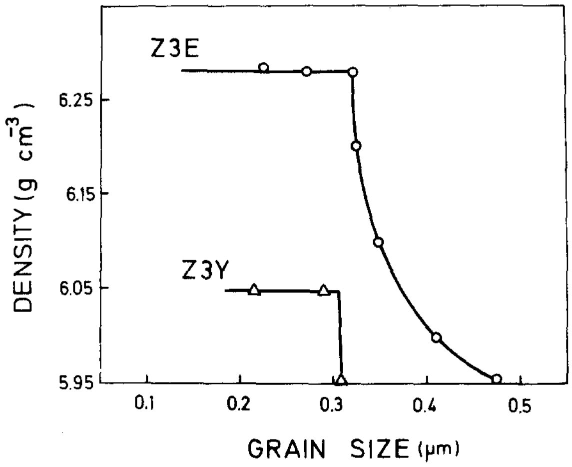

Figure 4 Density plotted against grain size of the (Y, Er)$_2$O$_3$-TZP ceramics.

microcracks and an additional porosity would be possible and, therefore, the density will decrease. On the other hand, the presence of cubic phase grains could diminish the average elastic modulus of the tetragonal constraining matrix, by which the transformability of the tetragonal phase will be favoured.

From Fig. 1a and b it could be assumed that the influence of sintering time for a specific temperature is more drastic in decreasing the density than the sintering temperature. Fig. 3 shows the variation of grain size as a function of sintering temperature for the different tetragonal zirconia compositions. As can be seen the grain size slowly increases up to the higher sintering temperature for the Z2Y and Z3Y compositions; however, in the case of Z2E and Z3E compositions, the tetragonal grains increase significantly beyond 1400° C. The grain size (critical size) at which a decrease in density took place (see Fig. 4) is larger in the case of the Z2E and Z3E (0.35 to 0.40 μm) compositions, which gives rise to a relatively higher stability of the tetragonal phase. Contrary to the report of Lange [6], the critical grain size for Z2Y and Z3Y is smaller, which could be related to the full density achieved in our samples. In any case, it seems clear that a grain size higher than 0.2 to 0.3 μm in the case of ZY tetragonal zirconia solid solutions, and higher than 0.3 to 0.4 μm for ZE tetragonal zirconia solid solutions, produces a strong microcracking accompanied by the tetragonal–monoclinic phase transformation during cooling.

Detailed retained tetragonal content measurements were made on the Z3E composition as a function of grain size; the monoclinic phase was never detected by X-ray diffraction on the surface of the as-sintered samples. After polishing, a certain amount of monoclinic phase was observed; however, it is a consequence of the tetragonal–monoclinic transformation which can be stress-induced by surface grinding. Although the monoclinic phase was not observed over the whole grain-size range explored, it was noticed that the cubic phase increased as the sintering temperature was increased above 1400° C, which is in close agreement with previous studies of the phase equilibrium diagrams [14–17]. In the case of the Z3Y sample, a similar behaviour was found. For the

