

Sintering of heterogeneous ceramic compacts

Part 2 $ZrO_2-Al_2O_3$

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Local differences in the density, grain size or chemical composition within a sintering compact can seriously limit the final densities which can be achieved. Experiments on zirconia-alumina composites have been conducted to test the influence of such variations. Experiments are described which measure the stresses produced in the sample as a consequence of local differences in the sintering rate, and which indicate variations in the accumulated density change occurring in the composites and in single-phase standards. An estimate is given for the acceptable degree of inhomogeneity if full density is to be achieved.

1. Introduction

It is known that local variations of either grain size, density or chemical composition can limit the ability of a sintering compact to reach high density. For many zirconia systems, chemical variations will be particularly significant and much progress has been made in the preparation of powders in which a high degree of homogeneity has been achieved.

Theoretical analyses [1-5] have considered the case of local variations in density and grain size. Experimental works which study the effect of inhomogeneity on sintering are relatively few, particularly with respect to any estimation of the stresses arising from the presence of the heterogeneities [6-10]. Local variations in density, usually formed during powder preparation or during compacting procedures, give rise to differential sintering rates within a compact. Thus stresses develop, densification is retarded and structural damage can be caused. These problems tend to prevent the attainment of the theoretical density and to limit mechanical strength.

The purpose of the present experiments has been to test the importance of inhomogeneities using the example of zirconia-alumina composite ceramics in which deliberate density inhomogeneities are introduced by means of the inclusion of large alumina powder grains (Fig. 1). Abnormal grain growth, which is encountered in $Al_2O_3-Al_2O_3$ studies [10], is not a problem for the two-phase system.

2. Experimental procedure

The composites have been manufactured using Toyo Soda TZ-3Y zirconia powder (Toyo Soda Mfg Co. Ltd, Japan) to form the matrix and either recrystallized alumina (200 μm) or 140 μm poly(methylmethacrylate) (PMMA) spheres (BDH Chemical Co., UK) to form inclusions. The fine-grained zirconia matrix powder, and the coarse second-phase additions were mixed in a beaker, and stirred with an aluminium rod

by hand for about 10 min. From 0.05 to 0.15 volume fraction of the second phase was added. The volume fraction was calculated using the weight and theoretical density of the materials used: 6.05 gcm^{-3} for zirconia, 3.986 for alumina and 1.19 for the polymer spheres.

The specimens were uniaxially pressed at 60 MPa. Two 15% composites containing 200 μm alumina particles were pressed respectively at 20 MPa and at 100 MPa to test the influence of the green density. The specimens were pre-fired at 800°C for 1 h with heating and cooling rates of 2°C min^{-1} , to increase the handling strength and, where appropriate, to burn away the polymer spheres. The green densities of the specimens were then determined. The pre-fired compacts had a relative density of about 44% and dimensions of 10 mm in diameter and about 6 mm in height. Specimens containing different amounts of the second phases were prepared at the same time; several compacts were also prepared without second phase as standards. The sintering behaviour of the composites was always compared with that of specimens free from second phase and prepared at the same time. Examples of the composites containing different types of coarse second phase are shown in Fig. 1.

Sintering was performed in a differential dilatometer. To explore the effect of the sintering temperature, experiments were conducted at temperatures between 1250 and 1500°C, the heating rate being 20°C min^{-1} . Changes in dimension of the specimens during sintering were monitored with a microcomputer. The final density and dimensions were measured after sintering. The instantaneous density during sintering was then calculated from the recorded shrinkage and from the final density. The relative density of the zirconia matrix in the zirconia-alumina composite can be calculated [10] as

