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Sintering and microstructure of ultrafine yttria–zirconia compacts

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Sintering behaviour of ultrafine yttria–zirconia solid solution compacts, with yttria contents ranging between 4 and 10 mol % have been investigated and the microstructural developments during sintering were followed. The 4 mol % yttria–zirconia compacts sinter at 1200° C to a high density with a relatively fine uniform microstructure. Firing at 1400° C produces no improvement in densification and discontinuous grain growth develops. The lowest density values are obtained with the 10 mol % yttria–zirconia compacts, with clustering in the grains and greater porosity in the microstructure. The activation energies were determined for both 4 and 10 mol % Y_2O_3-containing bodies in the temperature range 800 to 1000° C.

1. Introduction

Stabilized zirconia has been widely used for many years and with the ever increasing application of the oxide in high-technology ceramics, particularly in wear parts and as solid electrolytes, it has attracted widespread attention [1–3]. Owing to their important application as high-temperature materials, zirconia ceramics have received considerable attention from the view point of their sintering behaviour and control of the microstructures which develop during the sintering process, so that the resulting materials meet the requirements needed for these applications. In order to produce high-performance zirconia ceramics, solid-state sintering has traditionally been adopted as the favoured fabrication route. However, this route has presented some degree of difficulty and the achievement of high density in zirconia has often required the use of high firing temperatures (> 1700° C) [4].

Several approaches have proved to be effective in reducing these temperatures. Amongst these approaches, the use of fine reactive powders prepared by wet chemical methods has received considerable attention among investigators [5–8]. The objective behind this approach is to prepare powders that are ultrafine, uniform in particle size, free from hard agglomerates, and homogeneous with respect to composition. These powders, having such high surface areas, are sinterable at considerably lower temperatures offering high-density bodies with fine, uniform microstructures. However, the existence of agglomerates in wet chemically prepared powders, which is still expected, leads to the formation of rather strong aggregates during the calcination step [9, 10]. These aggregates do not usually break down during the forming process and consequently microstructural inhomogeneities develop in the ceramic bodies during sintering. Furthermore, the large active surface areas of such powders showed that the powder behaviour is sensitive to the atmosphere [11], to washing media [12], and to residual chemical species [13] and careful process control is therefore needed. It is generally believed amongst researchers that the sintering properties are dependent on the preparation procedure and that highly dense single-phase ceramics of stabilized zirconia are attainable if suitable attention is given both to the precise preparation conditions and to the subsequent handling processes [14–16].

In a previous work [17], ultrafine yttria-stabilized zirconia powders have been prepared by autoclaving intimate mixes of their corresponding hydroxides at 200° C for 2 h. Homogeneous yttria–zirconia solid solutions, with as little as 4 mol % Y_2O_3 content, having rounded particulates and noticeably high surface areas [18] have been achieved by this hydrolysis technique. The aim of the present work was to study the sintering behaviour of the yttria–zirconia powder compacts prepared by the above hydrolysis technique. The microstructural developments during the sintering process were also followed. Different firing temperatures were used to determine the optimum conditions to attain the desired dense ZrO_2–Y_2O_3 solid solutions. The activation energies of densification were determined for the zirconia containing 4 and 10 mol % yttria. The relationship between densification properties and microstructure of the bodies obtained have been discussed.

2. Experimental procedure

The ultrafine zirconia powders doped with various amounts of yttria (4, 6, 8 and 10 mol %) were prepared by autoclaving of their corresponding hydroxides at 200° C for 2 h. The method of preparation is described in detail elsewhere [17]. X-ray diffraction (XRD) and infrared (IR) analyses showed that the prepared materials have the cubic fluorite structure of stabilized zirconia. The prepared materials are denoted as 4 mol % Y_2O_3–ZrO_2, 6 mol % Y_2O_3–ZrO_2, and so on, throughout this investigation.

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The powders were then cold-pressed uniaxially in the form of pellets of 12 mm diameter and ~2 mm thick, in a stainless steel die, using a hydraulic press under a pressure of 5000 p.s.i. (34.45 N mm^{-2}). The green pellets were fired in platinum boats using a "Heraues" muffle furnace with "crusilite" heating elements at temperatures between 900 and 1400° C.

The bulk densities of the sintered pellets were determined by the mercury immersion method. Apparent porosity (using the parafin oil displacement method) and linear shrinkage were also measured.

