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Effect of Heating Schedule on the Microstructure and Fracture Toughness of alpha-SiAlON--Cause and Solution

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Abstract

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Effect of Heating Schedule on the Microstructure and Fracture Toughness of α-SiAlON—Cause and Solution

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The effect of heating schedule on microstructure and fracture resistance has been investigated in single-phase Nd-, Y-, and Yb-α-SiAlON. Such effect is strongly system dependent, reflecting the strong influence of phase stability on α-SiAON nucleation and the amount of transient/residual liquid during processing. The addition of 1% of α-SiAlON seeds to the starting powders nearly completely obliterates such effect, while it simultaneously improves microstructure homogeneity and fracture resistance. SENB toughness of 7 MPa·m$^{1/2}$ and peak *R*-curve toughness of ∼11 MPa·m$^{1/2}$ have been obtained for seeded Y-α-SiAlON ceramics using heating rates from 1°C/min to 25°C/min.

I. Introduction

Solid solutions of α-Si_3N_4, known as α-SiAlONs, are very attractive ceramics for applications where high hardness, wear durability, and oxidation resistance are needed. The recent development of *in situ*-toughened α-SiAlON with whiskerlike microstructure has further increased the appeal of these ceramics and generated much interest.[1] A central focus of the development effort of toughened α-SiAlON is on nucleation control that promotes the formation of whiskerlike grains. A two-step heating schedule, which includes a low-temperature nucleation step, has been shown to be effective for this purpose when either β-Si_3N_4[1] or α-Si_3N_4[2] starting powders are used. Komeya and co-workers[3] also have reported rather different microstructures of Ca-α-SiAlON obtained under different heating schedules, finding exaggerated whiskerlike microstructure at very high heating rates. Such sensitivity to heating schedule is obviously an important issue that affects the manufacturability of α-SiAlON. Here we address this issue by first investigating the heating schedule effect in various α-SiAlONs. We further demonstrate that the mere addition of 1% α-SiAlON seeds to the starting powder can obliterate such effect and improve microstructure homogeneity as well as fracture properties.

II. Experimental Procedure

The compositions investigated here are represented by the formula: $(Nd,Y,Yb)_{m/3}Si_{12-(m+n)}Al_{(m+n)}O_nN_{(16-n)}$. Here, the interstitial cations are listed in the order of decreasing ionic radius and (*m*, *n*) is set to be (1.5, 1.2), which was referred to as 1512 composition in our earlier publications.[1,2,4–6] For Y-1512 composition, we also prepared small crystals (0.3–0.7 μm in width and 2–5 μm in length) of the same composition, which were then used as α-SiAlON seeds in the starting powders. These seed crystals were grown from a liquid phase in a nitrogen atmosphere and later separated from the residual phases by chemical washing. The details of this procedure are available elsewhere.[4,5]

Starting compositions were prepared from powder mixtures of α-Si_3N_4 (SE-E-10, Ube Industries, Tokyo, Japan), AlN (Type F, Tokuyama Soda Co., Tokyo, Japan), Al_2O_3 (AKP50, Sumitomo Chemical America, New York), and rare-earth oxides Nd_2O_3, Y_2O_3, and Yb_2O_3 (all 99.9%, Alfa–Johnson Matthew Co., Danvers, MA). The oxygen content in α-Si_3N_4 (1.24 wt%) and AlN (0.88 wt%) was taken into account in the formulation. Powder mixtures were attrition milled in isopropyl alcohol for 2 h with high-purity Si_3N_4 milling media in a Teflon-coated jar. They were subsequently dried under a halogen lamp during stirring. When desired, charges of seeds were added to the powder slurries 10–15 min before the end of milling.

Powder mixtures were hot-pressed under a uniaxial pressure of 30 MPa in a graphite resistance furnace following various firing schedules. Samples were typically heated with a constant heating rate (from 1°C/min to 25°C/min) to 1900°C and held there for 1 h. In the two-step process, samples were first heated at 15°C/min to 1500°C, held for 1 h, then heated at the same rate to 1900°C, and held there again for 1 h. Full densification was observed in all cases unless otherwise noted.

