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Microstructure control of α-Sialon ceramics by seeding with α-Sialon particles

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A proper powder preparation was used to develop α-Sialon single crystals as seeds. The microstructure and fracture toughness of seed-containing α-Sialon ceramics sintered by hot-pressing were investigated. The specimen without seeding consisted of fine grains and a small amount of coarse grains. Specimens seeded with α-Sialon single crystal particles presented a large amount of elongated α-Sialon grains. The aspect ratio and the amount of elongated α-Sialon grains can be tailored by using different sizes and amounts of the seeds. The fracture toughness of seed-containing α-Sialon ceramics is improved, which is attributed to grain pullout and bridging of elongated grains.

1. Introduction

There are two polymorphs of silicon nitride, α-Si_3N_4 and β-Si_3N_4, which differ in structure by stacking sequences. They each form solid solution commonly referred to as α-Sialon and β-Sialon, whose general formulas are represented as $M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ (M = Li, Ca, Mg, Y and most of the lanthanide elements) and $Si_{6-z}Al_zO_zN_{8-z}$ respectively. Commercial silicon nitride ceramics are based on β-Si_3N_4/β-Sialon systems because elongated grains can be obtained in these materials, resulting in toughening effects by crack deflection and grain pullout. In comparison to β-Si_3N_4/β-Sialon ceramics, α-Sialon exhibits excellent hardness, oxidation and thermal shock resistance, but its lower fracture toughness, owing to its equi-axed grains, hinders its wide use. Recently, some literatures [1–3] have shown that α-Sialon can also obtain a microstructure of elongated grains and, hence, the high toughness, which opens up the possibility of fabrication of α-Sialon with combined high toughness and high hardness.

So far, the studies on self-toughened α-Sialons are concentrated on starting powders [1, 4], sintering additives and processing conditions [5, 6]. However, the study on the effect of seeding is very few [7], which is mainly due to the difficulty in the preparation of α-Sialon single-crystal particles. The effects of seeding on the development of microstructure and mechanical properties of β-Si_3N_4/β-Sialon materials have been intensively studied [8–11]. A bimodal microstructure in β-Si_3N_4 containing rod-like β-Si_3N_4 seeding was observed. The amount and size of elongated grains can be controlled by the amount and size of rod-like β-Si_3N_4 seeds introduced into the system. By optimizing the amount and size distribution of elongated grains, β-Si_3N_4/β-Sialon ceramics with improved fracture toughness can be obtained.

Recently, we have prepared α-Sialon single-crystal particles by a method of pressure-less sintering and acid rinsing treatment. By using the morphologically regulated particles as seed crystals, it is expected that the microstructure of α-Sialon could be tailored, thus improving the toughness of the material. The present paper describes our preliminary results on both preparation of seed crystal particles and microstructural features of seeded α-Sialon ceramics.

2. Experimental procedures

2.1. Preparation of seed particles

A nominal composition $Y_{0.33}Si_{9.3}Al_{2.7}O_{1.7}N_{14.3}$ was used for the preparation of α-Sialon seeds. Sm_2O_3 was also added as an additive with a weight ratio of α-Sialon to Sm_2O_3 as 9 to 1. Starting powders of α-Si_3N_4 (SN-E-10, Ube Industries, Yamaguchi, Japan, 2.0 wt%O), AlN (Type A, Wuxi Chemical Co, Wuxi,

China, 1.3 wt%O), Y_2O_3 and Sm_2O_3 (99.9%, Yaolong Chemical Co, Shanghai, China), Al_2O_3 (99.9%, Wusong Chemical Co, Shanghai, China) were used to achieve the desired composition. The oxygen content existing on the surface of nitride powders was taken into account in the calculation of the composition.