The structure of the investigated materials was analysed using D 500 Siemens X-ray diffractometer (CuK_α radiation and nickel filter). Infrared spectra were obtained with a Beckman IR 4250 absorption spectrophotometer. The microstructure of the fired bodies was studied using reflected light microscopy for the polished samples. Etching of the polished samples was conducted using a boiling 1 : 1 ammonium flouride solution for 3 to 5 min.

3. Results and discussion

Fig. 1 shows the relative densities of the 4, 6, 8 and 10 mol % yttria-stabilized zirconia compacts sintered at the different firing temperatures. It can be seen from the figure that the density values of the four investigated zirconias display the same trend as a function of temperature on firing. A sharp and regular increase in densification is observed between 900 and 1200° C, reaching in most cases a maximum, after which a more or less flat plateau is maintained up to 1400° C. The 4 mol % yttria-zirconia specimens exhibit the highest densities at all firing temperatures and the 10 mol % yttria-zirconia have the lowest values, with the 6 and 8 mol % yttria-zirconia specimens in between. A relative density of 95.6% theoretical is achieved by the 4 moll% Y_2O_3-ZrO_2 specimens at 1200° C, and is maintained almost unchanged as the temperature is raised to 1400° C. At the same firing temperatures, the 10 mol % yttria-zirconia specimens exhibit values of 91.2 and 92.8% theoretical, respectively. Again the 6 and 8 mol % yttria-zirconias show intermediate values, with the 8 mol % samples much nearer in their values to those of the 10 mol % Y_2O_3-ZrO_2 solid solutions. These results indicate that as the yttria content increases in the solid solutions, less densification is obtained and in all cases the theoretical density is not reached.

The opposite behaviour is observed from the results of the apparent porosity of the sintered compacts (Fig. 2). A noticeable decrease in porosities accompanies the increase in firing temperature up to 1200° C, then the porosities decrease only very slightly depending on the amount of the stabilizing yttria present in the specimens. A higher amount of stabilizer is accompanied by an increase in the porosity of the specimens at all firing temperatures. A similar trend (increase in density and decrease in porosity as the dopant content is raised) has been found by Karaulov and Rudjak [19] in a work on solid-state densification of Y_2O_3-ZrO_2 bodies. The results of density and porosity measurements are substantiated by the linear shrinkage data for the sintered pellets (Fig. 3). Linear shrinkage values ranging between 22.5% and 26.5% are seen at 1200° C (1 h) for the four doped compacts. These values remained within the same range as the firing temperature is raised to 1400° C.

The achievement of 95.6% theoretical density of

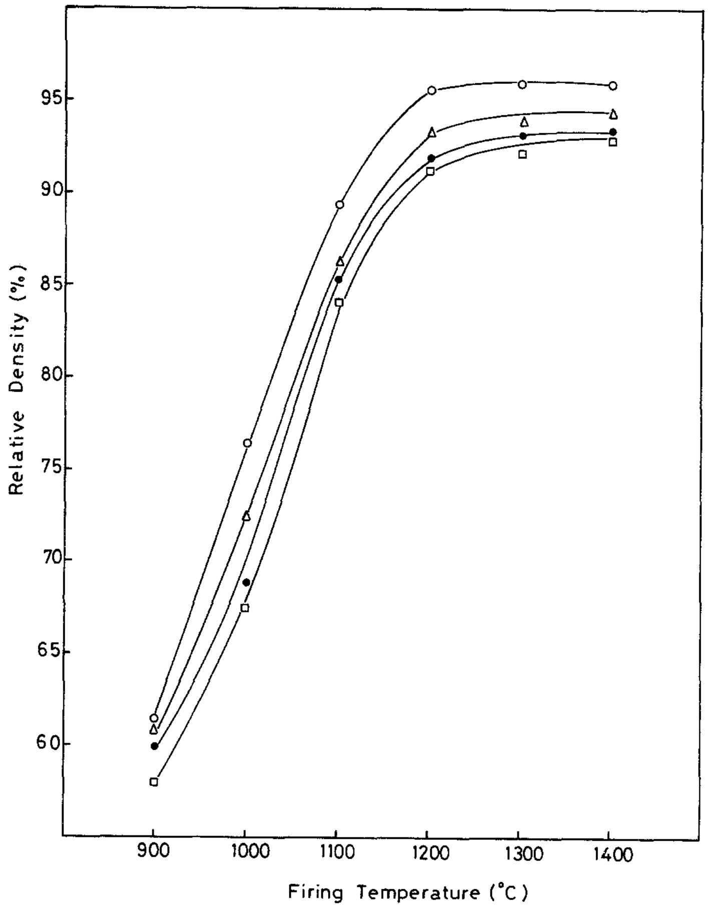

Figure 1 Influence of firing temperature on the densification of yttria-zirconia compacts (1 h soaking time). Yttria contents: (○) 4 mol %, (△) 6 mol %, (●) 8 mol %, (□) 10 mol %.

