LBL-27643

Center for Advanced Materials

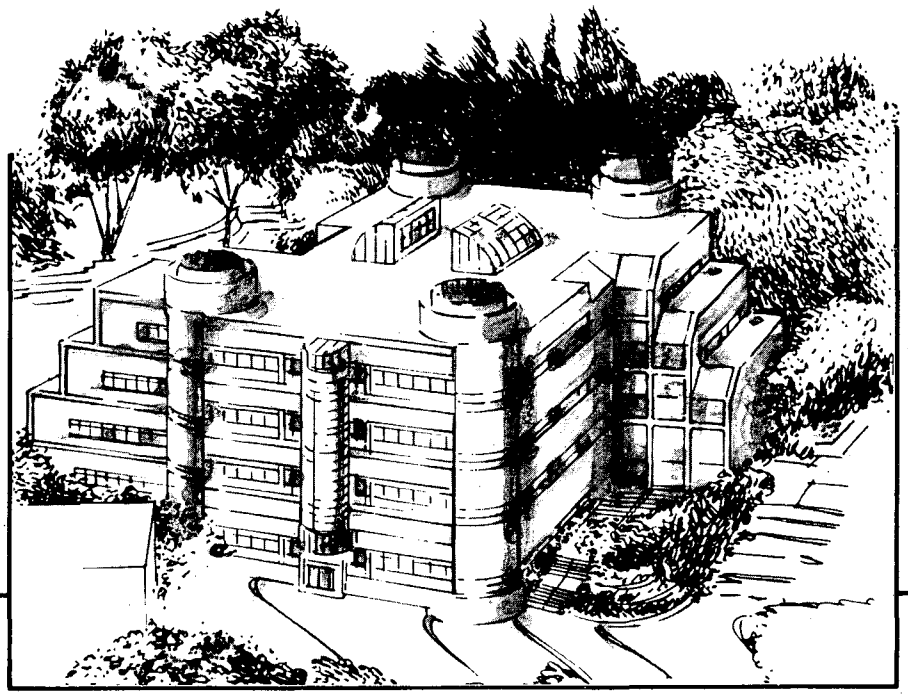
CAM

Presented at the Materials Research Society Spring Meeting, San Diego, CA, April 24–29, 1989

Densification of Particulate Ceramic Composites: the Role of Heterogeneities

L.C. De Jonghe and M.N. Rahaman

August 1989



Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LOAN COPY
Circulates
for 2 weeks
Bldg. 50 Library.
LBL-27643
Copy 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL # 27643

DENSIFICATION OF PARTICULATE CERAMIC COMPOSITES: THE ROLE OF HETEROGENEITIES

Lutgard C. De Jonghe

Center for Advanced Materials, Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, One Cyclotron Road, Berkeley, CA 94720

and

Mohamed N. Rahaman

Department of Ceramic Engineering, The University of Missouri-Rolla, Rolla, Missouri 65401

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, United States Department of Energy, under Contract Number DE-AC03-76SF00098.

ABSTRACT

Inert particulate inclusions in ceramic powder compacts can obstruct densification behavior significantly. The factors that are the causes of this decrease in the sinterability are reviewed. It is concluded that the origin of the sintering difficulty resides in defects that processes such as die compaction introduce during the initial forming of the composite powder compact. Alternative processing methods are suggested that should minimize the negative effects of the dispersed inclusion phase on densification.

