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The reaction hot-pressing of compositions in the system Al-Si-N-O corresponding to β'-sialon

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The reaction hot-pressing at 1700 and 1750° C of a number of compositions in the system Al–Si–N–O corresponding to points spanning the β'-sialon phase line in the region of $z = 0.8$ has been studied. Measurements have been made of densification rate and of the rate of conversion of α-Si_3N_4 to β'-sialon. The densification process for these compositions may be described in terms of a liquid-phase assisted fast particle rearrangement process succeeded by Coble creep. The rates of these processes are sensitive to the volume of grain-boundary liquid phase present, which in turn is determined by the position of the compositional point in relation to the β'-sialon line. For systems containing very little grain-boundary phase, the vapour-phase transport of material may become important.

1. Introduction

Hot-pressing is an established and reliable technique for the production of high-density high-strength nitrogen ceramics based on the Si–N and Al–Si–N–O systems. Such ceramics are of considerable interest as potential high-temperature engineering materials [1]. Hot-pressed silicon nitride has already found commercial application. More recently, attention has been directed at the production of materials consisting essentially of the β'-sialon phase. This phase, the first to be identified in the aluminium- and oxygen-containing system [2], has a considerable compositional range with retention of the β-silicon nitride crystal structure, and can be formulated as $Al_zSi_{6-z}N_{8-z}O_z$ [3] where z takes values up to approximately 4.2. Materials based on the β'-sialon phase have rapidly attracted interest because of their apparently general sinterability [4] and the ease with which they can be hot-pressed to high density at temperatures in the region of 1700° C in contrast to silicon nitride, and because of the readiness with which they are formed from starting mixtures of, for example, silicon nitride, aluminium nitride and aluminium oxide powders.

The kinetics of densification of silicon nitride during hot-pressing have been examined in detail with regard both to the important roles played by additives such as MgO, Y_2O_3 or Li_2O and to the associated α-phase to β-phase transformation [5, 6]. Data have been interpreted in terms of rapid initial particle rearrangement, which is followed by a solution–diffusion–reprecipitation process in which the diffusion rate is rate controlling and where the reprecipitation step results in the formation of the β-phase. During the intermediate stage of densification the densification rate ($d\rho/dt$) may be described by the Coble creep Equation [7]:

$$\frac{d\rho}{dt} = \frac{47.5 D_b w \Omega P_a}{G^3 kT} \qquad (1)$$

where D_b is the diffusion coefficient in the grain-boundary second phase ($m^2 \sec^{-1}$), w is the width of the grain boundary phase (m), G is the grain size (m), h is Boltzmann's constant ($J K^{-1}$), P_a is the applied pressure ($MN m^{-2}$) and Ω is the volume (m^3) of Si_3N_4 transported by each atom of the rate controlling species (Si or N). The surface energy contribution, γ/r, is assumed to be negligible

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by comparison with the applied pressure P_a. In accordance with this model, simple relationships have been observed between the densification rate and both the volume of second phase added and the applied stress. The α-Si_3N_4 to β-Si_3N_4 transformation likewise appears to be controlled by a grain-boundary diffusion process, as required by the Coble model.

It would be expected that useful comparisons could be made between β'-sialon systems with relatively low z values and the well-explored silicon nitride system. The two systems would appear to be broadly similar, in that the silicon nitride hot-pressing system consists in reality of, for example, the mixture SiO_2–Si_3N_4–MgO, while a commonly used starting point for β'-sialon materials is the mixture SiO_2–Si_3N_4–AlN–Al_2O_3. The silica is inevitably introduced, as a surface film on the silicon nitride particles. Both systems would be expected initially to consist at pressing temperatures of predominantly silicon nitride, with a liquid second phase derived from the minor constituents. It is, in fact, generally assumed that the rapid densification rates obtainable with β'-sialon compositions are the result of the early formation of liquid phases [8]. Such phases may subsequently remain in the fully dense material as grain-boundary phases. Recent work has been concerned with the mapping of liquid-phase regions in the AlN–Al_2O_3–SiO_2–Si_3N_4 system, and has revealed melting temperatures as low as 1480° C [9].

Preliminary quantitative comparisons of the dependence of densification rate during hot-pressing on the position of the calculated compositional point in relation to the β'-sialon phase line have indicated that the densification rate is very sensitive to composition [10]. Small deviations towards the oxide-rich side of the β'-line result in markedly enhanced densification rates, which have been associated with the presence of an SiO_2-rich liquid second phase. What has not been made clear is whether the α-Si_3N_4 to β'-sialon conversion is similarly sensitive to composition, or whether the densification model successfully applied to silicon nitride, and other systems, is equally appropriate for the β'-sialon system.

This paper is concerned with the results of a more detailed examination of the densification and conversion rates obtained during the reaction hot-pressing of selected β'-sialon compositions. These compositions correspond to theoretical z values in the region of 0.8, and were chosen so that the compositional points traversed the β'-sialon phase line (Fig. 1). It was thereby hoped to obtain by extrapolation information about the hot-pressing behaviour of systems corresponding to phase pure β'-sialon.

