Journal of the European Ceramic Society 18 (1998) 275–278
© 1997 Elsevier Science Limited
Printed in Great Britain. All rights reserved
0955-2219/98/$19.00 + 0.00
PII: S0955-2219(97)00108-8

A Rule-of-mixtures Model for Sintering of Particle-reinforced Ceramic-matrix Composites

H. J. Edrees,* A. C. Smith† and A. Hendry

Metallurgy and Engineering Materials Group, University of Strathclyde, Glasgow, UK

(Received 10 July 1996; accepted 30 May 1997)

Abstract

A model is described for the densification of ceramics and particle-reinforced ceramic-matrix composites when the degree of shrinkage is large. A rule of mixtures model can be used to describe the degree of densification in cases where there is no interfacial reaction between the reinforcement and the matrix. These models are illustrated by the reaction sintering of sialon and of sialon with titanium nitride, and also by the sintering of clay containing silicon carbide. The extent of linear shrinkage and also the rate of densification decrease with increasing volume fraction of reinforcement and these effects are explained on the basis of the model. The correspondence between the data and the model allow the prediction of shrinkage in particle-reinforced composite systems where there is no interfacial reaction during the densification process. © 1997 Elsevier Science Limited.

1 Introduction

Densification of covalent ceramics without additives is extremely difficult due to the low diffusivity in the solid state following from the nature of bonding in such materials. To overcome these difficulties, compounds are added which create a liquid phase during densification and this process is referred to as liquid phase sintering or LPS. The major advantage of this technique is the speed with which full densification can be achieved; it is widely used in the fabrication of, for example, silicon nitride and related ceramics.[1–4]

During LPS the liquid formed must wet the solid particles, and particle movement and densification occur initially by capillary pressure. Kingery[5] proposed that densification in the presence of liquids occurs by three distinct processes, an initial stage of particle rearrangement, a second step of solution and reprecipitation, and a final stage of pore closure. Although there have been many modifications of the original Kingery model (see for example Handwerker and Blendel,[2] German,[6] and Li Nan,[7] the essential features of the approach remain valid.

There is an extensive amount of work which has been carried out on LPS systems of interest in structural engineering ceramics[2,4,8–11] where the extent of shrinkage varies from a few percent up to about 40%. However, the above discussion and literature is based on monolithic materials whereas the present paper will examine ceramic matrix composites (CMC) and the influence of the addition of secondary phases on the shrinkage behaviour of structural engineering ceramic materials where liquid phases are present.

2 Theory

2.1 Shrinkage

Densification is related to both starting density and linear shrinkage as follows,

$$\rho_s = \frac{\rho_g}{\left(1 - \frac{\Delta L}{Lo}\right)^3} \tag{1}$$

where ρ_s is the sintered sample density, ρ_g is the green sample density and $\Delta L/Lo$ the linear shrinkage. The relationship of volumetric to linear shrinkage, S, is given by

$$\frac{\Delta V}{Vo} = 3\frac{\Delta L}{Lo} = 3S \tag{2}$$

for small values of shrinkage. For larger values, the shrinkage will be given by,

---

*To whom correspondence should be addressed.
†Current address: GE Superabrasives, Dublin, Eire.

$$\frac{\Delta V}{Vo} = 1 - (1 - S)^3 \qquad (3)$$

For a cylindrical sample with shrinkage along the diameter and the length of the sample

$$\frac{\Delta V}{V_o} = 1 - \left(1 - \frac{\Delta D}{D_o}\right)^2 \left(1 - \frac{\Delta L}{L_o}\right) \qquad (4)$$

2.2 Composites

The volume fraction of a particulate second phase present in a composite is an important factor in sintering and resultant shrinkage, and the shape and size of the reinforcing phase may also influence the sintering behaviour of the matrix material. A simple model for particulate composites can be proposed based on the rule of mixtures. The rule of mixtures gives

$$\left(\frac{\Delta V}{Vo}\right)_c = \left(\frac{\Delta V}{Vo}\right)_m (1 - f) \qquad (5)$$

where the subscripts c and m refer to composite and matrix, respectively, and where f is the volume fraction of reinforcing phase in the solid phase in the solid phases of the composite; that is, the shrinkage of the composite after sintering is equal to the shrinkage that would be found in the isolated matrix times the matrix volume fraction in the solid phases of the composite. The above equation is only applicable to composites where no interfacial reaction occurs.