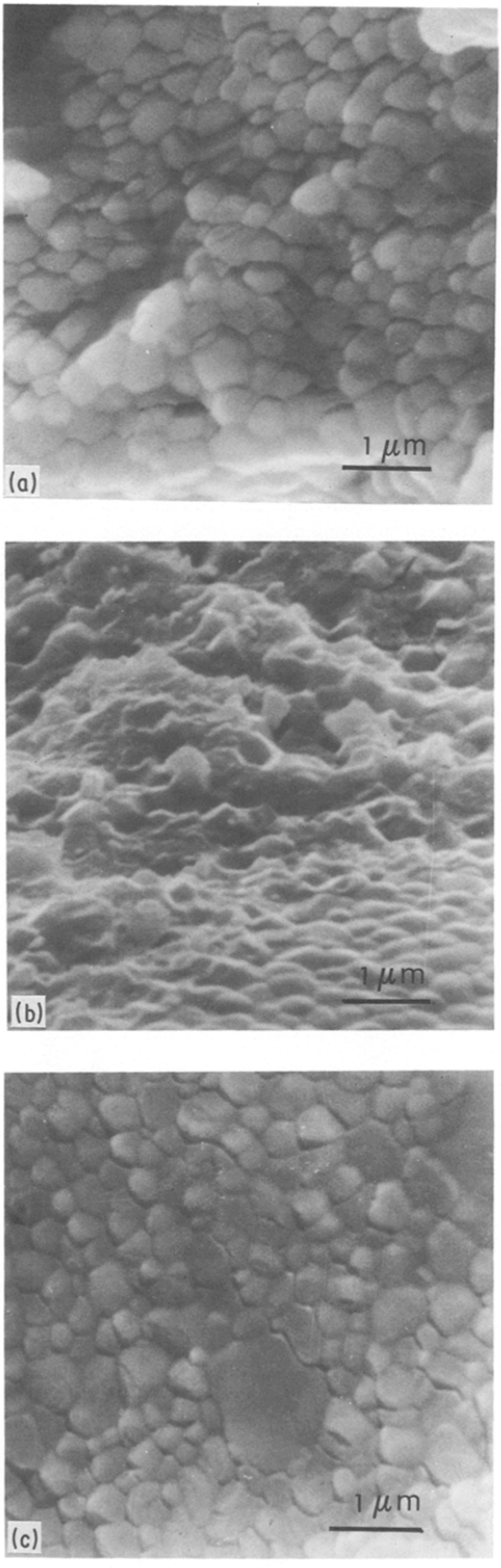

Figure 5 Fracture surface in Y-TZP as a function of sintering temperature: (a) 1400° C, (b) 1500° C, and (c) 1600° C.

tetragonal zirconia alloyed with 2 mol % $(Y, Er)_2O_3$, the critical grain size at which the tetragonal–monoclinic transformation takes place was lower than 0.3 μm at the same critical temperature of 1400° C.

The above results enables us to deduce that two density decreasing mechanisms could be operating in the sintered bodies at temperature higher than 1400° C. One is related to the grain growth as the only factor in decreasing density for the cases of tetragonal single-phase Z2Y and Z2E compositions. In the case of the Z3Y and Z3E compositions, another mechanism related to the partitioning reaction in the cubic phase formation could participate strongly in the decreasing density of the sintered bodies. Both effects contribute to a greater transformability of the tetragonal zirconia to monoclinic phase during the cooling process.

3.2. Microstructural development

Both the mechanical and electrical properties of tetragonal zirconia strongly depend on its microstructure, therefore its control is of primary importance in enhancing them. Fig. 5 shows the fracture surface of Y-TZP at different temperatures, in which it can be observed that below 1400° C, tetragonal zirconia being the only phase present, an intergranular fracture is predominant and no cracks were observed. Above that temperature a mixture of transgranular and intergranular fracture was present, and two types of grain, angular and rounded, were observed. It can be seen that microcracks along the grain boundaries are present as consequence of the cubic phase formation.

Fig. 6 shows typical microstructures of several Y(Er)-TZP samples that were thermally etched. The microstructural evolution is in agreement with that predicted from the phase equilibrium diagram. A very uniform microstructure of equiaxed grains was observed when tetragonal zirconia was the only phase present (1400° C). At higher temperatures a bimodal distribution was present. Such a distribution was attributed to the presence of cubic phase in the sample. The grains corresponding to the cubic phase in the sample. The grains corresponding to the cubic phase were much larger than those of the tetragonal phase. In all cases the grain size was larger for TZP alloyed with Er_2O_3 and a bimodal distribution was never observed in Z2E in the temperature range studied here. From the microstructural observations it seems that the nucleation and growth of the cubic phase grains follows a different kinetics than that for the tetragonal zirconia grains. The abnormally large grains of cubic phase are probably produced as a consequence of a rapid interdiffusion of yttrium and zirconium cations at the same time that a fast grain-boundary movement took place. The presence of some tetragonal grains embedded within the cubic grains corroborates this assumption.

3.3. Fracture toughness

In close agreement with the Evans and Charles [12] suggestions, the indentation technique was used to study the fracture toughness behaviour of our samples. Fig. 7a shows the K_{IC} measurements as a function of the temperature and sintering time. As can be seen, a maximum K_{IC} value was found at ~ 1400° C in all cases. Larger K_{IC} values were also found for lower Y_2O_3 (Er_2O_3) contents, i.e. 2 mol % Y_2O_3 (Y_2) and 2 mol % Er_2O_3 (E_2). At temperatures higher than 1400° C the fracture toughness quickly decreases and such a decrease was more sudden in the case of the tetragonal zirconia alloyed with Y_2O_3. In isothermal heat-treatment at the critical temperature of 1400° C (Fig. 7b), it was found that a maximum K_{IC} value was measured for 4 h in the case of Y-TZP samples, and for 2 h in the case of E-TZP. In both cases the maximum K_{IC} values coincided with the higher density in the Y(Er)-TZP sintered bodies. The increase in K_{IC} with sintering temperatures up to 1400° C could be explained by the increase in the density of the sintered bodies. Above that temperature the decreasing in fracture toughness could be attributed to both the growth of the tetragonal grains beyond the critical size, and to the presence of the cubic phase that, having a different Young modulus, could affect the elastic conditions of the constraining tetragonal zirconia matrix.

