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Variation of aluminium concentration in β′-sialon grains formed during liquid-phase sintering of Si_3N_4–Al_2O_3–Nd_2O_3

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The aluminium concentration in β′-sialon grains of the $74Si_3N_4$ (α)-$6Al_2O_3$–$20Nd_2O_3$ (wt %) specimen has been determined. As the α–β′ transformation proceeded, the average aluminium concentration in β′-sialon grains decreased. For individual β′ grains, the aluminium concentration at the centre was higher than that at the edge. The observed variation of aluminium concentration has been explained in terms of the compositional change of the liquid matrix during sintering.

1. Introduction

During the preparation of β′-sialon, because we usually use α-Si_3N_4 powder as starting material, the phase transformation from α to β′ occurs in the presence of a liquid formed by reactions between Si_3N_4, sintering additives such as Al_2O_3, and SiO_2 impurity [1–3]. Because β′-sialon contains aluminium supplied from the liquid phase, the formation of β′-sialon, i.e. α–β′ transformation, is expected to cause a variation in aluminium concentration in the liquid matrix and, therefore, in the β′-sialon formed with sintering time. Indeed, previous investigations on the Si–Al–O–N [4, 5] and Mg–Si–Al–O–N systems [6, 7] showed that the average concentration of aluminium in β′-sialon grains or z-value of $Si_{6-z}Al_zO_zN_{8-z}$ decreased with sintering time. Subsequently, Bonnell *et al.* [8] also demonstrated an uneven distribution of aluminium concentration in individual β′-sialon grains by an EDS analysis on thin foils of hot-pressed β′-YAG (yttrium aluminium garnet: $Y_3Al_5O_{12}$) and β′-cordierite samples.

In the present study, the variation of aluminium concentration in β′-sialon in the Si_3N_4–Al_2O_3–Nd_2O_3 specimen has been measured and explained, based on a proposed composition change in liquid phase during sintering. The Si_3N_4–Al_2O_3–Nd_2O_3 system was selected because neodymium is not soluble in β′-sialon and remains in the liquid phase. A neodymium-rich persistent liquid is expected to promote the α–β′ transformation during sintering.

2. Experimental procedure

Specimens were prepared from 74 wt % α-Si_3N_4 (LC12, H. C. Starck), 6 wt % Al_2O_3 (A16, Alcoa) and 20 wt % Nd_2O_3 (99.9%, Morton Thiokol Inc.). 100 g proportioned powder was wet-milled in an alumina attritor for 150 min using alumina balls and isopropanol. The alumina pick-up during milling was about 0.7 g. After drying and sieving through 0.102 mm apertures, the powders were cold-isostatically pressed at 200 MPa into compacts about 14 mm diameter and 13 mm high.

Powder compacts were sintered in a graphite furnace either at 1500 °C for various times from 12–450 min, or at various temperatures from 1500–1700 °C for 3 min under 160 kPa static nitrogen. The compacts were heated to the sintering temperature at 5 $K\,min^{-1}$ and cooled down by switching-off the electric power. The cooling rate from the sintering temperature to 1300 °C was about 60 $K\,min^{-1}$. After thermal cycling, the specimens were polished and X-ray diffracted for the range 15°–50° in 2θ with a step-width of 0.01°, using CuK_α. Two strong peaks of α- and β-Si_3N_4 phases (α(1 0 2), α(2 1 0), β(1 0 1), and

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β(2 1 0)) were chosen for the calculation of phase fractions as well as lattice parameters. The aluminium content in the β′-phase was determined from the calculated lattice parameters using the results of Gauckler *et al.* [9]. The fraction of β′ phase was calculated from

$$V_\beta = \frac{(I\beta_{(1\,0\,1)}/10.90) + (I\beta_{(2\,1\,0)}/11.21)}{(I\alpha_{(1\,0\,2)}/6.66) + (I\alpha_{(2\,1\,0)}/6.79) + (I\beta_{(1\,0\,1)}/10.90) + (I\beta_{(2\,1\,0)}/11.21)} \qquad (1)$$

where $I\beta_{(1\,0\,1)}$ is the measured intensity of the β(1 0 1) plane, and the constant of 10.90 is its normalized peak height [10].