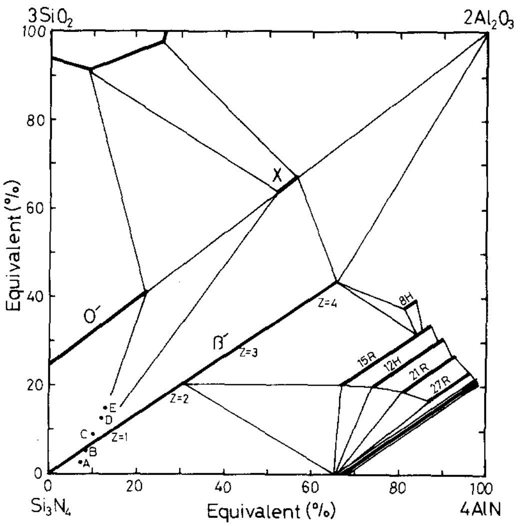


Figure 1 The SiO_2–Si_3N_4–AlN–Al_2O_3 behaviour diagram [1], showing the theoretical locations of the β'-sialon compositions studied.

2. Experimental details

The starting compositions of the systems examined are shown in Table I, and the compositional points are plotted in Fig. 1. These compositions were prepared from silicon nitride, aluminium nitride and alumina powders, the specifications for which are given in Table II. It was assumed that the aluminium nitride contained 6 wt % alumina, and the silicon nitride 4 wt % silica [11].

Powder mixing was carried out in propan-2-ol using a polythene container, in a vibro-mill. Alumina grinding media were used, and the mixing time was kept constant at 30 min. Loss from the alumina elements was allowed for in calculations of the above compositions. 6 g samples of powder were pressed in an induction-heated graphite die which had an internal diameter of 25 mm. The inner surfaces of the die and punches were coated with a film of boron nitride powder to prevent contact of the material with the graphite. Details of the apparatus and standard hot-pressing procedures have been described elsewhere [12]. In this study the standard pressure was 20 MPa, at temperatures of 1700 and 1750° C. In a limited number of experiments pressures were extended to

TABLE I Sample compositions expressed in terms of the starting materials (as mixed) and calculated phase compositions

Sample	Powder composition (wt %)			Phase composition (eq %)		
	AlN	Al_2O_3	Si_3N_4	Al	O	[O]/[Al]
A	7.6	1.1	91.3	7.4	2.7	0.36
B	6.0	4.7	89.3	8.6	5.4	0.63
C	3.6	10.0	86.4	10.3	9.1	0.88
D	1.4	14.9	83.7	12.0	12.8	1.07
E	0.0	18.1	81.9	13.2	15.2	1.15

cover the range 8 to 30 MPa. For the examination of the phase transformation the amounts of α-Si_3N_4, β-Si_3N_4 and β'-sialon were determined by X-ray diffractometry with Ni filtered Cu$K\alpha$ radiation (50 kV, 60 mA). Integrated intensities of the α_{201} and β_{101} and β'_{101} reflections were used in conjunction with calibration curves prepared from constant weights of standard mixtures. Fracture surfaces of hot-pressed material were observed both before and after etching, by means of scanning electron microscopy. Etching was carried out in NH_4FHF solution (20 wt %) for 5 min at 80° C.

3. Results

A typical family of densification curves is shown in Fig. 2 for compositions A, B, C and E pressed at 1700° C, and in Fig. 3 for compositions B, C, D and E pressed at 1750° C. Each curve represents the smoothed average of several runs. These clearly indicate the marked sensitivity of the densification rate to the composition, and the trend towards more rapid densification as the compositions move towards the SiO_2–Al_2O_3 boundary. Fig. 4 shows the variation of densification rate at a fixed relative density of 0.70, as a function of the equivalent oxygen/equivalent aluminium ratio. Since all the materials have similar z values, this ratio is used as a convenient indication of the amount of second phase likely to be present. On this scale the theoretical β'-sialon composition corresponds to an [O]/[Al] ratio of 0.67. Both curves approach the compositional axis in the region 0.63, indicating that the presence of a permanent oxide-rich second phase is necessary for appreciable densification to occur. A nitride-rich second phase is completely ineffective in this respect. These densification rates appear to increase more rapidly at 1750° C than at 1700° C, with increasing values of this ratio. Since the pressure dependence of densification rate can provide an important indication of the dominant densification mechanism, composition E was hot-pressed at a number of pressures in the range 8 to 30 MPa. The log–log plot of densification rate at a relative density of 0.70 as a function of pressure is shown in Fig. 5. The line drawn through the points has a slope of 1.0.