In an attempt to clarify such fracture toughness behaviour, K_{IC} and Vickers hardness (20 kg) as a function of grain size were studied. Fig. 8 shows the results obtained on Z3Y and Z3E sintered bodies, and it can be observed that in a narrow grain size range (0.22 to 0.30 μm) a considerable increase in K_{IC} (of 4 to 8 $MPa\,m^{1/2}$) occurs, and beyond that critical grain size a steep decrease was produced. A similar variation took place for Z3E sintered samples although the changes in K_{IC} are not so pronounced. In this case the critical grain size is displaced to a higher value. It is noticeable that the K_{IC} value remains almost constant beyond the critical grain size, and a small change (~ 1 $MPa\,m^{1/2}$) in the grain size range 0.33 to 0.48 μm took place.

The hardness measurements made on the polished surfaces showed a similar variation to that occurring in the fracture toughness behaviour. As before, the higher hardness was obtained at the higher density value and for a grain size close to the critical grain size. Beyond the critical grain size (0.29 μm) the decrease in density is responsible for the strong decrease in hardness (~ 30%) in the case of Z3Y. Despite the decrease in density produced in the Z3E samples, nonappreciable change in hardness took place.

4. Discussion

In Part 1 of this series of papers [1] the importance of avoiding both the presence of agglomerates and the formation of inhomogeneities during powder preparation was shown. These two processing parameters strongly influence the microstructure, mechanical properties and, therefore, the structure reliability of the fabricated ceramics. By assuming the non-existence, as in the present case, of these two negative factors in the prepared powder, then other parameters should be controlled leading to the production of ceramics with improved characteristics. In this way control of the microstructure developed during the sintering process was chosen as the key for improving the mechanical properties of the ceramic materials studied.