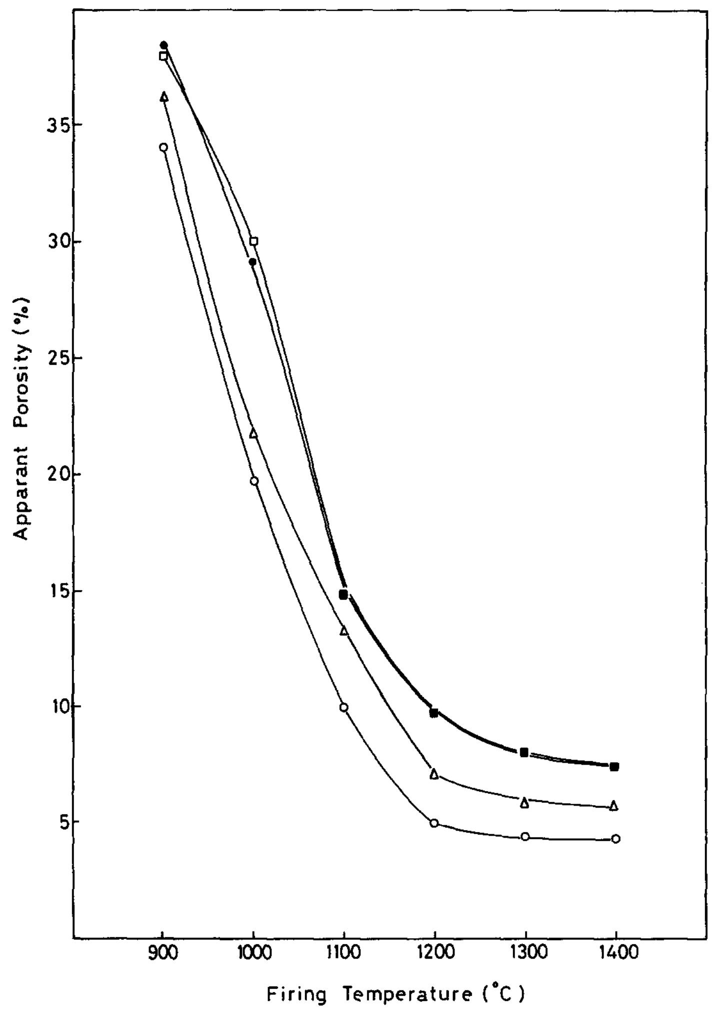

Figure 2 Effect of firing temperature on apparant porosity of yttria–zirconia compacts (1 h soaking time). For key, see Fig. 1.

zirconia at as low as 1200° C with 4 mol % Y_2O_3 in the solid solution is mostly attributed to the highly sinter-active nature of the ultrafine particles (5 to 20 nm) and the rather high surface area (266 ± 10 $m^2 g^{-1}$) powder prepared by the hydrolysis technique [17] that was adopted in the present work. It is generally accepted [1, 15, 20] that the driving force for sintering arises from the tendency of a powder compact to reduce its solid–vapour surface area, and hence to reduce the total surface energy. So, fine powders have better sinterability, i.e. faster and at lower temperatures, than the coarse ones. As a consequency, the powder preparation procedure has a noticeable influence upon the sintering behaviour. Mazdiyasni *et al.* [5], using their excellent alkoxy method, obtained highly dense (~ 95% theoretical) fully stabilized solid solution of 6 mol % Y_2O_3–ZrO_2 by sintering the compacts at as high as 1450° C for 16 h. Haberko *et al.* [6] achieved 95% theoretical for ZrO_2–6 mol % Y_2O_3 composition by sintering at 1500° C (19 h) of the calcined coprecipitated hydroxide material. Majani *et al.* [21] found that a sintering temperature of 1500° C is not sufficient to sinter effectively 6 mol % Y_2O_3–ZrO_2 powder prepared by a sol–gel process. They attributed this behaviour to the low compactibility and the poor bonding between the spherical particles forming the powder.