TABLE II Starting materials specification

Material	Specification
Silicon nitride	Lucas Industries Ltd (courtesy Dr R. J. Lumby) median size 6.6 μm, α/β ratio 91 : 9, metallic purity 99.5%
Aluminium nitride	Koch-Light, 99%, < 50 μm
Alumina	Alcoa A-16 Superground, median size 1 μm, purity > 99.9%

Fig. 6 shows the variations in the amounts of α-Si_3N_4 and β'-sialon present, as a function of time at 1700° C. The small amount of the β-Si_3N_4 initially present in the silicon nitride appeared to remain unchanged over this period of time. Small peaks corresponding to α-Al_2O_3 and AlN had disappeared after 10 min. The points for zero time were obtained by heating the powder mixture to temperature at the standard rate of 100° C min^{-1} and then immediately cooling again. Fig. 7 shows data for the amount of residual α-phase plotted in accordance with a first order rate equation, and the first order rate constants are plotted as a function of composition in Fig. 8. That the mean z value of the β'-sialon formed was not independent of time is shown in Fig. 9. It is seen that the mean z values tend to decrease rapidly with hot-pressing time and eventually level off in the region of 1.0. A comparison between densification rate and α-phase to β'-sialon conversion rate is provided by Fig. 10, where sets of data for 1700° C are superimposed. This suggests that, while the conversion rate is sensitive to the composition of the system, this is not so marked an effect as the dependence of the densification rate on composition.

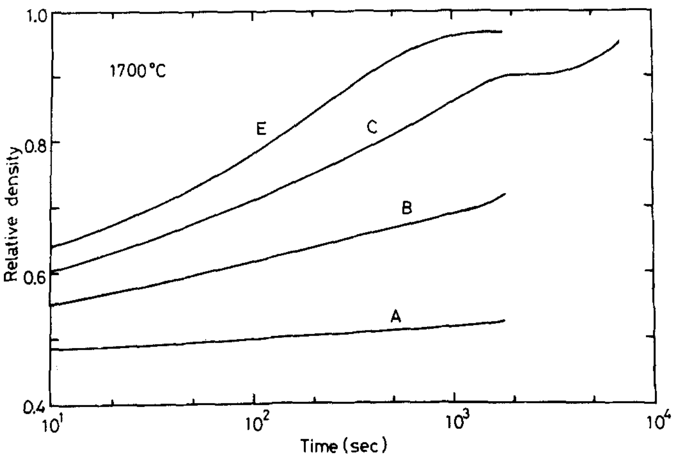


Figure 2 Relative density (ρ/ρ_{th}) plotted as a function of time for four compositions hot-pressed under 20 MPa at 1700° C.

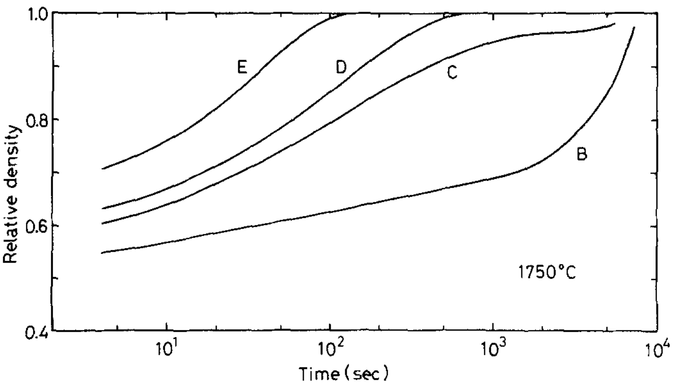


Figure 3 Relative density (ρ/ρ_{th}) plotted as a function of time for four compositions hot-pressed under 20 MPa at 1750° C.

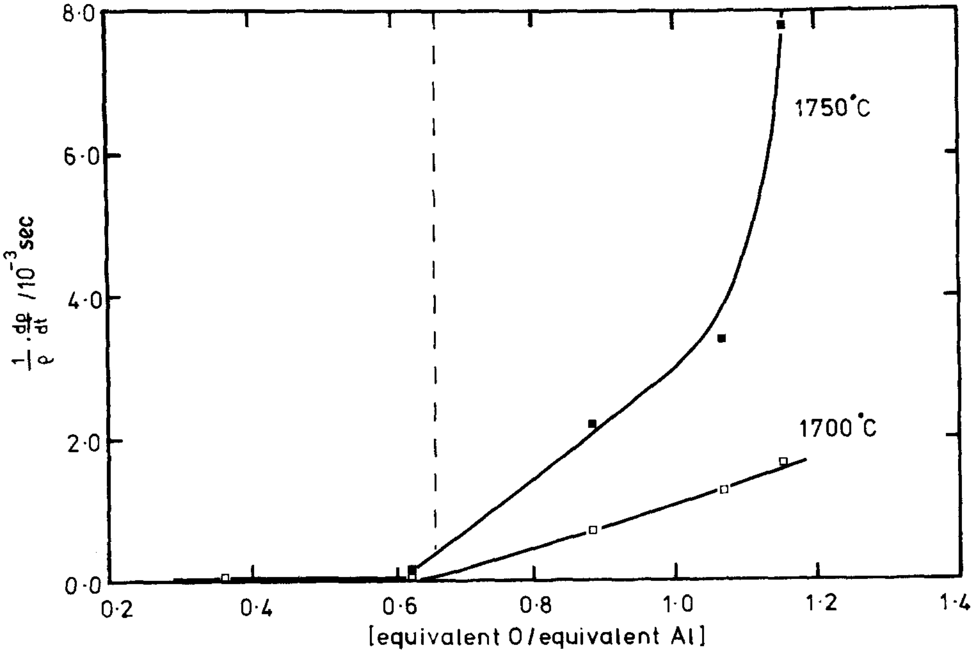


Figure 4 Instantaneous densification rates $[(1/\rho_t)(d\rho/dt)]$ at a relative density of 0.70 for 1700 and 1750° C plotted as a function of composition expressed in terms of the [equivalent oxygen]/[equivalent aluminium] ratio.