$$\rho_m = 1 - \frac{1 - \rho_i}{1 - \rho_i F} \quad (1)$$

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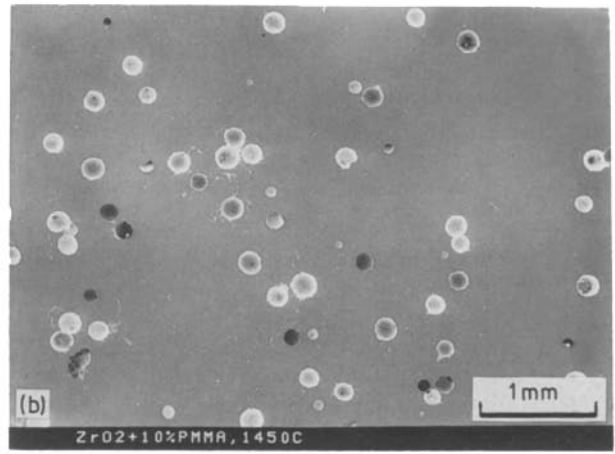
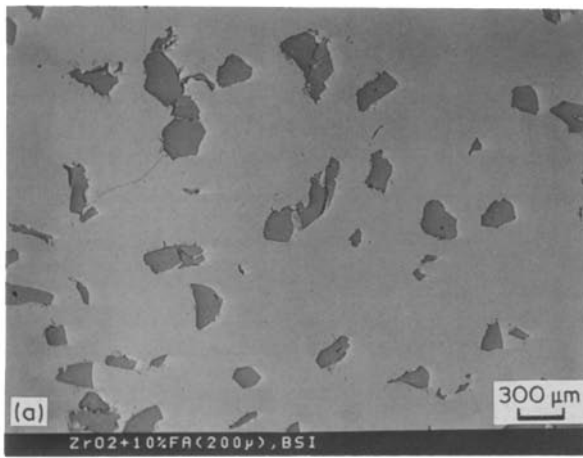


Figure 1 Micrographs of the composite systems studied. The specimens contained 10 vol% of the second phase sintered at 1450°C. The second phases were (a) 200 μm alumina particles, (b) 140 μm polymer spheres.

where ρ_m is the instantaneous relative density of the matrix, ρ_t is the instantaneous relative density of the composite and F is the solid volume fraction of alumina.

Densification rates were calculated from the respective density/time values by polynomial curve-fitting and differentiation. The densification rate can be expressed as a function of sintering stress [1, 11], and the influence of the coarse aggregates can then be represented in terms of an effective back stress which opposes the sintering stress; therefore when comparison is made at the same density between the densification rates in a homogeneous zirconia standard material and in the zirconia matrix of a zirconia-alumina composite, the normalized back stress can be estimated [10] as

$$\frac{\sigma_m}{\Sigma} = 1 - \left(\frac{\dot{\rho}_m}{\dot{\rho}_b} \right)_\rho \quad (2)$$

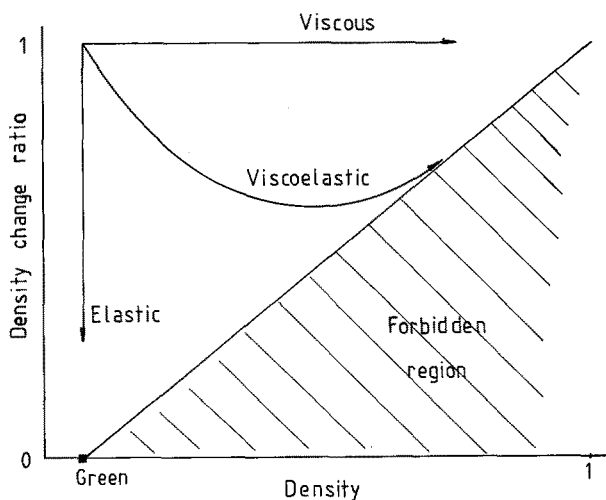


Figure 2 The possible trajectories for the density change ratio lie between two extremes. If the matrix is only capable of an elastic response to stresses arising from differences in densification rate then a back stress opposing the sintering stress accumulates very rapidly and sintering stops. If the matrix shows a viscous response, the back stress is fully relaxed and no slowing of matrix sintering is observed. Viscoelastic behaviour lies between the two. The forbidden region arises from the fact that the density of the inclusion-free samples cannot be greater than unity.

where σ_m is the effective back stress originating from the inhomogeneities, Σ is the sintering stress (the driving force for sintering), $\dot{\rho}_m$ and $\dot{\rho}_b$ are the densification rates of the matrix of the composite and of the standard specimen, respectively, and the subscript ρ means calculations based on comparison at the same density.

