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Abstract

Various procedures of mixing starting powders for hot-pressing α -SiAlON ceramics were studied. They included different milling methods (attrition milling, ball milling, and sonication), liquid medium (water, isopropyl alcohol, and pyridine), and atmospheres (ambient air and nitrogen). These mixing procedures resulted in markedly different densification behavior and fired ceramics. As the powders experienced increasing oxidation because of mixing, the densification temperature decreased, the amount of residual glass increased, and α -SiAlON was destabilized and replaced by β -SiAlON and AlN polytypes during hot pressing. These effects were mitigated when pyridine, nitrogen, and sonication were used. Several protocols that yielded nearly phase-pure, glass-free dense α -SiAlON were thus identified.

Comments

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The Effect of Powder Mixing Procedures on α -SiAlON

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Various procedures of mixing starting powders for hot-pressing α -SiAlON ceramics were studied. They included different milling methods (attrition milling, ball milling, and sonication), liquid medium (water, isopropyl alcohol, and pyridine), and atmospheres (ambient air and nitrogen). These mixing procedures resulted in markedly different densification behavior and fired ceramics. As the powders experienced increasing oxidation because of mixing, the densification temperature decreased, the amount of residual glass increased, and α -SiAlON was destabilized and replaced by β -SiAlON and AlN polytypes during hot pressing. These effects were mitigated when pyridine, nitrogen, and sonication were used. Several protocols that yielded nearly phase-pure, glass-free dense α -SiAlON were thus identified.

I. Introduction

PROCESSING silicon nitride or SiAlON begins with mixing nitride and oxide powders that are prescribed by the SiAlON formulation or by the sintering needs. The particle size is often reduced in this step, which may improve powder compaction and densification because of faster dissolution of smaller particles during liquid phase sintering.^{1–4} Using energetic mechanical mixing methods, such as 24 h of attrition milling (AM) or 300 h of ball milling (BM), the particle size of Si₃N₄^{1,2,5–8} and AlN^{3,9,10} powders can be reduced to tens of nanometers, accompanied by an increase in surface area to 50–60 m²/g, the size reduction of AlN being comparable or greater than that of Si₃N₄ under similar conditions. A significant fraction of amorphous phase may also form during mixing,⁵ further assisting sintering. On the other hand, Si₃N₄ and AlN powders experience oxidation during mixing, if it is performed in water- or oxygen-containing atmosphere or liquid medium. This is because of the reactivity of the very large surface area of the powder and the freshly cleaved new surfaces created by particle break-up. As Si₃N₄^{1,2,5,8,11} and AlN^{3,10,12} readily react with water forming oxide/hydroxide surface layer, anhydrous alcohol is commonly used as a milling medium. However, oxygen content does increase during milling in alcohol for both Si₃N₄^{2,5,9,11,12} and AlN.^{3,12} Some authors attributed this to the small amount of water contained in alcohol or atmosphere moisture,^{2,3,5,12} while reaction of powder with alcohol is also possible,^{9,11,12} producing ester and hydroxide surface groups. As a result of nitride powders hydrolysis, phase assemblage in the fired ceramics may differ from the intended one.^{4,12} In addition, the excess oxides may leave an appreciable amount of residual glass, which is detrimental for high-temperature properties.^{13–17}

Compared with β -Si₃N₄/SiAlON, α -SiAlON is much more susceptible to the adverse effects caused by powder oxidation. In the case of β -Si₃N₄, powder oxidation typically only affects the

ratio of β -Si₃N₄/glass and the composition of the glass. For α -SiAlON, as the single-phase composition is more limited in range, even a modest increase in O/N ratio may in some cases destabilize α -SiAlON enough to bring about other unintended phases, such as β -SiAlON and AlN polytypes, which have lower hardness or are less refractory.^{18–20} The literature concerning these effects, however, is not sufficient to form a basis for optimal processing of α -SiAlON. Therefore, we have investigated the influence of the milling method, liquid medium, and gas atmosphere on the densification, phase assemblage, and amount of residual glass of hot-pressed β -SiAlON. Our intent was to identify effective mixing protocols that incur minimal oxidation. In particular, we investigated pyridine as a liquid medium that proves advantageous for the above purpose.