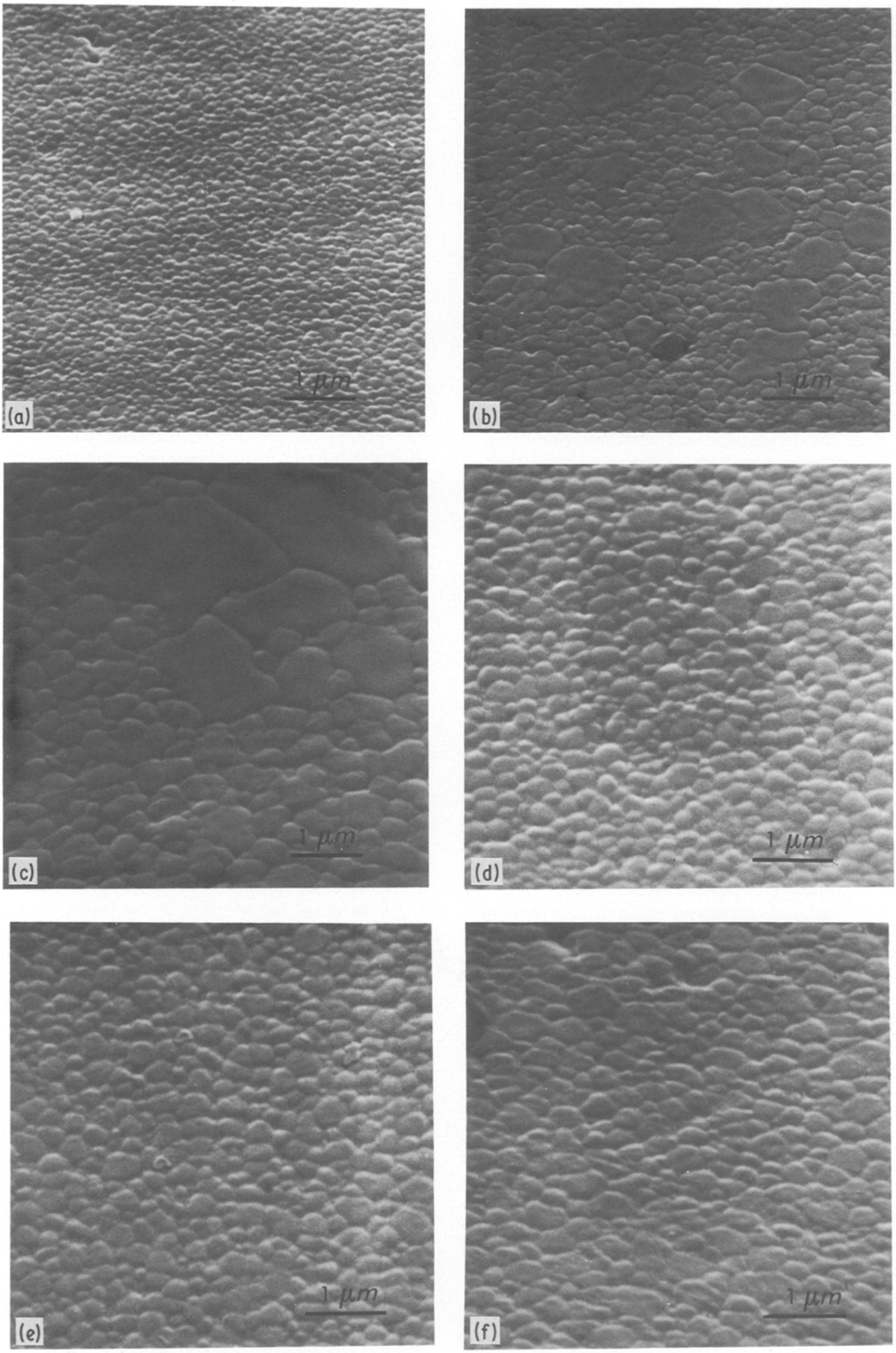

Figure 6 Microstructural evolution of Y-TZP ceramics at several temperatures, (a) 1400° C, (b) 1500° C and (c) 1600° C, and grain size evolution, (d) 1400° C, (e) 1500° C, and (f) 1600° C in Z2E as a function of the sintering temperature.

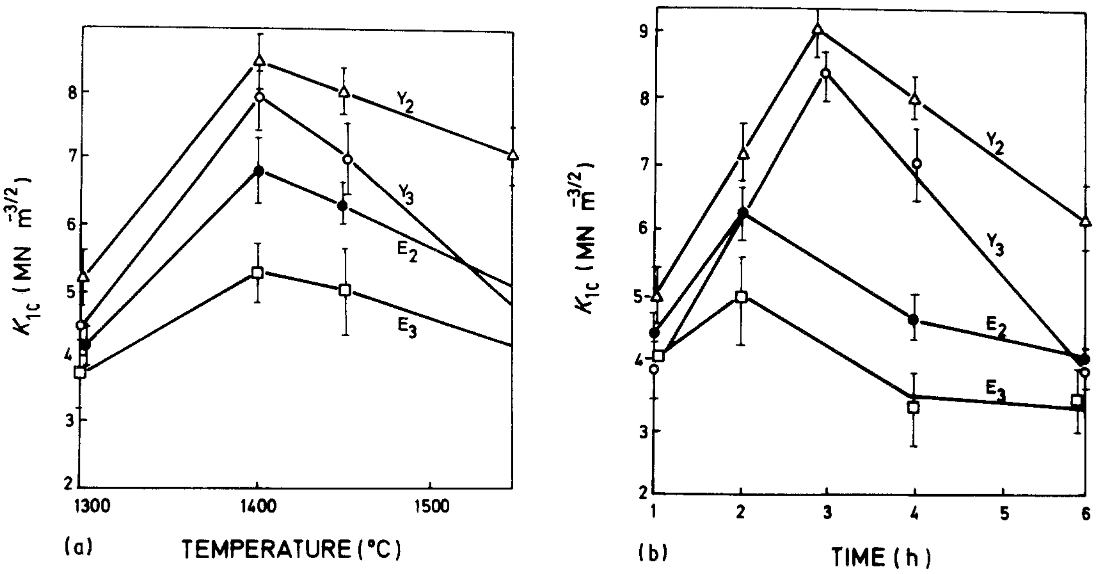

Figure 7 Fracture toughness evolution in Y(Er)-TZP as a function of the sintering temperature (a), and sintering time at 1400° C (b).

As previously established by Gupta *et al.* [3] for tetragonal zirconia alloyed with yttria, the strength and fracture toughness of such ceramics can be improved by the presence of a stress-induced phase transformation (SIPT) phenomenon; nevertheless, the contribution of SIPT is strongly conditioned by a number of factors as density, grain size, temperature and alloy additions.