Trends in density with time can also be used to study any decay of the back stress [3]. The evolution of the effective back stress may be defined by the value of the “density change ratio” during sintering. This ratio at a given value of process time is the density change of the composite divided by the density change of a reference specimen (without second phase) at the same process time, that is

$$\frac{\Delta\rho}{(\Delta\rho)_{F=0}} = \frac{\rho_t - \rho_0}{(\rho_t - \rho_0)_{F=0}} \quad (3)$$

where ρ_t is the density at a given time and ρ_0 is the green density. The higher the value of the density change ratio, the lower the effective back stress. When the value is unity, the back stress has either been

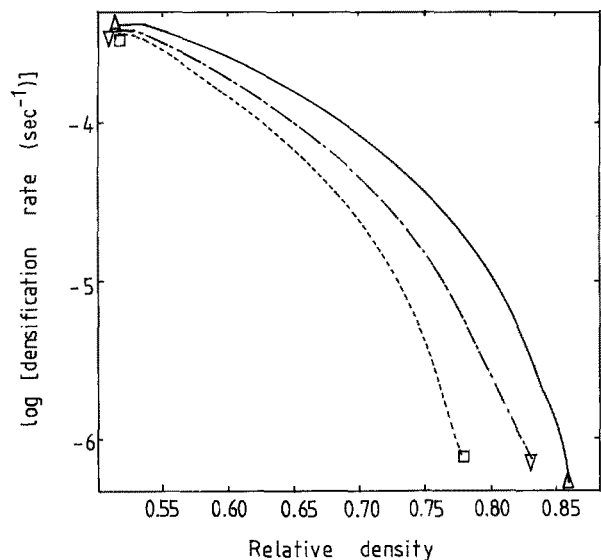


Figure 3 Variation of the densification rate with relative density of the zirconia matrix for specimens containing various amounts of 200 μm alumina particles sintered at 1250°C: (Δ , —) 0 vol%; (∇ , ---) 5 vol%; (\square , -.-) 10 vol%.

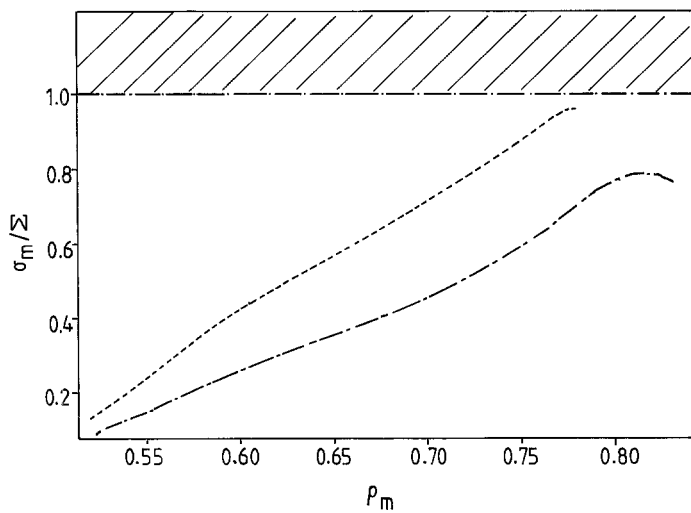


Figure 4 The variation of the normalized back stress with relative matrix density (specimens were sintered at 1250°C): (---) 5 vol %, (-.-) 10 vol %.

fully relaxed by the matrix or has had negligible significance. A schematic diagram for the form of plot expected is shown in Fig. 2.