3 Experimental

Samples of sialon matrix composites were prepared using Cookson Zyalon Ltd, Syalon grade 201 ($z = 0{\cdot}75$) and Goodfellow Metals titanium nitride as the reinforcing phase. The composition of all materials used is given in Table 1. The sialon precursor powder and the appropriate amount of the reinforcing phase were wet-milled in iso-propanol using alumina milling media for 24 h. The resulting slip was dried and subsequently dry-mixed for 1 h.

The sialon/reinforcement mix was uniaxially pressed to a pressure of 3 MPa into cylindrical compacts approximately 10 mm in diameter by 20 mm in height. This initial pressing was followed by an isostatic pressing to a pressure of 250 MPa. The green samples were weighed and their exact dimensions noted.

The green compacts were packed in a powder bed of Cookson Minerals Ltd Syalon grade 401 ($z = 3$) in a graphite crucible and fired in a graphite element furnace under 1 atmosphere of nitrogen. All samples were heated at a rate of 60°C min^{-1}, and samples containing titanium nitride were fired at 1650°C for 2 h. All samples were furnace-cooled. After firing, the samples were carefully removed from their powder bed and weighed. The dimensions of the sintered samples was measured and their density determined using the Archimedes method.

Table 1. Experimental materials

Material	*Source*	*Composition (wt%)*	*Mean particle size (μm)*
Kaolin clay	ECC International	$SiO_2 = 47$ $Al_2O_3 = 38{\cdot}3$ $Fe_2O_3 = 0{\cdot}5$ $K_2O/Na_2O = 0{\cdot}8$ $H_2O = 13{\cdot}3$	Not determined
Silicon carbide	Goodfellow Metals	$SiC = 99{\cdot}0$ $(Fe_2O_3 = 0{\cdot}15$ $SiO_2 = 0{\cdot}85)$	5 and 40
Titanium nitride	Goodfellow Metals	$TiN = 99{\cdot}5\%$	20 and 45
Syalon 201	Cookson Zyalon	$Si_3N_4 = 80{\cdot}3$ 'AlN' $= 3{\cdot}4$ $Al_2O_3 = 8{\cdot}3$ $Y_2O_3 = 8{\cdot}0$	8

Samples of clay with silicon carbide reinforcement were prepared from ECC International, Grade D china clay and Goodfellow Metals Ltd silicon carbide. The green preparation was the same as that for sialon composites. The test samples were fired *in situ* in a Thermal Sciences Ltd TMA1500 thermo-mechanical analyser at various heating rates and maximum temperatures as detailed in the Results section below.

All samples were analysed by X-ray powder diffraction to confirm that no alteration had occured in the reinforcing phase by reaction during sintering.

4 Results and Discussion

Experimental results on sintering of monolithic sialon (Cookson Minerals Ltd, Syalon grade 201) show that shrinkage is homogeneous along both the diameter and length of the sample during the course of sintering. It is well established that sintering of sialons of this type occurs by a liquid-phase mechanism.[2–4] Around 20% linear shrinkage on both the diameter and the length of the specimen is observed for fully densified samples in agreement with the green density values and eqn (1).

In the case of composite materials, the change in dimensions during the course of sintering is strongly dependent on the volume fraction of the reinforcing phase and its chemical compatibility with the matrix. The changes in sample dimensions of composite materials are compared with those predicted by the model in Fig. 1 for the case of sialon–TiN. Sialon reinforced by different percentages of TiN was used to study the shrinkage behaviour as this system shows no chemical reaction during the course of sintering. With additions of TiN, it is necessary to adjust the sintering temperature to attain near theoretical density. All experiments were carried out at temperatures between 1600 and 1750°C in a nitrogen gas atmosphere and samples were embedded in sialon powder to minimize weight loss during the course of sintering. Sintered sample densities are 97–99% of theoretical. Figure 1 also shows that within experimental error, shrinkage along the diameter of the specimens is equal to that along the length as was observed for monolithic sialon. Volume measurements before and after sintering carried out on these materials are presented in Fig. 2 showing agreement between the experimental and the theoretical values of eqn (5).

Particle size of the reinforcement has an effect on sintering. Two different batches of TiN powder with average particle sizes of 45 μm and 20 μm were used to reinforce the sialon matrix. The effect of the larger particle size was to increase by 30–50°C the sintering temperature which was necessary to achieve density equivalent to that of the specimen with smaller TiN particle size. Experimental observations show that there is no effect of TiN particle size on the degree of shrinkage after sintering, and for a constant amount of TiN the rate of shrinkage increases with increasing TiN particle size in contradiction to previous work on this system.[11] The discrepancy results from the experimental methods employed in the two studies. Whereas Herrman *et al.*[11] measured only the isothermal shrinkage, it is clear from the present study that a significant part of the total shrinkage takes place during heating to the isothermal hold temperature. For larger reinforcement particle sizes, the shrinkage is almost complete during heating and so the rate measured in the isothermal part of the cycle is apparently low. In the present work, the *maximum* sintering rate was recorded.