The deterioration in densification properties of the sintered specimens as the yttria content increases from 4 to 10 mol % cannot be interpreted on the difference between the powders' characteristics alone. The surface areas (S_{BET}), for example, of the 4 mol % Y_2O_3–ZrO_2 and 10 mol % Y_2O_3–ZrO_2 powders are 266.2 and 239.8 $m^2 g^{-1}$, respectively. This difference in the surface areas of the powders, as well as the slight increase in the average particle size as yttria content is raised [18], is not sufficient alone to explain the difference in the densification behaviour of the two solid solutions on sintering.

The majority of the fundamental kinetic studies on sintering of stabilized zirconia [4, 22–24] have considered that the densification mechanism is controlled by lattice diffusion of the cations, and that the rate controlling species is the cation moving by an interstitial mechanism rather than by a vacancy mechanism; the controlling lattice diffusion coefficient is determined by the concentration of the stabilizing dopant. Furthermore, maxima in density values have been frequently observed at certain concentrations for each of the stabilizing oxides. Additional dopant contents are accompanied by a decrease in density. In the case of Y_2O_3, 6 to 7 mol l% has been suggested [5, 11, 16, 25] as the optimum content for maximum densification. In this study, 4 mol % Y_2O_3 has offered the maximum densification. This result suggests that the solid solution obtained by the hydrolysis of the coprecipitated hydroxides is homogeneous on an atomic scale, leading to the reduction in the amount of Y_2O_3 needed for maximum densification of firing. However, there are few data available in the literature on which to base firm interpretation for the existence of this maximum.

Activation energies of densification for the 4 and

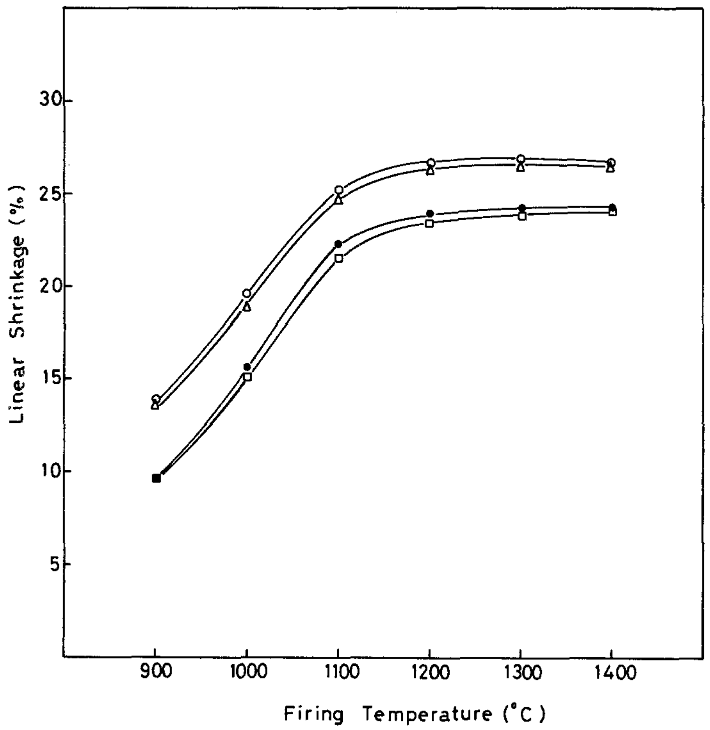

Figure 3 Per cent linear shrinkage at different firing temperatures (1 h) for yttria–zirconia compacts. For key, see Fig. 1.

10 mol % yttria–zirconia solid solutions, were calculated in the range between 800 and 1000° C. Fig. 4 shows the logarithm of density rate constant (log K) plotted against $1/T$, where K was calculated from the following equation

$$D^2 - D_0^2 = Kt$$

where $D - D_0$ is the increase in density of compacts at each temperature with time, and t is the heating time. The data in Fig. 4 show a straight line for each mix whose slope equals the activation energy value. These values are 11.5 and 19.7 kcal mol^{-1} for 4 and

