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Sintering of heterogeneous ceramic compacts

Part 1 Al_2O_3-Al_2O_3

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The sintering behaviour of alumina powder compacts containing inclusions has been studied. The densification rate is significantly retarded by the addition of coarse, dense, fused alumina particles. The influences of inclusion volume fraction, of inclusion size, of matrix density and of temperature on the reduction in densification rate are reported. A method is proposed for the evaluation of an effective "back stress" which opposes densification and which is generated by the presence of the inclusions.

1. Introduction

A common objective in the preparation of ceramic products is the attainment of high density during the heat treatment process. It is now recognized that inhomogeneities – local variations of chemical composition, grain size or density – within the green compact can limit the extent of densification attained.

During powder preparation, for example in a calcination step, or during compacting procedures, inhomogeneities such as agglomerates or non-uniform particle packing can readily occur. These constitute sources of local variation in density. Such differences in density from region to region cause local variations in densification rate, thus giving rise to stresses within and between the regions. If, for example, a powder compact contains relatively dense inclusions, the shrinkage of the matrix during sintering and the resulting constraint imposed by the inclusions will generate stresses in the matrix, in the inclusions, and at the inclusion–matrix interface. These stresses have been given the overall term "back stresses". Unless the stresses can be relaxed in the matrix, they will cause a fall in densification rate and structural damage, which may even remain after densification. Some investigators [1, 2] have shown that the removal of inhomogeneities, especially of hard aggregates, brings about improved final densities and mechanical properties.

Recent emphasis [3] has been placed on ceramic matrix composites incorporating dense fibre or whisker inclusions as an effective option for the improvement in toughness of ceramic products. The growing interest in such composites, where density variations are an intrinsic feature of the unfired structure, emphasizes the need for an understanding of the densification behaviour of non-uniform powder compacts.

Several initial studies, using either theoretical [4–8] or experimental [9–14] approaches, have explored the nature of the stresses developed in inhomogeneous systems. Evans [4] has developed an analysis for a spherical inhomogeneity within a matrix and used formalisms for creep and sintering dominated by grain-boundary diffusion to obtain solutions for the stress. Raj and Bordia [5] have considered a spherical heterogeneity in a viscoelastic medium, and evaluated the resulting transient and steady-state stresses. Their analysis suggests a parameter, the ratio of the shear creep rate to the densification rate in the porous body, which can be used as a measure of the degree of stress development likely during the densification of a non-uniform compact. Hsueh *et al.* [6] have approached the problem using the constitutive laws for a viscoelastic body coupled with phenomenological expressions for the required materials response parameters to evaluate the stresses by numerical analysis. A more recent analysis [7] has proposed a simplification of the stress calculations by noting the relatively rapid relaxation of the stresses in comparison with the rate of stress accumulation. In common with the other treatments, a measure of the ability of a system to surmount problems arising from inhomogeneity is seen to lie in the ratio η_d/η_c where η_c, η_d are the respective viscosities for the creep and densification processes in the system. The most recent study [8] has suggested that the stresses arising from these treatments are generally too small to account for the severe reductions in densification rate encountered.

Experimental observations of non-uniform sintering have been made by Lange and Metcalf [9] (Al_2O_3–ZrO_2), by Kellet and Lange [10] (Al_2O_3), by De Jonghe and co-workers [11–13] (ZnO–SiC, glass–SiC) and by Ostertag [14] (SiC whiskers in Al_2O_3). Kellet and Lange [10] prepare two specimens with different green densities and then measure the load required to force the specimen with high green density to densify as fast as the sample with low green density. De Jonghe and co-workers [11–13] introduce hard agreegates into powder compacts and measure the reduction in densification rate and final density. Their results show that the densification behaviour of the

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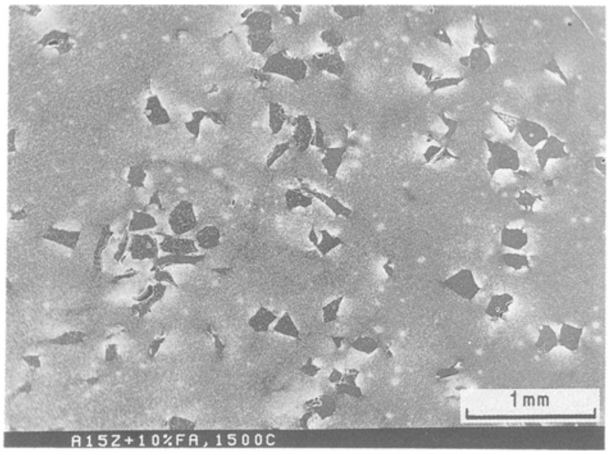

Figure 1 Micrograph of composite containing 10 vol % of fused alumina, sintered at 1500° C.