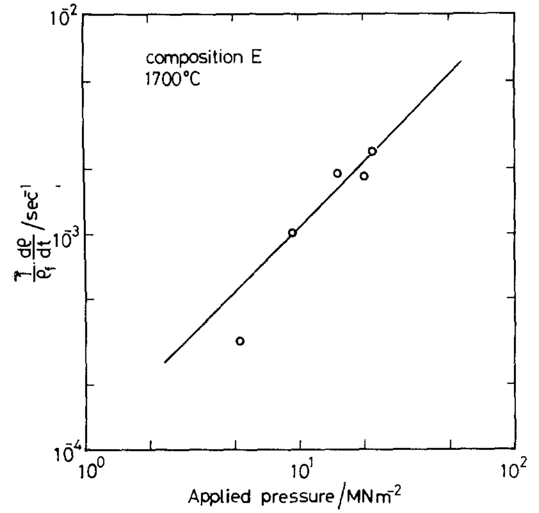


Figure 5 Instantaneous densification rate $[(1/\rho_t)(d\rho/dt)]$ at a relative density of 0.70 plotted in log–log form, as a function of applied pressure, at 1700° C for composition E.

Samples of compositions A and E, chosen because they would be expected to show the most extreme microstructural features, were hot-pressed for varying lengths of time at 1700° C and then fractured for examination by scanning electron microscopy. Fracture faces were subsequently chemically etched and then re-examined. Examples of micrographs of composition A are shown in Fig. 11 and of composition E in Fig. 12. A feature of these micrographs is the underlying coarsening of the grain structure revealed by the etch treatment. Otherwise it is clear that the void fraction remains approximately constant in composition A, while the voids are rapidly eliminated in composition E. Fracture occurs preferentially through the finer grain matrix so that the presence of the coarser grain structure tends not to be apparent until the etch treatment is applied.

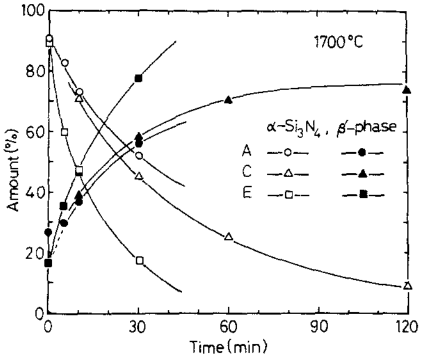


Figure 6 The conversion of α-Si_3N_4 to β'-sialon during hot-pressing under 20 MPa at 1700° C, plotted in terms of the proportion of each phase present, as a function of time.

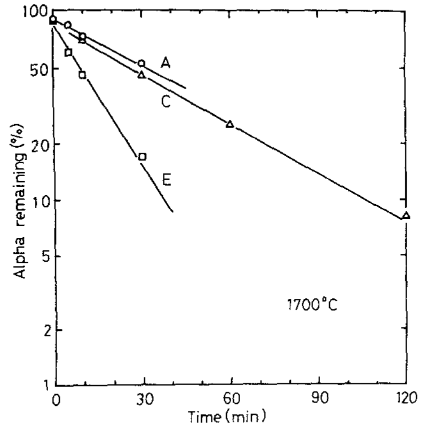


Figure 7 Data presented in Fig. 6 for α-Si_3N_4 plotted according to a first order rate law.

4. Discussion

The reaction hot-pressing behaviour of powder mixtures of overall compositions corresponding approximately to β'-sialon is shown clearly in Figs. 2, 3 and 8 to be markedly sensitive to slight changes in the nominal composition. Both the rate of densification and the rate of β'-sialon formation are influenced considerably by small movements of the compositional point away from the β'-sialon phase line. This corresponds broadly to the pattern of behaviour to be expected from a series of reacting and densifying systems in which the proportion of liquid phase present is progressively increased. Because of the similarity to be expected between the systems, it is of interest to make qualitative comparisons with the hot-pressing behaviour of silicon nitride in the presence of 5 wt% MgO (generating some 12 vol% liquid phase), under identical conditions of temperature (1700 to 1750° C) and pressure (20 MPa) [5]. Although for a fully quantitative comparison of these reaction rates it is necessary to make certain important assumptions, particularly with regard to the real particle size of the silicon nitride powder used, it appears that the conversion and densification rates of compositions D and E are close to those of the α-Si_3N_4–MgO system, and the times required for theoretical density to be attained, and the rates of disappearance of α-Si_3N_4, are very similar in both these β'-sialon and silicon nitride systems. In this respect, therefore, the simplifying assumption made initially, that the β'-sialon system could, in practice, be regarded as an