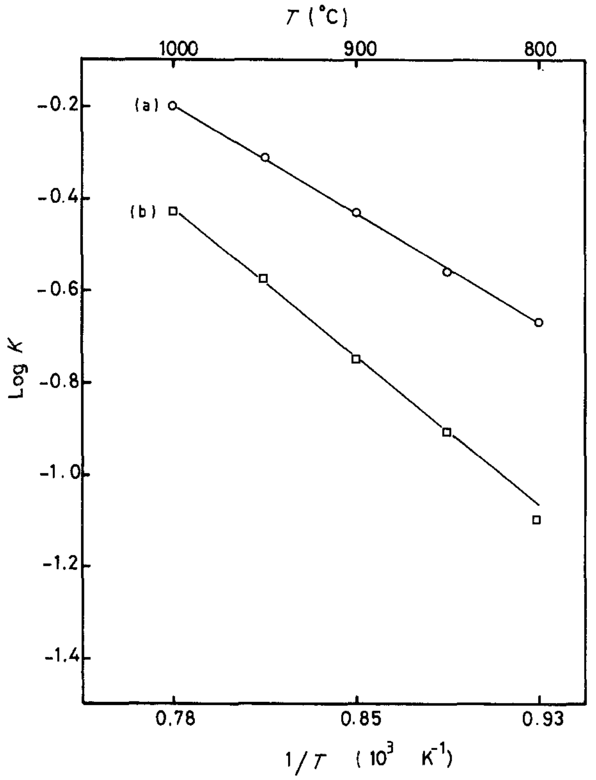

Figure 4 Logarithm of density rate constant (log K) plotted against $1/T$ for isothermal heatings for (a) 4 mol % Y_2O_3-ZrO_2 and (b) 10 mol % Y_2O_3–ZrO_2 compacts.

10 mol % yttria–zirconia solid solutions, respectively. These results confirm the role of yttria content in decreasing the sintering rate as mentioned above. The present values are lower than those obtained by Karaulev *et al.* [26] (24 and 60.5 kcal mol^{-1} for 4 and 8 mol % yttria–zirconia specimens, respectively) using traditional solid state sintering.

In order to find a possible explanation for the limited densification of the doped samples, the microstructures of the sintered pellets were examined. Fig. 5 and 6 show some of the photomicrographs obtained for the 4 and 10 mol % Y_2O_3–ZrO_2 compacts sintered at 1200 and 1400° C. From Figs 5a and b it is evident that the 4 mol %-containing compacts, when sintered at 1200° C (1 h), offered a generally fine-grained texture with somewhat larger crystals embedded within the fine-grained matrix. The microstructure shows negligible internal porosity and that porosity at grain boundaries is not significant. It seems apparent that two grain size groups coexist in the microstructure of the bodies, each having a somewhat different sintering behaviour: one is relatively large crystals ($> 10\,\mu$m) and the other is a rather continuous matrix of small grains ($< 5\,\mu$m). In such a texture, it is to be expected that the sintering would proceed differently in the two groups of crystals. The crystals in the matrix, being of different sizes, would grow at the expense of the smaller ones. This is, in fact, the case; an exaggerated grain growth is observed (Figs 5c and d) in the samples as the firing temperature increased to 1400° C. Noticeably larger grains, or groups of connected grains, are observed within the finer matrix. The developed grain growth is also accompanied by the evolution of microporosity which is different in various areas from that seen for samples fired at 1200° C. Isolated entrapped pores are also seen and are separated, with variable distances, from boundaries of the growing grains. The high-purity, fine-grained, and highly sinter-active nature of the powder used is the motive behind development of such discontinuous grain growth

