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Effect of grain-boundary crystallization on the high-temperature strength of silicon nitride

LAURIE A. PIERCE, DIANE M. MIESKOWSKI, WILLIAM A. SANDERS
National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio 44135, USA

Si_3N_4 specimens having the composition 88.7 wt% Si_3N_4–4.9 wt% SiO_2–6.4 wt% Y_2O_3 (85.1 mol% Si_3N_4–11.1 mol% SiO_2–3.8 mol% Y_2O_3) were sintered at 2140° C under 25 atm N_2 for 1 h and then subjected to a 5 h anneal at 1500° C. Crystallization of an amorphous grain-boundary phase resulted in the formation of $Y_2Si_2O_7$. The short-time 1370° C strength of this material was compared with that of material of the same composition having no annealing treatment. No change in strength was noted. This is attributed to the refractory nature of the yttrium-rich grain-boundary phase (apparently identical in both glassy and crystalline phases) and the subsequent domination of the failure process by common processing flaws.

1. Introduction

Silicon nitride is currently under consideration for use in high-temperature engineering applications due to its superior high-temperature properties. However, the Si_3N_4 usage temperature may ultimately be limited by the properties of its grain-boundary phase. This results from softening of the grain-boundary phase and resultant slow crack growth at high temperatures. This problem has been addressed by several investigators [1–6] who have examined the effect of additive type, amount of additive, and crystallinity of the grain-boundary phase, largely in hot-pressed materials. Grain-boundary phase softening is especially important in sintered parts since greater additive levels are used here than in hot pressing.

Crystallization of the grain-boundary phase has been promoted by several researchers [1–4] as a method for increasing the high-temperature strength of Si_3N_4. In order to investigate its effect on the high-temperature strength of an experimental composition, a comparison was made between specimens processed to contain an extensive glassy phase (sintered at 2140° C, 1 h, 25 atm N_2) and specimens processed to produce a partially crystalline grain-boundary phase (annealed at 1500° C for 5 h after sintering). The composition was held at 88.7 wt% Si_3N_4–4.9 wt% SiO_2–6.4 wt% Y_2O_3 (85.1 mol% Si_3N_4–11.1 mol% SiO_2–3.8 mol% Y_2O_3). Evaluation primarily involved X-ray diffraction (XRD) and measuring the modulus of rupture (MOR) at 1370° C.

2. Experimental procedure

The initial experimental work of this study involved the determination of a crystallizing heat treatment. For this, three trial compositions (Table I) were chosen from the Si_3N_4–Si_2N_2O–$Y_2Si_2O_7$ compatibility triangle of the Si_3N_4–SiO_2–Y_2O_3 system [7] in such a way as to provide varying amounts of grain-boundary phase. This was done so that the effect of second-phase quantity, if any, could be determined. The trial compositions were mixed in 50 g batches from as-received Si_3N_4, SiO_2, and Y_2O_3 (see Table I for chemical analyses). Mixing time was 3 h in 500 ml polyethylene bottles with HPSN milling medium (Advanced Ceramic Systems, Ypsilanti, Michigan)* and 250 ml pure ethanol as mixing fluid. After mixing, the ethanol was evaporated from the powder slurries using a Rotavapor drying apparatus (Preiser Scientific, Louisville, Kentucky). The powders were dried further in a vacuum oven at 110° C and then sieved through a 100 mesh stainless steel screen.

Rectangular test bars (3.81 cm by 0.79 cm by 0.45 cm) were formed by compacting 2.6 g charges of each powder composition at 42 MPa in a two-way action tungsten carbide-lined die. The green bars were then vacuum-sealed in latex tubing and isostatically cold-pressed at 414 MPa. The relative density of the green compacts averaged 57.5 ± 0.7% for these compositions. The bars were sintered and annealed in a double-walled, water-cooled furnace with a 10.2 cm diameter tungsten mesh heater and concentric tungsten and molybdenum radiation shields. W–5 Re/W–26 Re thermocouples were used for monitoring and controlling the temperature. The specimens were positioned on and separated by BN discs inside a capped tungsten cup which was placed on a tungsten pedestal inside the heater.