In a general manner the densification behaviour of the tetragonal zirconia sintered bodies alloyed with a low percentage of yttria (erbia) was parallel to that reported by Gupta *et al.* [3], see Fig. 1, in which the density of samples increased as the sintering temperature was increased up to a critical temperature (~ 1400° C) beyond which a sudden density decrease was produced. Gupta *et al.* [3] attributed such behaviour to a change in grain size, and concluded that a critical grain size existed (0.32 μm) beyond which a spontaneous phase transformation, tetragonal–monoclinic, during cooling from the sintering temperature took place. From the beginning it seems clear that the grain size is the only cause for the decrease of the retained tetragonal phase as the sintering temperature was increased. However, it must be mentioned that the compositions of Gupta *et al.* [2] contained some monoclinic phase which, on cooling, could act as active nucleation sites for phase transformation. On the other hand, the density of his samples (5.6 g cm^{-3}) is very far of the theoretical density (D_T = 6.09 g cm^{-3}) and this is another factor leading to the formation of monoclinic phase during the cooling process. Furthermore the variation of strength as a function of the grain size could not have been studied at a fixed temperature and, in that case, the temperature is other parameter favouring, on cooling, the tetragonal–monoclinic transformation and microcracking. Then by assuming that near fully densified bodies is the prime factor required for tetragonal retention and constraint, the samples studied here were higher than 98% theoretical density. On this basis it is believed that below a critical temperature (~ 1400° C), for a determined content of alloying additive, the retention of tetragonal zirconia at room temperature will be conditioned by a critical grain size which, on the other hand, will also depend on the kind of additive, the density of the sintered body and the uniformity of the grain size distribution. In our case, a critical grain size of 0.29 μm was found in the Z3Y ceramics, and 0.38 μm when the zirconia was alloyed with the same content of Er_2O_3. These results could be closely related to the ability of the additive in decreasing the structural free energy change at room temperature. Beyond those critical grain sizes a dramatic density degradation was produced as a consequence of the large microcracking which takes place on cooling in the tetragonal–monoclinic transformation.

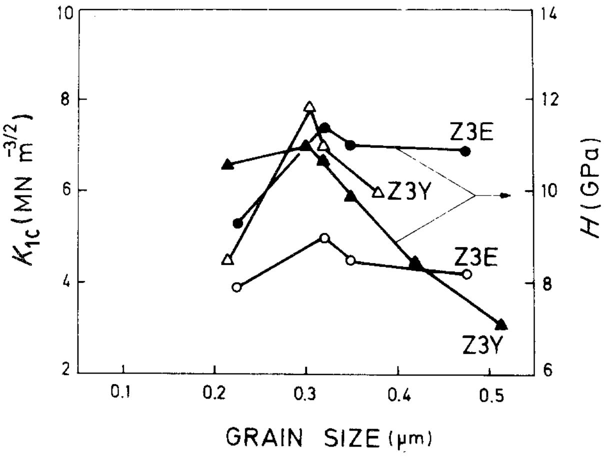

Figure 8 Fracture toughness (K_{IC}) and hardness variations as a function of the grain growth size.

Above the critical temperature of ~ 1400° C, in those cases in which tetragonal zirconia is the only phase present, i.e. for Z2Y and Z2E compositions, the density degradation could be produced by a nucleation and rapid grain growth above the critical grain size for retention of tetragonal phase. In those cases in which a new phase, cubic phase, is formed the mechanism for the density degradation process could take place via a partitioning reaction in which the low-temperature tetragonal zircoinia (T) converts, above 1400° C, to two phases: tetragonal zirconia (T′) + cubic phase (C). On cooling, the new tetragonal phase (T′), having an yttria content lower than 3 mol % but a grain size corresponding to the tetragonal phase (T), will transform spontaneously to the monoclinic phase with a large microcracking formation. On the other hand, the cubic zirconia phase is formed from tetragonal zirconia phase (T) by rejecting zirconium and oxygen ions and, in that case, a pressure gas is probably generated. In agreement to the suggestions of Lange *et al.* [18], the loss of such oxygen pressure can originate the formation of additional porosity. Fig. 9 shows a picture of the microstructure supporting our arguments. It can be seen that, like up to 1400° C, just below the interphase separating the tetragonal single-phase field of the two phases field (T + C), the density increases achieving the theoretical density value, and no phase transformation takes place. Above that temperature, in Fig. 9e, a spontaneous transformation of tetragonal zirconia (T′) to monoclinic phase takes place mainly in the grain boundary. It must be mentioned that at 1500° C the massive formation of cubic zirconia phase was not observed; however, it can be seen that the smaller tetragonal grains are joined, constituting a germ, in a first step, for the cubic zirconia formation. At 1600° C the partitioning reaction for the cubic zirconia formation seems complete and a strong increase in porosity takes place. As can be seen, no monoclinic precipitation on the cubic surface grains was observed which indicates that the partitioning reaction is responsible for the density degradation at this temperature.