Powder mixtures were milled in alcohol for 24 h with Si_3N_4 milling media. After drying, the powder mixture was lightly pressed by fingers into a cylinder, and heated without pressure at 1800°C for 0.5 h and 3 h respectively in a graphite furnace under a nitrogen atmosphere of 0.1 MPa. The corresponding products were respectively denoted as SA and SB. The samples were then crushed and screened through a 60-mesh sieve. The screened powders were subjected to two successive rinsing treatments as follows: (1) a mixed solution of concentrated hydrofluoric acid (HF) and nitric acid (HNO_3) at 60°C for 48 h; (2) a concentrated sulfuric acid (H_2SO_4) solution at 160°C for 8 h. Following each acid rinsing treatment, the powders were washed in distilled water at room temperature for 8 times.

2.2. Preparation of bulk specimens

The nominal composition for bulk α-Sialon samples was $Y_{0.165}Sm_{0.165}Si_{9.3}Al_{2.7}O_{1.7}N_{14.3}$, in which 1.5 wt% $SmAlO_3$ and 1.5 wt% YAG were added as sintering additives. The starting powders are similar to those described above. The powder mixture was milled under absolute alcohol for 24 h in a plastic jar, using Si_3N_4 milling media. After drying, the prepared α-Sialon single crystal particles were added into the powder mixture, which was again stirred under absolute alcohol for 24 h. The amount of added seeds was 5, 10 wt% for SA and 2.5, 5, 7.5 and 10 wt% for SB in the nominal α-Sialon composition respectively. Pellets of dried powder were hot-pressed under nitrogen atmosphere in a graphite resistance furnace at 1800°C for 1 h.

2.3. Microstructure analysis and mechanical properties measurement

The bulk densities of the samples were measured in water by Archimede's principle. Phase assemblages of the fired specimens and seed particles were characterized by XRD using a Guinier-Hägg camera with Cu $K_{\alpha 1}$ radiation and Si as an internal standard. The measurement of X-ray film was completed by a computer-linked line scanner system (LS-18). The microstructure of the fired specimens and the morphology of seed particles were observed using a HITACHI S-570 scanning electron microscope (SEM). Polished surfaces of the prepared samples were etched in molten NaOH for a few seconds and carbon coated prior to observation. An image analyzer (IRAS/C, Kontron Elektronik, Munich, Germany) was used for measuring the grain size and distribution. The diameter (d) and length (l) of each grain were determined from the shortest and the longest diagonal of the grain respectively. The aspect ratio of each grain was obtained from l/d. At least 500 grains were measured for statistical analysis of each specimen. Indentation fracture toughness was determined using a Vickers indenter at a load of 10 kg.

3. Results and discussion

3.1. Preparation and characteristics of seed particles

Table I shows phase assembly of synthesized powders before and after acid rinsing treatment. Synthesized powders before acid rinsing treatment consisted of minor amounts of H ($Y_{10}(SiO_4)_6N_2$) phase and J ($Y_4Si_2O_7N_2$) phase, along with α-Sialon as a major phase. After HF + HNO_3 mixture acid rinsing, the H phase and J phase disappeared, but a minor unknown phase was still present. This unknown phase eventually disappeared after a further acid rinsing treatment in the H_2SO_4 solution at 160°C. Thus, after two successive rinsing treatments, only a single α-Sialon phase remained.

Fig. 1 shows SEM micrographs of α-Sialon single crystal particles after two successive acid rinsing treatments. It can be seen that the size of α-Sialon seed particles increases with an increase in sintering time. The characteristics of synthesized seed particles are listed in Table II.

3.2. Phase assembly and microstructure of seeded α-Sialon

The phase composition and relative densities of Y, Sm-α-Sialon specimens with and without seeding is listed in Table III. It can be seen that the densities of Y, Sm-α-Sialon specimens are not affected by the amount of seed particles. Phase assemblages of Y, Sm-α-Sialon with seeding after sintering are the same to those without seeding, which consist of α-Sialon and a minor amount of melilite phase.