In order to determine a crystallizing heat treatment, specimens from each composition were first subjected to a normal sintering cycle (2140° C, 1 h, 25 atm N_2) and then cooled to one of eight annealing temperatures in the range 1000 to 1600° C. They were held at these temperatures for 1 h, then ground with a 400 grit diamond wheel and the ground surfaces examined

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*Chemical analysis of the medium indicated 5.25 wt% O_2, 0.46 wt% C, 0.8 wt% Al, and expressed in p.p.m. 670 Ca, 30 Cu, 2000 Fe, < 2 Ti, 370 Cr, 130 Mg, 90 Mn, < 10 V, < 20 Zr, 2000 Mo, 240 Ni, 130 Zn, < 30 Pb, < 60 Sn.

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TABLE I Characterization of silicon nitride, oxide powders and Si_3N_4–SiO_2–Y_2O_3 compositions after milling and sintering

Material or composition	Mill charge (wt %)			As-received or milled condition chemical analysis			Specific surface area, ($m^2 g m^{-1}$)	Sintered condition phase content,* (wt %)		
	Si_3N_4	SiO_2	Y_2O_3	Oxygen (wt %)	Carbon (wt %)	Spectrographic analysis (p.p.m.)		Si_3N_4	SiO_2	Y_2O_3
Si_3N_4†	–	–	–	0.90	0.14	860 Al, 140 Ca, 20 Co, 60 Cr, 2140 Fe, 30 Mg, 60 Mn, 140 Ti, 280 V, 600 Y, 50 Zn, 20 Zr	4.6	–	–	–
SiO_2‡	–	–	–	–	0.16	220 Al, 190 Ca, 30 Cr, 50 Cu, 50 Fe, 130 Mg, 90 Mn, 340 Na, 40 Ti	166	–	–	–
Y_2O_3§	–	–	–	–	0.11	60 Cu, 60 Mg, 40 rare earth oxides	7.5	–	–	–
Comp. A	84.78	8.32	6.90	5.90	0.13	210 Al, 40 Cr, 10 Cu, 1070 Fe, 20 Mo	–	88.48	4.38	7.14
Comp. B	90.93	5.37	3.70	3.66	0.13	210 Al, 50 Cr, 10 Cu, 1180 Fe, 30 Mo	–	93.05	3.25	3.70
Comp. C	93.85	3.66	2.49	2.48	0.13	220 Al, 40 Cr, < 10 Cu, 1170 Fe	–	95.10	2.86	2.04
Comp. 6Y	87.93	5.84	6.23	4.74	0.13	490 Al, 120 Cr, 110 Cu, 1240 Fe, 90 Mo	15.3	88.69	4.94	6.37

*Calculated allowing for Si_3N_4 pickup during milling, weight loss during sintering, and oxygen, carbon and yttrium analyses after sintering.
†AME-KBI High Purity, 99.5%; 83.7% α, 15.7% β, 0.6 percent free silicon.
‡Apache Chemical Inc. Code 6846, 99.99%.
§Molycorp 5600, 99.9%.

using XRD. The crystalline grain-boundary phase resulting from these heat treatments was 10 $Y_2O_3 \cdot 9\, SiO_2 \cdot Si_3N_4$, as identified by Wills *et al.* in a study of the Si_3N_4–Y_2O_3–SiO_2 system [8]. The XRD data from the present study showed that the most extensive crystallization occurred at 1500° C, independently of composition. (This was based on relative 10 • 9 • 1 peak intensities.) No effect of second-phase quantity was noted. Since $Y_2Si_2O_7$ was one of the expected crystalline grain-boundary phases [4], the 10 • 9 • 1 phase was considered to be a non-equilibrium phase. Additional specimens were subjected to a longer anneal at 1500° C (5 h) to confirm this expectation, with the reuslt that $Y_2Si_2O_7$ was produced instead of the 10 • 9 • 1 phase. In no instance was Si_2N_2O found by XRD. This is not completely surprising because of the proximity of the experimental compositions to the Si_3N_4–$Y_2Si_2O_7$ tie line [7].