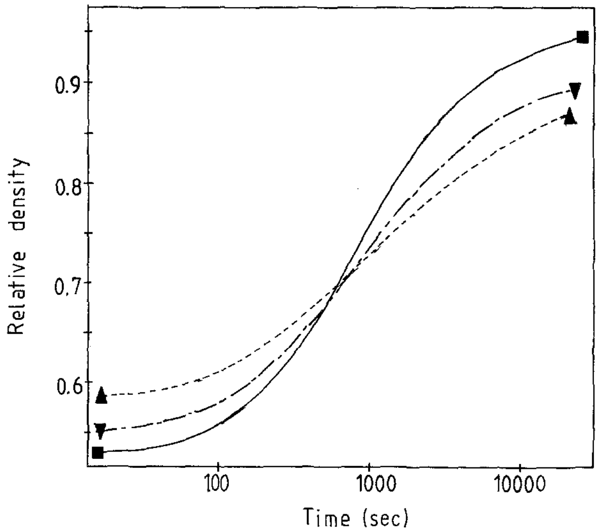

Figure 2 Variation of the density of specimens containing various amounts of 200 μm alumina particles, sintered at 1500° C, with the log isothermal sintering time: (□, ——) 0 vol %; (▼, - - -) 5 vol %; (▲, - - -) 10 vol %.

non-uniform powder compacts deviates considerably from the simple rule of mixtures. Ostertag [14] has provided direct evidence for the reality of stress development during sintering.

The present study describes inhibition of densification by deliberate introduction of coarse particles and proposes a simple method to evaluate the development of "back stress" arising from the existence of hard inclusions. The relative significance of inclusion volume fraction and inclusion size and of other processing conditions (matrix density, temperature) is examined.

2. Experimental procedure

The system studied was a fine-grained alumina with inclusions of coarse fused alumina. Fine, high-purity alumina powder* with mean size about 0.5 μm, was used as the matrix material. Coarse and dense fused alumina grains, classified to a narrow size range around 200 μm and washed in hot acid (HNO_3:HCl = 1 : 1) for 60 h, acted as the deliberately introduced inhomogeneities.

The fine-grained alumina powder and the coarse particles were mixed together in a beaker, and stirred with an aluminium rod by hand for about 10 min. One example of the distribution of 10% fused alumina in the fine-grained alumina matrix is shown in Fig. 1; this material was sintered at 1500° C for 10 h and reached a relative density of 80%. Since good mixing was difficult to obtain, a relatively small fraction of coarse particles was used to avoid any tendency of the coarse particles to touch during sintering. Different volume fractions, 2.5 to 15% of fused alumina, were mixed with the fine powder. The volume fraction was calculated on the basis of the known weights and a theoretical density of 3.986 g cm^{-3}.

The specimens were all die-pressed at the same pressure of 100 MPa. The size of the compacts was 1 cm in diameter and about 0.6 cm in height. The compacts were all prefired at 800° C for 1 h with heating and cooling rates of 2° C min^{-1}, in order to increase the green strength of the specimens. The green densities of the compacts were determined from the dimensions and weights. The relative green density of the specimens ranged from 41 to 45%. The compacts were sintered at temperatures from 1300 to 1550° C in a dilatometer. The specimens were heated at 25° C min^{-1} from 300° C to a point 400° C below the desired sintering temperature; they were then maintained at this temperature for 10 min to equilibrate the system, before being heated at 20° C min^{-1} to the sintering temperature. The linear shrinkage of specimens was monitored continuously by a microcomputer. The final density was measured from the final dimensions, the density of the compact at any earlier time being then determined from the final density and the recorded shrinkage.

For the fine-grained alumina–fused alumina system, it may be assumed that the fused alumina is completely dense and chemically inert to the fine-grained matrix. As porosity is entirely within the fine-grained alumina matrix, the density of the matrix can be calculated as

$$\varrho_m = 1 - \frac{1 - \varrho_t}{1 - f} \qquad (1)$$

where ϱ_m is the instantaneous density of the matrix, ϱ_t is the instantaneous relative density of the composite, and f is the instantaneous volume proportion of the fused alumina. Since the volume of the composite continually decreases during sintering, the volume proportion of fused alumina increases. When the specimen reaches full density, the volume proportion will equal the solid volume fraction, F, so that

$$f = F\varrho_t \qquad (2)$$

The densification rates of both the composite and the fine-grained matrix fraction of the composite are calculated from the changes in compact density and in matrix density with time, respectively.