INTRODUCTION

Particulate ceramic composites can offer important performance advantages in that they may have a higher fracture toughness and creep resistance at elevated temperatures than single phase ceramics. The potential for improved performance is, however, offset by the increased difficulties that the processing of such composites present. In particular, it has been commonly observed that free sintering of particulate composites is significantly hampered, even at modest volume fractions of the dispersed inclusions [1-3]. One way to report the retardation effects is to regard densification as driven by an externally applied, effective mechanical stress, (referred to as the sintering stress, Σ), that reproduces the combined action of surface and grain boundary tensions [4]. The relative reluctance with which the composites densify can then be expressed in terms of a hydrostatic backstress that opposes the intrinsic sintering stress that would densify an inclusion-free matrix of identical microstructure as that of the composite. The decrease of the densification rate, however, might well reside in a modification of the kinetic factors rather than of the sintering stress; and further experimentation is required to reveal the actual cause of the effective backstress. The origin of such an effective backstress has been attributed to various factors including significant viscoeleastic backstresses originating in densification incompatibilites between the matrix and the dispersed phase [5,6], the formation of an undeformable network of the dispersed inclusions [7], the effects of dispersed phase clustering [8,9], and more recently, the adverse effects of micro-crack or crack-like defects promoted by the presence of the dispersed inclusions either in the initial cold compaction or during sintering of the composite [10].

Various authors have concluded that large viscoelastic backstresses cannot realistically develop in densifying particulate composites [4,11,12]. Only those incompatibility stresses corresponding to the instantaneous viscous limit should be expected rather than those arising from a cumulative viscolelastic process. The constrained network model developed by Lange [7] offers an attractive alternative explanation for the retarding effects of the dispersed phase on the densification rate, especially at high volume fractions.

While particulate composites can usually be densified without much difficulty by pressure-assisted sintering, it would be clearly advantageous to achieve adequate densification by free sintering. The processes that oppose free densification when a useful volume fraction of the inclusion phase is present must therefore be understood so that they can be minimized or avoided altogether.

In this paper we review our understanding of the factors that can contribute to the modification of the sintering behavior of ceramic powder compact, by dispersed particulate inclusions.

EXPERIMENTAL

Apart from the usual dilatometric measurements that can be used to elucidate densification mechanisms and the factors that affect them, one can determine the low-load constant-stress creep rate of the composites as they are densifying. This technique has been described earlier [13,14], and adds an additional probe for clarifying sintering processes. In a typical experiment samples, prepared by mechanical mixing and cold die

compacting, are measured by standard dilatometric methods, but controlled stresses up to a few hundred kilopascal are applied. This low applied stress superimposes a nearly constant-volume creep onto the densification, and the creep rate can be determined straightforwardly. The densification and simultaneous creep rates of single phase and particulate composite samples can then be compared.

DISCUSSION

The linear densification strain rate, $\dot{\epsilon}_d$, and the creep strain rate, $\dot{\epsilon}_c$, of a densifying powder compact can be written parametrically as

$$\dot{\epsilon}_d = \Sigma/\eta_d \qquad (1)$$

and

$$\dot{\epsilon}_c = \sigma_a/\eta_c \qquad (2)$$

where Σ is the sintering stress and σ_a is the applied uniaxial stress. Equations (1) and (2) also define the meaning of the densification and the creep viscosities, η_d and η_c.

Under the assumption that the densification rate of the inclusion-free, identical matrix, $\dot{\epsilon}_m$, is known, the instantaneous matrix densification rate, $\dot{\epsilon}_{com}$ of a particulate composite containing a volume fraction, f, of the dispersed phase can be shown to be [4]

$$\dot{\epsilon}_{com} = \dot{\epsilon}_m\{1 + 4[\eta_c/\eta_d][f/(1 - f)]\}^{-1} \qquad (3)$$

This equation is based on the critical assumption that the densifying compact is quantitatively represented by the behavior of an inert spherical particle surrounded by a densifying, uniform mantle of matrix material. It further is based on a continuum model in which, necessarily, particle size or transport mechanism considerations must be absent. This is equivalent to the assumption that all the inclusions are of uniform size and are spacially ordered in a uniform matrix. This situation is clearly not realized in normal mixing processes where, at best, complete spacial randomness (CSR) can be achieved. Normally, the particles will be non-uniformly distributed and will not be monosized. The compact can then be regarded as consisting of an irregular space-filling assemblage of Voronoi cells each with one inclusion inside. The cell size and the inclusion size distribution represent a corresponding distribution in local volume fraction of the dispersed inclusions. Compatibility stresses must then arise during densification, opposing the driving force for sintering and leading to somewhat lower densification rates than those predicted by Eqn. (3). It is difficult to assess the magnitude of such compatibility backstresses quantitatively; at high volume fractions they could be expected to be significant, when the system approaches the constrained network sintering model proposed by Lange [7]. The effects of non-uniform distribution of the inclusion may be estimated by considering two equal volume elements of the composite containing different fractions, f_1 and f_2, of inclusions such that the average remains f. These volume elements would need to