The aluminium concentration in specific areas of β′-sialon grains was measured by energy-dispersive X-ray analysis attached to a transmission electron microscope (Model 200CX, Jeol). Grains with a regular hexagonal shape in the specimen sintered at 1700 °C for 1 h were analysed.

3. Results and discussion

During sintering of the specimens, the α to β′ transformation occurred rapidly as in many other Si_3N_4-oxide systems [1, 2, 11, 12]. Fig. 1 shows calculated aluminium concentration of the β′ grains and the transformed β′ fraction after sintering at various temperatures for 3 min. The transformation is almost completed at 1700 °C within 3 min, while the average aluminium concentration in β′ grains decreases from 8.3 at % at 1500 °C to 2.8 at % at 1700 °C. As shown in Fig. 2, a similar decrease in the average aluminium concentration with transformed β′ fraction was observed during sintering of specimens at 1500 °C. The present results on the variation of aluminium concentration with the phase transformation in Nd–Si–Al–O–N are in agreement with the previous ones for the Si–Al–O–N [4, 5] and Mg–Si–Al–O–N [6, 7] systems. It appears, therefore, common that the β′-sialon grains formed at the beginning of the transformation contain a higher aluminium content than those formed at a later stage.

Fig. 3 shows a transmission electron micrograph together with measured aluminium concentration at various sites in β′ grains of the specimen sintered at 1700 °C for 1 h. The aluminium concentration of the larger grains is higher than that of the smaller ones, and the centre of a grain also has a higher aluminium concentration than its edge region. This result is similar to the previous one for hot-pressed β′-YAG and β′-cordierite specimens [8].

The observed variation of aluminium concentration in the β′ grains implies that the material precipitated earlier contains higher aluminium contents, because β′-grains are believed to grow by the precipitation of materials from a liquid phase during the α–β′ transformation [1, 2]. (Of the two possibilities suggested by Bonnell *et al.* [8], precipitation of material with different aluminium contents and diffusion-out of aluminium into the glass phase during cooling, the first possibility is believed to be reasonable by taking into account the fast cooling rate in our experiment and the low diffusivity of aluminium in β′-sialon [13].) The aluminium variation in β′ grains is, therefore, a consequence of the variation of the liquid composition during the α–β′ transformation. Note that the chemical composition of the material precipitated from a liquid phase will be determined by the chemical composition of the liquid.

Based on the liquidus and tie lines in Si_3N_4–β′-cordierite [8], Si_3N_4–β′-$Y_2Si_2O_7$ [14], Si_3N_4–β′-$Y_3Al_5O_{12}$ [14, 15], Si–Al–O–N [16], and Nd–Si–Al–O–N [17] systems, a behaviour diagram (Fig. 4) of liquid and solid during heating and isothermal holding of Si_3N_4–β′-oxide systems can be drawn. The left-hand corner of Fig. 4 corresponds to pure Si_3N_4 and the initial composition of the powder mixture is given by point C_0.

As the specimen temperature reaches the lowest liquid formation temperature, T_i, a liquid phase forms by the reaction between Al_2O_3, impurity SiO_2, other oxides, and also possibly Si_3N_4 (The actual composition of the liquid is, in general, not on the plane of the