Fig. 2 shows SEM photographs of α-Sialons sintered at 1800°C for 1 h without and with different amounts of α-Sialon seed particles SB. The specimen without seeding consists of relatively fine elongated grains and a

TABLE II Characteristics of synthesized seed particles under different conditions

Symbol	Soaking time (h)	Average diameter (μm)	Average length (μm)	Average aspect ratio
SA	0.5	0.4	0.8	2
SB	3	1	4	4

TABLE I Phase assembly of synthesized powders during acid rinsing treatment

Symbol	Sintering time (h)	Phase assembly of powder: Before acid rinsing treatment	After acid rinsing treatment (HF + HNO_3 mixed solution)	After further acid rinsing treatment (H_2SO_4 solution)
SA	0.5	α'/vs + H/vw + J/vvw	α' + U	α'
SB	3	α'/vs + H/vw + J/vvw	α' + U	α'

Note: $\alpha' = \alpha$-Sialon, H = $Y_{10}(SiO_4)_6N_2$, J = $Y_4Si_2O_7N_2$, v = very, s = strong, w = weak, m = medium, U = an unknown phase.

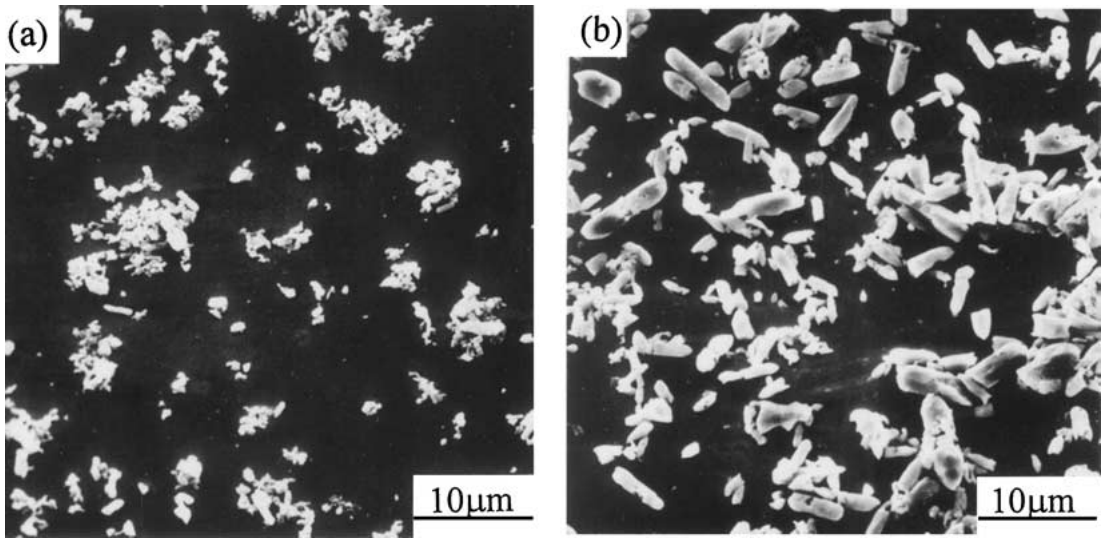

Figure 1 SEM micrographs of α-Sialon single crystal particles: (a) SA and (b) SB.

TABLE III Phase assembly and relative density of Y, Sm-α-Sialon specimens with and without seeding

Specimens	Added seeds (wt%)	Relatively density (g/cm^3)	Phase compositions
YS1	0	3.44	α'/s + M/w
YS2	2.5SB	3.46	α'/s + M/w
YS3	5SB	3.45	α'/s + M/w
YS4	7.5SB	3.44	α'/s + M/w
YS5	10SB	3.45	α'/s + M/w
YS6	5SA	3.46	α'/s + M/w
YS7	10SA	3.43	α'/s + M/w

Note: $M = R_2Si_{3-x}Al_xO_{3+x}N_{4-x}$, w = weak, s = strong.

