

Synthesis of α -SiAlON Seed Crystals

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Single-phase seed crystals of Ca- and Y- α -SiAlONs have been synthesized for tailoring microstructure of α -SiAlON ceramics. The influence of composition, sintering temperature, and nitrogen pressure on the size and morphology of seeds has been explored. Guidelines for α -SiAlON seed preparation and morphology control are provided.

I. Introduction

SEEDING is an effective method for microstructure control of Si_3N_4 -based ceramics. It is well known that a small amount of native β - Si_3N_4 particles that exist in the α - Si_3N_4 powders serve as seeds for β - Si_3N_4 or β -SiAlON grains in the fired ceramics. For α -SiAlON, Chen and Rosenflanz¹ used β - Si_3N_4 starting powder (containing 5%–7% of native α - Si_3N_4 seeds) to obtain a coarse microstructure with elongated α -SiAlON grains. Intentionally added artificial seed crystals may overtake the native nuclei in the starting powders and are especially effective. Liquid-grown, micrometer-sized elongated β - Si_3N_4 seeds^{2–4} can result in β - Si_3N_4 ceramics with excellent mechanical properties.^{5–7} For α -SiAlON ceramics, seeding with pulverized α -SiAlON ceramic fragments can also yield ceramics with a desirable microstructure and improved fracture toughness.⁸

Seed preparation is intrinsically more difficult for α -SiAlON because the parent structure, α - Si_3N_4 , is unstable under typical processing conditions. Only by forming a solid solution with the formula $\text{Me}_{m/2}\text{Si}_{12-m-n}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$ (here Me is a metal ion with a valence z) can the α structure be stabilized. Therefore, α - Si_3N_4 crystals cannot be grown by particle coarsening in a liquid; neither are they useful as seeds for α -SiAlON. This is unlike the case of β - Si_3N_4 and β -SiAlON. Moreover, the present information on the phase relations between α -SiAlON and oxynitride liquid^{9,10} is insufficient to guide seed processing. In this communication, we report the synthesis conditions for several α -SiAlON seeds of different compositions, morphologies, and sizes. They have been used to obtain Y- and Ca- α -SiAlON ceramics with a pronounced *R*-curve behavior.¹¹

II. Experimental Procedure

Seed crystals with chemical formulas $\text{Ca}_{m/2}\text{Si}_{12-m-n}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$ and $\text{Y}_{m/3}\text{Si}_{12-m-n}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$ were prepared by liquid-phase sintering. The intended compositions were $m = 0.8$, $n = 0.9$ (CS-1) and $m = 1.5$, $n = 1.2$ (CS-2, CS-3, CS-4) for Ca-SiAlON, and $m = 1.5$, $n = 1.2$ (YS-1, YS-2, YS-3, YS-4) for

Y-SiAlON. The formulations of the starting powders are listed in Table I, which take into account the oxygen content in the starting powders, α - Si_3N_4 (1.24 wt%, SE-E-10, Ube Industries, Japan) and AlN (0.88 wt%, type F, Tokuyama Soda Co., CA). These powders, along with metal oxides, 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.

Seed crystals could grow in both pellets and powder mixtures (YS-2 and YS-3). Pellets of powder mixtures were pressed under 30 MPa of uniaxial pressure at room temperature. Sintering was performed in a graphite resistance furnace for 2 h using the conditions listed in Table I. Pellets of YS-1, which has a very low liquid content, were first hot-pressed at 1500°C for 0.5 h under 10 MPa pressure to achieve a higher density. After sintering, all the compacts were still porous and could be easily crushed and sieved through a 125-mesh sieve. Treating with various chemical solutions and washing in ultrasonicated water yielded separated seeds.

The phase compositions of sintered samples and harvested crystals were analyzed by X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation. For reference, we used pulverized powders of fully dense single-phase ceramics (hot-pressed at 1900°C, at 30 MPa, for 1 h) with the intended seed compositions. For morphology characterization, a scanning electron microscope (SEM) was used. Dimensional statistics of seed crystals were collected by measuring SEM images of 150–200 grains.