Since specific composition within the Si_3N_4–Si_2N_2O–$Y_2Si_2O_7$ compatibility triangle was not considered a strong variable, the 1500° C, 5 h anneal was applied to a baseline composition similar to Composition A in Table I. This consisted of 88.7 wt % Si_3N_4–4.9 wt % SiO_2–6.4 wt % Y_2O_3 (85.1 mol % Si_3N_4–11.1 mol % SiO_2–3.8 mol % Y_2O_3) and is denoted as 6Y. It was processed in the same manner as the trial compositions discussed above (2140° C, 1 h, 25 atm N_2) with the following exceptions. The starting powders for the 6Y composition were ground for 24 h in an HPSN mill (Ceramic Systems Inc., Detroit, Michigan).† A mill charge included 100 g of the starting powders, 800 g of 1 cm by 1 cm HPSN cylinders (see above) as grinding medium and 0.51 ethanol as the milling fluid. After pressing, the green density averaged 61.0 ± 0.3%. Twenty-four bars received no annealing treatment beyond sintering and served as experimental controls. Thirty more bars received the 1500° C, 5 h anneal. Prior to XRD and MOR determination, all bars were ground to 3.29 cm by 0.56 cm by 0.28 cm and the long edges bevelled to a 0.12 mm radius. Modulus of rupture was measured at 1370° C using SiC test fixtures (9.53 mm inner span, 19.05 mm outer span) in an SiC muffle furnace mounted on a testing machine (Instron Corporation, Canton, Massachusetts). All tests were conducted in air with a crosshead speed of 0.51 mm min^{-1}. Scanning electron microscopy (SEM) was used to identify fracture origins.

3. Results and discussion

This section discusses the effect of the 1500° C, 5 h anneal on the high-temperature strength of NASA experimental composition 6Y.

XRD data for annealed and non-annealed 6Y are shown in Fig. 1. From this it can be seen that the only crystalline phase present in the non-annealed material is β-Si_3N_4. After the 1500° C/5 h anneal, however, $Y_2Si_2O_7$ peaks appear due to crystallization of the previously amorphous grain-boundary phase. The expected Si_2N_2O phase was not observed.

Strength data for annealed and non-annealed 6Y at 1370° C are presented in Table II. A statistical analysis, consisting of an *F*-test and a Student's *t*-test, indicated no difference in the average strength of the two materials. In order to determine the basis for this unexpected similarity in strength, the following are

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†Chemical analysis of the mill indicated < 0.005 wt % C, 1.04 wt % O_2, and expressed in p.p.m. 1000 Al, 710 Ca, 410 Cr, 500 Cu, 6000 Fe, 350 Mg, 310 Mn, 70 Ni, 250 Ti, and 110 V.

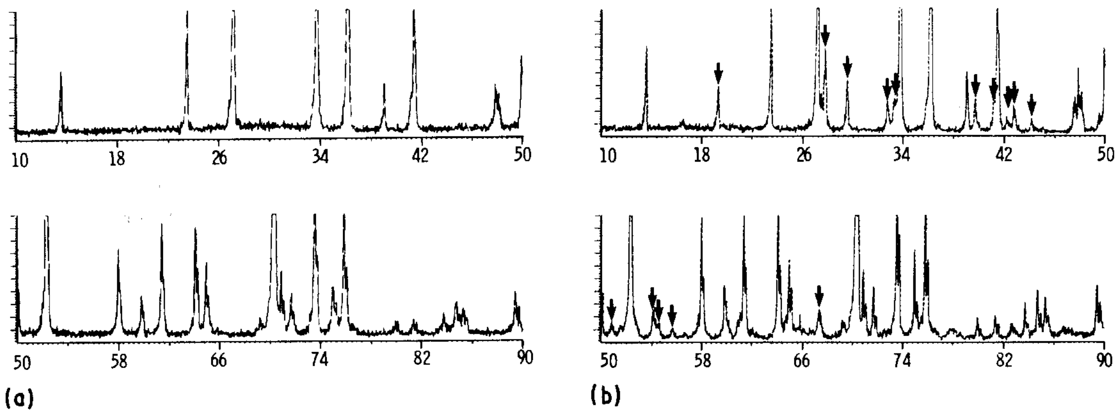

Figure 1 X-ray patterns for 6Y Si_3N_4. All peaks are β-Si_3N_4 except those labelled with an arrow, which are $Y_2Si_2O_7$. (a) Non-annealed, (b) annealed at 1500° C for 5 h.

examined: (i) fracture surfaces (using SEM) and (ii) the shapes of the MOR load–deflection traces. Typical fractographs are shown in Fig. 2 for both materials. As the cause of failure, these show common processing flaws (typical of room-temperature failure) instead of large areas of slow crack growth (often typical of high-temperature failure). The load–deflection traces were linear in all instances, again indicating the absence of extensive slow crack growth [9].