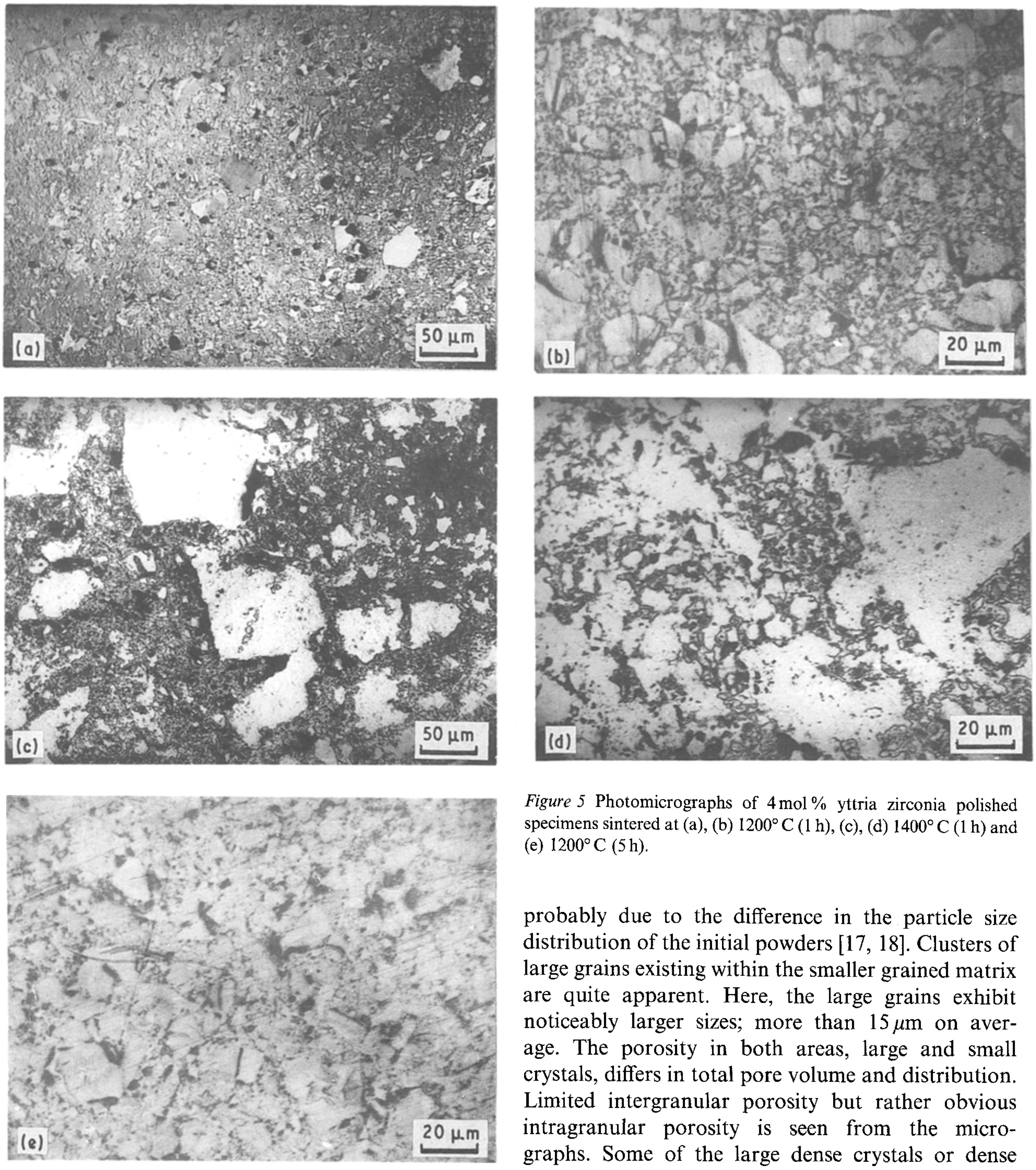

Figure 5 Photomicrographs of 4 mol % yttria zirconia polished specimens sintered at (a), (b) 1200° C (1 h), (c), (d) 1400° C (1 h) and (e) 1200° C (5 h).

on sintering at 1400° C. It is believed that the non-uniform distribution of the neighbouring areas of different crystal sizes as the bodies are sintered to 1400° C is responsible for arrest of the densification process. To substantiate the above-mentioned conclusion, the microstructure of a sample fired at 1200° C for 5 h is investigated and its photomicrograph is shown in Fig. 5e. A more or less uniform grain size appears, indicating dominance of the normal grain growth mechanism. A relative density of 96.2% theoretical is obtained with this sample. The remaining porosity appears at grain corners, indicating that further densification is possible.

The photomicrographs of the 10 mol % yttria–zirconia samples sintered at 1200° C (Figs 6a and b) display an overall grain-size increase compared with the 4 mol % yttria-containing bodies sintered at the same temperature (see Figs 5a and b). This increase is probably due to the difference in the particle size distribution of the initial powders [17, 18]. Clusters of large grains existing within the smaller grained matrix are quite apparent. Here, the large grains exhibit noticeably larger sizes; more than 15 μm on average. The porosity in both areas, large and small crystals, differs in total pore volume and distribution. Limited intergranular porosity but rather obvious intragranular porosity is seen from the micrographs. Some of the large dense crystals or dense zones, are partially attached to lenticular voids indicating that some sort of intraagglomerate sintering took place partly in the bodies [25]. These zones could be multigrained areas that were detached from the surrounding matrix in the early stages of sintering due to differential shrinkage rates between them and the matrix. It seems that the presence of two different inter- and intra-multigrained pore sizes has led to severe fluctuations of the sintering driving force across the body and poor densification resulted (91.2% theoretical) at 1200° C. This situation is not observed with the 4 mol % Y_2O_3–ZrO_2 samples and it seems that the low yttria content has inhibited the grain growth up to 1200° C, but at 1400° C the growth rates have exceeded the inhibiting effect of the stabilizing yttria.