The same arguments could be applied to explain the K_{IC} decreasing process. Just below 1400° C, assuming isotropic thermal expansion, a tetragonal zirconia constraining matrix could prevent the volume change associated with the phase transformation and, in such a case, by applying an external stress the tetragonal to monoclinic transformation could be induced in the vicinity of the crack during indentation. The ability of the tetragonal zirconia constraining matrix to arrest

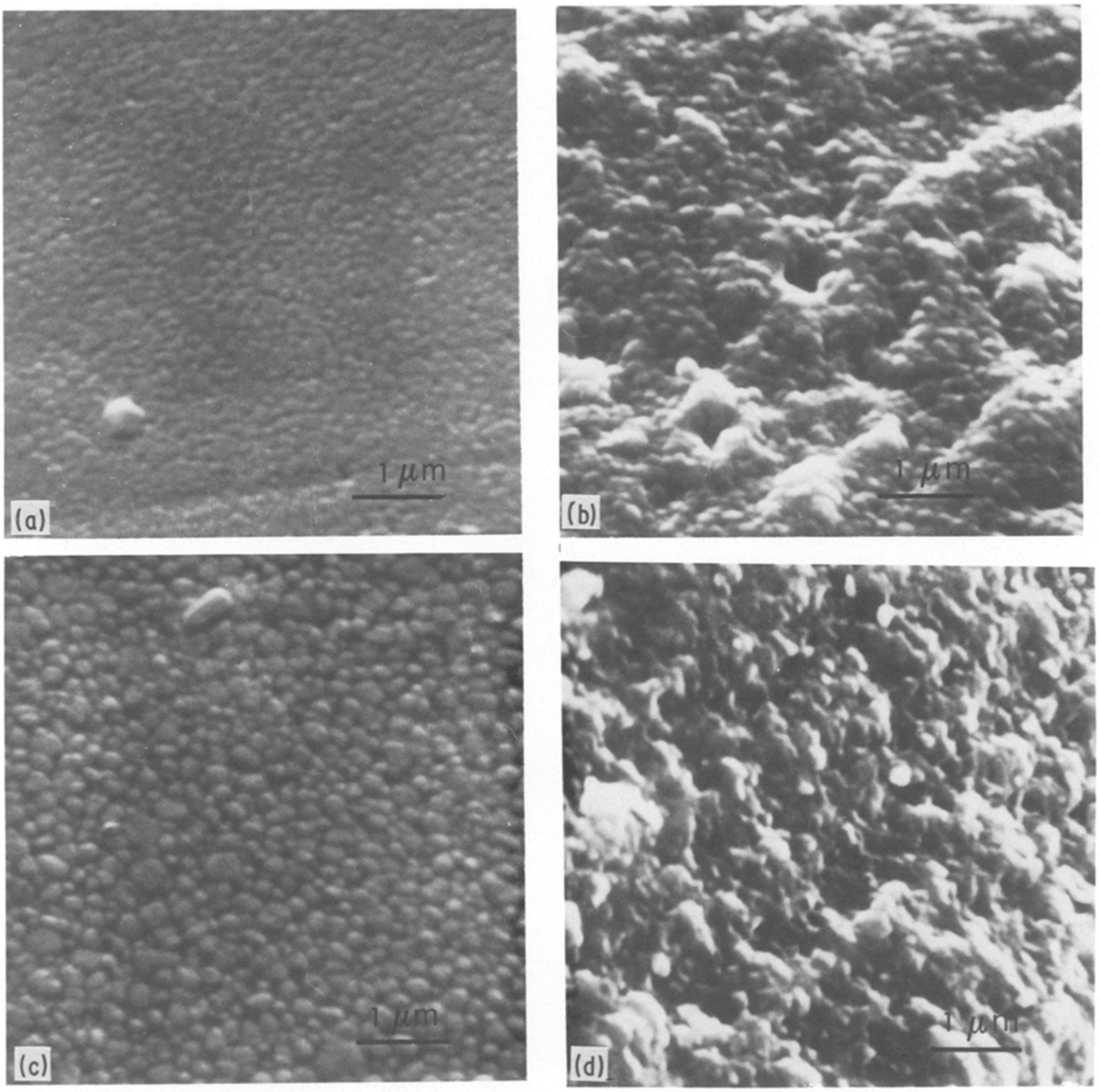

Figure 9 Microstructure of thermally etched and fracture surface of TZP as a function of the sintering temperature. (a), (b), (c), and (d) at 1400° C, and (e), (f), (g) and (h) above 1400° C.