densify compatibly requiring that their overall volumetric strain rate be equal. This is achieved by the generation of self-stresses that increase the densification rate of the slow volume element and decreases the densification rate of the fast one. The new densification rate $\dot{\epsilon}_{nm}$ of the matrix of these two volume elements can then be calculated and compared with the densification rate, $\dot{\epsilon}_{mo}$, of the volume elements if they had equal inclusion contents. After some algebra, this leads to

$$\dot{\epsilon}_{nm}/\dot{\epsilon}_{mo} = 2\ F_1F_2/[(F_1 + F_2)F] \qquad (4)$$

where, following Eqn 3, with $\eta_c/\eta_d = 2$,

$$F_1 = [1 + 8f_1/(1 - f_1)] \qquad (5)$$

with similar expressions for F_2 and F corresponding to f_2 and f.

Figure 1 shows a plot of the densification rate ratios using Eqn. (4), for various values of f, as a function of f_1/f. It is evident from this representation that the retarding effects due to heterogeneous distributions of inclusions is most serious at high inclusion contents and for large variations in the local inclusion contents. At low volume fractions of inclusions, say below 10-15 vol%, this calculation indicates that the opposition to densification from this type of backstress is relatively minor.

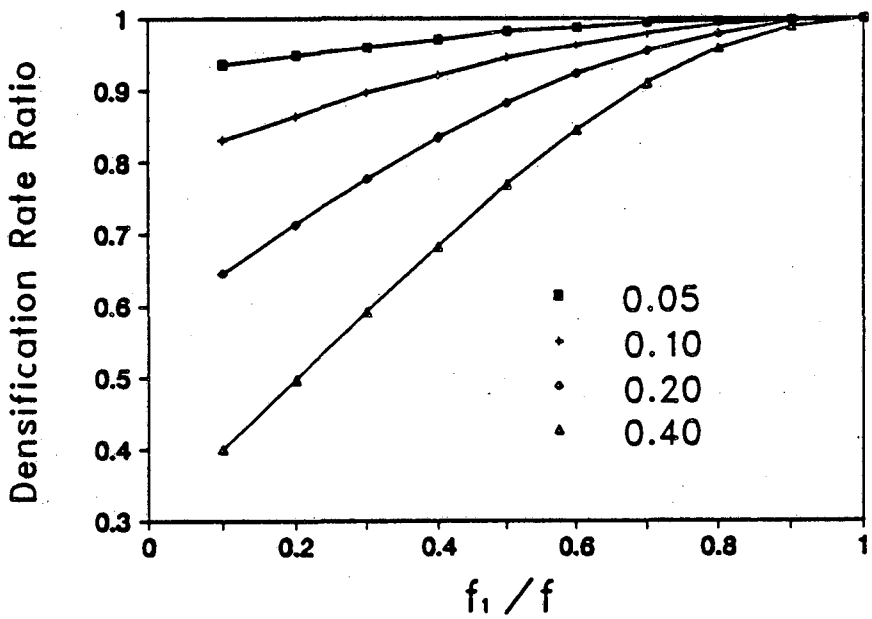


Figure 1. Densification ratio, $\dot{\epsilon}_{nm}/\dot{\epsilon}_{mo}$, as a function of f_1/f calculated from Equation (4).

Estimates of how varied the spacial density distribution of the inclusions or their network formation can be in the case of CSR can be deduced from the available expressions for the probability distribution of finding a neighbor to a particle at a distance equal to its diameter. This probability is given by [15]

$$P(d) = 1 - \exp(-\lambda\pi d^3) \qquad (6)$$

where λ is the inclusion number density per unit volume or intensity of the composite, and d is the center to center distance between the dispersed inclusions.

