PII: S0955-2219(98)00168-X
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0955-2219/98/$—see front matter

Effect of Sedimentation and Flocculation Pre-treatment of Starting Si_3N_4 and Al_2O_3 Powders on Room Temperature Strength of β-sialon ($z=1$)

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(Received 9 February 1998; accepted 29 June 1998)

Abstract

The room temperature strength of β*-sialon fabricated using a mixture of sedimented and flocculated* Si_3N_4*, and* Al_2O_3 *powders was investigated, in comparison with that achieved using* Si_3N_4 *and aluminum iso-propoxide solution, and that using as-mixed* Si_3N_4*, and* Al_2O_3*, respectively. This* β*-sialon showed an average strength of about 990 MPa. It was slightly lower than that when using an aluminum iso-propoxide solution, but approximately twice that of the sample using an as-mixed powder. The difference in strength among the specimens is interpreted in terms of the size and number of process-related internal defects resulting in a fracture origin. It could be concluded that the sedimentation and flocculation pre-treatment of the starting powders was very effective to increase the strength of* β*-sialon due to removing internal defects. © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

β-sialon($Si_{6-z}Al_zO_zN_{8-z}$) is of interest for use in ceramic components for engines and other high temperature engineering applications.[1] The authors have reported that the strength of β-sialon fabricated from Si_3N_4 and aluminum iso-propoxide (Al (Oi-Pr)$_3$) solution was much improved compared to that from Si_3N_4 and Al_2O_3 powders.[2–5] This improvement in strength was due to decreased size of defects as fracture origins. The formation of defects was assumed to originate from inhomogeneous dispersion of Al_2O_3 which formed liquid phase during sintering. So, it is considered that if sufficiently homogeneous dispersion of Al_2O_3 can be attained, the strength of β-sialon should be improved even when powder is used as an Al_2O_3 source. Using $A1_2O_3$ powder is more appropriate from commercial aspect than Al(Oi-Pr)$_3$ as a starting material. Carlström and Lange reported that the sedimentation and flocculation pre-treatment of a starting powder was effective to get a homogenous mixture of two kinds of powders.[6] It is considered that analogous procedure can be applied to remove the inhomogeneities that might be fracture origins in a β-sialon sintered body also in the case where the material will be fabricated from Si_3N_4 and Al_2O_3 powders.

This paper describes the effect of sedimentation and flocculation pretreatment of starting Si_3N_4 and Al_2O_3 powders on room temperature strength of β-sialon with $z=1$, in comparison with β-sialon made using as-mixed Si_3N_4 and Al_2O_3 powders[2] and a spray dried mixture of Si_3N_4 and Al(Oi-Pr)$_3$ solution.[7]

The α-Si_3N_4 raw material used was from Tosoh Co., Ltd (Tokyo, Japan, grade TS-7) and α-Al_2O_3 was from Sumitomo Chemicals Co., Ltd (Tokyo, Japan, grade AKP-50). Si_3N_4 was dispersed and stirred in water at pH 10·5. The suspension was sedimented for 15 h to remove particles and/or hard agglomerates greater than 1·8 μm. The pH of decanted retaining dispersion was changed to 7 for flocculation. The clear supernatant was removed and the flocculated suspension was washed with distilled water. The solid concentration of flocculated suspension was determined by measuring

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weight of suspension and dehydrated powder. The sedimented and flocculated suspension of Al_2O_3 was prepared at pH 11·5 and 9 by the same procedure as Si_3N_4. The pH was adjusted with either NH_4OH or HCl in all cases. The flocculated Si_3N_4 suspension was weighted into a plastic container followed by the Al_2O_3 flocculated suspension with the Si/Al ratio set to $z=1$ in the formula of $Si_{6-z}Al_zO_zN_{8-z}$, and stirred. The dispersion medium of the mixed, flocculated suspension was replaced with ethanol and it was dried up for hot-pressing. Hot-pressing was carried out at 1850°C for 1 h under the pressure of 30 MPa in N_2 atmosphere. A hot-pressed β-sialon using a spray dried mixture of α-Si_3N_4 powder and Al (Oi–Pr)$_3$ solution was prepared by previously reported procedure.[3,7] A powders mixture of α-Al_2O_3 (Iwatani Chemicals Co., Ltd. Tokyo, Japan, grade RA-40) and α-Si_3N_4 which was mixed with Si_3N_4 balls in ethanol for 20 h and immediately dried up in a stainless steel tray was hot-pressed with same condition.[2] Hereinafter, the samples are indicated as sample-A, -B and -C, respectively, as shown in Table 1. The specimens with a size of 3×3×30 mm for bending test were prepared by previously reported machining[4] from each hot-pressed plate. These specimens were heattreated at 1200°C for 2 h in air to decrease the influence of surface grinding flaws. The bending test was carried out using 3-point loading device with a span of 20 mm and a cross-head speed of 0·5 mm min^{-1} at room temperature. The K_{IC} was measured by Vicker's indentation method with load of 10 kg by using Nilhara's equation.[8] The fracture origins were observed with an optical microscope.