II. Experimental Procedure

The nominal composition of all samples was Y- α -SiAlON represented by the formula Y_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n} with $m = 1.5$, $n = 1.15$, which lies near the border of the single-phase α -SiAlON region at above 1800°C. The starting powders used were α -Si₃N₄ (SN-E10, UBE Industries, Ube, Japan), AlN (Type F, Tokuyama Soda Co., Burlingame, CA), and Y₂O₃ (99.995%, APS 25–50 nm, Alfa-Johnson Matthew Co., Ward Hill, MA). The oxygen content in α -Si₃N₄ (1.26 wt%) and AlN (0.82 wt%) was taken into account in the formulation.

Three types of milling procedures were compared: (a) ultrasonic milling (US) in a 500 mL polyethylene jar using sonication by a VirSonic 450 (Virtis, Gardiner, NY) at 60% power output with a 3/4" titanium probe; (b) BM at 150 rpm in a 1000 mL polyethylene jar filled with ~1.5 kg of 10 mm Si₃N₄ balls; and (c) AM at 600 rpm in a 700 mL Teflon-coated jar with a polyetheretherketone (PEEK, C₁₉H₁₂O₃) attritor and 1 mm Si₃N₄ balls. Compared with other plastics, PEEK was chosen because of its relatively high strength and toughness, while containing very little oxygen. Three types of mixing medium were compared: (a) distilled water; (b) isopropyl alcohol, (CH₃)₂CHOH, 99.5% with 50 ppm of water; and (c) pyridine, C₅H₅N, 99+ % and distilled over CaH₂ prior to use. For atmosphere control, the processing steps for powder mixing, as well as subsequent die pressing and loading into a hot-pressing furnace, were performed in (a) ambient air and (b) nitrogen (industrial grade) for comparison. When nitrogen processing was used, the powders in transfer were packed in a latex bag, which later decomposed during heating.

After mixing, the powder/liquid suspensions were dried in a rotary evaporator and sifted through a 325-mesh stainless-steel sieve (45 μ m openings). The powder was placed in a graphite die and hot-pressed in a graphite resistance furnace. Hot pressing was performed in a nitrogen atmosphere (1 atm) at a uniaxial pressure of 30 MPa. The heating rate was 15°C/min, followed by holding at 1900°C for 1 h and cooling with the furnace (approximately 50°C/min down to 1500°C). During hot pressing the chamber was filled with nitrogen and mechanical pressure was applied at 1000°C, after 1 h holding in vacuum at this temperature to remove absorbed organic residues from the powder surface. Full density (99+%) was achieved in all cases.

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Table I. Mixing Conditions and Properties of Hot-Pressed Ceramics

#	Milling method	Mixing time (h)	Gas	Liquid medium	T_1^\ddagger	T_2^\ddagger	Phases [‡]
1	AM	4	Air	Water	1055	—	β' (vs), ? (w)
2	AM	24	Air	Alcohol	1230	1475	α' (w), β' (vs), ? (s)
3	AM	24	Air	Pyridine	1190	1535	α' (w), β' (vs), K (s), ? (m)
4	AM	24	Nitrogen	Alcohol	1280	1550	α' (vs), β' (vs), 21R (s), 15R (m), K (s)
5	AM	4	Nitrogen	Pyridine	1465	1645	α' (vs), 21R (m), ? (w)
6	AM	24	Nitrogen	Pyridine	1340	1545	α' (vs), β' (w), 21R (s), K (w)
7	BM	24	Air	Alcohol	1515	1720	α' (vs), 21R (w)
8	BM	24	Air	Pyridine	1535	1725	α' (vs), 27R (vw)
9	BM	24	Nitrogen	Alcohol	1520	1725	α' (vs), 21R (w), ? (vw)
10	BM	24	Nitrogen	Pyridine	1555	1735	α' (vs), 27R (vw), 21R (tr), ? (vw)
11	BM	48	Nitrogen	Pyridine	1540	1715	α' (vs), 21R (m)
12	BM	72	Nitrogen	Pyridine	1530	1730	α' (vs), 21R (m)
13	BM	168	Nitrogen	Pyridine	1545	1705	α' (vs), 21R (m)
14	US	1	Air	Alcohol	1570	1730	α' (vs), 27R (vw)
15	US	1	Air	Pyridine	1575	1730	α' (vs), 27R (tr)
16	US	1	Nitrogen	Alcohol	1565	1735	α' (vs), 27R (vw)