Equation (6) can be rewritten in terms of inclusion radius, r, and volume fraction, f, when it is assumed that the dispersed inclusions are spherical and monosized:

$$P(d) = 1 - \exp\{-(3/4).f.(d/r)^3\} \qquad (7)$$

In the case of CSR the probability distribution function $P(d)$ is unaffected by inclusion size; however, in the case of clustering this may not be the case and inclusion size as well as volume fraction may affect $P(d)$. For 10 vol% of inclusion, for example, the probability of having a touching neighbor is less than 10%. This consideration again underscores that rigid network formation arguments cannot account for the strong retardation of densification at inclusion volume fractions of below about 0.1, unless there is pronounced clustering. In practice, a detailed study of the distribution of the inclusion density as a function of the sampling area or volume can be used to characterize the homogeneity of the distribution. For CSR this sampling (quadrat count in two dimensions) would follow a Poisson distribution; for non-CSR distribution, the variance-to-mean ratio would be used as a measure of heterogeneity (or index of dispersion).

The data considered here are those in which clustering was not detected. It should be noted, however, that in another study, [8] clustering was shown to increase with decreasing inclusion size leading to increasing obstruction of densification at constant volume fraction. A significant inclusion size effect was also reported [9].

When clustering or unusual spacial density variation of the inclusions are largely absent, an evaluation of the experimental ratio $\dot{\epsilon}_{com}/\dot{\epsilon}_m$ in Eqn. (3), would indicate to what extent the experiments agree with the analysis that led to Eqn. (3). Data from earlier experiments by De Jonghe and coworkers [1] are shown in Table 1. The viscosity ratios, η_c/η_d, commensurate with Eqn. 3 range from near 20 at 3 vol% inclusions to about 80 at 20 vol % inclusions. This is a factor of 10 to 40 larger than the theoretically possible value of 2 deduced by Scherer [11] and also significantly more than what might be attributable to the spacial variations in inclusion density discussed above, except at the high volume fractions.

Table 1: Experimental data for the matrix densification rate of the composite after a sintering time of twenty minutes, relative to the unreinforced matrix, $(\epsilon_{com}/\epsilon_m)_{20}$, and the ratio of the creep viscosity to the densification viscosity, η_c/η_d, calculated from Equation (3) for different inclusion volume fraction, f.

f	$(\epsilon_{com}/\epsilon_m)_{20}$	η_c/η_d

0.03	0.69	19
0.06	0.51	19
0.09	0.36	24
0.13	0.26	26
0.19	0.07	81

Further insight into the origin of the strong decreases in the densification rates of ceramic matrix particulate composites may be found in a study of their creep/sintering behavior. The creep/sintering studies are done by loading dilatometry in which the creep and densification strain rates are simultaneously determined. In porous materials, the viscosity of creep and of densification are intimately related, unless stress-driven rearrangement is rapid, and it becomes possible to determine whether the obstruction to densification in a particulate composite is due to altered viscosities, e.g. by preventing inclusion-network shear, or if it involves modification of the sintering stress itself.

Some recent data [16] were obtained on creep/sintering of a particulate composite of ZnO with 10 vol% silicon carbide. The data are shown in Fig. (2). A remarkable feature of the creep data is that the time dependence of the creep rate appear to be unaffected, although the time dependence of the densification rate is significantly different. The creep rate can be written in terms of the material's structural parameters as [4]

$$\dot{\epsilon}_c = \sigma_a/\eta_c = \sigma_a(K.\Phi^{(n-1/2)}/X^n) \qquad (8)$$

where K is a constant, X is the interpore distance, Φ is the stress intensification factor [17], and n is a transport mechanism dependent parameter. For ZnO, with volume diffusion as the dominant tansport mechanism, n is equal to 2. X is determined by the coarsening processes and is therefore a function of time. Φ is determined by the overall porosity and has been found to be well represented by $\Phi = \exp(aP)$, with $a \approx 5$ for ZnO. The time-sensitivity of the viscosity must then be regarded as resulting from a fortuitous compensation between ϕ and X. The densification of the matrix would also be expressible by an equation very similar to Eqn 8, when the creep and densification are effected by the same transport mechanisms:

$$\dot{\epsilon}_m = \Sigma(1/\eta_m) = K\Phi^{(n-1/2)}/X^n \qquad (9)$$

where Σ is the sintering stress. The ratio of the instantaneous densification rate to the constant stress creep rate can then give a measure of how the sintering stress is modified by the presence of the inclusions. The results indicated that the sintering stress of the composite was decreased by a factor of approximately 2, from the very onset of densification throughout the measurement range Fig. (3). At the same time, the above considerations indicate that the origin of the effective backstress cannot be sought in the viscous mismatch stresses generated by the particles since, according to Eqn. (3), it can only account for a decrease of about 20 % in Σ at 10 vol% inclusions; also, the spacial variation of the inclusion distribution at this inclusion content is also unlikely to account directly for the decrease. Another cause therefore produces the observed strong decreases in the densification rates of composites at modest inclusion content. This cause must also be present from the beginning of densification.

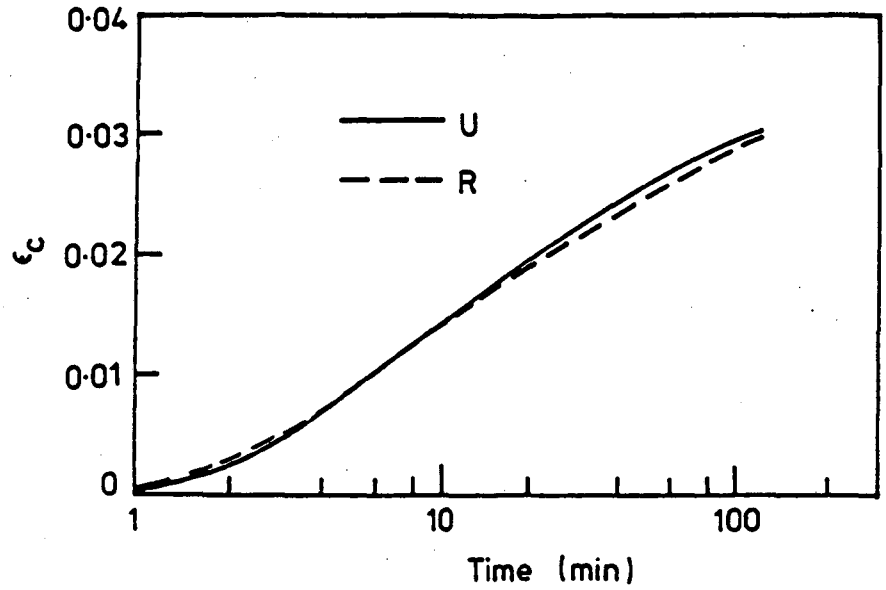


Figure 2(a). Creep strain as a function of time for unreinforced ZnO (referred to as sample U) and ZnO reinforced 10 v% SiC (sample R) sintered at 725°C under a uniaxial stress of 250 kPa.