Microstructures of the specimens were observed by scanning electron microscopy. Polished samples were heated at 1250°C for 1 h to reveal the grain boundaries.

3. Results

The densification rate of the zirconia matrix in composites sintered at 1250°C, and containing 5 and 10 vol% of 200 μm alumina particles, is illustrated in Fig. 3 as a function of the matrix density. The densification curve of a reference specimen is also shown in the figure. These curves clearly show that the introduction of the coarse alumina particles inhibits the densification of the zirconia matrix. The densification rate of the matrix is decreased substantially as the coarse alumina particles are added.

The normalized back stress of the composites can be calculated on the basis of Equation 2 and is illustrated as a function of matrix density in Fig. 4. A strong dependence is found on the amount of coarse particles added.

Evaluation of the normalized back-stress shows that it grows continuously during sintering until the point is approached where further densification is prevented (normalized back stress equal to unity). By reading the critical matrix density as the point where

an extrapolation of the back stress becomes equal to the driving force for sintering in the unconstrained matrix, it is possible to find a measure for the influence of each experimental variable, such as the volume fraction of inclusions or the sintering temperature. From Fig. 4, this critical density can be obtained by taking the intercepts of least-squares-fitted lines with the line for unit normalized back stress. Values for the composites containing different amounts of coarse alumina particles and sintered at 1250 and 1450°C are shown in Fig. 5. From the figure, it is possible to determine that about 0.09 volume fraction of coarse particle is sufficient to prevent full densification in a specimen sintered at 1450°C. For specimens sintered at 1250°C, the fraction is only about 0.02.

The zirconia powder used is rather readily sintered. When higher sintering temperatures are used, the compacts are already well densified during heating up to the isothermal temperature. Therefore, fewer data are available for evaluation in the case of samples taken to a higher sintering temperature. None the less, the critical matrix density for 10% composites containing 200 μm alumina particles is illustrated as a function of sintering temperature in Fig. 6. The figure shows that the limits for acceptable degrees of inhomogeneity are increased with increasing sintering temperature.

The density change ratio of composites containing 200 μm alumina particles or 140 μm polymer spheres

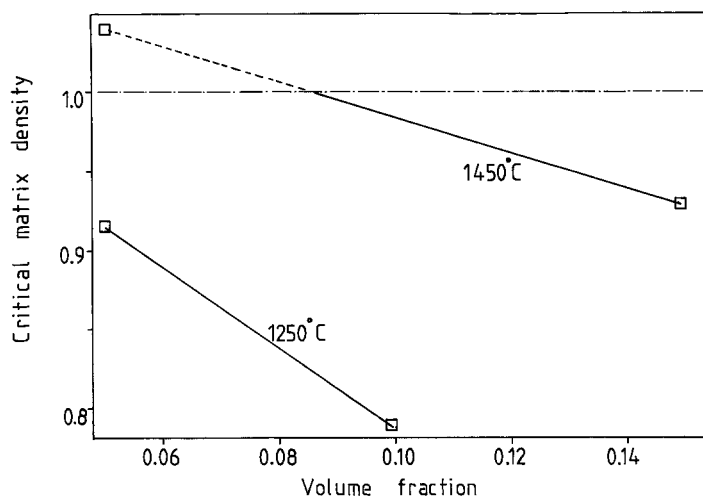


Figure 5 The variation of the critical matrix density of the specimens containing alumina particles and sintered at various temperatures as a function of the volume fraction of alumina particles.