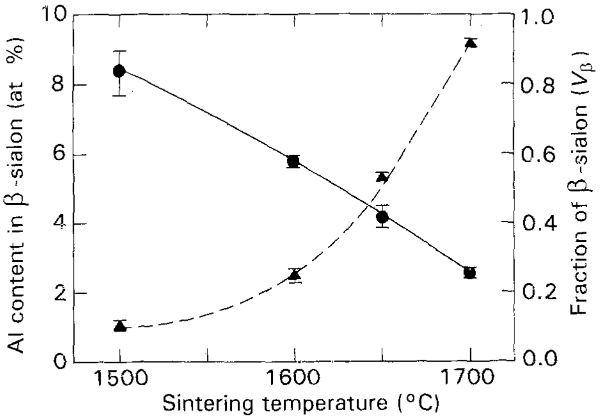

Figure 1 Changes of (●) the average aluminium content in β′-sialon and (▲) the volume fraction of β′ (V_β) with the sintering temperature in $74Si_3N_4$–$6Al_2O_3$–$20Nd_2O_3$ (wt %) specimens sintered for 3 min.

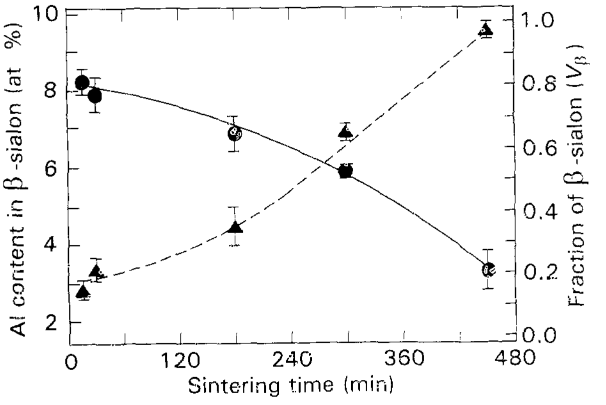

Figure 2 Changes of (●) the average aluminium content in β′-sialon and (▲) the volume fraction of β′ (V_β) with sintering time in $74Si_3N_4$–$6Al_2O_3$–$20Nd_2O_3$ (wt %) specimens sintered at 1500 °C.

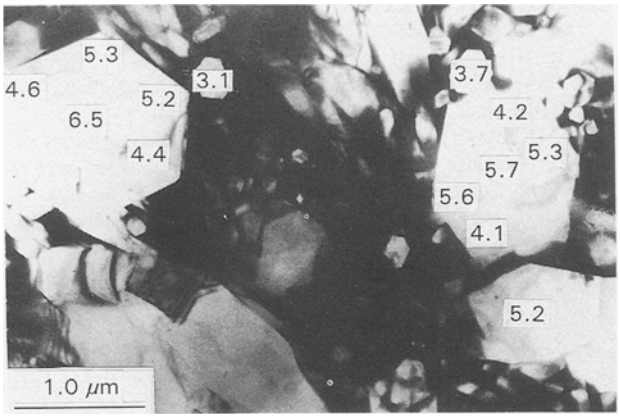

Figure 3 Transmission electron micrograph of $74Si_3N_4$–$6Al_2O_3$–$20Nd_2O_3$ specimen sintered at 1700 °C for 1 h. The figures show measured aluminium concentration (wt %) at various sites in β′ grains.

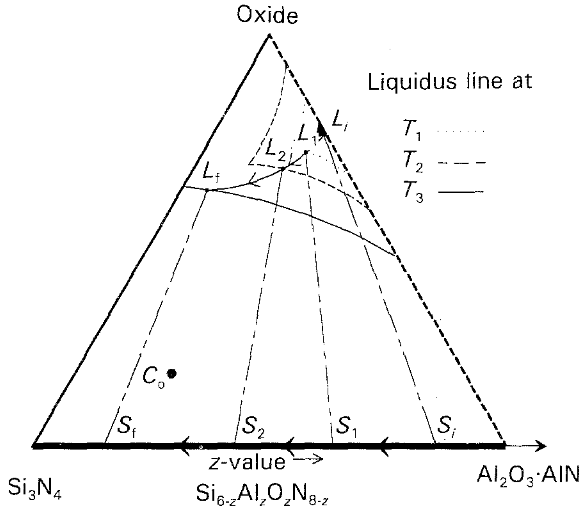

Figure 4 Schematic diagram illustrating the compositional variation of liquid and β′-sialon with α–β′ transformation in a Si_3N_4–β′-oxide system during heating.