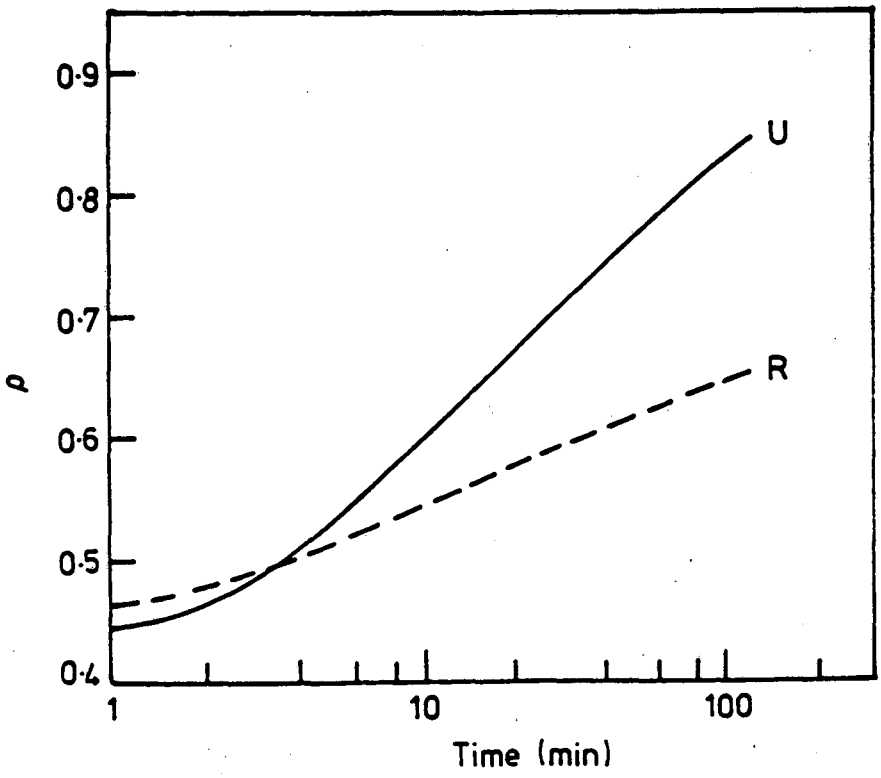


Figure 2(b). Density as function of time for samples U and R described in Fig. 2(a).

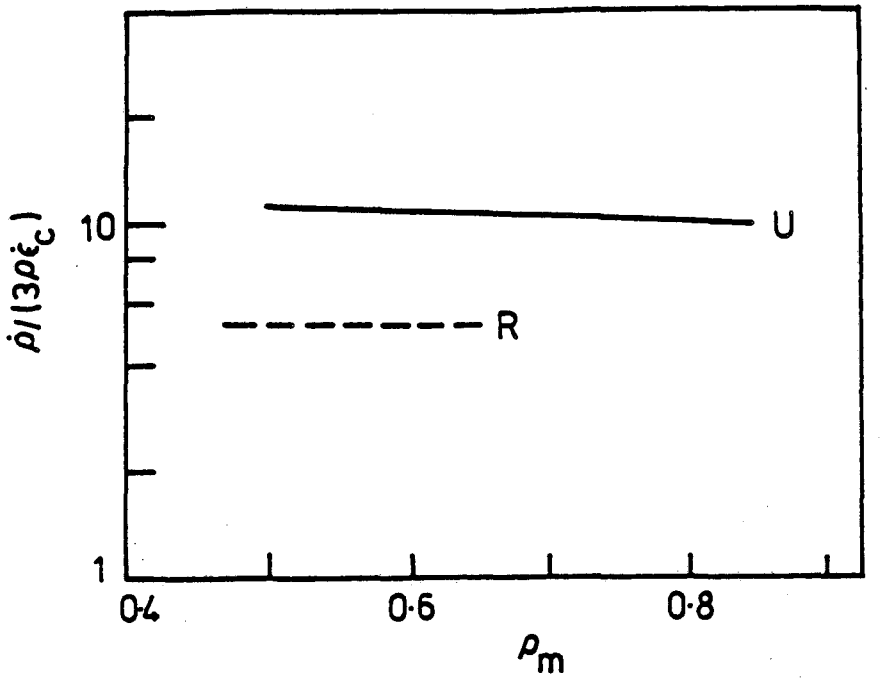


Figure 3. Ratio of the densification rate to the creep rate as a function of the matrix relative density for sampes U and R described in Fig. 2(a).

Figure 3. Ratio of the densification rate to the creep rate as a function of the matrix relative density for sampes U and R described in Fig. 2(a).