minor amount of coarse grains. However, specimens with seed particles, as expected, have large amounts of elongated grains, which increase with increasing the amount of seed particles. It is obvious that the elongated grains in all seed-containing α-Sialon specimens are much larger both in length and width than the seed particles, indicating the growth of seed particles during sintering. It has been known that during liquid phase sintering of nitrogen ceramics, there are two distinct stages: the phase transformation (namely α-$Si_3N_4 \rightarrow \beta$-$Si_3N_4$, α-$Si_3N_4 \rightarrow \beta$-Sialon or α-$Si_3N_4 \rightarrow \alpha$-Sialon) driven by the difference in free energy between the two phases [12], and the subsequent grain growth driven by the difference in grain size [13]. Our previous work on Ca, and Nd/Er α-Sialon compositions revealed a nearly equi-axed α-Sialon grain morphology after the $\alpha \rightarrow \alpha'$ transformation and a gradual increase of the aspect ratio during the subsequent grain growth stage [14, 15]. The addition of α-Sialon seed particles with an elongated morphology in α-Sialon compositions would be beneficial to elongated grain growth as the transformation of α-$Si_3N_4 \rightarrow \alpha$-Sialon has been completed for the seed particles although the same transformation will be carried out for α-Si_3N_4 starting powders during liquid phase sintering. The α-Sialon seeds are thermodynamically stable at the temperature where the transformation from α-Si_3N_4 powder to α-Sialon takes place (around 1500°C for the present system). It is therefore reasonable to assume that the α-Sialon grain growth would preferentially take place at the sites of α-Sialon seeds. The increase in the amount and size of elongated grains in the seed-containing α-Sialon ceramics has further confirmed the effect of seed particles on the α-Sialon grain growth.

The size distributions of elongated grains as a function of grain diameters for specimens with 0 wt%, 2.5 wt%, 5 wt% and 10 wt% addition of seeds SB are shown in Fig. 3. The curve for the specimen without seeding presents a single modality in the distribution (the maximum frequency locates at around 0.7 μm). However, grain size distribution of seed-containing α-Sialon shows a dual modality, existing two maximum frequencies at around 0.7 μm and 2 μm respectively. It is noted that the distribution peaks representing smaller grains in all four specimens locate almost at the same diameter value ($\sim$0.7 μm). It is thought that these smaller grains occur as a result of dissolution and precipitation involving α-Si_3N_4 to α-Sialon transformation, but their growth is not affected by the seeds. This can explain why the amount of the small grains is high in the seed-free sample, but decreases with increase in the amount of seeds (Fig. 3). It is also seen that the height of the second peaks, representing the large grains, in the seed-containing specimens increases with seed concentration, which indicates that the more seed particles are added into the α-Sialon composition, the more grains with large diameter. It is reasonable to suggest that the grains with higher aspect ratio and larger diameter are attributed to the growth on seeds. Meanwhile, the length of elongated grains in the seed-containing samples decreases with increase of seed particles due to grain impingement, but the grain diameter remains constant, which results in a decrease of aspect ratio (see Fig. 4).

The microstructure of seed-containing α-Sialons is not only affected by the amount of seed particles, but also by the size of seed particles. Fig. 5 shows the SEM photographs of specimen YS6 with 5 wt% SA seed particles, which have smaller size than SB seed particles. For the same composition and added amount of seeds, both the length and width of elongated grains in YS6 specimen are smaller in comparison to YS3 (the ones in Fig. 2c).