behaviour diagram; however, it is drawn on the diagram for convenience in explanation.) Because the liquid region extends from the right-hand edge of the triangle during heating for the systems mentioned above [8, 14–17], the liquid formed at the early stage of sintering contains a higher aluminium content. The precipitation of aluminium-rich β′-sialon which might be in equilibrium with the aluminium-rich liquid will occur with the dissolution of α-Si_3N_4. Upon continuous heating, the composition of liquid changes towards the Si_3N_4–oxide line of the triangle along the path from L_i to L_f and accordingly the composition of precipitating β′-sialon from S_i to S_f. L_f can be closer to the Si_3N_4–oxide line than the equilibrium composition for the indicated composition C_o.

The same reasoning can be applied for the case of isothermal holding. Because the formation of β′ is believed to occur by dissolution of α-Si_3N_4 and precipitation a β′, and aluminium is continuously consumed by the precipitation of β′ phase, the material precipitated during the later stage of sintering contains less aluminium. As a consequence, the aluminium concentration decreases gradually from the centre of a grain towards the edge, as shown in Fig. 3. Similarly, small β′ grains which should be formed at a later stage contain less aluminium than large β′ grains formed earlier.

During sintering, a small amount of *N*-apatite phase ($Nd_4Si_3O_{12}$ or $Nd_5Si_3O_{12}$ N [17]) also appears in the specimens sintered for 3 min at 1500, 1600 and 1650 °C. In the specimen sintered at 1700 °C for 1 h, however, no *N*-apatite phase was detected, implying that *N*-apatite phase is a metastable phase existing below 1700 °C in $74Si_3N_4$–$6Al_2O_3$–$20Nd_2O_3$. This result differs from the previous one [17] which reported the existence of metastable *N*-melilite. Nevertheless, the presence of *N*-melilite or *N*-apatite may not be relevant to the proposed explanation for the variation of aluminium in β′-sialon because these phases do not contain any aluminium.

Uneven composition in single crystals, such as in this β′-sialon, can result from the liquid-phase sintering, if the liquid composition changes with the sintering time and the diffusion of atoms in the solid solution is slow. In this respect, this phenomenon is expected to be difficult to observe because the ceramic crystalline phases are usually compounds with limited solubility. However, the TiC–Mo–Ni cermet system is a well-known example [18–20]. When molybdenum is added for the sintering of TiC–Ni, a new (Ti, Mo)C solid solution forms on TiC grains and results in cored structure: TiC cores and surrounding (Ti, Mo)C solid solution. It has been demonstrated [20] that the small TiC grains dissolve into the liquid matrix and precipitate as (Ti, Mo)C on the surface of large TiC grains during sintering. Meanwhile, the molybdenum concentration in the liquid decreases by the precipitation of (Ti, Mo)C [18–20]. Because the concentration gradient in (Ti, Mo)C cannot be removed by the usual heat-treatment [18], the variation of aluminium concentration in β′-sialon also seems to be maintained during the sintering.

4. Conclusion

The average aluminium concentration in β′ grains decreases with the transformation from α to β′ in the Si_3N_4 (α)-Al_2O_3–Nd_2O_3 system. Because the aluminium in the liquid matrix is consumed with the formation of β′-sialon, the liquid contains less aluminium as the transformation progresses. The result of this process is a gradual decrease of the aluminium concentration from the centre of β′ grains and with their decreasing size, as observed in the present and previous investigation [8]. The observed concentration gradient in β′-sialon can, in turn, be further experimental evidence for the solution–reprecipitation process of the α–β′ phase transformation through the liquid.

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