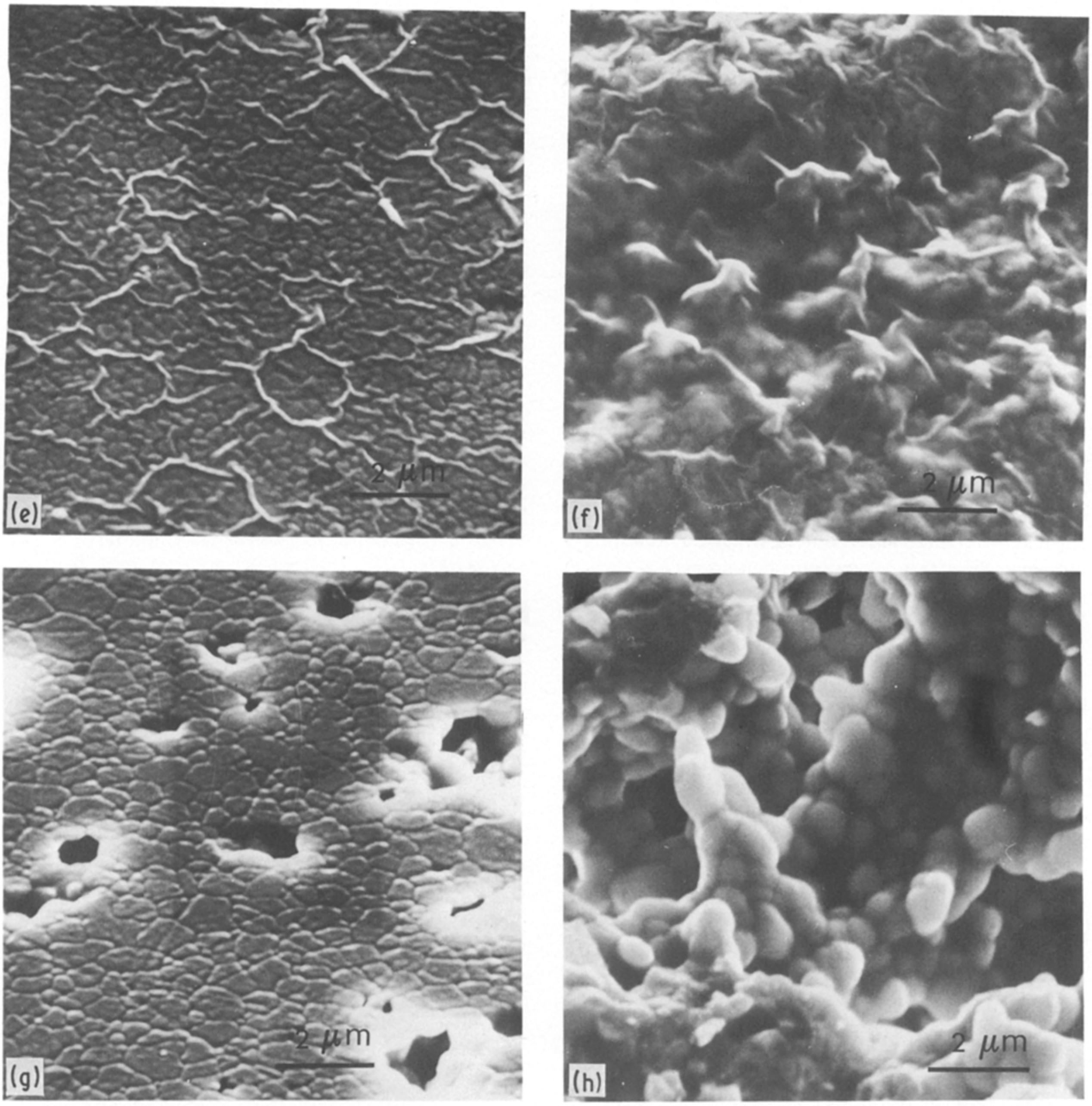

Figure 9 Continued

the initiation of the crack will depend not only on its grain size but also on its uniformity. It seems clear from Fig. 8 that there is a critical grain size beyond which a sudden decrease in K_{IC} takes place. However, the existence of some abnormally large tetragonal grains could also be a cause for K_{IC} degradation. In such a case the assumption of isotropic matrix dilation could not be valid, and another analysis would have to be applied. The larger tetragonal grains could be considered like inclusions in the tetragonal zirconia constraining matrix and, probably, the differential thermal expansion of both could originate crack formation and K_{IC} degradation. This will be the case if the inclusion (larger tetragonal grains) size is higher than a critical size which will coincide with the critical grain size. On the other hand, if the inclusions are not uniformly distributed in the matrix, a tetragonal–monoclinic transformation by zones will be produced. Fig. 10 is an illustrative example supporting our suggestions. This zonal transformation produces an

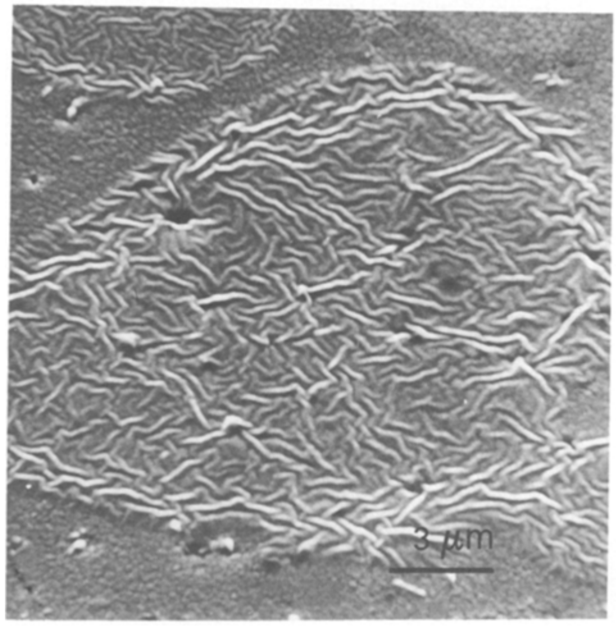

Figure 10 Spontaneous tetragonal–monoclinic transformation in thermally etched TZP sample.

inhomogeneous crack distribution leading to a strong decrease in K_{IC}.

At temperatures higher than 1400° C, i.e. well into the two-phase (tetragonal + cubic) field, the K_{IC} degradation process is dominated by the partitioning reaction in the cubic phase formation. In this case the cubic phase could be considered to be an inclusion in the tetragonal zirconia constraining matrix. The anisotropic thermal contraction which takes place on cooling can produce a large microcracking and subsequently a K_{IC} decrease. Furthermore, the presence of cubic phase grains, with a Young modulus lower than that of the tetragonal zirconia constraining matrix, could change strongly the average elastic properties of the matrix itself. In such conditions the fracture toughness will be lower. Lange *et al.