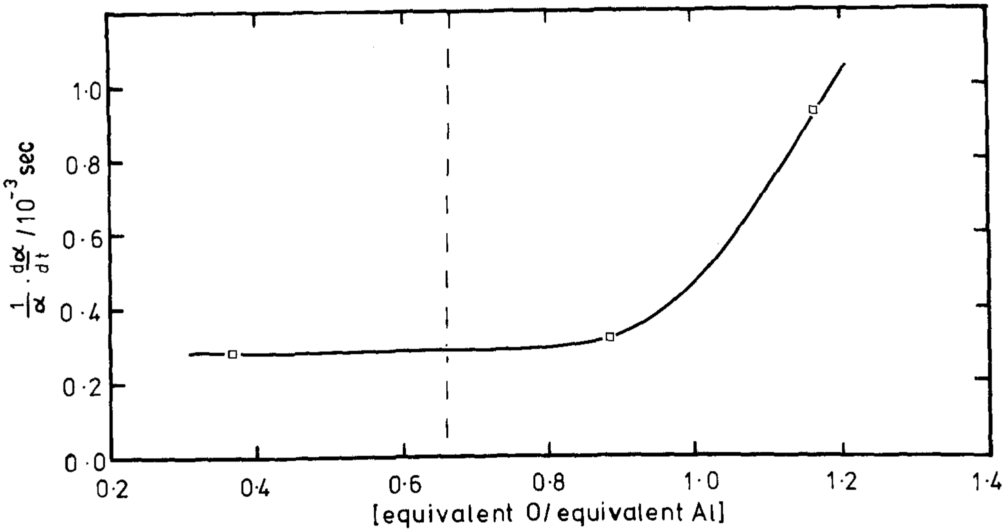


Figure 8 First order rate constants $[(1/\alpha)(d\alpha/dt)]$ for the α-Si_3N_4 to β'-sialon conversion at 1700° C plotted as a function of composition expressed in terms of the [equivalent oxygen] / [equivalent aluminium] ratio.

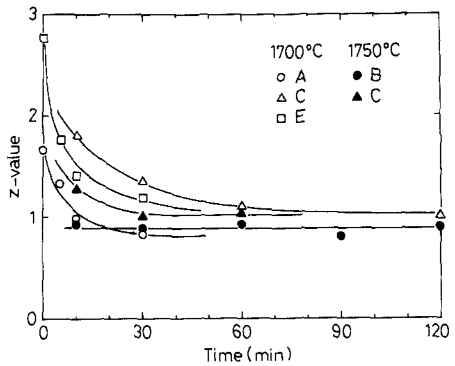


Figure 9 Mean z values for the β'-sialon phase, as determined from X-ray diffraction 2θ values, plotted as a function of time, for selected compositions hot-pressed under 20 MPa at 1700 and 1750° C.

α-Si_3N_4 liquid-phase system, would appear to be justified. On the other hand, compositions B and C are much less reactive, and practically no densification is obtained at 1700° C with composition A although interestingly the rate of the α-Si_3N_4 to β'-sialon conversion is still appreciable. This pattern of behaviour is qualitatively similar to the pattern observed with the silicon nitride system as the magnesium oxide content is progressively reduced. The further implication arising from the behaviour of composition A, however, is that mechanisms are still available for the α-Si_3N_4 to β'-sialon transformation other than that of solution-reprecipitation. Further evidence for the marked chemical reactivity of this system is

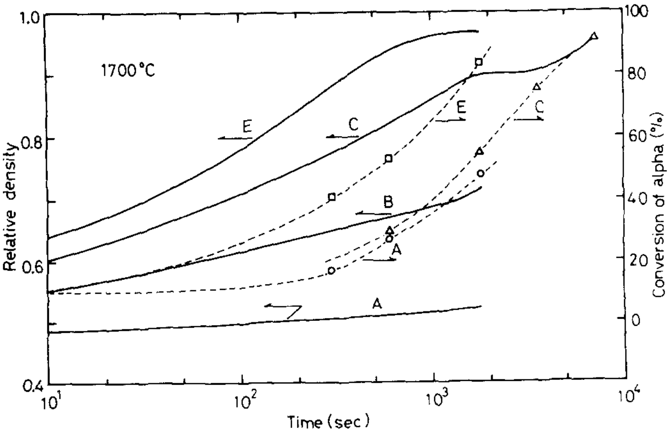
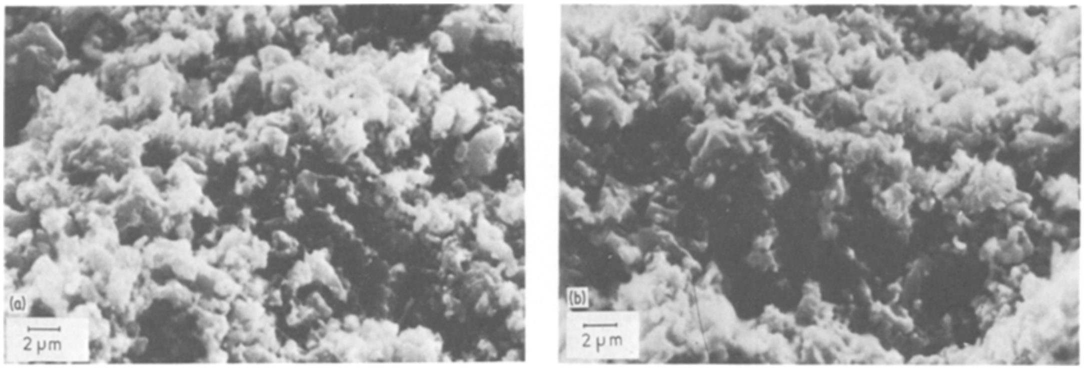


