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o′–β′ sialon ceramics

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Powders of Si_3N_4, Al_2O_3 and SiO_2 were mixed with Y_2O_3 as sintering aid and hot-pressed to form o′–β′ sialon. During sintering, the o′ phase preferentially precipitated in the temperature region of 1550 to 1600 °C, and the β′ phase precipitated at temperatures of 1700 °C and above. The resultant microstructure consisted of dual phases of o′ and β′. The mechanical properties of o′–β′ sialon were improved with increasing amount of the β′ phase. When SiO_2 required for the formation of the o′ phase was all included in the grain boundary phase, o′–β′ sialon exhibited a three-point bending strength as much as 1400 MPa. The oxidation resistance of o′–β′ sialon is expected to improve due to the presence of the o′ phase, but actually was not so good due to the presence of the grain-boundary glassy phase and impurities.

1. Introduction

The β′ phase, Si_2N_2O phase (o′ phase), AlN polymorphic phase, an unknown phase named the X phase, and their mixtures appear on the behaviour diagram [1] for the Si–Al–O–N system at 1700 °C. The region composed of the β′ phase is relatively narrow, and phases other than β′ are likely to appear due to a slight deviation in the amount mixed. Since the sialon ceramic is sintered through the liquid phase, it undergoes dissolving of α-Si_3N_4 into the liquid phase and re-precipitation as β′-sialon in the sintering process. Sialon can precipitate two or more phases at the same time. As a result, such a material may be called an *in situ* composite ceramic.

Among the phases which are able to be combined with the β′ phase, such as α′ phase, o′ phase and AlN polymorphic phase, the o′ phase is focused on in the present work and the correlation between the mechanical properties and the o′/β′ phase ratio was investigated. The α′–β′ composite sialon has already been studied by Mitomo *et al.* [2], who reported that the mechanical properties of AlN–β′ composite were inferior. Sun *et al.* [3] indicated the possibility of combination with the o′ phase, but the mechanical properties of the resultant composite were not examined. Both the AlN polymorphic phase and the α′ phase are basically nitrides, but the Si_2N_2O phase is an oxynitride. Therefore the properties of Si_2N_2O–β′ composite sialon are interesting to note. Yabuta *et al.* [4] have consolidated o′–β′ sialon ceramics by a sinter–HIP method. They carried out quantitative analysis of both the phases of o′ and β′ using an image analysis technique. According to their findings, the o′ phase contents determined were correlated with those calculated from the X-ray diffraction results. They have also studied [5] the effect of process-related oxidation on the microstructure and mechanical properties of o′–β′ sialon ceramics, and clarified that the amount of o′ phase increased and the grain size of o′ phase was changed with progressive oxidation of the silicon nitride powder.

2. Materials and preliminary experiments

Powders of α-Si_3N_4 (Ube SN-E10), Al_2O_3 (Sumitomo AKP-50), and SiO_2 (Nipsil E220) were weighed to the desired composition. After ball-milling in acetone for 24 h, the mixed powder was dried, crushed and then hot-pressed. The mix proportions of the component powders were calculated from

$$\frac{6X}{11.937 + 6X + 4Y} = \frac{a}{100} \qquad (1)$$

$$\frac{11.716}{11.937 + 6X + 4Y} = 1 - \frac{b}{100} \qquad (2)$$

where X (mole) is the ratio of Al_2O_3 to 1 mole (140 g) of Si_3N_4; Y (mole) is the ratio of SiO_2 to 1 mole (140 g) of Si_3N_4; a (eq %) is the $Si^{4+} \rightarrow Al^{3+}$ substitution on the phase diagram; and b (eq %) is the $N^{3-} \rightarrow O^{2-}$ substitution on the phase diagram. The above equations include compensation for the surface-oxidized layer (SiO_2) formed in the α-Si_3N_4 powder.

The Si_3N_4–SiO_2–Al_2O_3 system partly melts at around 1550 °C and starts liquid-phase sintering. This system is inferior in sinterability to the Si_3N_4–SiO_2–Al_2O_3–Y_2O_3 system described later.