At 1400° C (see Fig. 6c), the dense large-grained zones of the 10 mol % yttria–zirconia samples grow larger and densify better and trap pores within the

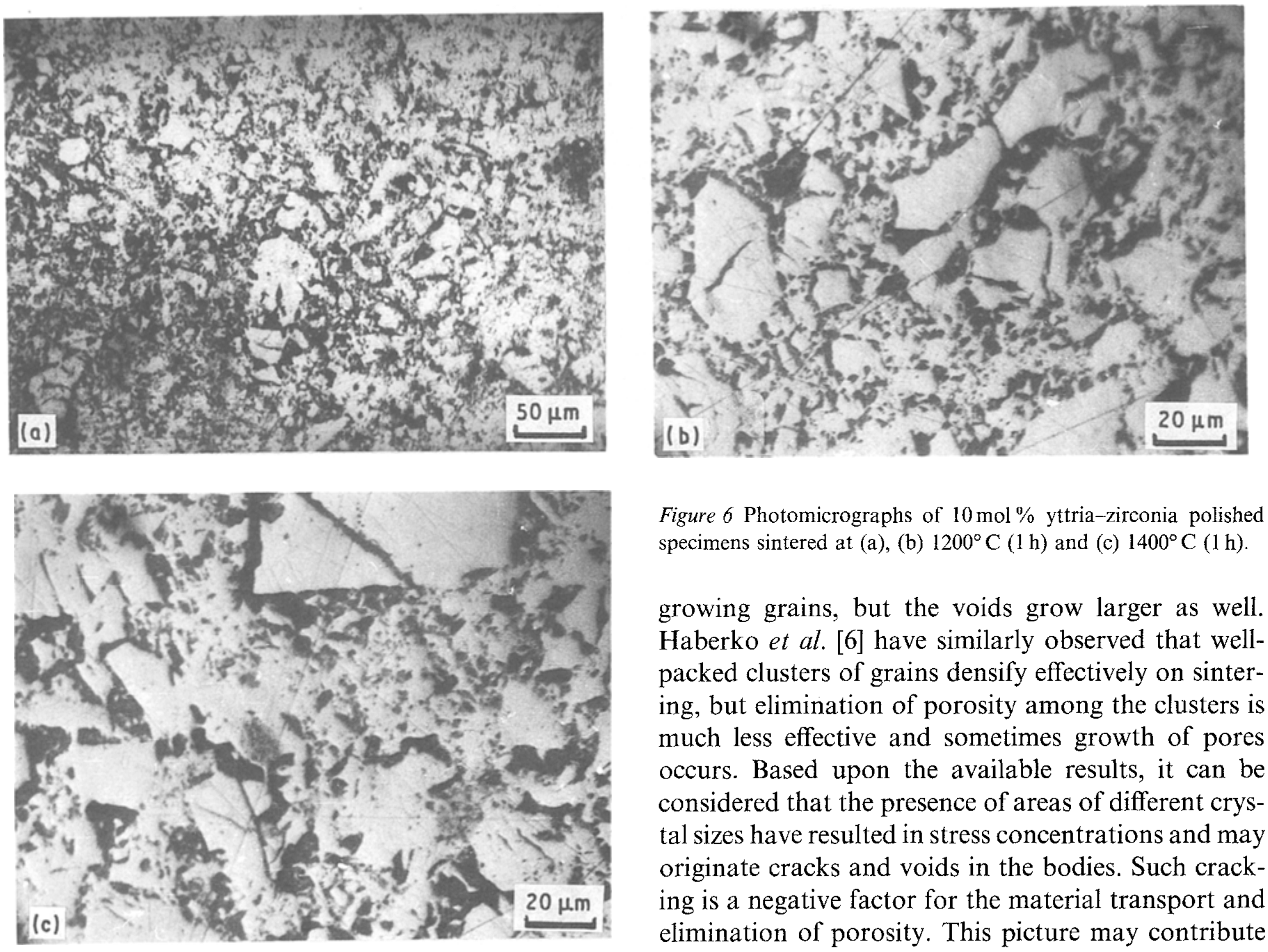

Figure 6 Photomicrographs of 10 mol % yttria–zirconia polished specimens sintered at (a), (b) 1200° C (1 h) and (c) 1400° C (1 h).

growing grains, but the voids grow larger as well. Haberko *et al.* [6] have similarly observed that well-packed clusters of grains densify effectively on sintering, but elimination of porosity among the clusters is much less effective and sometimes growth of pores occurs. Based upon the available results, it can be considered that the presence of areas of different crystal sizes have resulted in stress concentrations and may originate cracks and voids in the bodies. Such cracking is a negative factor for the material transport and elimination of porosity. This picture may contribute