Table 2 shows the properties of hot-pressed samples. All samples showed complete densification with water absorption percentage of less than 0·01%, however the densities of samples were 3·13, 3·12 and 3·14 Mg m^{-3}, respectively. All samples consisted of β-sialon and X-phase, however, the amount of X-phase by XRD study was decreasing in the order of sample-B, -A and -C. This difference in the amount of X-phase was in direct correspondence with the difference in the densities of samples. Sample-A showed the strength of 985 (1180–839) MPa and this value was approximately the same with sample-B [1001 (1319–831) MPa],[7] however, that was much higher than sample-C [496 (424–529) MPa].[2] All samples showed similar values of fracture toughness and hardness. Figure 1 showed optical micrographs Vickers indentation on the surfaces of the samples. The size of the black spots that could be observed in sample-A and -B was clearly smaller than that in sample-C as shown in Fig. 1. This indicated that sample-A and -B had more homogeneous microstructures than sample-C. Figure 2 showed optical micrographs of typical fracture origins of the samples. About half the numbers of the bend test specimens were fractured from internal defects [Fig. 2(a) and (c)] and

Table 1. Designation of samples

Sample name	*Starting materials*	*References*
A	$Si_3N_4 + Al_2O_3$ flocculated powders	Present work
B	$Si_3N_4 + Al(Oi\text{-}Pr)_3$ solution	7
C	$Si_3N_4 + Al_2O_3$ as-mixed powders	2

Table 2. Properties of samples

Sample	*Density ($Mg\,m^{-3}$)*	*Bending strength (MPa)*	*K_{IC} ($MPa\,m^{1/2}$)*	*Hv (GPa)*
A	3·13	985	3·2	15·3
B	3·12	1001	3·5	14·9
C	3·14	496	3·2	14·9

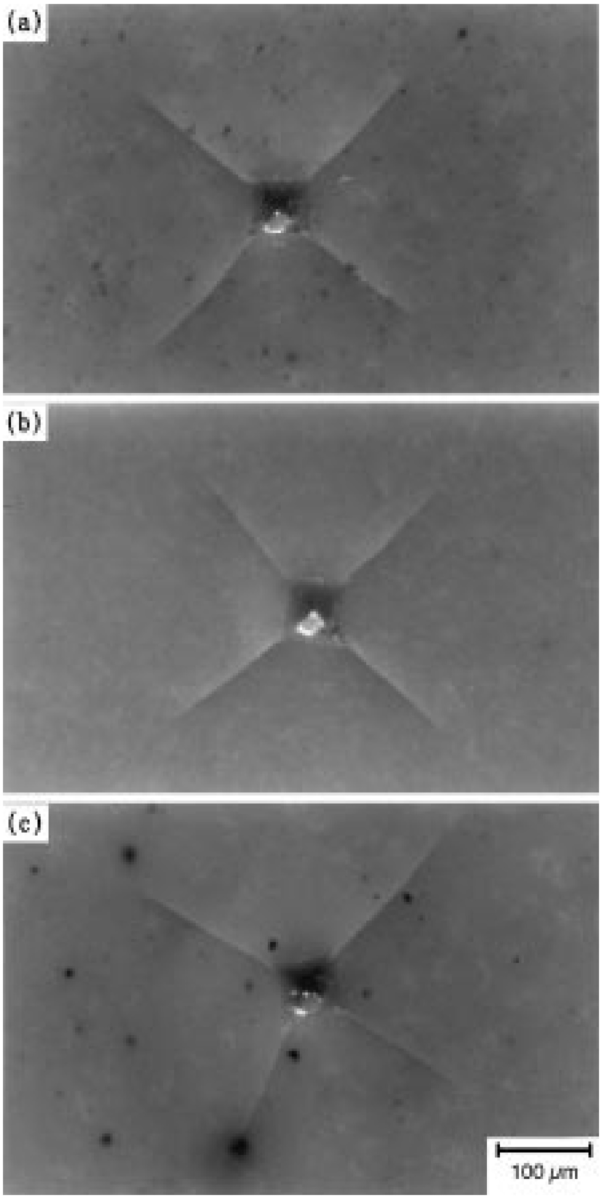

Fig. 1. Optical micrographs of surfaces of samples with Vickers indentations: (a) sample-A; (b) sample-B; (c) sample-C.

the remainder from surface flaw [Fig. 2(b) and (d)] in the case of sample-A and -B. All specimens of sample-C were fractured from internal defects [Fig. 2(e)].