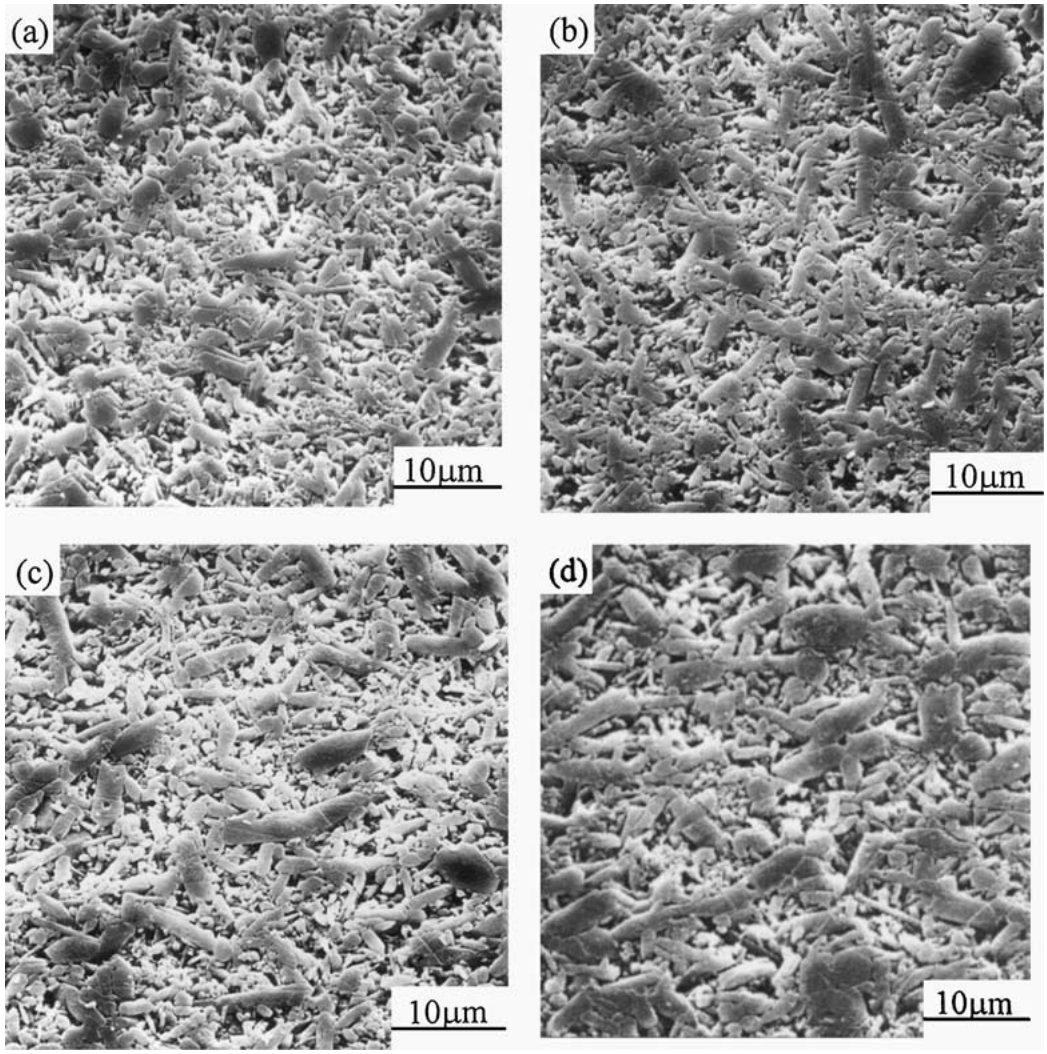

Figure 2 Microstructure of α-Sialons hot-pressed at 1800°C for 1 h: (a) YS1, (b) YS2, (c) YS3, and (d) YS5.

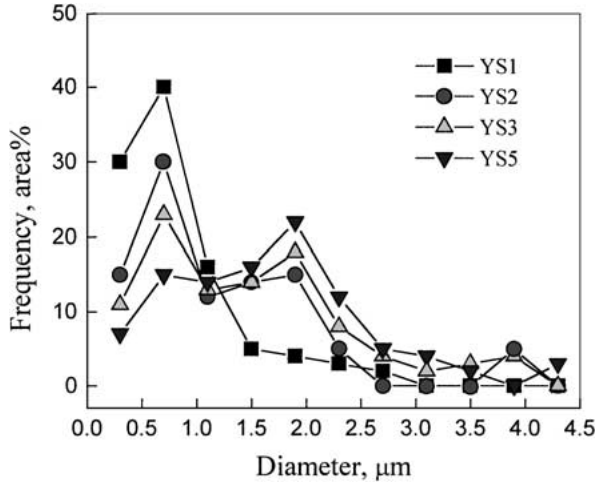

Figure 3 Grain size distribution of α-Sialons hot-pressed at 1800°C for 1 h.