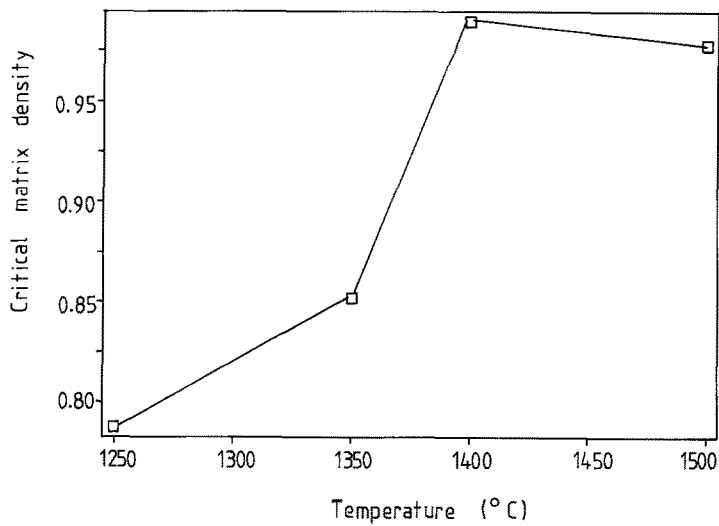
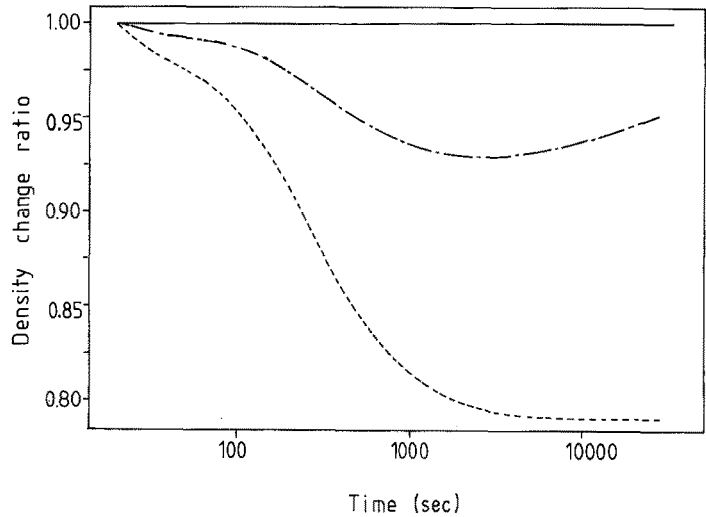


Figure 6 The variation of the critical matrix density of the composites containing 10% alumina particles with sintering temperature.

Figure 7 The variation of the density change ratio with isothermal sintering time. The specimens were sintered at 1250°C. The values are normalized to unit density change ratio at the beginning of the sintering to demonstrate the effects imposed by the dense inclusions: (—) 10 vol% PMMA, (---) 5 vol% alumina, (- - -) 10 vol% alumina.



and sintered at 1250°C is shown as a function of processing time in Fig. 7. In contrast to the zirconia-alumina system, the zirconia-polymer-sphere system displays no effective back stress. Fig. 7 shows the difference between the two systems. It can be seen that the value of the density change ratio decreases with increasing volume fraction of the inert coarse particles, this indicating an effective back stress increasing with increasing volume fraction of the coarse particles.

The effect of sintering temperature on the density change ratio is illustrated in Fig. 8. This shows that the density ratio drops in the early stages of sintering, but eventually climbs as sintering progresses, i.e. the consequences of the back stress are partially recovered for this system in the later stages of sintering.

The effect of green density, as observed in 15% composites containing 200 μm alumina particles die-pressed at various pressures, can be seen in Fig. 9. The specimens are pressed at 20, 60 and 100 MPa, the