In general it is accepted that the following relationship holds between K_{IC} and strength (σ_f);[9]

$$K_{IC} = \sigma_f Y c^{1/2} \tag{1}$$

where c is size of a fracture origin and Y is a dimensionless constant.

Since all samples consisted of β-sialon and X-phase and their fracture toughness were almost same, it is considered that the difference in strength depended primary on the size of the fracture origins. The original size of surface flaw as a fracture origin could not be measured exactly, however, in the case of the specimens fractured from internal defects, it is considered that this relationship between σ_f, and c could be estimated. It is known that the stress applied at the internal fracture origin (σ) hold the following relationship with width of a specimen (a), thickness of a specimen, (h), applied load (P), a span (L) and distance of a fracture origin from tensiled surface (y).[10]

$$\sigma = \frac{3PL}{ah^3} \times (h/2 - y) = \sigma_f(1 - 2y/h) \tag{2}$$

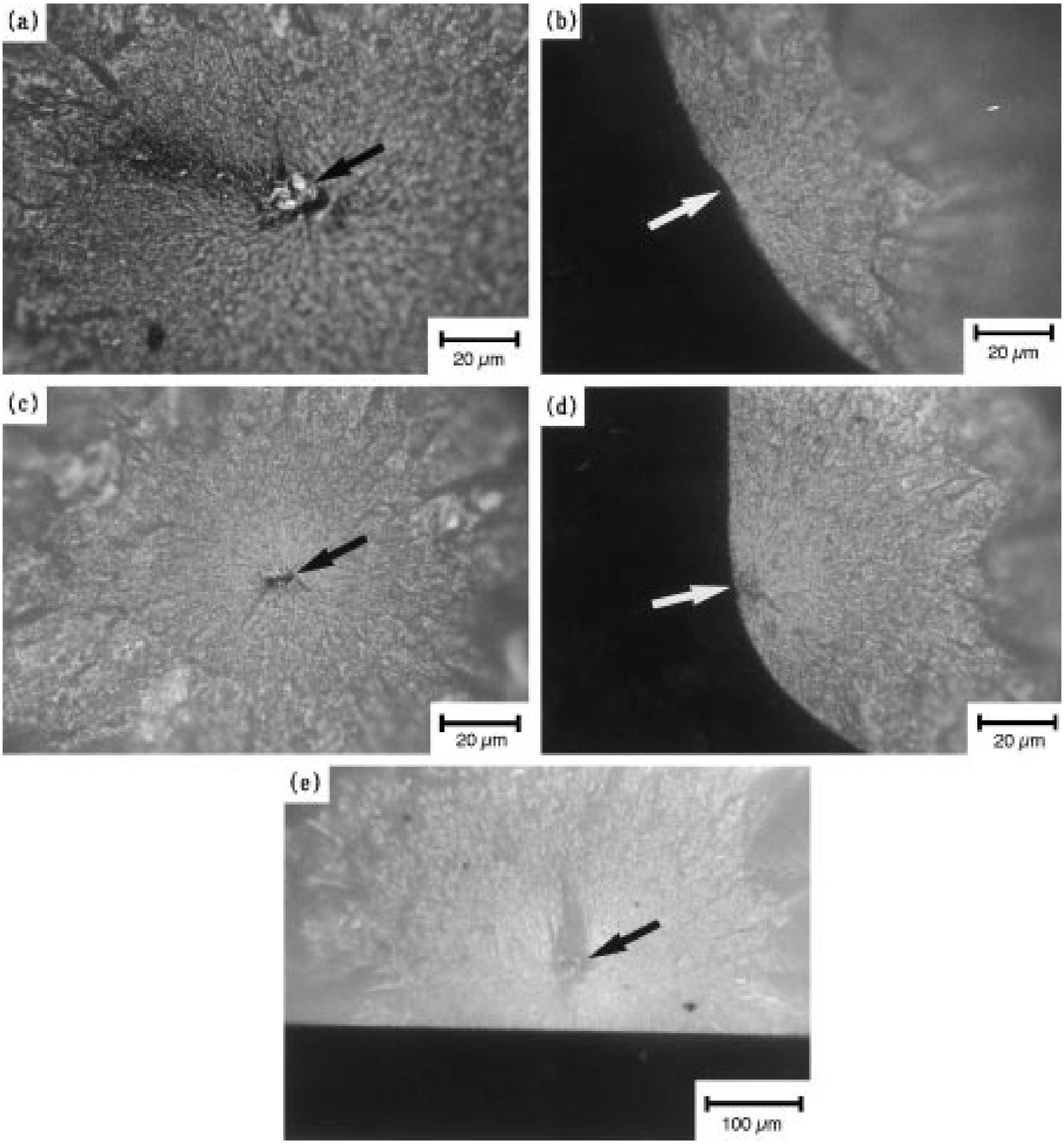

Fig. 2. Optical microgaphs of typical fracture origins of samples (arrows indicate fracture origins): (a) sample-A (fractured from an internal defect, $\sigma_f = 955$ MPa); (b) sample-A (fractured from a surface flaw, $\sigma_f = 1118$ MPa); (c) sample-B (fractured from an internal defect, $\sigma_f = 1319$ MPa); (d) sample-B (fractured from a surface flaw, σ_f, = 956 MPa); (e) sample-C (fractured from an internal defect, $\sigma_f = 488$ MPa).

Since y was about 260, 240 and 70 μm for the specimens shown in Fig. 2(a), (c) and (e), respectively, estimated σ using eqn (2) was 790, 1100 and 470 MPa, respectively. On the other hand, the size of fracture origins showing Fig. 2(a), (c) and (e) was about 18, 8 and 45 μm, respectively. The estimated strength by using eqn (1) and the size of fracture origins was about 740 and 1100 MPa for the specimens shown in Fig. 2(a) and (c), respectively on the basis of the strength of the specimen shown in Fig. 2(e). These values corresponded to the stress applied at a fracture origin above mentioned approximately.

The authors have reported that the size of surface machining flaws which lead to be a fracture origin was a particular factor where the clack grew wider and deeper than that expected with average surface condition in case of pure β-sialon, and the original size of flaws have not been decreased by heat treatment in air.[8] Whether or not a particular surface flaw resulted in a fracture origin as an enlarged and grown clack depended on the machining condition. In other words, if there was ideally a homogeneous sintered body without any internal defects, its strength distribution would be controlled by the difference of the surface machining condition. On the contrary, if highly perfect surface finishing was achieved, all fracture origins shall basically due to an internal, processing-related defect. Consequently, the strength of the specimens fractured from an internal defect could be more as a material related strength than that where a surface flaw was fracture origin.