From the preceding summary of results, it appears that the glassy grain-boundary phase in the non-annealed material resists slow crack growth to the same degree as the crystallized phase in the annealed material. This is attributed to the refractory nature of the yttrium-rich grain-boundary phase [10, 11]. By raising the melting point of the grain-boundary phase, Y_2O_3 additions to Si_3N_4 reduce the degree of grain-boundary softening, and consequently the extent of slow crack growth (based on results generally reported for MgO- and Y_2O_3/Al_2O_3-doped Si_3N_4).

In another study [12], processing flaw characteristics were found to have little or no influence on slow crack growth. This study involved a comparison of

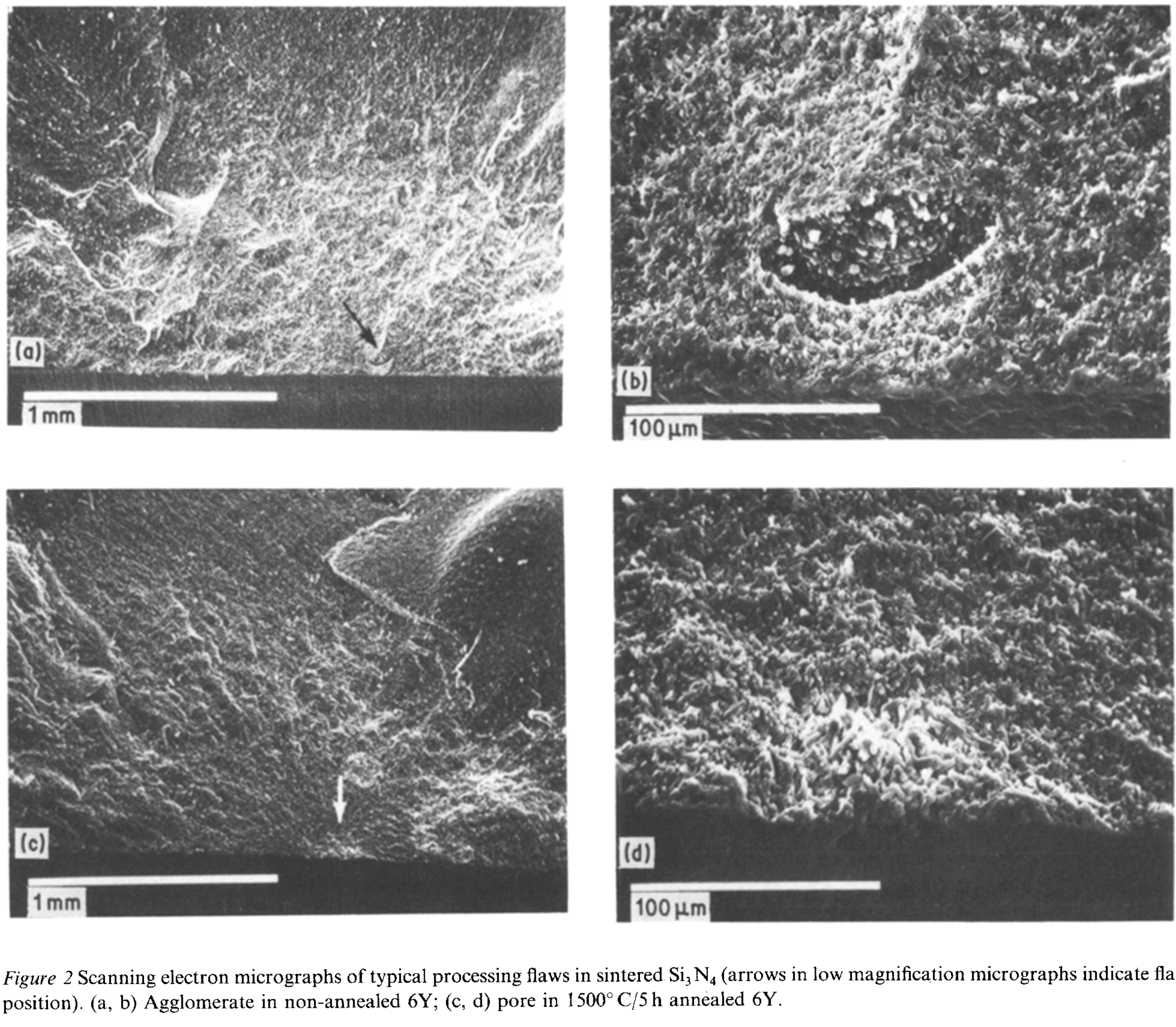

Figure 2 Scanning electron micrographs of typical processing flaws in sintered Si_3N_4 (arrows in low magnification micrographs indicate flaw position). (a, b) Agglomerate in non-annealed 6Y; (c, d) pore in 1500° C/5 h annealed 6Y.

TABLE II 1370° C strength statistics for annealed and non-annealed 6Y

	Annealed	Non-annealed
Average strength (MPa)	334.0	338.4
Standard deviation (MPa)	41.95	34.61
Number of tests	30	24

strength between Composition 6Y (Si_3N_4–SiO_2–Y_2O_3) and General Telephone and Electronic Composition AY–6 (Si_3N_4–Al_2O_3–Y_2O_3 with SiO_2 from powder processing) at room temperature, 1200 and 1370° C. Despite the fact that AY–6 and 6Y room-temperature strengths were statistically equal for given flaw populations, the AY–6 1200 and 1370° C strengths were found to be significantly lower. Because of the strength equality at room temperature, these differences were attributed to the extensive slow crack growth exhibited by AY–6 at 1200 and 1370° C rather than to differences between processing flaw populations.

In studies on the high-temperature strength of hot-pressed Si_3N_4, Tsuge and co-workers [1, 2] found that strength was increased by crystallization of the glassy grain-boundary phase. In the first of these studies, the grain-boundary phase of a composition consisting of Si_3N_4–5 wt % Y_2O_3 was crystallized by the application of a pre-sinter prior to hot-pressing. Slow crack growth was observed in non-crystallized specimens with a more brittle fracture character