Phase analysis was performed using X-ray diffractometry (Rigaku Co., Tokyo, Japan) with CuK_α radiation. In all cases, single-phase α-SiAlON was found. Microstructures of sintered samples were observed on polished and etched sections. Etchants

Table I. Fracture Toughness of α-SiAlON Ceramics $(Nd,Yb,Y)_{0.5}Si_{9.3}Al_{2.7}O_{1.2}N_{14.8}$

Sample†	SENB fracture toughness, K_{IC} (MPa·m$^{1/2}$)‡
Nd-25	6.1
Nd-15	6.1
Nd-5	6.1
Nd-1	6.1
Nd-2st	6.3
Yb-25	4.3
Yb-15	3.6
Y-25	5.3
Y-15	5.9
Y-5	6.1
Y-1	5.9
Y-2st	6.1
YS-25	6.7
YS-15	7.1
YS-5	7.0
YS-1	6.9

†Designated by the cation and the heating rate. Thus, Nd-15 is an Nd-α-SiAlON heated at 15°C/min. Two-step heating schedule is indicated by 2st; e.g., Nd-2st. YS indicates Y-α-SiAlON with 1% seeds. ‡±0.1 MPa·m$^{1/2}$.

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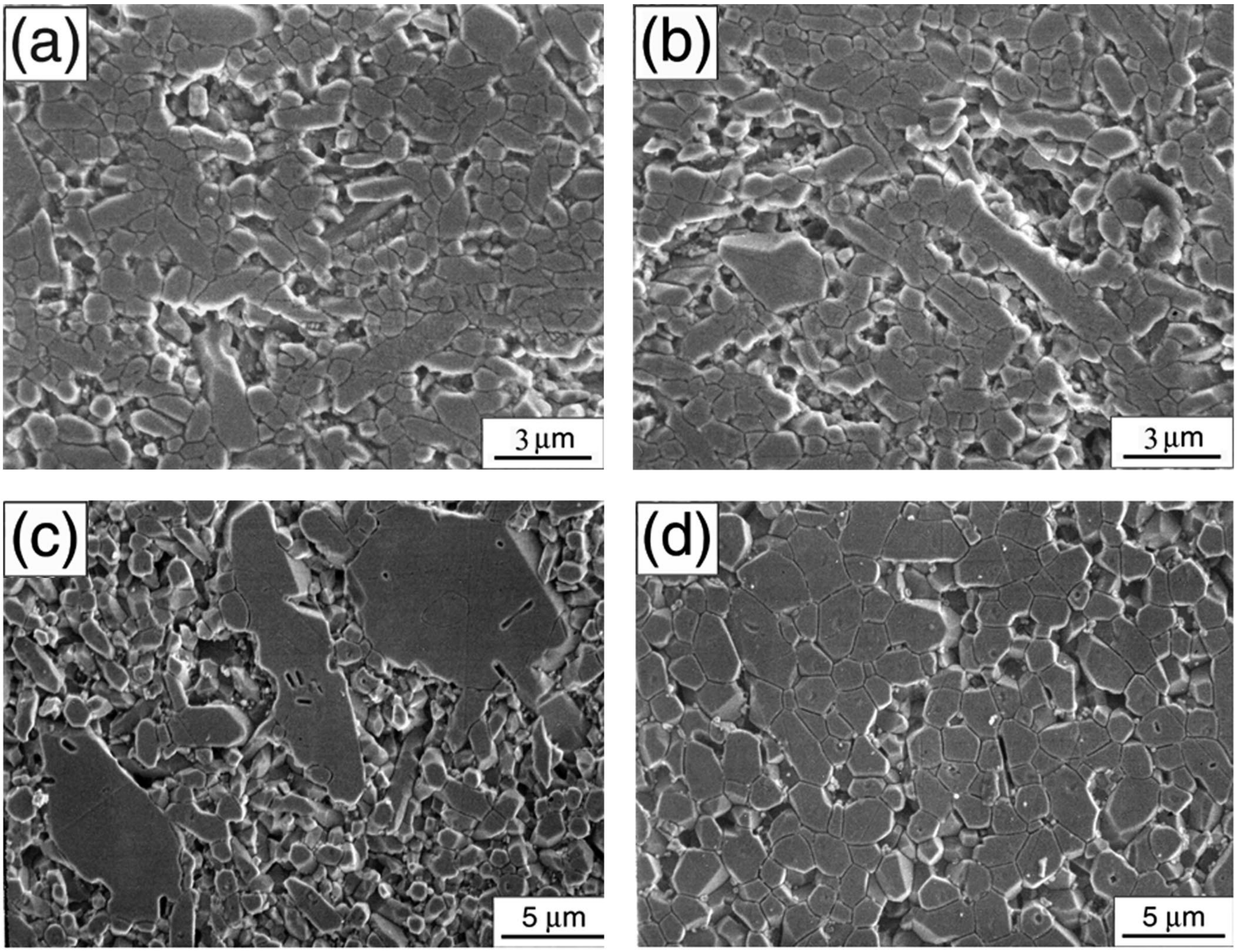

Fig. 1. SEM micrographs of Nd-1512 ceramics heated at (a) 25°C/min and (b) 5°C/min and of Yb-1512 ceramics heated at (c) 15°C/min and (d) 5°C/min. Micrographs correspond to Nd-25, Nd-5, Yb-15, and Yb-5 in Table I.

used were boiling solutions of NH_4F (20 g) in HNO_3 (50 mL). Scanning electron microscopy (SEM; Model 6300-F, JEOL, Tokyo, Japan) was used for microstructure characterization.