Figure 10 Relative density (ρ/ρ_{th}) and simultaneous proportion of α-Si_3N_4 converted to β'-sialon during hot-pressing under 20 MPa at 1700° C, plotted as a function of time.



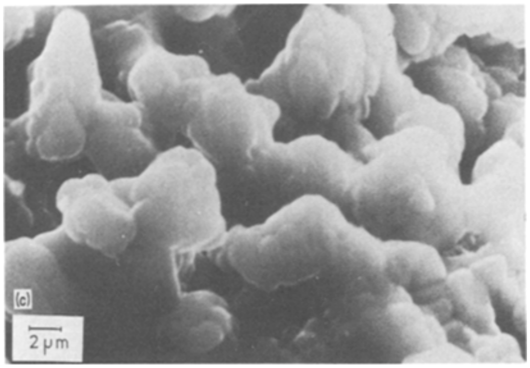


Figure 11 Composition A hot-pressed under 20 MPa at 1700° C for (a) 0 min, unetched fracture surface; (b) 30 min, unetched fracture surface; (c) 30 min, etched fracture surface.

provided by the shift in mean z value with time for composition A, shown in Fig. 9. This suggests that β'-sialon first formed may be subsequently re-dissolved, and reprecipitated as β'-sialon of a lower z value.

It has been suggested that in the α-Si_3N_4–MgO system the initial hot-pressing densification stage consists of a particle rearrangement process, leading to relative densities of the order of 0.65 within times of 3 sec [5]. Subsequent densification requires sequential particle deformation and grain-boundary sliding processes [13]. The Coble intermediate stage hot-pressing model has been found to give a generally satisfactory fit to the experimental data, indicating that the particle deformation process is rate controlling and that grain-boundary sliding is relatively fast. In the present study of the β'-sialon system it was not felt that sufficient reliability could be placed on densification data obtained at pressing times of less than 10 sec for their use in quantitative support of a particle rearrangement, or indeed any other, densification mechanism. However, in view of the nature of the system and the likelihood of the rapid generation of a liquid phase from interaction of the amorphous silica film on the surface of the silicon nitride particles with AlN and Al_2O_3 [9], as well as from the eutectic at 1595° C in the sample SiO_2–Al_2O_3 system [14], a liquid-phase assisted particle rearrangement process seems intrinsically probable. Fig. 3 indicates that at very short times (~ 1 sec) a spread of relative densities has been obtained, the relative density increasing in proportion to the volume of liquid phase to be expected, even though the initial cold compact relative densities (~ 0.48) were identical. In keeping with this argument for an initial very fast particle rearrangement process, it can be seen that the short time relative densities are higher at 1750° C than at 1700° C. Only composition A has retained its cold density after a time of 10 sec.

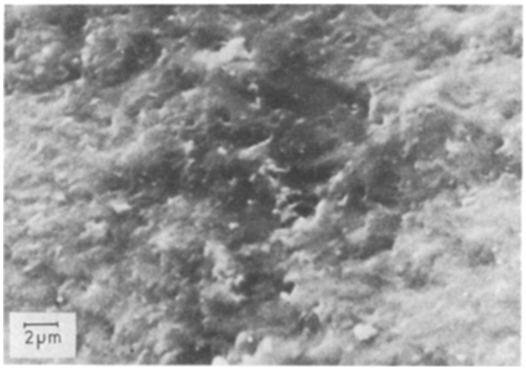


Figure 12 Composition E hot-pressed under 20 MPa at 1700° C for 30 min – unetched fracture surface.

Tests of the applicability of the Coble hot-pressing model to the intermediate stage of densification in the β'-sialon system may be applied by considering the pressure dependence of the densification rate (Equation 1), and the effects on densification rate of small variations in composition (and by implication, therefore, the volume of liquid present). The applied pressure dependence was tested on composition E which would be expected to contain the largest volume of liquid phase. Satisfactory agreement with the requirement of the model is observed indicating that a solution-reprecipitation process in the presence of a stress gradient is rate-controlling.