Fig. 1 shows the temperature dependence of bending strength (JIS-R1601 and 1604) in the Si_3N_4–SiO_2–Al_2O_3 system sialon. The lowering of the strength does not occur until 1300 °C. This means that the amount of the grain-boundary glassy phase is small in this temperature region. The strength starts to decline from 1400 °C, and is not high enough for a structural material at temperatures even lower than 1400 °C. When the grain boundary between the o′ phase and β′ phase of o′–β′ sialon was observed using a high-resolution transmission electron microscope, the mismatch between certain facets of o′ and β′ phases was found to be relatively small, as shown in Fig. 2.

Next, Y_2O_3 was selected as a sintering aid, and the Si_3N_4–SiO_2–Al_2O_3–Y_2O_3 system was studied. The raw powders were weighed to the mix proportions calculated by Equations 1 and 2, mixed with 7.7 wt % of Y_2O_3 powder (Nippon yttrium, purity: 99.9%, finely ground grade), ball-milled, dried, crushed, and hot-pressed at 40 MPa.

3. Experimental results and discussion

3.1. Sintering behaviour

Raw powders of compositions having 5 eq % $Si^{4+} \rightarrow Al^{3+}$ substitution and 17 eq % $N^{3-} \rightarrow O^{2-}$ substitution on the phase diagram were mixed with 7.7 wt % of Y_2O_3 and hot-pressed at 1500, 1600 or 1750 °C for 2 h. Specimens were machined from the hot-pressed discs (90 mm $\phi \times 10$ mm) in the direction normal to the pressure axis and were examined by X-ray diffraction (XRD). From the XRD patterns shown in Fig. 3, it is evident that α-Si_3N_4 slightly remains at 1500 °C but disappears at 1600 °C. In the phase diagram of the Y_2O_3–SiO_2–Al_2O_3 ternary system, the initial liquid phase appears at 1400 °C on heating. At 1650 °C, the liquid phase increases in amount and decreases in viscosity with the addition of the glass modifier Y_2O_3. The original form of o′–β′ sialon is almost produced at 1650 °C. The peak intensity of the β′ phase slightly increases further at 1750 °C.

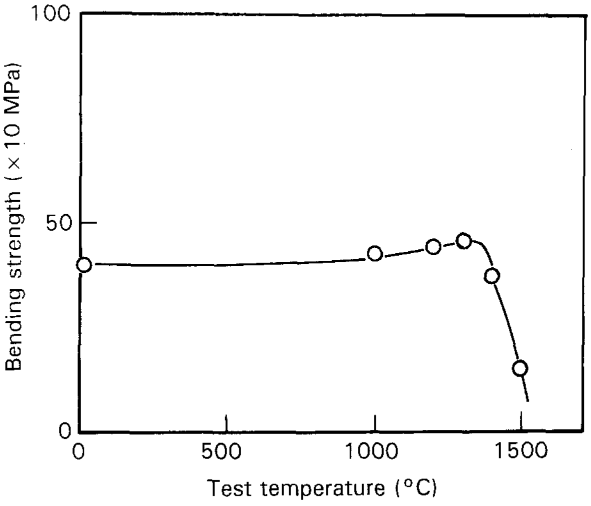

Figure 1 Temperature dependence of bending strength of Si_3N_4–SiO_2–Al_2O_3 system sialon.

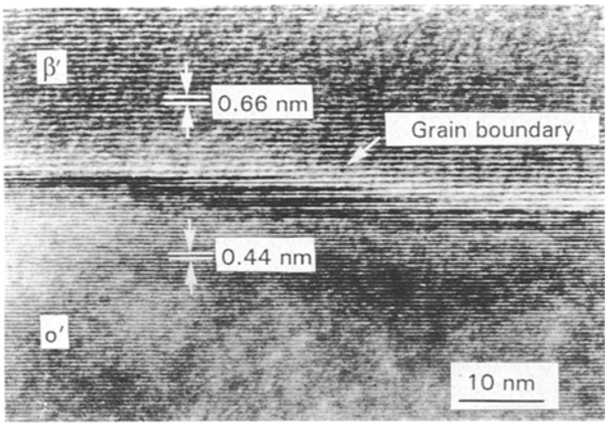

Figure 2 Lattice image of interface between o′ and β′ phases observed by high-resolution transmission electron microscope.

