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High-strength silicon nitride ceramics obtained by grain-boundary crystallization

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A monolithic type of toughened silicon nitride ceramics has been developed from Si_3N_4–Y_2O_3 systems. However, because of the existence of a second phase, the fracture strength decreases at elevated temperatures. To improve the high-temperature strength of silicon nitride, some additional components were investigated. It was found that the addition of hafnia to the Si_3N_4–Y_2O_3–AlN system gave a greater high-temperature strength based on the promotion of grain-boundary phase crystallization: namely, 126 kg mm^{-2} in 3-point bend strength at 1300 °C for the hot-pressed specimen, and 90 kg mm^{-2} at 1300 °C for the pressureless sintered specimen. The role of the hafnia in crystallization is not yet clear, and is being characterized by electron microscopy and microanalysis.

1. Introduction

Elongated-grain structured silicon nitride ceramics have been developed by the sintering of powder compacts of the system Si_3N_4–Y_2O_3–Al_2O_3/AlN, which have high strength and high toughness [1, 2]. As a result both of these materials and of technological developments, silicon nitrides are now being applied to areas such as automotive engine components, bearings and other wear/heat-resistant parts in engineering systems.

However, silicon nitride ceramics generally deteriorate in strength above 1000–1200 °C, due to the softening of grain-boundary phases consisting of Si–Al–Y–O–N glass and/or crystalline compounds, as indicated by extensive microscopic analysis [3, 4]. To reduce this strength degradation at high temperatures, elimination of the grain-boundary phases or of grain-boundary phase crystallization has been considered [5].

After preliminary experimental research, it was found that hafnia might be a suitable additive for crystallization. This paper is concerned with the improvement of high-temperature strength by such crystallization, which was investigated by the selection of available additives.

2. Experimental procedure

Three kinds of compositions were selected in the system Si_3N_4–Y_2O_3: (A) Si_3N_4–Y_2O_3–Al_2O_3; (B) Si_3N_4–Y_2O_3–Al_2O_3–AlN; and (C) Si_3N_4–Y_2O_3–AlN–HfO_2. Commercially available silicon nitride powder, UBE E-10, and high-purity yttria, alumina, aluminium nitride and hafnia powders were used. In these experiments, the compositions included 5 wt % yttria for each specimen. Alumina and aluminium nitride were below 5 wt %, and hafnia was just a few percent. After mixing and adding an organic binder, green compacts of 50 × 50 × 5 mm were prepared by die pressing, and pressureless sintered at 1700–1750 °C in 1 atm nitrogen, followed by hot-pressing at 1750 °C under 400 kg cm^{-2} in 1 atm nitrogen. For the finally sintered specimens, density (by the Archimedes method), Vickers hardness, fracture toughness, K_{Ic} (by the indentation fracture method), and microstructure (by electron microscopy) were evaluated. Three-point bend strengths at room temperature to 1300 °C were measured according to Japanese standards (R1601).

3. Results and discussion

3.1. Fracture strength

The temperature dependence of the strengths of hot-pressed and pressureless sintered specimens are shown in Fig. 1. These results reveal that high-temperature strength depends on the composition. It is notable that high-temperature strength has been effectively increased by the addition of small amounts of hafnia – the strength of the hot-pressed specimen of composition (C) was very high, 126 kg mm^{-2} at 1300 °C. In the case of pressureless sintered samples, compositions were changed toward higher contents of oxide additives to achieve full densification without pressure. The highest strength was obtained in specimen (C), in which the strength at 1300 °C was 90 kg mm^{-2}.