The effect of variations in the liquid-phase content on densification behaviour is less easy to examine quantitatively for several reasons, each having a small but a cumulatively significant effect. These may be enumerated as follows: (i) the uncertainties with regard to the exact starting composition arising from variations in the amount of oxide present in the nitride powders after milling; (ii) slight losses in material, principally SiO and Al_2O, during pressing, which would be expected to cause a drift in composition towards the AlN corner of the phase diagram; (iii) the lack of knowledge of how close the system is to equilibrium during the early stages of the pressing process; (iv) the progressive change in the volume of the liquid phase during the reaction in which Al and O are withdrawn in the conversion of α-Si_3N_4 to β'-sialon. Point (iv) may not, however, in practice be a significant cause of uncertainty because at the relative density of 0.70 used for comparison purposes very little phase conversion has occurred with compositions B, C, D and E. At 1700° C, for densification rates measured at a relative density of 0.70, a reasonably straight line may be drawn through the data points and which intersects the composition axis at a point close to the theoretical value for β'-sialon. At 1750° C it appears that composition points close to the theoretical β'-sialon composition also provide a reasonably linear relationship between the densification rate and the volume of liquid phase present. The line curves sharply upwards, however, for compositional points further away from the β'-sialon line. This suggests that at a temperature between 1700 and 1750° C, a significant change occurs in the volume of liquid phase present for compositions well removed from that of β'-sialon, consequent possibly on shifts in phase field boundaries with increasing temperature. It is also clear from the behaviour of compositions A and B, which theoretically correspond to compositions on the nitride-rich side of the β'-sialon line, that the rapid removal of surplus silica through reaction with the excess aluminium nitride and silicon nitride seriously retards the densification process. Thus it must be assumed from a consideration of Fig. 4 that pure single phase β'-sialon material would be intrinsically no more easy to densify by hot-pressing than is α-silicon nitride in the absence of oxide pressing aids.

The behaviour of composition B at long pressing time ($> 10^3$ sec) does not conform to the pattern set by compositions C, D and E. This in itself indicates a discontinuity in hot-pressing characteristics as the β'-sialon line is crossed, although the precise reason for the later stage changes in curve gradient leading to the attainment of theoretical density at 1700° C in times of the order of 10^4 sec is not clear. It is possible that at these long times other compositional changes occur due to interactions with the hot-press environment. Sample weight losses were slight over the time scale of most interest in this work ($< 10^2$ sec), but approached 2 wt% after times of the order of 10^4 sec.

The model proposed for the intermediate stage of hot-pressing in silicon nitride [5] indicates that the α-Si_3N_4 to β'-Si_3N_4 transformation should initially follow the same pattern of kinetic behaviour as the densification process. This view follows from the assumption that the α-Si_3N_4 entering the liquid phase under the influence of the stress gradient and allowing densification to occur, reprecipitates as the β'-phase. In the silicon nitride case significant common features of the densification and transformation processes were observed, and which were taken to indicate that the common rate controlling step for both processes was the diffusion of material along the grain boundaries. The transformation rate law was, however, observed to be first order with respect to the disappearance of α-Si_3N_4, and the first order rate constant was independent of applied pressure [5]. It thus appeared that the time between the application of pressure and achievement of full density was too short to allow sufficiently accurate recording of transformation data at this stage of the process, and the first order kinetics observed were assumed to relate therefore to the α-Si_3N_4 to β-Si_3N_4 transformation after full density had been obtained. In the present case of the β'-sialon system, measurement of the transformation rate at different pressures was not attempted. It was clear, however, that the transformation at 1700° C accurately followed first order kinetics over a very wide range of conversion, and independently of composition. In this respect also, therefore, the silicon nitride and the β'-sialon systems appear to behave in a similar way. In the Si_3N_4–MgO system there was a clear linear dependence of the transformation first order rate constant on the volume of liquid phase present. In the β'-sialon system the same difficulties apply in making quantitative comparison between the transformation rate constants and the volume of liquid present, as in the densification rate comparisons. Nonetheless, Figs. 4 and 8 show that there is a significant difference in behaviour between the different compositions, and that the trends are in line with the expected change in liquid-phase level. However, the transformation rate of composition A is still appreciable, even though the extent of densification obtained after 10^3 sec is negligible. This provides a strong indication that other material transport processes are occurring, and which lead to a phase transformation, but not to densification. Two such processes are surface diffusion, and the vapour-phase transport of material. Additional information is needed in order to assess the relative importances of these processes in this system, but it is worth observing that at temperatures of 1700° C and above, the volatility of the reactants is becoming appreciable. A practical indication of this fact is the tendency for weight losses to be obtained at long hot-pressing times. Reaction 2 for example leads to theoretical vapour pressures of the order of 10^{-3} atm [15],