The microstructures of polished surfaces were observed by scanning electron microscopy (Hitachi S-700 and Camscan 3-30 BM). Etched microstructures

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*A15Z: impurities (p.p.m.) Ca < 3, Cr < 2, Cu < 1, Fe < 5, Ga < 17, Mg < 1, Mn < 1, Mo < 5, Na < 25, Ni < 3, Pb < 2, Si < 35, Ti < 3, V < 3; Criceram, Courberoie, France.

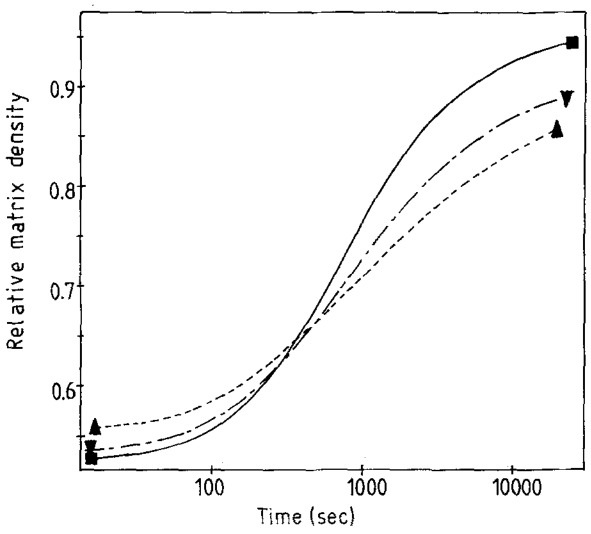

Figure 3 Variation of the matrix density of the specimens in Fig. 2 with the log isothermal sintering time: (■, ——) 0 vol %; (▼, - - -) 5 vol %; (▲, – – –) 10 vol %.

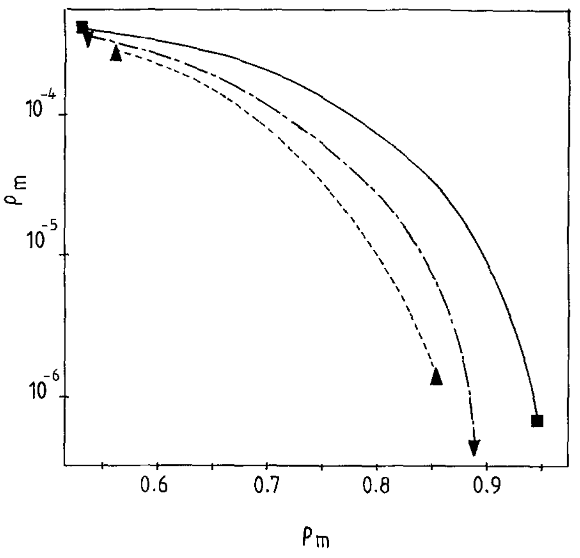

Figure 4 Variation of the densification rate of the specimens in Fig. 3 with matrix density: (■, ——) 0 vol %; (▼, - - -) 5 vol %; (▲, – – –) 10 vol %.

were prepared by thermal etching, the polished specimens being heated at 1350° C for 1 h.

3. Results

The relative density of composites containing 0, 5 and 10% fused alumina is shown as a function of isothermal sintering time in Fig. 2. The three compacts were sintered at 1500° C. It is noted that, as the fused alumina is added, the starting density is slightly increased, but the final density is drastically reduced.

The relative density of the fine-grained matrix phase in the composites, shown in Fig. 2, is shown as a function of time in Fig. 3. The result from a compact without fused alumina is also shown for reference. As shown in Fig. 3, the fused alumina does not affect the starting density of the matrix, but the final matrix density is dramatically decreased with increasing fused alumina content. The final relative density of the matrix in the 5% and 10% composites is 5.9% and 9.4% less than the relative density of compacts without fused alumina, respectively.

The most direct presentation of the influence of the inclusions on densification behaviour is to compare the densification rate of the composite at a given matrix density with the densification rate found in an inclusion-free sample of the same density. The two rates can be readily taken from plots of the densification behaviour as a function of matrix density as shown in Fig. 4. At a given value of ϱ_m, the ratio $\dot{\varrho}_m/\dot{\varrho}_b$ can be evaluated where ϱ_m is the matrix density in the composite and ϱ_b is the density of the inclusion-free sample.