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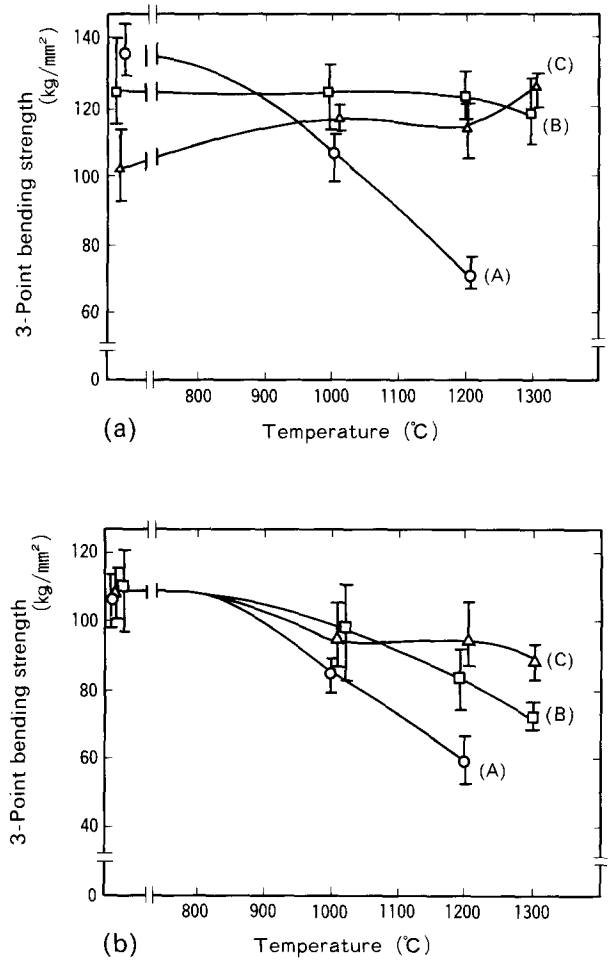

Figure 1 Temperature dependence of 3-point bend strengths for (a) hot-pressed and (b) pressureless sintered specimens.

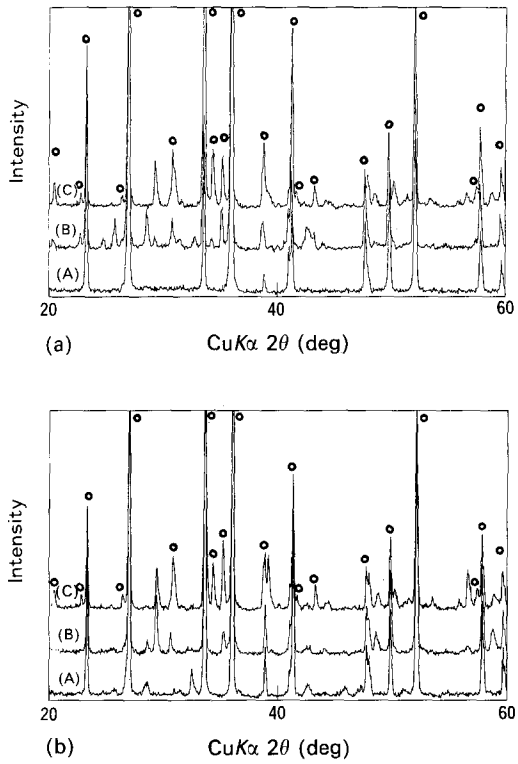

Figure 3 X-ray diffraction patterns of (a) hot-pressed and (b) pressureless sintered specimens. ○, Si_3N_4 or sialon; no mark, unknown.

3.2. Micrographs and X-ray diffraction analysis

Typical fractographs of hot-pressed specimens, fractured at 1300 °C, are illustrated in Fig. 2. From these micrographs, it is seen that the strength degradation at higher temperatures in specimen (A) is based on softening of the grain-boundary phase. On the other hand, it is observed that the specimen with added hafnia has highly refractory grain-boundary phase compounds. These phenomena are consistent with the results of the X-ray diffraction (XRD) analyses shown in Fig. 3a. According to the typical XRD patterns of hot-pressed materials, specimen (A) consists of β-sialon and glassy phase; and (B) consists of β-, α-sialon, glassy and crystalline phases; and (C) is