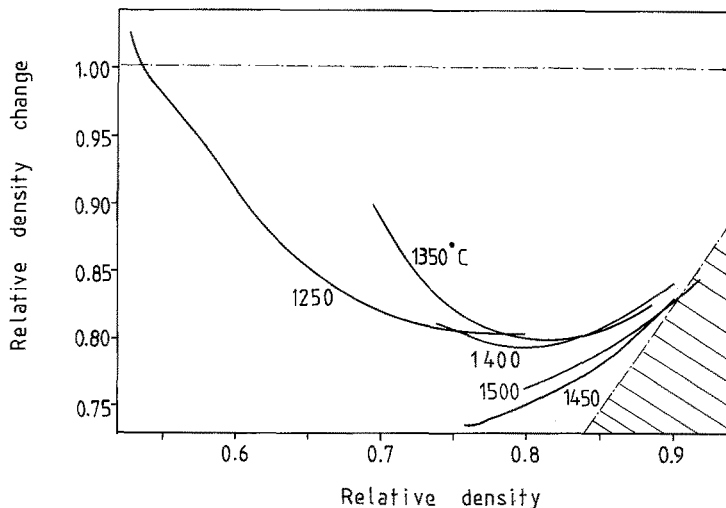


Figure 8 The variation of the density change ratio with time (represented as the attained relative density of the composites). The sintering temperature of the specimens is indicated in the figure.

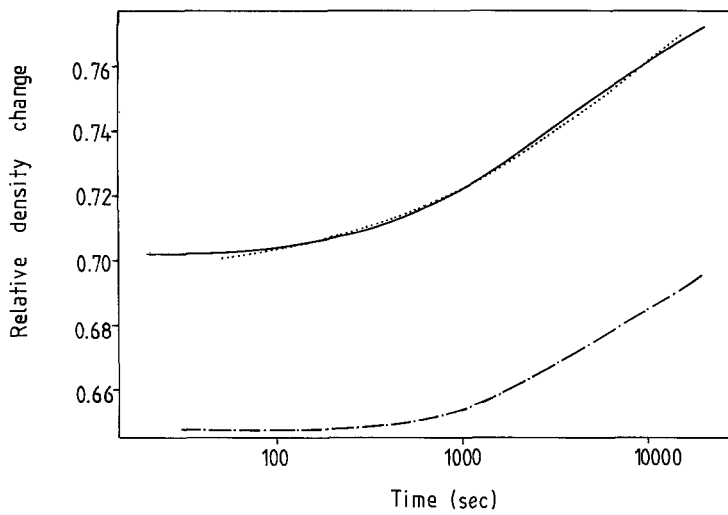


Figure 9 The variation of the density change ratio with time. The specimens were pressed at various pressures and sintered at 1450°C: (---) 20 MPa, (—) 60 MPa, (···) 100 MPa.

relative green densities being 43.0, 46.8 and 48.2%, respectively. It is noted that the lower the green density, the higher the back stress. Since similar values are found for the green densities of specimens pressed at 60 MPa and at 100 MPa, no difference is detected between the values of density change ratio for these specimens.

4. Discussion

The development and evolution of the back stresses caused by density inhomogeneities in green compacts have been evaluated in terms of two parameters, based on experimental measurements, namely the normalized back stress and the density change ratio. The method using the density change ratio is the more indirect of the two approaches, even though it offers the advantage of simpler experimental requirements (density measurement after known times); however, the direct estima-

tion of the normalized back stress (which requires dilatometry, preferably with facilities for data processing) and the predictions of the density change ratio are for the most part consistent with each other. The apparent recovery shown in Fig. 8 requires long times and occurs because the sample without inclusions has reached a final density and the composite is continuing to densify, even at the very low rates attainable under conditions where the back stress has reached more than 90% of the sintering stress value. The critical density concept (e.g. Fig. 5) is therefore to be interpreted as the point where the densification rate becomes inconveniently slow (the extrapolation to unit back stress in Fig. 4 is to this extent an approximation). Both plots can be seen to involve an asymptotic approach to an end-point density lower than the theoretical value (Figs 4, and 8).