Using this procedure, the influence of the inclusions on sintering behaviour can be evaluated as a function of matrix density as in Fig. 5. Notable features are (i) that the impact of the inclusions becomes progressively more severe as densification proceeds, (ii) that higher volume fractions of inclusion phase cause more severe reduction in the observed rates, and (iii) that the compact densification rate can fall to zero before full matrix density is achieved.

The influence of inclusion volume fraction can be shown for given values of matrix density as in Fig. 6. These data are for 1500° C and are taken at 75% of the theoretical density. Larger volume fractions cause progressively serious restriction to the observed rates.

The size of the inclusions relative to the matrix particle size is varied in the data shown in Fig. 7. Two features are (i) that inclusions even as little as six times the matrix grain size are capable of causing severe

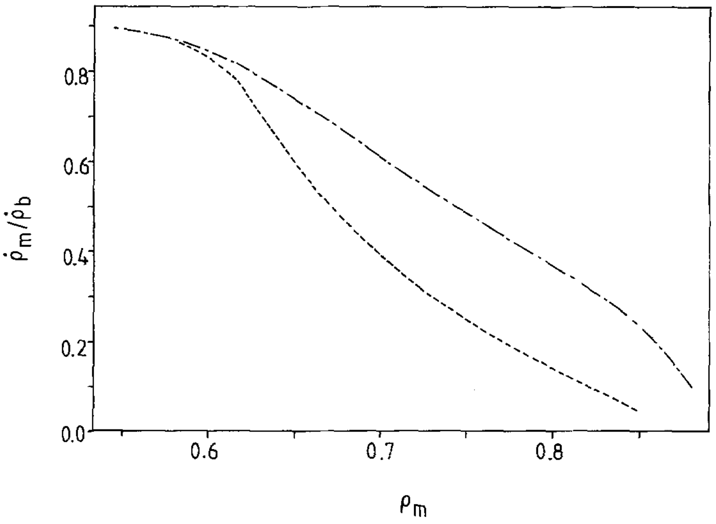

Figure 5 Variation of the densification rate ratio (the ratio of the densification rate of the matrix in the composite to that of the inclusion-free sample) of the specimens in Fig. 4 as a function of matrix density: (- - -) 5 vol %, (– – –) 10 vol %.

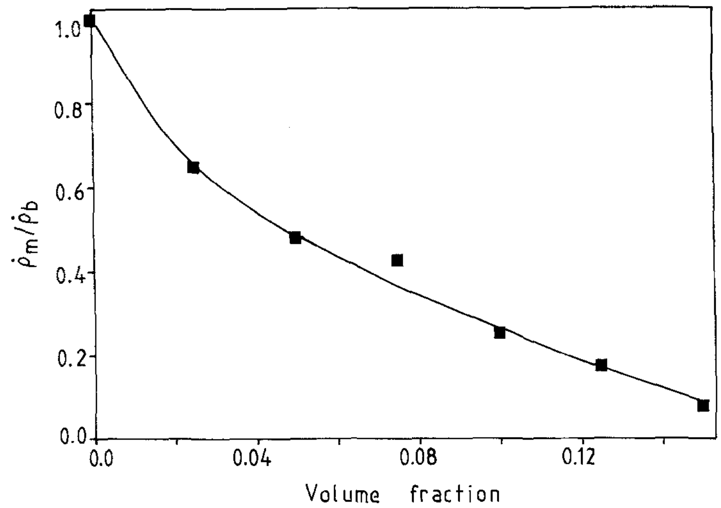

Figure 6 Variation of the densification rate ratio at 75% matrix density with volume fraction of inclusions (1500° C).

reduction in densification rate in samples with a matrix density of 75%, and (ii) that the severity of the effect is then reduced as the inclusion size further increases, i.e. as the number density of inclusion centres is reduced (constant volume fraction).

The microstructure of a polished and thermally etched surface is shown in Fig. 1. The compact, containing 10% fused alumina, has been sintered at 1500° C for 10 h, and the relative density is 80%. The fused alumina particles are seen to be angular and relatively well dispersed. The contrast in the micrograph has been intentionally exaggerated to show the density distribution within the composite. The density distribution of the matrix is found to be inhomogeneous, the white regions in the figure being less dense regions found around the fused alumina particles. This local effect arises most probably from initial packing problems around the angular particles in die-pressing.