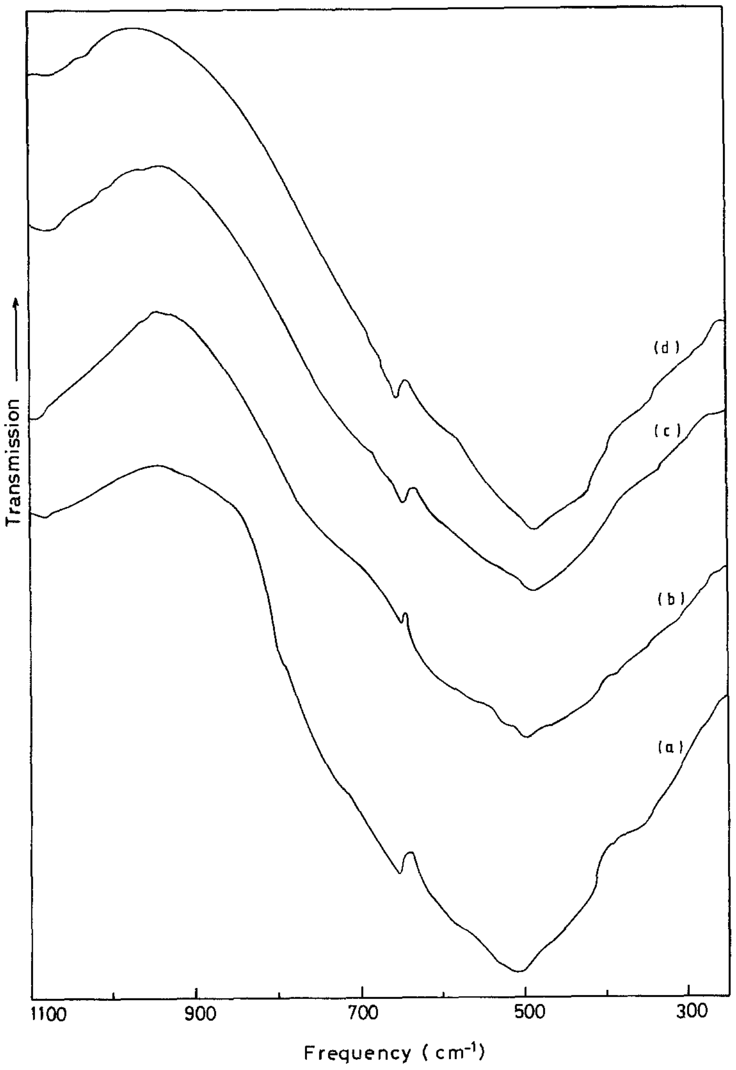

Figure 7 Medium infrared spectra of yttria–zirconia specimens sintered at 1400° C (1 h). Yttria contents: (a) 4 mol %, (b) 6 mol %, (c) 8 mol %, (d) 10 mol %.

to the explanation of the densification halt well below the theoretical density on firing and to the remaining porosity.

It was thought that the above-mentioned dense large zones (Figs 6b and c) derived from compositional inhomogeneities. However, the X-ray patterns of the sintered samples (not presented here) showed no signs of destabilization and the mixed oxide remained in the cubic phase after firing to 1400° C. In Fig. 7 the IR spectra of the sintered oxides are shown in the medium range, where the appearance of the broad absorption band at 620 and 400 cm^{-1} with its weak shoulder at 630 cm^{-1} confirms the XRD results. The absence of any microcracking or disintegration in the crystals, as manifested from the photomicrographs, also substantiates the above data.

4. Conclusions

Highly sinterable compacts have been obtained from the ultrafine homogeneous yttria–zirconia solid solution powders, prepared by autoclaving of their corresponding hydroxides. Dense bodies having 95.6% theoretical and fine-grained microstructure have been achieved at temperatures as low as 1200° C (1 h) and with 4 mol % Y_2O_3 content only. Higher temperatures and higher yttria contents are not recommended to avoid development of abnormal grain growth and clustering of large grains. Longer firing times at 1200° C may produce better sintering results.

Activation energies of densification were determined: 11.5 and 19.7 $\mathrm{kcal\,mol^{-1}}$ for 4 and 10 mol % Y_2O_3–ZrO_2 solid solutions, respectively, in the temperature range 800 to 1000° C. Such low values denote the sinter-active nature of the original powders. Increasing yttria from 4 to 10 mol % in the bodies introduced more defects into the structure of zirconia and consequently more energy is needed for densification.

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