III. Results and Discussion

(1) Compositions of Seed Crystals

The starting compositions were selected assuming α -SiAlON is compatible with a certain liquid composition.^{9,10,12,13} The liquids chosen were a gehlenite-based glass (G) in the case of Ca- α -SiAlON, and melilite (M) or AlN-polytype glass + melilite in the case of Y- α -SiAlON. After sintering, XRD analysis showed mostly α -SiAlON. Some second phases, mainly 12 H and melilite, were also present in the YS compositions (Fig. 1). Gehlenite-based glass did not devitrify with α -SiAlON and its reflections were absent in the XRD patterns.

Chemical treatments in the following order separated α -SiAlON seed from other phases: (a) For melilite and glassy phase removal,

Table I. Compositions and Processing Conditions

Sample	Composition [†]	<i>T</i> (°C)/ <i>P</i> _{N₂} (MPa)
CS-1	80Ca-0809+20 G	1700 /10
CS-2	80Ca-1512+20 G	1700 /10
CS-3	80Ca-1512+20 G	1900 /10
CS-4	80Ca-1512+20 G	1700 /0.2
YS-1	97 Y-1512+ 3M	1700 /0.2
YS-2	80 Y-1512+20 gl	1700 /0.2
YS-3	80 Y-1512+20 gl	1700 /10
YS-4	80 Y-1512+20M	1900 /10

[†]Expressed in wt% of intended α -SiAlON + wt% of forming liquid. G: 2CaO·Al₂O₃·SiO₂; M: Y₂O₃·Si₃N₄; gl: 0.34Al₂O₃·0.31Y₂O₃·0.35Si₃N₄.

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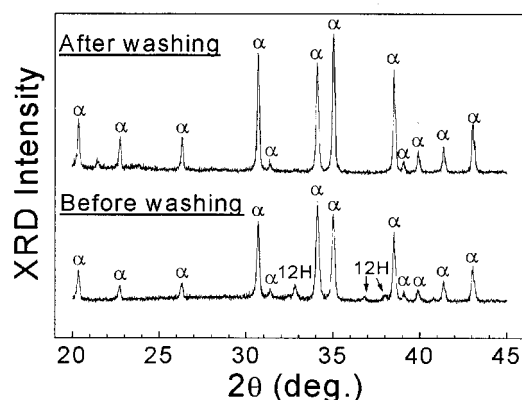


Fig. 1. XRD patterns of YS-3 before and after chemical treatments and washing.

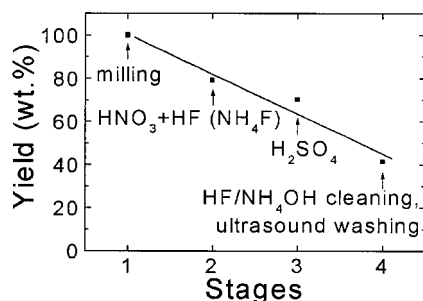


Fig. 2. Yield (in wt%) after each step of chemical treatment of YS-3.

we used mixtures of HNO_3 and HF held at room temperature, or HNO_3 and NH_4F at 250°C for faster dissolution. (b) For removal of Y-containing compounds formed after the first step of washing, we used H_2SO_4 at room temperature. (c) For surface SiO_2 removal, we used 3% HF at room temperature. (d) For final removal of HF residue, we used 1% NH_4OH at room temperature. These procedures left single-phase α - SiAlON seed crystals (upper XRD pattern shown in Fig. 1). Figure 2 shows the typical yield after each chemical treatment; the final yield was about 40%.

Calculated lattice parameters for seeds nearly equal those of hot-pressed reference ceramics of the intended compositions (Table II) and agree with those calculated from m and n using the empirical relations.^{9,14} Although the lattice parameters are not very sensitive to n (oxygen content), the near coincidence of the unit cell dimensions of the seed crystals and the reference ceramics suggests that the seeds do have the intended compositions. Thus, the liquid compositions in Table I are probably compatible with the respective α - SiAlON at the temperatures and pressures used.