3.2. Properties of sintered bodies

Fig. 4 shows the effect of hot-pressing temperature on the bulk density and bending strength (JIS-R1601) of o′–β′ sialon. The ratio $I_{\beta'(200)}/[I_{\beta'(200)} + I_{o'(200)}]$ is calculated from the (200) peak intensities of the β′ phase and o′ phase in the XRD patterns and is shown as a measure of the ratio of the β′ phase to the o′ phase in Fig. 4. The bulk density decreases with increasing hot-pressing temperature above 1500 °C. At this temperature, although sintering does not proceed much, the pressing forcibly rearranges the powder particles,

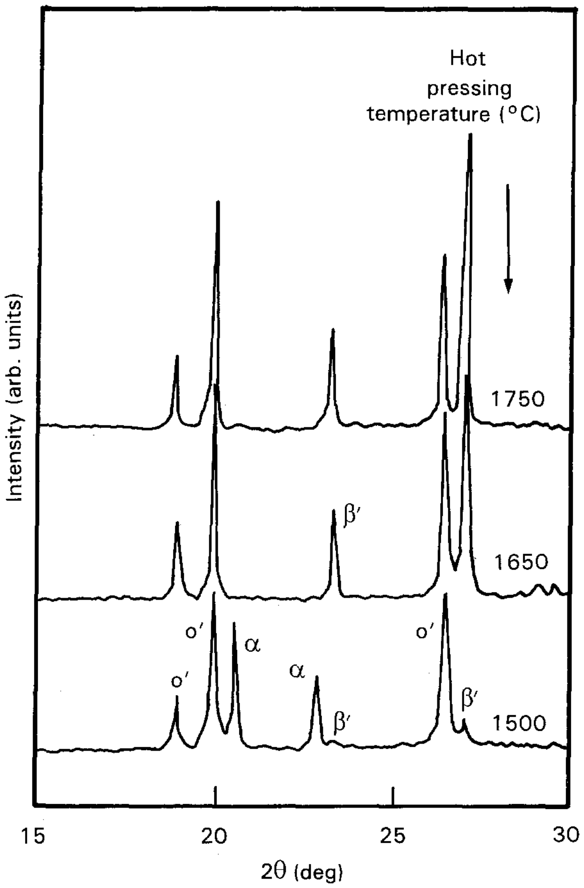

Figure 3 Variation of the X-ray diffraction patterns of Si_3N_4–SiO_2–Al_2O_3–Y_2O_3 system sialon with hot-pressing temperatures, 1500 to 1750 °C.

resulting in an increase of packing density. At 1600 °C, sintering advances, the thermal decomposition of the liquid phase and o′ phase begins to occur, and an o′ phase of relatively low theoretical density increases in amount. The bending strength thus increases, regardless of the magnitude of the bulk density. The proportion of the β′ phase gradually increases with increasing temperature up to 1700 °C, which in turn increases the bending strength. With the composition being the same, the change in the volume ratio of the o′ phase to the β′ phase is considered to change the composition of the glassy phase. Although the change in matching between the crystalline phase and grain-boundary glassy phase is one of the resultant problems, its effect on the bending strength is not evaluated. The reduction of bending strength of materials hot-pressed at 1750 °C is attributable to the thermal decomposition of part of the o′ phase. The room-temperature three-point bending strength of specimens hot pressed at 1700 °C was 921 MPa.