A polished but unetched surface of a 10% composite is shown in Fig. 8. Fig. 8a shows the microstructure around a single fused alumina particle. Fig. 8b shows at higher magnification the microstructure at one area near the fused alumina particle of Fig. 8a. The density shown in the figure is much less than the relative density of the specimen, namely 80%. The initial structural fault has intensified as sintering has proceeded [15]. It is also noted that the matrix density near the angular corner of the particle is higher than elsewhere, and that abnormal grain growth can be observed in these regions. During sintering, the matrix applies a compressive stress on the hard inclusions, and initial density variations become more pronounced. That big grains provide nuclei for abnormal grain growth has been commonly recognized. Fig. 9 shows one example observed in this study (5% composite, sintered at 1500° C to a relative density of 84%).

4. Discussion

Densification rates during sintering have been related in the literature to a sintering stress [16], or sintering potential [6]. This provides a convenient normalizing parameter for discussion of the severity of problems caused by the presence of the inclusions. For a powder compact containing no second-phase particles, the initial density is ϱ_0 and the instantaneous density during sintering is ϱ_b. Then the densification rate during sintering may be expressed in the form of the generalized equation

$$\dot{\varrho}_b = KF(\varrho_0, \varrho_b, G_b)\,\Sigma_b \qquad (3)$$

where K is a kinetic constant and $F(\varrho_0, \varrho_b, G_b)$ is a function of the initial density, the instantaneous density and the instantaneous grain size G_b; the specific function depends on the dominant sintering mechanism involved in the sintering process. Σ_b is the sintering stress or driving force responsible for sintering.

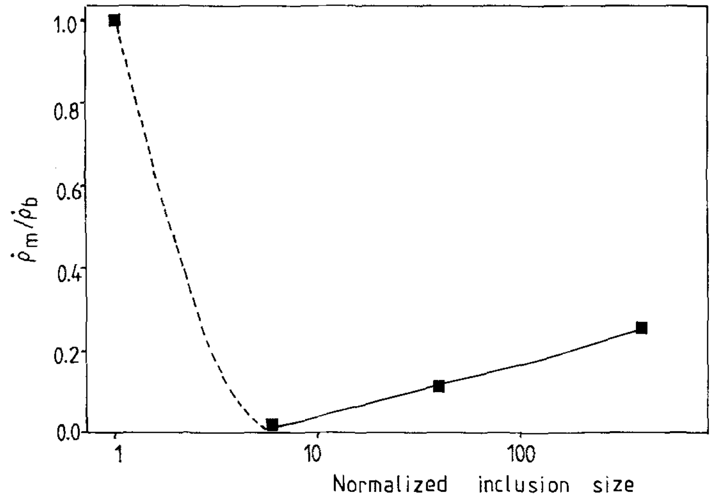

Figure 7 Variation of the densification rate ratio at 75% matrix density in composites containing 10 vol % of fused alumina as a function of normalized inclusion size (1500° C).