The sintering stress can be lowered by several factors. A strong factor is the initial compact density; recent results indicate that the sintering stress decreases with decreasing density [18]. A lesser decrease of the sintering stress can be brought about by prolonged coarsening at low temperatures; however, since the effects are present from the very onset of densification it is difficult to maintain a coarsening-based argument. It is therefore concluded that the origin of the apparent backstress resides in difference in the microstructure that the presence of the inclusions has brought about during the cold compaction of the composite. Several effects can be considered: die compaction is likely to lead to larger variations in the spatial distribution of the matrix green density when a inclusion phase is present than without. In addition, during cold compaction the mismatch between the undeformable inclusions and the compacting matrix must also be accommodated, and this accommodation can be accomplished by local matrix density gradients as well as by matrix shear. Inhomogenous compaction will then introduce residual stresses in the green compact that upon unloading may lead to matrix microcracking. This, in turn, can constitute a non-recoverable damage that makes the sintering process less successful, e.g., by developing a large-pore tail in the pore size distribution. Such damage has not yet been detected directly in partly sintered particulate composites, although it has been postulated by Lange [19] and shown to be present in model experiments [10] in which a large, undeformable core was included in a sintering cylindrical specimens.

The road to increasing the sinterability of particulate composites lies

therefore in the improvement of the distribution of the inclusion phase and in selecting forming processes, such as slip casting and wet pressing, in which residual stresses are kept at a minimum. The present experiments indicate that such processing methods will lead to particulate composites that can be free-sintered at useful inclusion contents.

CONCLUSIONS

The arguments advanced for the explanation of the retarding effect of inclusions on densification of ceramic matrix particulate composites have been reviewed. It is concluded that the origin of the retardating effects must be sought in the pre-sintering microstructure, and methods have been indicated that could minimize the sintering difficulties.

ACKNOWLEDGEMENT

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

REFERENCES

1. L. C. De Jonghe, M. N. Rahaman, and C. H. Hsueh, Acta metall. 34, (7), 1467-1471 (1986).

2. R. K. Bordia and R. Raj, J. Am. Ceram. Soc. **71** (4), 302-310 (1988).

3. W. H. Tuan, E. Gilbart, and R. J. Brook, J. Mat. Sci. **24**, 1062-1068 (1989).

4. L. C. De Jonghe and M. N. Rahaman, Acta metall. **36** (1), 223-229 (1988).

5. R. Raj and R. K. Bordia, Acta metall., **32** (7), 1003-1019 (1984).

6. C. H. Hsueh, A. G. Evans, R. M. Cannon, and R. J. Brook, Acta metall. **34** (5), 927-936 (1986).

7. F. F. Lange, J. Mater. Res. **2** (1), 59-65 (1987).

8. M. W. Weiser, Ph.D. Thesis, University of California at Berkeley (1987).

9. M. W. Weiser and L. C. De Jonghe, J. Am. Ceram. Soc. **71** (3) C-125--C-127 (1988).

10. F. F. Lange, Acta metall. **37** (2), 697-704 (1989).

11. G. W. Scherer, J. Am. Ceram. Soc. **70** (10) 719-725 (1987).

12. R. K. Bordia and G. W. Scherer, Acta metall. **36** 2411-2416 (1988).

13. L. C. De Jonghe and M. N. Rahaman, Rev. Sci. Instrum.

14. M. N. Rahaman, L. C. De Jonghe, and R. J. Brook, J. Am. Ceram. Soc. **69** (1), 53-57 (1986).

15. J. Diggle, Statistical Analysis of Spatial Point Patterns, New York: Academic Press (1983).

16. M. N. Rahaman and L. C. De Jonghe, unpublished results, 1989.

17. J. M. Vieira and R. J. Brook, J. Am. Ceram. Soc. 67 (4), 245-249 (1984).

18. M.-Y. Chu and L. C. De Jonghe, unpublished results, 1989.

19. F. F. Lange, in Ceramic Transations: Ceramic Powder Science IIB, Gary L. Messing, Edwin R. Fuller, Jr., and Hans Hausner, eds. American Ceramic Society, Ohio, 1988.

LAWRENCE BERKELEY LABORATORY
CENTER FOR ADVANCED MATERIALS
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720