The kind of internal defect shown as the black spots in Fig. 1 is anticipated to be a fracture origin. Thus the decreasing size of this type of internal defects will be consistent with the increase of strength level in case of sample-A and -B compared with sample-C. In case of sample-A, the specimens which failed from internal defects showed the mean strength of 966 (1104–839) MPa which is slightly lower than those with surface flaws as fracture origins [1015 (1180–849) MPa]. However, in both cases, the maximum and the minimum values were approximately same, respectively. Thus it is considered that even when nearly perfect surface finishing will be achieved, no substantial improvement in strength is to be expected for sample-A material. Thus, the strength level will be exclusively controlled by the size of internal defects as a fracture origin. On the other hand, the mean strength of the specimens fractured from internal defects was 1182 (1319–963) MPa and that from surface flaws was 908 (955–831) MPa for sample-B. It is considered that the specimens fractured from a surface flaw also contained the similar internal defects as those fractured from an internal defect. However, in the case of these specimens, the fracture occurred from a surface flaw at a lower load than in the case of fracture from an internal defect. Thus, the lower strength of these specimens was due to the more rough machining condition that introduced larger surface flaws than in the specimens which fractured from an internal defect. Therefore, it is considered that if the surface conditions of these specimens will be improved, the strength will increase up to the level of those fractured from an internal defect, and, the sample-B material should show a higher strength level than the sample-A material.

The strength level of samples can be ranked in their order of sample-B > sample-A≫sample-C, ultimately due to the size and the number of internal defects resulting in a fracture origin. However, the inherent strength of sample-A was approximately a twice that of sample-C. So, it could be concluded that the sedimentation and flocculation pre-treatment on starting powders was very effective to increase the strength of β-sialon due to removing inhomogeneities which potentially became a fracture origin.

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