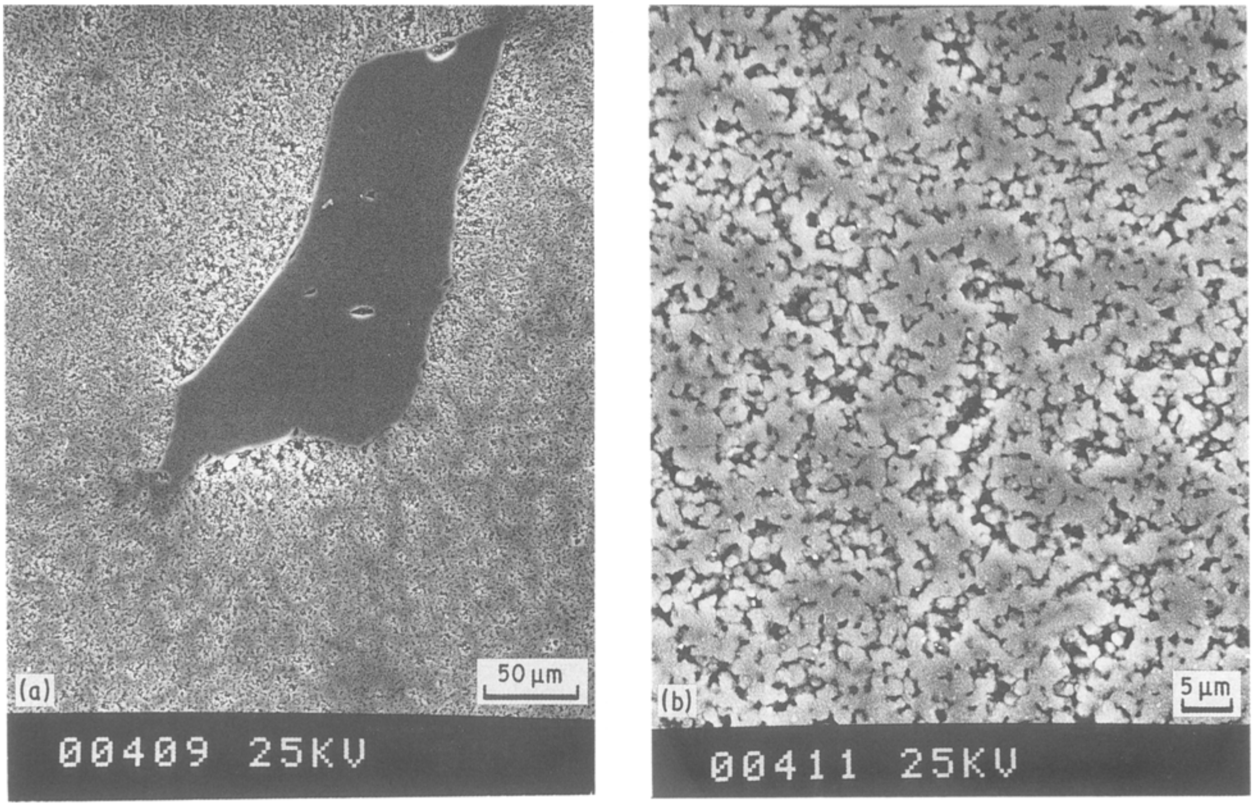

Figure 8 (a, b) Extreme density variation around a pore-free coarse grain.

For a compact containing high-density inhomogeneities, the initial matrix density is found (Fig. 3) to be ϱ_0; the instantaneous density of the matrix is ϱ_m. The effect of the hard aggregates in decreasing the sintering rate can be represented in terms of a back stress, σ_m, opposing the sintering stress. For the systems studied, assuming that the matrix grain size, for given conditions of composition and temperature, depends only on the instantaneous matrix density, $G_b = G_m$, where G_m is the grain size of the fine-grained matrix. The densification rate of the fine-grained matrix may then be expressed as follows [11-13]:

$$\dot{\varrho}_m = K'F'(\varrho_0, \varrho_m, G_m)(\Sigma_m - \sigma_m) \qquad (4)$$

where the subscript m represents the matrix, the other terms having the same meaning as in Equation 3.

Comparing, at a given matrix density, the densification rate of a compact without fused alumina with that of the fine-grained matrix in a composite, and assuming that the effect of the hard inclusions on the matrix is uniformly distributed, then $K = K'$, $F = F'$ and $\Sigma_b = \Sigma_m = \Sigma$, so that

$$\frac{\sigma_m}{\Sigma} = 1 - \left(\frac{\dot{\varrho}_m}{\dot{\varrho}_b}\right)_{\varrho,\varrho_0} \qquad (5)$$

where the subscripts ϱ and ϱ_0 mean that the two densification rates have been compared at the same density, and that the two specimens have been sintered from the same green density. The term σ_m/Σ is then a normalized back stress, i.e. a single term by which the influence of the inhomogeneity can be represented.

As well as supporting the value of the relative densification rate as a measure of the inhomogeneity problem, this approach indicates as in Fig. 10 the rise in back stress as densification proceeds, and the absence in this study of any stress diminution as has been suggested in the theoretical models for longer sintering times [6].

Although theoretical treatments show substantial differences in the approach adopted in evaluating the

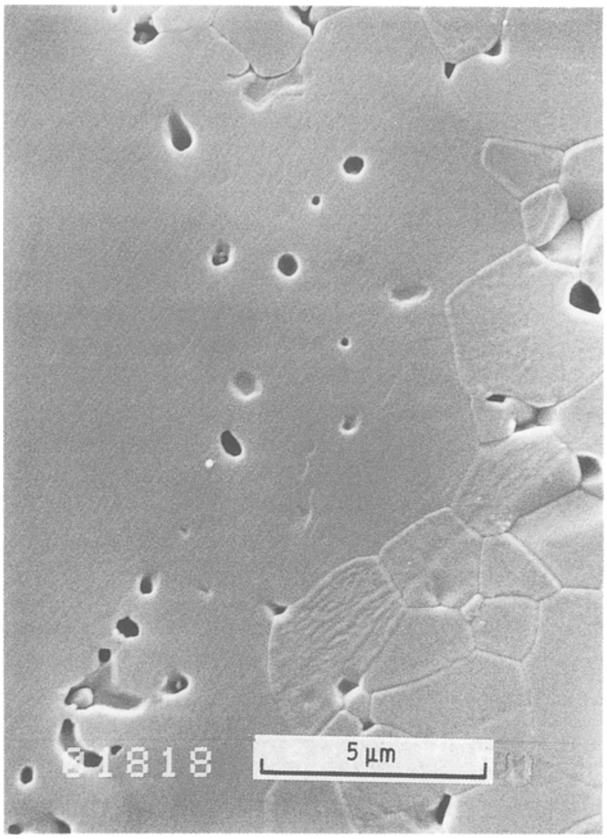

Figure 9 Abnormal grain growth at an angular corner of a coarse grain.

