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Publication Date

1987-11-01

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LIQUID PHASE SINTERING OF $\text{MgO-Bi}_2\text{O}_3$

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Introduction

Liquid phase sintering is often invoked to enhance the densification rates of ceramic or metal powder compacts and has been studied experimentally and modeled numerous times. It can also be useful in producing high density particulate composites without the need for applying stress. The recently developed technique of loading dilatometry^{1,2} which combines densification measurements with simultaneous, low-load uniaxial creep measurements can assist in clarifying some aspects of the liquid phase

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sintering process.

A variety of theoretical approaches, mostly based on the initial treatment of Kingery and his coworkers^{3,4} have been formulated. The importance of the rearrangement of the particles under the action of the liquid surface tension and the solution-precipitation mechanism have, since then, been considered essential features of the liquid phase sintering mechanisms. In addition, the simultaneous flow of the liquid phase from between the grain boundaries and its contribution to the overall densification rate has been considered recently by Marion et al.²¹

The interparticle forces resulting from liquid bridges, and driving the densification, have been examined by several workers. Consideration of the detailed geometry of the liquid menisci has provided calculated values of two-particle interaction forces as a function of wetting angles and volume fraction of liquid.⁶⁻⁹ A quantitative treatment of the redistribution of the liquid during densification is more problematic since this depends strongly on the initial particle packing which is difficult to quantify. Sequential pore filling has been considered, for example by Yoon^{10,11} et.al. and by Kaysser and his collaborators⁹. A two-dimensional model has been considered recently by Shaw¹². His treatment indicated sequential pore filling, and the possibility that the average liquid pressure might stay relatively constant during part of the pore filling process, or vary in accordance with the pore radius of the sequentially filled pores. In this latter respect, the driving force for densification, after the initial rearrangement process, should be expected to evolve in a manner qualitatively similar to that of solid state sintering. It should then also be possible to define the sintering stress¹³ Σ/Φ , the equivalent applied external stress, in a manner identical to that for solid state sintering. Σ is the effective stress on the grain boundaries and Φ is a geometrical factor that takes the porosity into account (the stress intensification factor^{14,15}). The consideration of a sintering stress as an equivalent externally applied stress, while receiving increased attention recently, was introduced by Kingery^{3,4}.

The examination of the evolution of the sintering stress in the intermediate stage of the liquid phase densification of MgO- 5wt% Bi₂O₃ is reported here.

Experimental

The MgO powder * had an average initial particle size of about 0.06 μm . 0.5 wt% of bismuth oxide was added while the MgO was in a concentrated alcohol suspension, and mixing was achieved by stir-drying. After drying, the powder mixture was broken up mechanically in a mortar and pestle, and compacted in a die at about 20 MPa, to a green density of 0.40 of the MgO theoretical density. The compacted pellets were 9.52 mm in diameter and about 6mm thick. For creep-sintering the samples, held in the loading dilatometer, were introduced rapidly in the dilatometer furnace which was kept at 1275K. The equilibrium temperature was reached in about 5 to 10 minutes. During this time the transient densification brought the samples to 0.50 of the theoretical density of MgO. For the creep-sintering experiments, constant loads of 200 or 400 g were applied, corresponding to initial stresses of 27.5 and 55.0 kPa. The densification temperature was chosen such as to be above the melting point of Bi_2O_3 (about 1025K), such that the densification occurred in 1 to 2 hours, but below the temperature where the pure MgO started densifying. The densification and creep could thus be attributed fully to the action of the liquid phase.

After sintering, the densities of the samples was verified by the Archimedes method, and some samples were polished and examined in a scanning electron microscope.

Results and Discussion

The measurement of the total dilatometric shrinkage as a function of applied uniaxial load and time at constant temperature, together with Archimedes density measurements of interrupted sintering at various times, readily yields the creep strain and

* Reagent grade, J.T.Baker Chemical Co., Phillipsburg, N.J.

the densification strain as a function of time.¹⁶ Fig 1 shows the density component of the sintering samples for 0, 27.5 and 55 kPa of initial applied stress, corresponding to 0, 200 and 400g loads. Pure MgO, without the Bi₂O₃ addition, does not show any measurable densification at this temperature. It is clear that a systematic increase in the densification rate has been caused by the applied uniaxial load. The simultaneous creep strains of the samples, at constant load are shown in Fig 2. From these data, the creep rates at constant applied stress and the densification rate can be derived, by taking into account the change in the sample diameter during the densification with the creep rate linearly proportional to the applied stress. These rates, as well as the densification rate at zero load and at a load of 55kPa are shown in Fig 3. Within the limits of accuracy of the experiments, the increased densification rate at a constant applied uniaxial stress is proportional to the densification rate at zero applied stress. A comparison of the microstructures of the compacts after 1 hr of sintering at 1275 K with zero applied stress and with a 55 kPa applied stress, Fig 4 a and b, shows that the grain sizes have been unaffected by the stress, but that the small applied stress has preferentially eliminated larger pores in the compact.

The creep strain rates and the lineal densification strain rates, at uniaxially applied stress σ_a , may be expressed simply in the following form:¹³

$$\dot{\epsilon}_\rho(\sigma_a) = [(\Sigma/\Phi) + (\sigma_a/3)] / \eta_\rho \quad \text{Eqn 1}$$

and

$$\dot{\epsilon}_c(\sigma_a) = \sigma_a / \eta_c \quad \text{Eqn 2}$$

where Σ/Φ , the sintering stress, is the equivalent externally applied stress, and η_ρ and η_c are viscosities. The ratio of the densification rate over the creep rate at applied stress σ_a is

$$\dot{\epsilon}_\rho(\sigma_a) / \dot{\epsilon}_c(\sigma_a) = (\eta_c / \eta_\rho) (\Sigma/\Phi) / \sigma_a + \eta_c / 3\eta_\rho \quad \text{Eqn 3}$$

and contains a stress dependent and a stress independent term. This latter term is the result of the incremental densification rate that is caused by the hydrostatic stress component of the applied uniaxial stress.