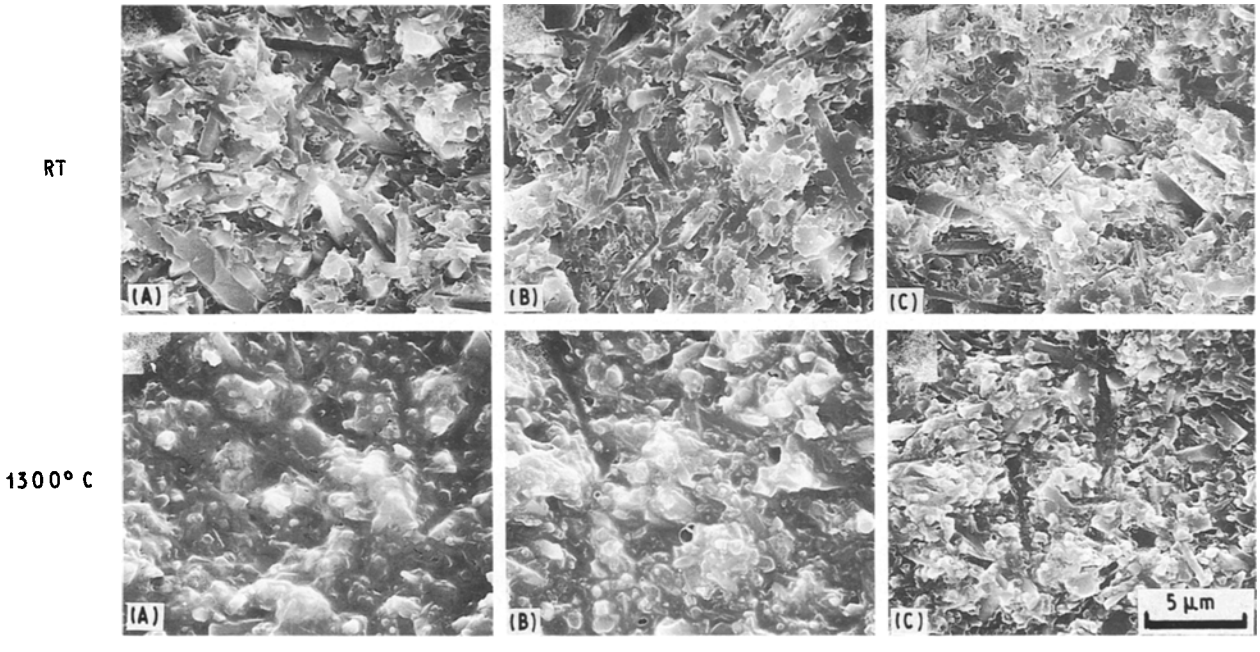

Figure 2 Fractured surfaces of bend-tested specimens (hot-pressed).

β-, α-sialon and crystalline. Grain-boundary phase crystallization was enhanced by the addition of hafnia. However the crystal structures of the new crystalline compounds were very complicated and have not yet been identified.

α-sialon, which seems to be of the composition Si–Y–Al–O–N, was formed as shown in Table I. It is notable that the amount of α-sialon increased with the increase in aluminium nitride and hafnia. However, the role of hafnia has not yet been clarified.

Fig. 3b shows XRD patterns for the pressureless sintered samples. These are similar to those for the hot-pressed samples, although they show more complicated profiles because of the difference in composition.

Fig. 4 shows typical micrographs of polished and etched specimens. The grains of the specimen (A) were the most developed, compared to those for (B) and (C): this may be due to the differences in mobility of atoms in the grain-boundary phases during sintering. The grains and grain-boundary phases were observed by transmission electron microscopy (TEM). It was found that the grain morphologies were very similar in each case, but the grain-boundary phases were different in (A) (glassy) and in (B) (crystalline). Further work is being done to characterize these by electron diffraction and spectroscopy analyses.

TABLE I Content of the α-sialon phase for hot-pressed and pressureless sintered specimens

Treatment	Content (%)		
	(A)	(B)	(C)
Hot-pressed	0	7	14
Pressureless sintered	0	3	15

3.3. Fracture toughness and hardness

The fracture toughness and micro-Vickers hardness values of hot-pressed and pressureless sintered specimens are shown in Table II. The highest fracture toughness is obtained for specimen (A). However, all of the values are in the range 6.8–7.4 MPa $m^{1/2}$. More precise measurements are required in order to understand the toughness mechanisms. The Vickers hardness decreases in the sequence (C) → (B) → (A). The highest value obtained in (C) is important, and is probably due to the existence of α-sialon, which is consistent with the work of Mitomo *et al.* [6]. This tendency is also observed in pressureless sintered specimens, as is shown in Table II.

Thus it is seen that hafnia doping is useful for higher strengthening, based on the promotion of grain-boundary phase crystallization. In the near future a much more detailed characterization of these samples will be reported from the electron microscopy and microanalytical data.