observed in crystallized specimens. The composition, Si_3N_4–5 wt % Y_2O_3, is similar to Composition 6Y; however, the former was milled in an Al_2O_3 mill and the level of SiO_2 pickup due to oxidation was not reported. As a result, a direct comparison is not possible. Other differences include the use of hot-pressing as opposed to high nitrogen pressure sintering, the use of a pre-sinter instead of an anneal to induce crystallization, and the use of three-point bend strength in place of four-point.

In their second study, Tsuge and Nishida [2] reported an increase in the 1200° C strength‡ of Si_3N_4 hot-pressed with additions of Y_2O_3 and Al_2O_3 as the result of their pre-sinter crystallizing heat treatment. The extent of slow crack growth was not examined in this study. Other than these two studies, the published research on grain-boundary crystallization in Si_3N_4 is not easily related to the present work. The study by Smith and Quackenbush [4] involved a comparison between Si_3N_4 sintered with Y_2O_3 and Al_2O_3 and Si_3N_4 sintered with Y_2O_3 alone,and is also not directly comparable to the current study.

An area for future research would be an investigation of the effects of grain-boundary crystallinity on high-temperature creep. Perhaps strength advantages exist for compositions such as annealed 6Y in the field of time-dependent properties. A second area for research would be on the effects of grain size and morphology. There has been some indication from other in-house research projects that these factors may affect the extent of slow crack growth at a given temperature, and consequently the degree to which grain-boundary crystallinity may have a beneficial effect.

In summary, the present research found no difference in the 1370° C strength of an Si_3N_4–SiO_2–Y_2O_3 composition having an amorphous grain-boundary phase and an identical material having a grain-boundary phase with crystalline character. This is attributed to the refractory nature of the yttrium-rich grain-boundary phase and the subsequent domination of the failure process by common processing flaws as in room-temperature fracture.

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‡Confirmed statistically by the present authors from the data of Tsuge and Nishida [2].