(2) Morphology and Growth Kinetics

The different compositions and heat treatments produced seed crystals of different sizes and morphologies. They varied from

equiaxed (YS-1, Fig. 3(d)) to highly elongated (e.g., all other samples in Fig. 3, especially CS-2), and their widths varied from about $0.4\ \mu\text{m}$ (CS-1, CS-2, YS-2), to about $1.5\ \mu\text{m}$ (CS-3), to more than $3\ \mu\text{m}$ (sample YS-4, not shown). Figure 4 exhibits a typical distribution of seed aspect ratio and crystal volume for sample YS-3. (Width and length follow from these two parameters.) Table II summarizes the average characteristic dimensions of all samples.

Temperature has a strong influence on the morphology and size according to Tables I and II. Seeds grown at 1900°C (CS-3 and YS-4) were larger than those grown at 1700°C (all other samples). The influence of the amount of forming liquid was also significant. For example, equiaxed seeds were obtained only in YS-1, which had the smallest amount (3 vs 20 wt% in all other cases) of liquid. The effect of nitrogen pressure, which favors the growth of larger crystals (comparing CS-2 at 10 MPa and CS-4 at 0.2 MPa, and likewise YS-3 at 10 MPa and YS-2 at 0.2 MPa), may operate indirectly through the liquid as well. This is because the liquid region in the $(\text{Me},\text{Si},\text{Al})(\text{O},\text{N})$ systems usually expands with nitrogen pressure.¹⁵ Lastly, the effect of the amount of metal oxide (e.g., CaO), which favors the growth of larger and more elongated crystals (comparing CS-2 at $m = 1.5$ and CS-1 at $m = 0.8$), may again be due to the volume of liquid, since more metal oxide would provide more liquid during sintering.

Other factors may also influence the formation and the morphology of liquid-grown crystals. These include viscosity of liquid,¹⁶ interface kinetics (both depending on temperature and composition),¹⁷ nucleation statistics (different populations of nuclei with α/β - Si_3N_4 structure and different particle sizes in the starting powders),^{16,18} and microstructure of compacts (porosity, connectivity, size, etc.). These effects will be reported elsewhere.

IV. Conclusions

(1) Seed crystals of α - SiAlON of controlled compositions have been synthesized using several compositions of compatible forming liquids.

(2) The size and shape of seed crystals can be varied using different amounts of liquid, firing temperature, and nitrogen pressure. Both equiaxed and elongated crystals have been obtained.

(3) A method for harvesting seed crystals has been developed. The yield is about 40% and is adequate for most applications.

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Table II. Unit Cell Dimensions and Average Characteristics of α - SiAlON Seed Crystals

Sample	Width (μm)	Aspect ratio	Aspect ratio–5% [†]	Volume (μm^3)	Lattice parameters			
					Seed		Reference	
					a (\AA)	c (\AA)	a (\AA)	c (\AA)
CS-1	0.41	2.5	4.6	0.20	7.806 (1)	5.674 (1)	7.804 (1)	5.676 (1)
CS-2	0.45	3.8	8.2	0.33	7.843 (1)	5.707 (1)	7.840 (1)	5.704 (2)
CS-3	1.61	2.7	5.4	11.93	7.841 (1)	5.704 (1)		
CS-4	0.33	2.6	5.8	0.12	7.837 (1)	5.701 (1)		
YS-1	0.51	1.3	2.4	0.13	7.830 (2)	5.705 (3)	7.826 (1)	5.707 (1)
YS-2	0.38	2.2	5.5	0.11	7.825 (3)	5.706 (4)		
YS-3	0.62	2.4	6.3	0.32	7.829 (2)	5.705 (3)		
YS-4	3.51	3.1	6.9	190.8	7.839 (3)	5.713 (2)		

[†]Value of the highest 5% of the distribution in Fig. 4. It is about 2.2 times the average aspect ratio.