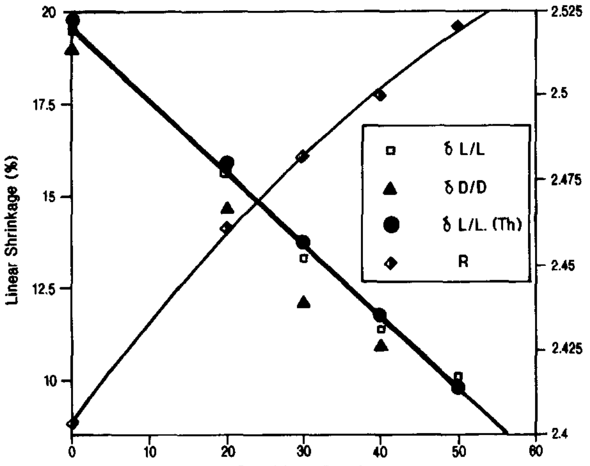

Fig. 1. Relation between linear shrinkage and TiN volume fraction in sialon/TiN composites.

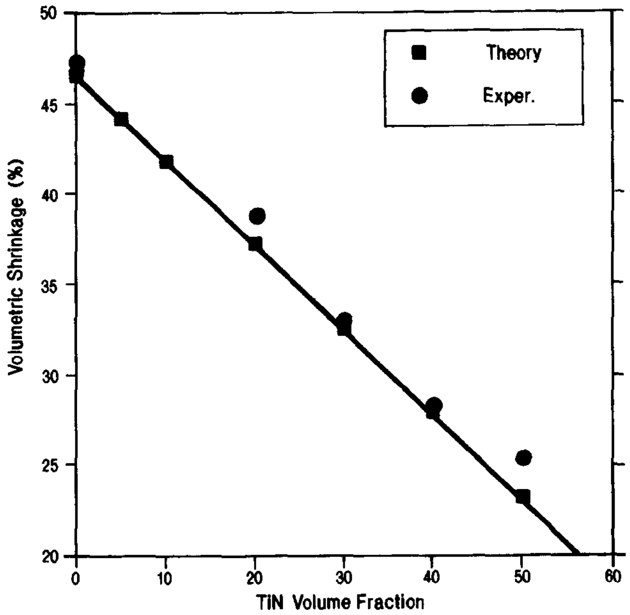

Fig. 2. Relation between volume shrinkage and amount of second phase in sialon matrix composites with TiN.

The behaviour of this model system in which an inert nitride is sintered in a sialon matrix supports the simple rule of mixtures densification model applied to a liquid-phase sintering system and is consistent with the behaviour of the monolithic matrix. Syalon 201 is, however, a reaction sintering powder mixture in which the individual components react during densification to form a sialon matrix of a specific composition. During the reaction, therefore, the volume of liquid phase active in promoting densification may vary. As this is a highly specific set of circumstances, it was decided to investigate a more conventional system to further test the present model of composite sintering.

The china-clay/SiC system was therefore chosen to evaluate the effect of reinforcement and also to further study the effect of reinforcement particle size on sintering. Phase diagrams of the kaolin clay used in this study[12] show that the solidus temperature is at 1310°C where the amount of liquid phase is approximately 30% for the amount of alkali present (Table 1).

TMA equipment was used to study the instantaneous dimensional changes in length of the sample during the course of sintering. The results for monolithic clay sintered at 20°C min^{-1} to 1480°C for 30 min show that the overall linear shrinkage is around 20%, part of which is due to loss of structural water and to phase changes, and that the main dimensional change is not isothermal but occurred on heating. Similar experiments were performed on clay containing 10, 20 and 30% silicon carbide. The densification behaviour in all of these samples is the same but the total amount of shrinkage, and rate of densification change with the volume fraction of reinforcement. Data for all of the composites show that linear dimensional change is essentially complete during the heating cycle with a negligible amount of shrinkage at isothermal sintering temperature. Under the conditions used in these experiments there is at least 30% of liquid phase present and this suggests therefore that the simple rule-of-mixtures model, which applies to the LPS system sialon/TiN, also applies to sintering by vitrification in the case of clay-based systems.