$$Si_3N_{4(c)} \rightleftharpoons 3Si_{(l)} + 2N_{2(g)}, \qquad (2)$$

while Reaction 3,

$$2Si_3N_{4(c)} + 3Al_2O_{3(c)} \rightleftharpoons 3Al_2O_{(g)} + 6SiO_{(g)} + 4N_{2(g)} \qquad (3)$$

if assumed to occur independently, would provide Al_2O and SiO partial pressures of the order of 10^{-5} atm. Even aluminium nitride becomes significantly unstable as aluminium and nitrogen at 1700° C ($\sim 10^{-3}$ atm). It has previously been suggested that the existence of a liquid phase is necessary for the conversion of α-silicon nitride to β-silicon nitride [16]. Subsequently, Greskovich and co-workers have presented evidence which indicates that the transformation can occur in the absence of liquid phases [17], and the importance of vapour-phase transport or surface diffusion processes is implied.

The action of competing material transport processes in determining the sintering behaviour of the predominantly covalent silicon carbide and silicon nitride has been examined in detail by Greskovich and Rosolowski, and the tendency for particle and porosity aggregation to occur without overall compact shrinkage commented on [18]. Similar behaviour is seen in the case of the sialon system of composition A, where considerable microstructural rearrangement has occurred with redistribution of the void space, even though overall densification is negligible. This similarity points to the importance of other material transport processes during the reaction hot-pressing, and which permit the redistribution of material with simultaneous chemical reaction, yet leave material at particle–particle contact points to inhibit compact shrinkage. The significant grain growth seen in the etched fracture face of composition A suggests that as in the silicon carbide case, grain-boundary mobility may nonetheless be appreciable.

5. Conclusions

The hot-pressing behaviour of β'-sialon- and MgO-doped silicon nitride systems show many points of similarity in those cases where the β'-sialon compositions contain an appreciable quantity of an oxide-rich grain-boundary phase. This pattern confirms the importance of the grain-boundary phase for densification in the sialon system. The rate-controlling densification step in such sialon compositions appears to be satisfactorily described by the Coble creep model.

In the cases of sialon compositions close to the theoretical β'-sialon line a different pattern of behaviour is seen. Densification rates tend to become negligible, although chemical interactions and microstructural rearrangement still occur at appreciable rates. These facts suggest that other material transport processes are potentially important in this system, although in the presence of large amounts of an oxide-rich grain-boundary phase they may be relatively unimportant because of the existence of an alternative, faster, material-transport route. Extrapolation of the sialon densification behaviour to compositions containing no grain-boundary phase indicates that pure β'-sialon should be effectively unsinterable unless special conditions obtain, such as, for example, the use of ultra fine powders.

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References

1. K. H. JACK, *J. Mater. Sci.* **11** (1976) 1135.
2. K. H. JACK and W. I. WILSON, *Nature* (*London*) *Phys. Sci.* **238** (1972) 28.
3. R. J. LUMBY, B. NORTH and A. J. TAYLOR, in "Special Ceramics", Vol. 6, edited by P. Popper (British Ceramic Research Association, Stoke-on-Trent, 1975) pp. 283–98.
4. A. W. J. M. RAE, D. P. THOMPSON and K. H. JACK, in Proceedings of the Army Material Technology Conference, Ceramics for High Performance Applications II, Newport R. I. (1977) p. 1039.
5. L. J. BOWEN, R. J. WESTON, T. G. CARRUTHERS and R. J. BROOK, *J. Mater. Sci.* **13** (1978) 341.
6. L. J. BOWEN, T. G. CARRUTHERS and R. J. BROOK, *J. Amer. Ceram. Soc.* **61** (1978) 335.
7. R. L. COBLE, *J. Appl. Phys.* **41** (1970) 4798.
8. M. H. LEWIS, B. D. POWELL, P. DREW, R. J. LUMBY, B. NORTH and A. J. TAYLOR, *J. Mater. Sci.* **12** (1977) 61.
9. I. K. NAIK, L. J. GAUCKLER and T. Y. TIEN, *J. Amer. Ceram. Soc.* **61** (1978) 332.
10. M. BENN, M. KUWABARA and F. L. RILEY, "Science of Ceramics", Vol. 9 (Nederlandse Keram, Vereniging, 1977) pp. 119–26.
11. B. NORTH, M.Sc. Thesis, University of Birmingham (1978).
12. T. G. CARRUTHERS and R. J. WESTON, *Proc. Brit. Ceram. Soc.* **22** (1973) 197.
13. W. BEERÉ, *Acta Met.* **24** (1976) 277.
14. "Phase Diagrams for Ceramists" (American Ceramics Society, Columbus, Ohio, 1964).
15. "JANAF Thermochemical Tables", 2nd edn. (US Department of Commerce, Washington, 1971).
16. D. R. MESSIER, F. L. RILEY and R. J. BROOK, *J. Mater. Sci.* **13** (1978) 1199.
17. C. GRESKOVICH and S. PROCHAZKA, *J. Amer. Ceram. Soc.* **60** (1977) 471.
18. C. GRESKOVICH and J. H. ROSOLOWSKI, *ibid* **59** (1976) 336.

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