It can be seen from Figs 5, 6 and 8 that the sintering

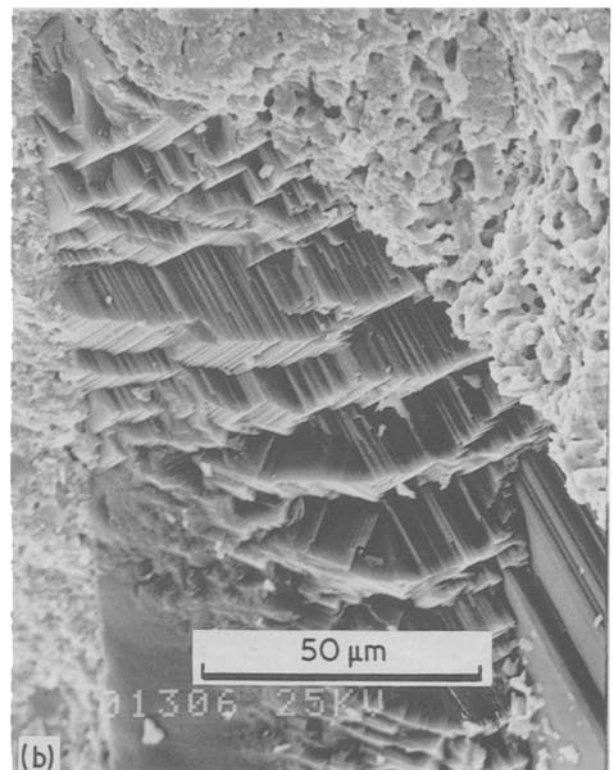
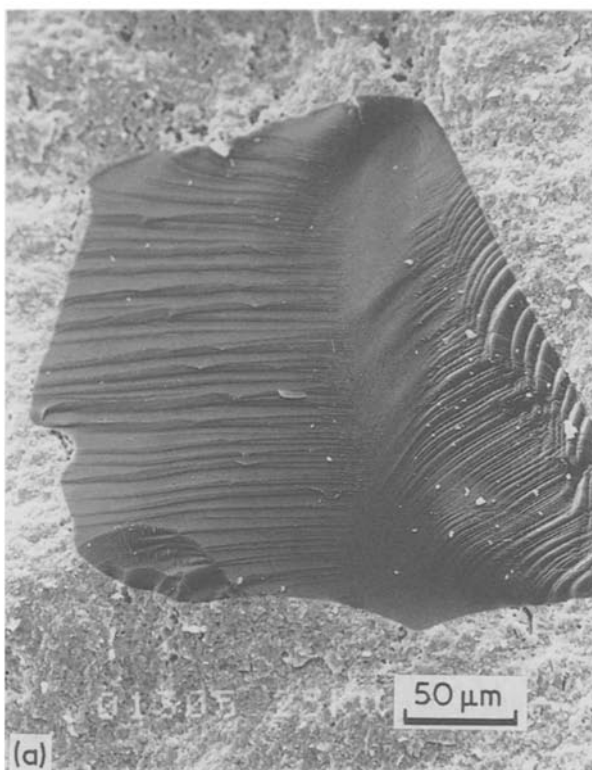


Figure 10 (a, b) Micrographs of the composite system. Extreme density variations are introduced by means of pore-free alumina grains within a porous zirconia matrix. The specimen was sintered at 1500°C for 10 h.