* [18] did not find any appreciable variation of K_{IC} as the temperature was increased above 1400° C, in spite of the density decrease produced. They attribute this fact to the existence of a large glass content which could strongly influence the stress relaxation phenomena.

5. Conclusions

1. In an agglomerate-free tetragonal zirconia powder the densification process is strongly dependent on both the temperature and time of sintering. The best sintering conditions to achieve full densification and 100% tetragonal retention were 1400° C for 2 h.

2. Just below 1400° C a critical grain size, 0.29 μm, exists in fully densified Y-TZP and 0.38 μm in fully densified Er-TZP, beyond which a dramatic density decrease takes place. Such critical grain size is lower for $(Y, Er)_2O_3$ contents lower than 3 mol %.

3. Above 1400° C, in TZP containing 3 mol % $(Y, Er)_2O_3$, a partitioning reaction with the cubic phase formation, dominates the density degradation process.

4. In fully densified Y-TZP a very high fracture toughness (9 to 10 MPa m$^{1/2}$) was attained as a consequence of the stress-induced phase transformation phenomenon. In fully densified Er-TZP the fracture toughness was never higher than 6 to 7 MPa m$^{1/2}$.

5. Below or above 1400° C a critical grain size or the partitioning reaction, respectively, strongly influences the fracture toughness behaviour of the fully densified Y(Er)-doped polycrystalline tetragonal zirconia.

The above conclusions enable one to think that, regardless of other thermodynamical factors such as chemical free energy, strain free energy and the surface free energy changes occurring in the tetragonal to monoclinic transformation, microstructure is the main factor which must be controlled in order to improve the mechanical properties of the TZP-based ceramics.

Acknowledgement

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