Raw powders with the $Si^{4+} \rightarrow Al^{3+}$ substitution set at 5 eq % and the $N^{3-} \rightarrow O^{2-}$ substitution set at 8, 13, 16.5 or 23 eq % were mixed with 7.7 wt % of Y_2O_3, hot-pressed at 1700 °C for 2 h, and tested for three-point bending strength at room temperature. The results are shown in Fig. 5. The phase diagram shows that increasing the amount of substitution increases the proportion of the o′ phase and decreases the bending strength. The presence of the o′ phase was not detected for 8 eq % from the XRD patterns. This is probably because excess SiO_2 does not form the o′ phase, but forms SiO_2-Al_2O_3-Y_2O_3 glass through the sintering aid Y_2O_3 and exists at the grain boundaries. The room-temperature bending strength of o′–β′ sialon is 1420 MPa on average and is comparable to that of sialon produced by the alkoxide process [6].

Fig. 6 shows a transmission electron micrograph (TEM) of o′–β′ sialon. The microstructure is a uniform mixture of grains, apparently those of the relatively acicular β′ phase, and of relatively equiaxed grains of the o′ phase (as well as the β′ phase probably), measuring 1 μm or less in diameter.

3.3 Oxidation resistance

The o′ phase is an oxynitride and is expected to be superior in resistance to oxidation. Fig. 7 shows the oxidation weight gain of o′–β′ sialon and Syalon 201 (Vesuvius Zyalons, Solihull, UK) that were hot-pressed at 1600 and 1700 °C and oxidation-tested in the atmosphere for 24 h at temperatures from 1200 to 1500 °C. The o′–β′ sialon specimens hot-pressed at 1600 °C are larger in the proportion of the o′ phase and are thus smaller in oxidation weight gain than those hot-pressed at 1700 °C.

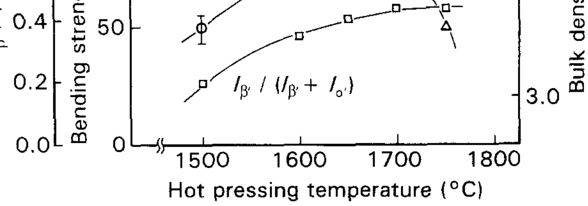

Figure 4 Effect of hot-pressing temperature on (△) density, (○) three-point bending strength and (□) phase ratio of o′–β′ sialon.

Fig. 8 is the cross-sectional SEM back-scattered electron image of o′–β′ sialon hot-pressed at 1700 °C and oxidation-tested. The normal microstructure is observed on the right-hand side and shows an oxide film of a few tens of micrometres in thickness on the left-hand side in contact with the atmosphere. Judging from the test duration of a mere 24 h, this result cannot be highly rated. The presence of the o′ phase

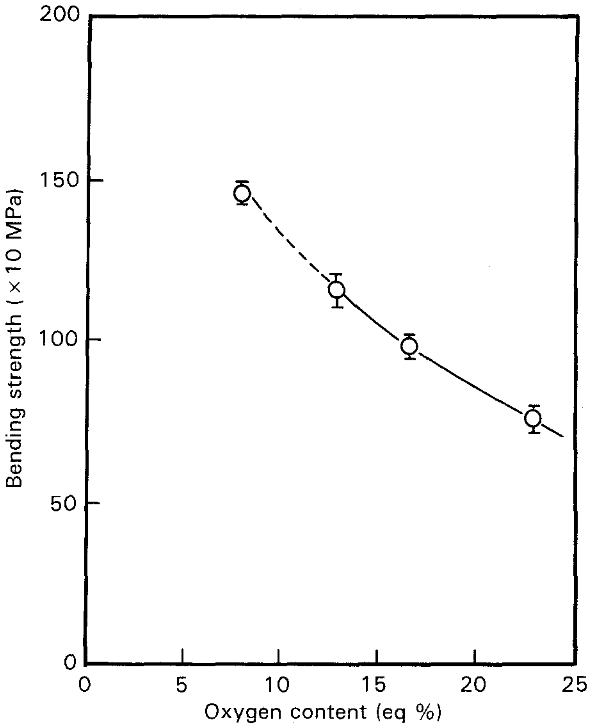

Figure 5 Effect of oxygen content on the three-point bending strength of o′–β′ sialon.