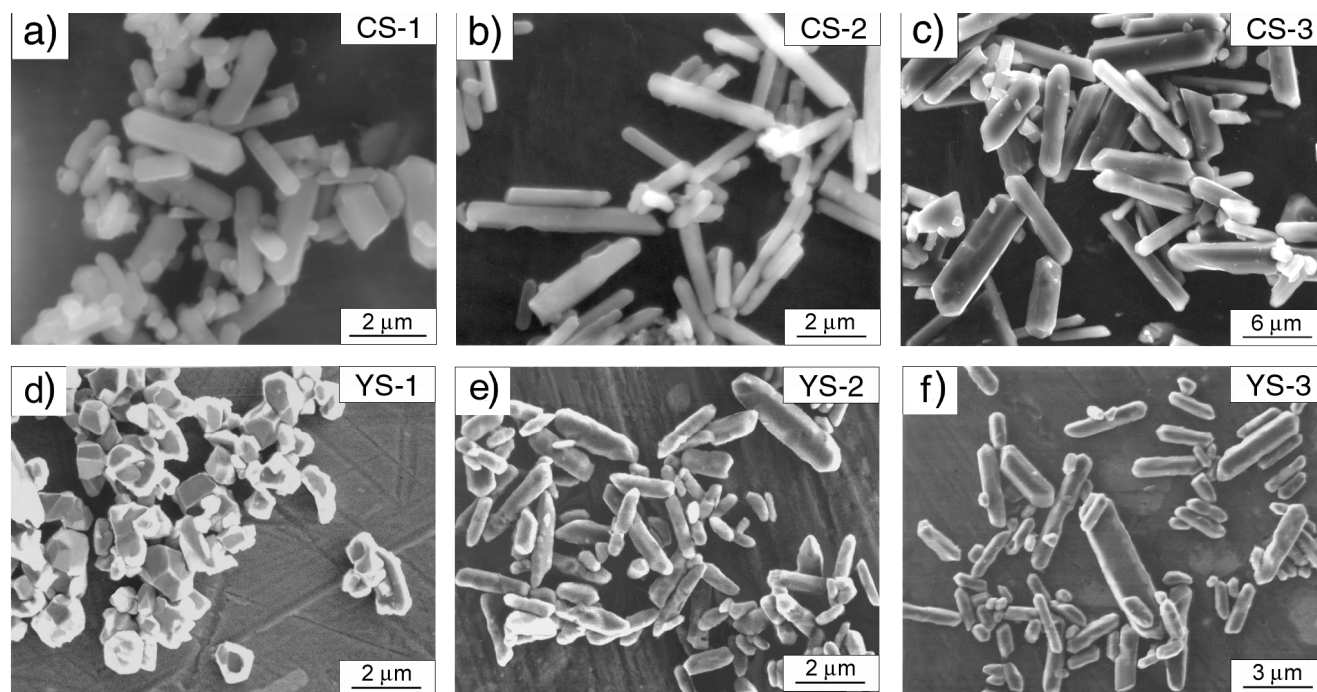


Fig. 3. SEM micrographs of seed crystals.

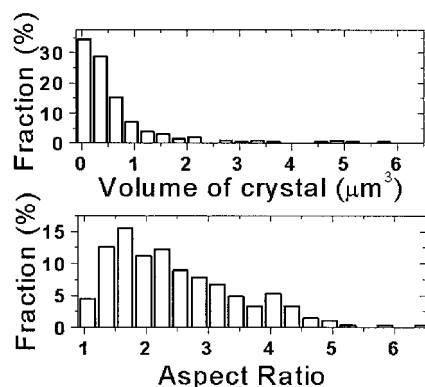


Fig. 4. Distribution of harvested seed crystals (YS-3) by aspect ratio and volume.

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