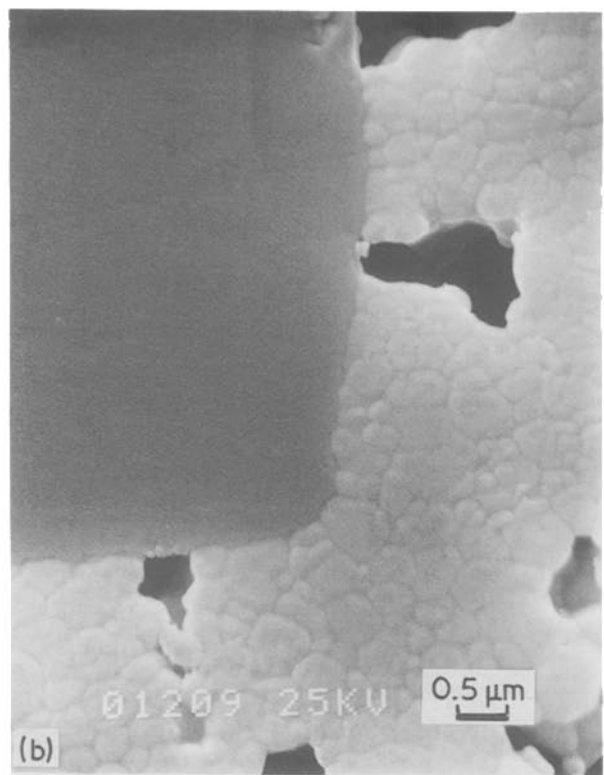
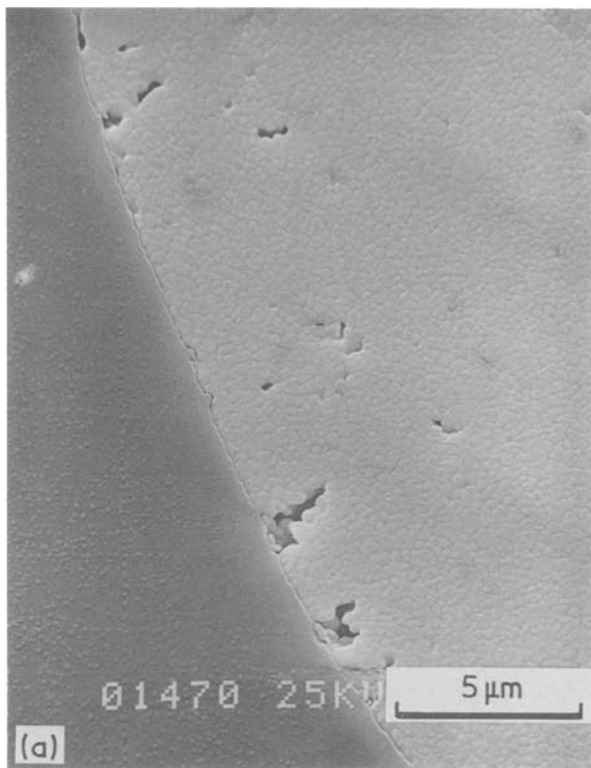


Figure 11 Micrographs of the polished surface of the composite systems. Note the cracks around the alumina particles. Specimens containing 10% 200 μm alumina particles sintered at (a) 1350°C and (b) 1450°C.

temperature plays an important role in the extent of stress development encountered during the densification of inhomogeneous ceramic compacts. The results indicate that increasing sintering temperature can decrease the ratio between the back stress and sintering stress, and can relax the back stress more effectively. This can be understood in terms of the predictions of the basic theoretical interpretation as discussed elsewhere [10].

It is worth considering the importance of the results in Figs 4, 5 and 6 for the microstructural development of bimodal compacts. The added hard aggregates give rise to back stresses which can in turn cause microstructural cracks in the compacts. Fig. 10 shows an alumina particle in a porous zirconia matrix (10 vol% of 200 μm alumina particles sintered at 1500°C for 10 h). Fig. 11 clearly shows cracks around the alumina particles in similar compacts sintered at 1350 and 1450°C. (The microstructures emphasize the role of temperature in determining the extent of matrix creep and hence of stress relaxation.)

5. Conclusions and implications

The ability of deliberately added inhomogeneities to limit the extent of densification in a zirconia matrix has been studied. The experimental results are presented either in the form of a normalized back stress or in the form of an evaluation of the density change ratio. Both methods suggest that the extent of recovery from the stresses developed by differences in densification rate within the sample is relatively limited. The results show that high sintering temperatures and high

green densities are helpful in limiting the effect of the back stress. In most practical conditions, the extent of initial inhomogeneity is much less severe than in the present experiments; however, the tendency of initial density variations to become more extreme during heat treatment [12] and the recognised problems of attaining chemical homogeneity in doped zirconia systems emphasize the value of efforts to obtain the greatest powder uniformity and green compact uniformity during processing.

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