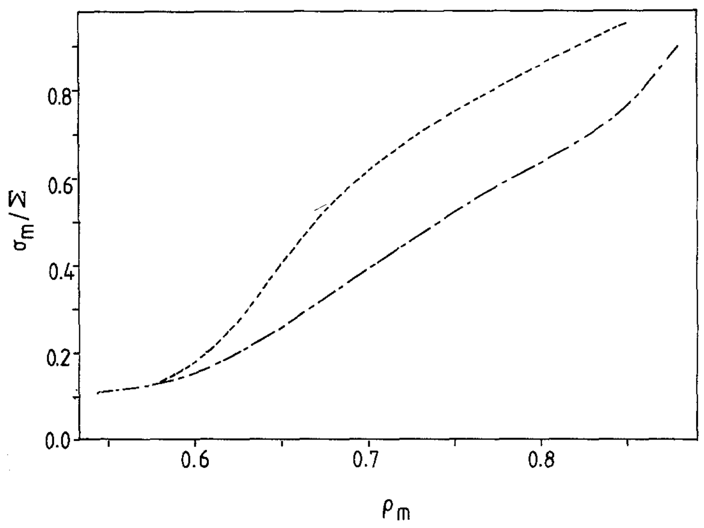

Figure 10 Variation of the normalized back stress with matrix density for the specimens in Fig. 3: (- - -) 5 vol %, (— — —) 10 vol %.

stresses, the various treatments stem from a common view of the viscoelastic origin of the stresses.

In the simplest approach, the solid is treated as a Maxwell system of series spring and dashpot [6]. The time dependence of the stress following imposition of unit stress, $\bar{\varepsilon}$, on such a system is

$$k = \left[G \exp\left(-\frac{G}{\eta}t\right)\right]\bar{\varepsilon} \qquad (6)$$

where G a modulus term, η the viscosity and t the time following imposition of the load. The accumulating hydrostatic strain arising from the unconstrained differences in shrinkage rate between adjacent regions in the composite is

$$\varepsilon = \int_0^t \Delta\dot{\varrho}\,\mathrm{d}t \qquad (7)$$

where $\Delta\dot{\varrho}$ is the difference in rates that would occur in the absence of interactions, i.e. back stresses. Force balance between the matrix and inclusions requires that

$$\bar{\sigma}_p f = -\bar{\sigma}_m(1-f) \qquad (8)$$

where $\bar{\sigma}_p$, $\bar{\sigma}_m$ are the mean stresses in the inclusion and matrix phases, respectively, and f is the instantaneous volume fraction.

Combining equations, the matrix stress takes the form

$$\sigma_m = \frac{4f}{1-f}\int_0^t G\,\Delta\dot{\varrho}\exp\left(\frac{-G(t-n)}{\eta}\right)\mathrm{d}n \qquad (9)$$

for solid inclusions. This stress is then to be compared with the experimentally derived form given in Equation 5.

From data such as those in Fig. 10 or in Fig. 5, it is possible to estimate for a given volume fraction of inclusions the matrix density at which the back stress rises to the point where it fully offsets the sintering stress, or at which the matrix densification rate in the composite falls to zero. This value of the matrix density is shown as a function of volume fraction in Fig. 11. The implication from the figure is that inclusion loadings above the indicated value (F at a matrix density of unity) will prevent the attainment of full density in the compact under the given conditions (1500° C).

A major issue then becomes the search for process improvements which allow an increase in the value of this critical matrix density. One factor is the temperature where, as shown in Fig. 12, higher temperatures reduce the severity of the problem. On the basis of a simple extrapolation, a temperature of 1700° C would be needed to achieve full density when 10 vol % inclusions are present.