It is obvious that the experimental ratio of the densification over the creep strain rate immediately puts an upper limit on the ratio of the viscosities defined by Eqns 1 and 2. For an applied stress of 27.5 kPa the ratio of the lineal densification rate at zero applied stress over the creep rate is found from the data of Fig. 3:

$$\dot{\epsilon}_{\rho}(0)/\dot{\epsilon}_c(27.5 \text{ kPa}) \approx 5.1 \quad \text{Eqn 4}$$

This ratio is nearly constant for the density interval examined here. Fig. 5 shows this ratio, together with the ratios for solid state sintering materials CdO,¹⁷ ZnO,¹⁸ and MgO,¹⁹ as well as a glass.²⁰ Thus, the constancy of this ratio over a wide density range in the intermediate stage of densification is emerging as a universal feature of sintering, regardless of the densification mechanism, with the value of the ratio being system specific. The low value of η_c/η_{ρ} is further in agreement with the predictions of Scherer²² which are based on a general consideration of effective viscoelastic moduli.

The ratio of the creep viscosity over the densification viscosity can be found from the incremental densification rate at a fixed applied stress, using Eqn 2 and 3. Using the data summarized in Fig 3 one obtains

$$\eta_c/\eta_{\rho} = 3[\dot{\epsilon}_{\rho}(\sigma_a) - \dot{\epsilon}_{\rho}(0)]/\dot{\epsilon}_c(\sigma_a) \approx 1.7 - 1.9 \quad \text{Eqn 5}$$

from the beginning of the measurements to a density of about 75% of theoretical. It is interesting to note that this ratio is nearly constant for the duration of the experiment. This implies, in addition, that the sintering stress, Σ/Φ , is nearly constant as well in this density interval since the ratio of the densification rate at zero applied stress over the creep rate is also constant.

From the values of the ratio of creep over the densification viscosity the magnitude of the sintering stress can be found readily:

$$\Sigma/\phi = [\dot{\epsilon}_\rho(0)/\dot{\epsilon}_c(\sigma_a)] \sigma_a [\eta_c/\eta_\rho]^{-1} \quad \text{Eqn 6}$$

In this case, the sintering stress is about 78 kPa. This is quite low. One might to a first approximation equate Σ/ϕ with $2\gamma/R$, where γ is the relevant surface tension, say 0.5 J/m^2 (500 erg/cm^2), and R is the radius of curvature of the relevant meniscus. This estimate would put R at about $6 \text{ }\mu\text{m}$, certainly larger than the particle size evident in Fig 4a and 4b. Such low sintering stress might, however, be expected on the basis of the sequential pore filling models. An additional consideration is that the liquid tends to promote the formation of large particle agglomerates, as discussed by Kaysser and his coworkers⁹ and also evident in this study. In this geometry, one should expect the sintering stress to relate to the solid/liquid agglomerate size rather than to the primary particle size, possibly causing the low values of the observed sintering stress.

Conclusions

The experiments indicate , as was the case for solid state sintering or for the sintering of glass, that the driving force for densification in liquid phase sintering is nearly constant over a significant range of the intermediate sintering stage. Further, the ratio of the densification viscosity over the creep viscosity in this liquid phase sintering system is also nearly constant in the densification interval examined and has a value of about 1.8. The constancy of the ratio of the densification strain rate over the creep strain rate gives increasing experimental support to the notion that it is a universal feature of sintering in a wide density range covering the intermediate stage of densification, regardless of the sintering mechanism. Further experimentation and analysis is necessary to test the materials and density range over which this possible universal characteristic of creep/sintering would extend.

Acknowledgements

This work was supported by the Division of Materials Science, Office of Basic Energy Sciences, U.S.Department of Energy under Contract No. DE-AC03-76SF00098.

Discussion with F.F.Lange are gratefully acknowledged.

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Figure Captions

Fig.1 Density versus time (log scale) for sintering of MgO , at 1000 °C, with and without 5 wt% Bi₂O₃. The applied loads are indicated in grams on the corresponding densification curves.

Fig.2 Creep strain for densification of MgO with 5 wt% Bi₂O₃, at 1000 °C ,the applied loads are indicated in grams.

Fig.3 Log₁₀ of the strain rates, in min⁻¹, versus density for MgO + 5 wt% bismuth oxide, at 1000 °C. The numbers in paretnesis are the corresponding applied uniaxial stresses in kPa. The subscript ρ refers to the densificaiton strain rate, while the subscript c refers to the creep strain rate.

Fig.4 Microstructure of MgO + 5 wt% Bismuth oxide after 1 hr at 1000 °C densified , A) with applied uniaxial load of 400 g (corresponding to a stress of about 55 kPa), and B) without applied load.

Fig.5 Ratio of the densification strain rate over the creep strain rate at a constant applied uniaxial stress of 200 kPa. The markers on the lines indicate the density interval over which the data were continuously collected by loading dilatometry.

XBL 8710-4514

Fig. 1

XBL 8710-4516

Fig. 2

XBL 8710-4517

Fig. 3

XBB870-9327

Fig. 4

XBL 8710-4515

Fig. 5

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