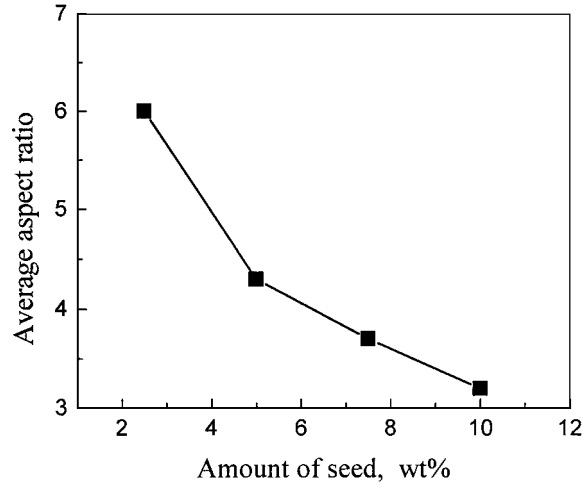

Figure 4 Average aspect ratio of elongated grains in the samples with different amounts of seed particles.

3.3. Mechanical properties

The variation of fracture toughness of α-Sialon ceramics as a function of the amount of seed particles is shown in Fig. 6. Specimen without seeds has relative low fracture toughness. By adding both SB and SA seed particles, the fracture toughness of α-Sialon ceramics is increased. When doped with the SB seed, the fracture toughness of specimens initially increase and then decrease when the amount of seed particle was more than 5 wt%. Samples seeded with SA particles have shown lower fracture toughness than the SB seeded specimens, reflecting the effect of grain size on mechanical properties.

Fig. 7 shows the propagating paths of cracks caused by the indentation test in α-Sialons specimens without seeding and with 5 wt% SB seed particles. The

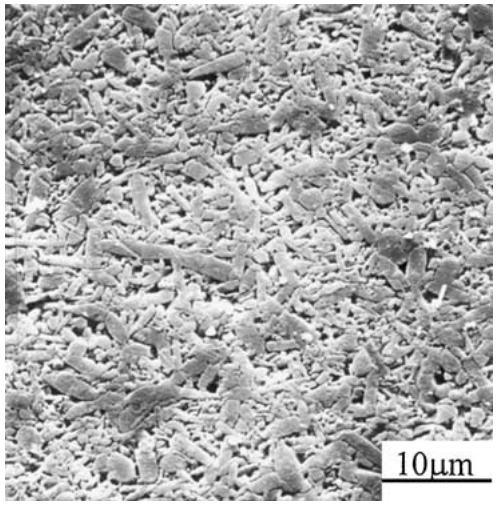

Figure 5 SEM micrographs of polished and chemically etched surfaces of YS6.

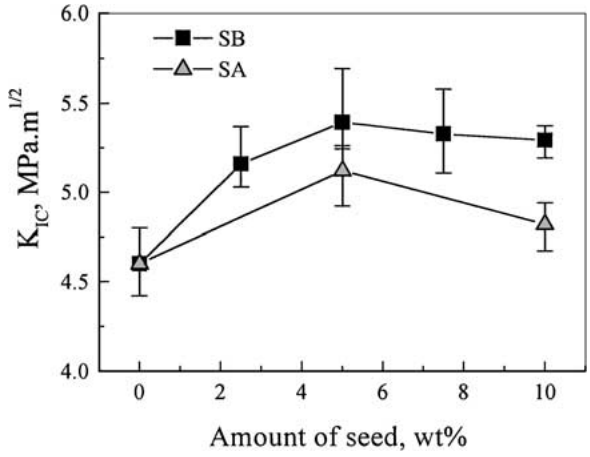

Figure 6 Fracture toughness of α-Sialons sintered at 1800°C for 1 h as a function of amounts of seed particles.

cracks in the specimen without seeds are relatively flat (Fig. 7a). On the other hand, the cracks in specimen with 5 wt% seeds show appreciable deflection by the larger grains developed from seed particles (Fig. 7b), which implies that the improved fracture toughness in the seeded specimens could be attributed to crack deflection and bridging by the larger elongated grains.