This can be understood in terms of Equation 9. Remedies for the inclusion stress can be seen as comprising the following:

(a) Reduction in $\Delta\dot{\varrho}$, i.e. elimination of inhomogeneity from monolithic powder compacts in the form of

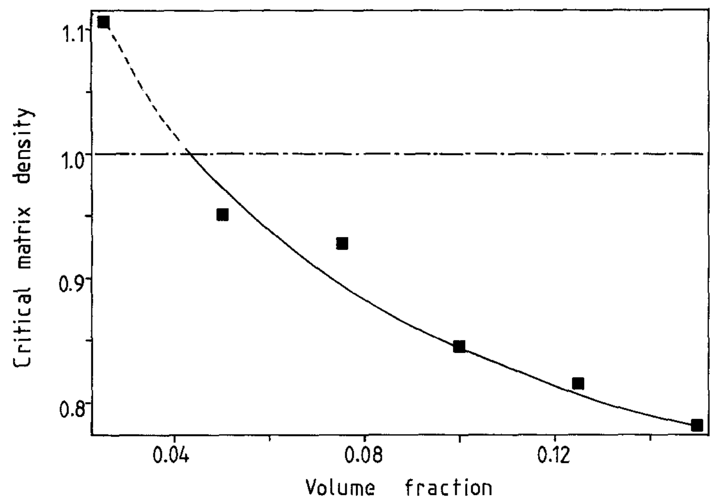

Figure 11 Variation of the critical matrix density with volume fraction of inclusions for composites containing 200 μm fused alumina (1500° C).

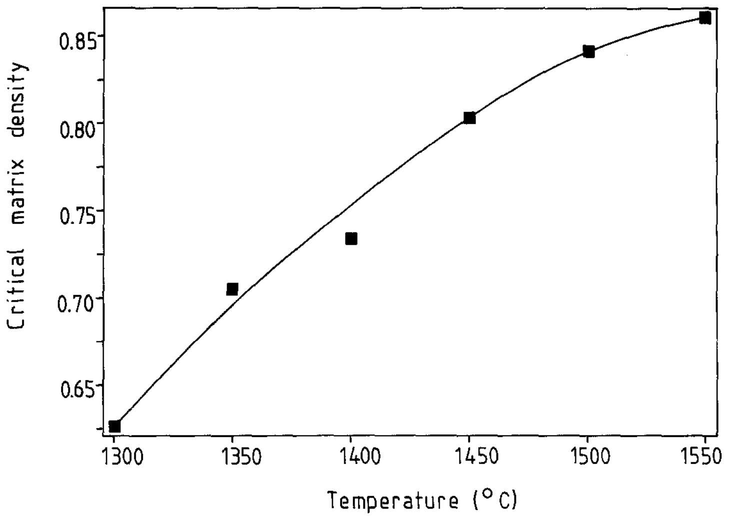

Figure 12 Variation of the critical matrix density with sintering temperature for composites containing 10 vol % of 200 μm fused alumina.

packing differences, grain size differences or compositional differences that would cause local variations in densification rate. For composite systems, the problem is intrinsic to the use of different phases and solutions must be found in additional treatments, say in the use of fugitive coatings on fibres which induce a virtual shrinkage which can be matched to that of the matrix.

(b) Increase in the stress relaxation rate, i.e. reduction in the matrix viscosity. For diffusional creep processes, this viscosity is given by a term of the form

$$\eta = \frac{L^n kT}{D\Omega}$$

where L is the matrix grain size, Ω the atom volume and D the process diffusion coefficient. Consequently benefit is to be seen in small grain size [17], and in diffusion enhancement either by the presence of a boundary liquid phase or as in Fig. 12 by temperature increase.

(c) Increase in the sintering stress Σ. Since the densification rate responds to $(\Sigma - \sigma_m)$, the use of techniques such as hot isostatic pressing which raise Σ can be seen as beneficial. This approach has been much adopted in industry for the resolution of the inhomogeneity problem for composites.

5. Conclusions

The existence of inhomogeneities in a given microstructure is a basis for differential sintering rates and for stress development within the compact. To alleviate the problem in non-uniform compacts, there are two approaches that can be adopted, namely first to increase the sintering stress, and secondly to decrease the back stress.

The use of a fine and active powder as matrix material is one method to increase the sintering stress, as is the use of pressure sintering.

To decrease the back stress, mechanisms for the promotion of stress relaxation are to be sought. On the basis of matrix relaxation by diffusional creep processes, benefit is expected from higher temperatures and from fine matrix grain size. Benefits have been found in the present study from higher temperatures.

The main conclusion from the work is the indication of the severity of the inhomogeneity problem. The absence of explicit stress release and the notable influence of inclusions even at the 3 μm size level (0.5 μm matrix grain size) underlines the benefits to be obtained from efforts to achieve high degrees of homogeneity in the preparation of the prefired green structure.

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