Single-edge notched-beam (SENB) fracture toughness was measured in four-point bending using bars of 30 mm × 4 mm × 2 mm, with their tensile surfaces lying parallel to the hot-pressing plane. A notch ~0.1–0.2 mm long was introduced to one side using a thin blade, followed by wire sawing to achieve a tip radius of 10 μm. To measure the *R*-curve, crack length was continuously monitored during loading using a microscope with a resolution of ~5 μm. Further details of this procedure are described elsewhere.[6]

III. Results and Discussion

The effect of heating rate on the microstructure varies greatly from ceramic to ceramic. Nd-1512 and Yb-1512 offer two extremes, because the stability of α-SiAlON is the lowest in Nd-SiAlON while the highest in Yb-SiAlON among all the rare-earth-stabilized systems. Microstructures of Nd-1512, heated at 25°C/min and 5°C/min (samples Nd-25 and Nd-5 in Table I), respectively, are shown in Figs. 1(a) and (b). Their microstructures appear similar, with a few large grains, some quite elongated. Both of these ceramics are dense, which is expected, because a relatively large amount of liquid is known to exist in this system because of the low stability of Nd-α-SiAlON.[7] In contrast, at the lower heating rate, i.e., 5°C/min, the Yb-1512 ceramic remains porous after hot-pressing. This is because of the higher stability of Yb-α-SiAlON, which forms much more readily and at a lower temperature during slow heating,[8] hence depriving the compact the transient liquid required for densification at higher temperatures. The microstructure of such a ceramic is shown in Fig. 1(d). At higher heating rates, the formation of Yb-α-SiAlON is delayed to a higher temperature so that more liquid is available for densification; thus, dense ceramics remain obtainable. Some large, blocky grains also form at the intermediate heating rate, 15°C/min, as shown in Fig. 1(c). However, at 25°C/min, the microstructure has only fine grains, similar to those shown in Figs. 1(c) and (d). The SENB fracture toughness, tabulated in Table I, reflects the above difference in microstructure. Nd-SiAlON has generally higher but similar toughness regardless of heating rate. Yb-SiAlON has lower toughness except at the intermediate heating rate (Yb-15 in Table I). Two-step hot-pressing of Nd-SiAlON leads to a microstructure similar to those of Figs. 1(a) and (b) and similar fracture toughness (Nd-2st in Table I).

Y-α-SiAlON has an intermediate stability[7,8] and can be densified at all heating rates from 1°C/min to 25°C/min. However, the microstructure varies systematically with the heating rate, as does the fracture toughness. As shown in Fig. 2, the fracture toughness throughout the *R*-curve is lower for the 25°C/min case than the 5°C/min case. This difference can be attributed to the different microstructure (see inset in Fig. 2): at 25°C/min it is comprised of mostly fine, equiaxed grains, whereas, at 5°C/min, many large, elongated grains are present. Two-step heating also generates a

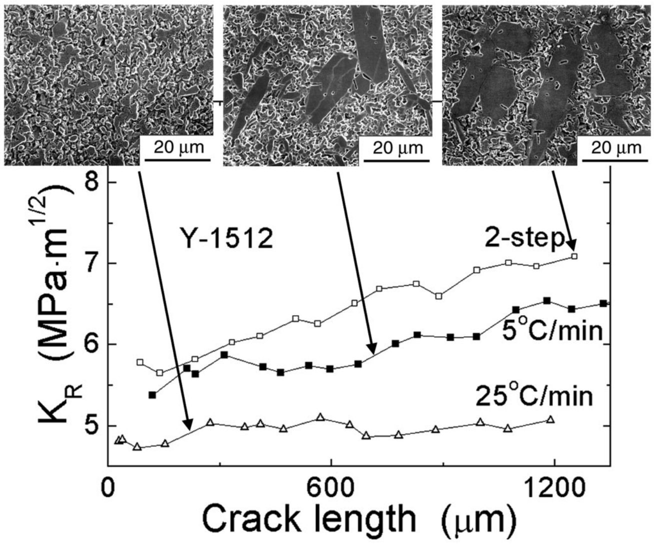

Fig. 2. *R*-curves and SEM micrographs of unseeded Y-1512 following three heating schedules as shown. Curves and micrographs correspond to Y-25, Y-5, and Y-2st in Table I.

microstructure with many large, elongated grains and higher toughness, as shown in Fig. 2. The microstructure and the toughness for 1°C/min heating are similar to those of two-step heating.