The experimental results on clay/SiC mixtures indicate that linear shrinkage decreases with increase of SiC volume fraction as seen in Fig. 3. This figure shows that around 35% reduction in the linear shrinkage follows when china clay is reinforced by 30% SiC and that the results of shrinkage reduction in the presence of inert reinforcements are in good agreement with the values calculated using the rule-of-mixtures model [eqn (5)]. The results also reveal that there is no influence of silicon carbide particle size on the degree of densification as it appears that clay reinforced by different amounts of SiC with 5 μm or 40 μm particle size has the same degree of shrinkage. This is consistent with the data reported above for sialon/TiN and is in agreement with the simple model based on a rule of mixtures provided that the reinforcement volume fraction is sufficiently low that particles of reinforcement do not influence one another. All samples presented in Fig. 3 were sintered to almost theoretical density.

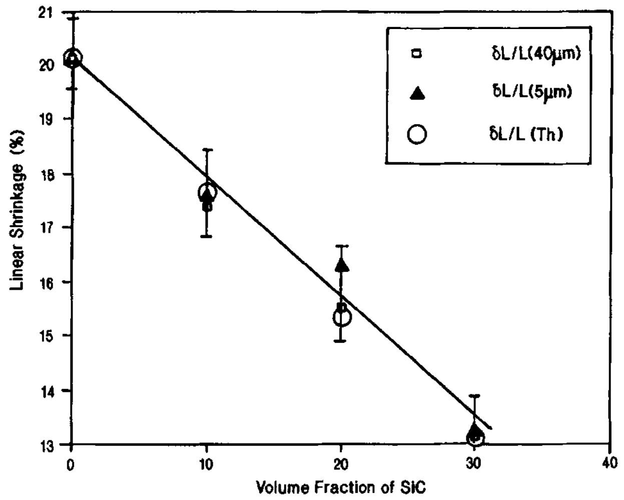

Fig. 3. Relation between shrinkage and volume fraction of SiC in clay/SiC sintered to 1480°C.

5 Conclusions

It has been shown that a description of sintering of particle-reinforced composites, where large extents of densification occur and no interfacial reaction occurs between the matrix and reinforcement, can be made in terms of a simple rule of mixtures approach

The model is illustrated by sialon–titanium nitride and clay–silicon carbide composites which show the effects of variation of the reinforcement volume fraction and of the mean particle size. In the former case the process of densification occurs by liquid-phase sintering with a rearrangement stage during heating followed by solution/re-precipitation to form the β'-sialon matrix. In the clay–silicon carbide system densification occurs by vitrification in the presence of a significant liquid fraction and the system is almost completely densified during the heating cycle to the optimum sintering temperature.

References

1. Abe, O. J., *Journal of Material Science*, 1990, **25**, 4018.
2. Takehashi, T., In *Sintering of Advanced Ceramics*. ed. C. A. Handwerker and J. Blendell. The American Ceramic Society, Ceramic Trans., 1990, Vol. 7, p. 230.
3. Edrees, H. J. and Hendry, A., In *Complex Microstructures*, ed. R. Stevens. Brit. Cer. Proc., Vol. 42, 1989, p. 49.
4. Hampshire, S. and Jack, K. H., In *Special Ceramics 7*. British Ceramic Society, 1981, p. 37.
5. Kingery, W. D., *J. Applied Physics*, 1959, **30**, 301.
6. German, R. M., *Liquid Phase Sintering*. Plenum Press, New York, 1985.
7. Li, Nan (ed.), Sintering and Materials. In *Proc. 6th Int. Symposium on the Science and Technology of Sintering*. Int. Academic Pub., Beijing, China, 1995.
8. Chang, G., Chun, X., Yuan-Lou and Li-min, C., *Euro Ceramics—Processing of Ceramics*, Vol. 1, ed. G. De Witt, R. A. Terpstra and R. Metselaar. Elsevier, Oxford, 1989, p. 426.
9. Anya, C. C. and Hendry, A., *Journal of the European Ceramic Society*, 1993, **12**, 297.
10. Watari, K., Nagaoka, T. and Kanzaki, S., *Journal of Material Science*, 1994, **29**, 5801.
11. Herrman, M., Baltzer, B., Schubert, C. and Hermel, W., *Journal of the European Ceramic Society*, 1993, **12**, 287.
12. Levin, E. M. and McMordie, H. F., *Phase Diagrams for Ceramists*. The American Ceramic Society, Columbus, OH, 1981.