It has been reported that the toughening contribution from crack bridging increases with an increase in both the diameter and volume content of the elongated grains [16, 17]. In this work, the maximum value in the grain size distribution of the smaller-grain group is not changed with an increase in the amount of seed particles, but the size and the amounts of the elongated grains are dependant on the seed particles, as discussed above. The increase in the diameter and amount of seed particles would facilitate grain growth in both length and width directions, thus resulting in more crack deflection and an increase in fracture toughness. However, the length of elongated grains would be decreased by adding too much seed particles in the starting composition, which makes crack deflection less effective and, hence, the lower fracture toughness. Thus, the optimum fracture toughness can be achieved in this material by tailoring the amount and size of seed particles.

4. Conclusions

1. Pure α-Sialon seed particles can be obtained by pressure-less sintering and subsequent acid rinsing treatment. The size and shape of α-Sialon seed particles can be controlled by sintering time.

2. The microstructure of Y, Sm-α-Sialon ceramic without seeding consists of fine elongated grains and a minor amount of relatively coarse grains. However, seed-containing α-Sialon specimen for the same composition presents large amounts of elongated grains. The amount and size of elongated grains can be tailored by the amount and size of seed particles.

3. The fracture toughness of Y, Sm-α-Sialon specimens is improved by adding with seed particles. The best fracture toughness, 5.4 MPa $\cdot$ m$^{1/2}$, can be obtained in the specimen with 5 wt% of seeds with larger size. The improved fracture toughness is attributed to crack deflection and bridging by larger elongated α-Sialon grains.

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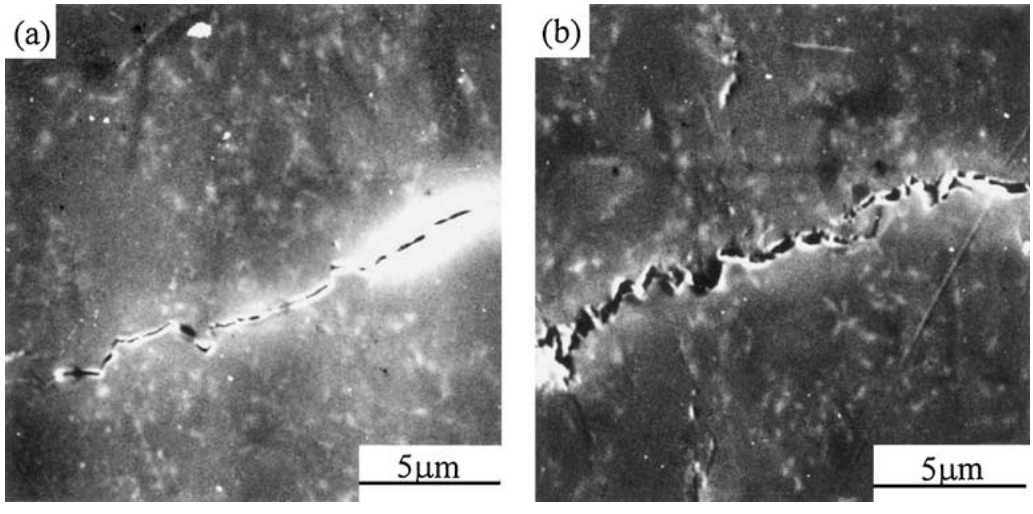

Figure 7 SEM micrographs of the crack propagation in (a) YS1 and (b) YS3.

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