The above results are consistent with the proposal of Chen, Rosenflanz, and Kim[1,2,9] regarding α-SiAlON nucleation, which was first demonstrated using β powders. Namely, the two-step heating treatment (or slow heating) allows the formation of a limited number of nuclei at low temperatures; such nuclei later dominate the growth at high temperature to develop a microstructure of elongated grains. For Yb-SiAlON, this strategy works for β-Si_3N_4 powders,[1,9] but it breaks down when α-Si_3N_4 powders are used. This is because α-Si_3N_4 powders have a higher driving force and reactivity than β-Si_3N_4 powders;[10] therefore, even at low temperature, α-SiAlON formation is too fast. For Nd-SiAlON, the driving force is so low that nucleation is always limited.[1,2,8,9] Therefore, elongated grains can always be obtained regardless of heating schedule. (Our unpublished study also has found that Ca-SiAlON is similar to Nd-SiAlON, and always forms elongated grains. If a very high heating rate is used so that the α formation reaction is delayed to very high temperatures, then the large amount of liquid present and the fast growth kinetics at high temperatures are conducive to abnormal grain growth. This leads to an exaggerated whiskerlike microstructure, as first reported by Komeya and co-workers.[3]) The case of Y-SiAlON is intermediate between the two limits and is most subject to influences caused by the heating schedule.

We have also investigated the combined effect of seeding (1% seeds) and heating rate on the microstructure and fracture toughness of Y-SiAlON. As shown in Fig. 3, at 5°C/min and 25°C/min, the microstructures are relatively uniform and similar, containing many elongated grains that are tightly packed. The observed *R*-curves are also similar. The fracture toughness on the *R*-curve is considerably higher than that without seeding (see Fig. 2). Table I shows that all the seeded Y-1512 ceramics have similar SENB fracture toughness higher than the values of unseeded ceramics. Thus, the large influence of the heating schedule on the microstructure and fracture properties of Y-SiAlON can be removed by the addition of only 1% seeds. This indicates that these α-SiAlON seeds are so thermodynamically stable at all temperatures that they are always able to grow and consume the driving force, rendering those potential nucleation sites among the starting powders inactive. The microstructure, therefore, is dominated by these seeds, which have a one-to-one correspondence to the elongated grains in the final microstructure, according to our recent study of seeding statistics.[11,12]

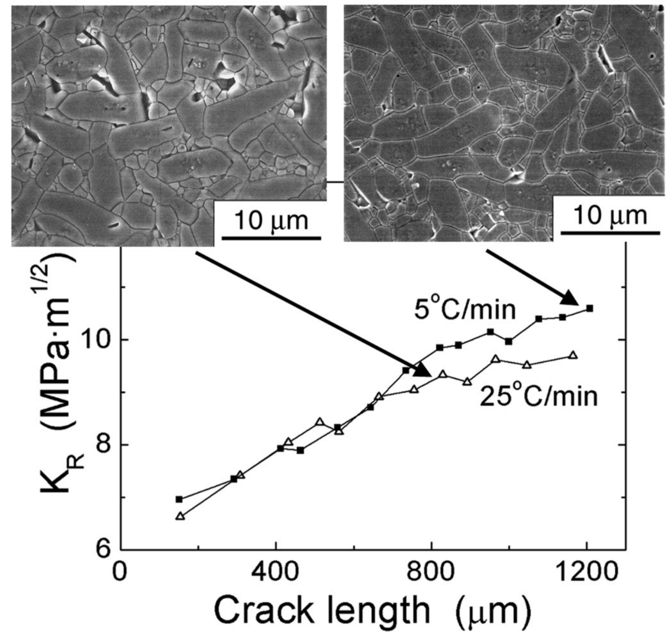

Fig. 3. *R*-curves and SEM micrographs of seeded Y-1512 heated at two rates. Curves and micrographs correspond to YS-25 and YS-5 in Table I.

IV. Conclusions

(1) Firing schedule has a profound influence on the microstructure of α-SiAlON. The influence systematically varies with the relative phase stability of α-SiAlON, which is composition dependent. To optimize densification and mechanical properties, it therefore is necessary to tailor the heating schedule for individual α-SiAlON systems.

(2) Seeding has a remarkable effect of removing the microstructure/property sensitivity to the firing schedule. As a result, higher toughness and more uniform microstructure can be readily obtained for seeded ceramics under a wide range of heating conditions.

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