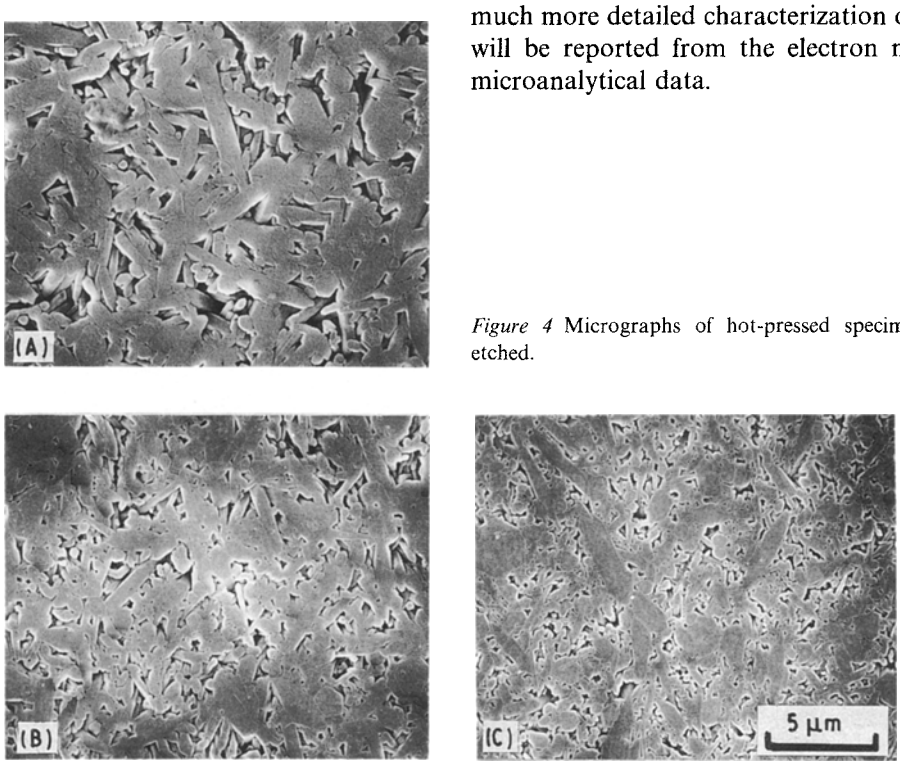

Figure 4 Micrographs of hot-pressed specimens, polished and etched.

TABLE II Vickers hardness and fracture toughness for hot-pressed and pressureless sintered specimens

Specimen	Hot-pressed		Pressureless sintered	
	H_v (500 g) kg mm^{-2}	K_{Ic} (MPa m^{-2})	H_v (500 g) kg mm^{-2}	K_{Ic} (MPa $m^{1/2}$)
(A)	1610 (1532–1644)	7.3 (7.2–7.4)	1570 (1454–1658)	6.9 (6.8–7.0)
(B)	1750 (1726–1779)	7.0 (6.8–7.2)	1500 (1466–1532)	7.2 (7.1–7.3)
(C)	1840 (1745–1924)	6.9 (6.8–6.9)	1730 (1686–1785)	7.2 (6.9–7.5)

4. Conclusions

The composition of the ceramic systems (A) Si_3N_4–Y_2O_3–Al_2O_3; (B) Si_3N_4–Y_2O_3–Al_2O_3–AlN; and (C) Si_3N_4–Y_2O_3–AlN–HfO_2 were investigated in order to improve high-temperature strength by controlling grain-boundary phase crystallization. The following results were confirmed.

1. Bend strengths at 1300 °C increase in the sequence (A) → (B) → (C). The hafnia-doped specimen (C) has the highest strength, 126 kg mm^{-2} at 1300 °C after hot pressing, and 90 kg mm^{-2} after pressureless sintering.
2. The increased strengthening is due to grain-boundary phase crystallization.
3. The microstructures consist of elongated grains and grain-boundary phases, in which grain sizes increase in the order (C) → (B) → (A).
4. The fracture toughness at room temperature is in the range of 6.8–7.4 MPa m$^{1/2}$ in the hot-pressed, and 6.8–7.5 MPa m$^{1/2}$ in the pressureless sintered specimens.
5. The micro-Vickers hardness at room temperature is in the range of 1450–1950 kg mm^{-2}. The hafnia-doped specimen has the highest value because of the increased amount of α-sialon.

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