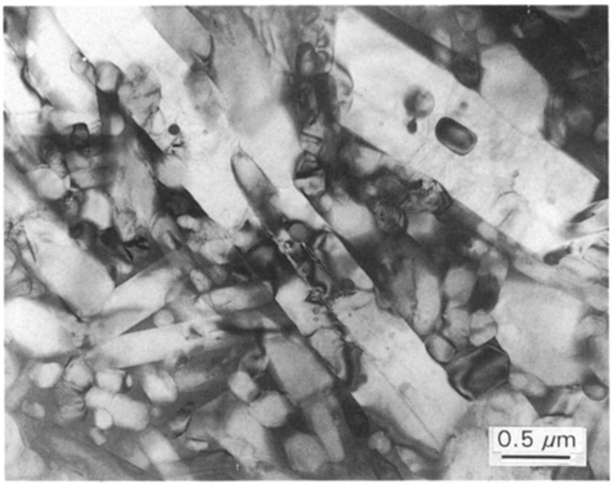

Figure 6 Transmission electron micrograph of o′–β′ sialon.

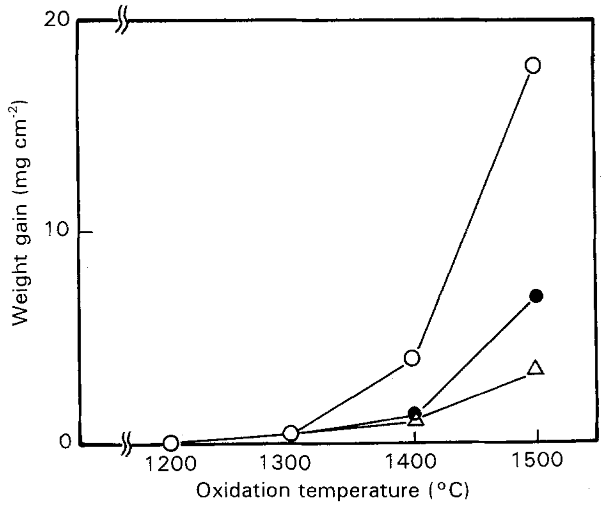

Figure 7 Comparison of oxidation weight gain of o′–β′ sialon hot-pressed at (△) 1600 °C and (●) 1700 °C with (○) Syalon 201.

Figure 8 Cross-sectional image o′–β′ sialon by scanning electron micrograph taken on the sample oxidation-tested at 1500 °C for 2 h.

was not effective enough, perhaps because the grain-boundary glassy phase partly melted at 1400 °C and oxygen attacked the β′ phase through the grain boundaries. Cross-sectional observation at 1500 °C revealed an yttrium-segregated layer (apparently $Y_2Si_2O_7$ phase) on the surface. This finding indicates active mass transfer within the surface oxide film. Syalon 201 was greater in oxidation weight gain than o′–β′ sialon, despite the extensive crystallization of grain boundaries as the YAG (yttrium aluminate garnet) phase. This is probably because Syalon 201 contains large amounts of impurities.

4. Conclusions

α-Si_3N_4, Al_2O_3, SiO_2 and Y_2O_3 powders were mixed, hot-pressed into o′–β′ sialon, and investigated for sintering behaviour, mechanical properties and oxidation resistance. The results obtained can be summarized as follows:

1. The o′ phase and β′ phase did not precipitate at the same time. The o′ phase was likely to appear in a relatively low-temperature region in the initial stage of sintering, while the β′ phase developed in the high-temperature region after the middle of the sintering process.
2. When Y_2O_3 was not added to o′–β′ sialon, the amount of the grain-boundary glassy phase was small, little or no decrease was observed in bending strength at high temperatures, and the absolute value of bending strength was also small.
3. The three-point bending strength of o′–β′ sialon depended on the amount of the β′ phase, and the contribution of the o′ phase to the mechanical properties of o′–β′ sialon was not so great.
4. Oxygen diffused into and oxidized the β′ phase due to the presence of the grain-boundary glassy phase and low-melting point substances from impurities. For this reason, improvement in oxidation resistance cannot be expected much from the presence of the o′ phase.

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