[‡] T_1 , temperature at which fast densification starts; T_2 , fast densification ends. T_1 and T_2 are the points of inflection on densification curves see Fig. 1. The systematic error in determining these temperatures is $\pm 10^\circ\text{C}$. [†]vs, very strong; s, strong; m, medium; w, weak; vw, very weak; tr, traces; (?), unidentified phase. 27R(8AlN:SiO₂), 21R(6AlN:SiO₂) and 15R(4AlN:SiO₂) are AlN polytypes, K, kyanite (Al₂O₃:SiO₂); β' , β -SiAlON.

Microstructure of sintered samples was characterized using a scanning electron microscope (SEM). Phase analysis of sintered ceramics was performed by X-ray diffraction (XRD) using CuK _{α} radiation. The results of phase analysis are summarized in Table I along with the mixing conditions.

III. Results and Discussion

(1) Powder Suspension in Liquid Medium

Suspension behavior was judged by sedimentation rate. Water suspension demonstrated the best stability, followed by pyridine and alcohol, which were very similar. These liquids are polar, their dipole moments being 2.3 D for pyridine, 1.87 D for water and 1.66 D for isopropanol.²¹ Although the larger dipole moment of pyridine should lead to better Si₃N₄/AlN powder dispersion,³ the presence of —OH bonds in water and alcohol allows for easy attachment to the siloxane Si—O—Si groups on the Si₃N₄ surface. Therefore, the observed dispersability correlated better with the polarity of solvents relative to water: 100 for water, 54.6 for alcohol, and 30.2 for pyridine.²¹ (Polarity is loosely used to cover a number of different effects including those related to dielectric constant and dipole.) In contrast, we found non-polar solvents, for example, hexane (0 D, polarity 0.9), had very poor dispersability and gave unsatisfactory results in AM.

(2) Densification Behavior

Examination of densification curves²² can offer insight into the liquid-phase sintering process of different powders. This is illustrated in Fig. 1 where the different temperatures at which rapid densification begins (T_1) and ends (T_2) were caused by different powder mixing. As shown in Table I, T_2 stood about 200°C above T_1 and was always lower than the final holding temperature (1900°C). These temperatures were accurate within $\pm 10^\circ\text{C}$ because of sensitivity to the heating rate,²³ packing density and loading train configurations. Nevertheless, it is clear that they generally decreased in the order of US, BM, and AM. A similar decrease with increasing mixing time under otherwise identical conditions was also seen. For example, compare mixing in pyridine for different time by AM (sample #5 and #6) and by ball milling (#10–13). In general, T_1 decreases with decreasing particle size as dissolution becomes easier, and both T_1 and T_2 decrease with increasing amount of sintering liquid, hence powder oxidation.²² This is consistent with the above result as both particle size decreased and oxidation increased with mixing time, at a rate that increased in the above order of milling methods.

Chemical environment was clearly important as reflected by pyridine mixing which, with few exceptions, gave the highest temperatures within each group where different types of liquid medium were compared. This influence was more pronounced in AM (e.g., compare sample #4 and #6) than in BM (compare #7–8 or #9–10). Compared with ambient air, nitrogen environment also increased T_1 and T_2 , more so in AM (e.g., compare sample #2 and #4, or #3 and #6) than in BM (e.g., compare #7 and #9, or #8 and #10). The higher chemical sensitivity in AM was because of the higher degree of particle cleavage and fresh surface creation. Indeed, using US, which caused dispersion and mixing but little particle cleavage, all the samples (#14–16) regardless of chemical environment showed similar T_1 (1565°–1575°C) and T_2 (1730°–1735°C) that were the highest recorded in this study.

The reported literature data for T_1 in Y- α -SiAlON system typically lie around 1450°–1550°C, for powders ball-milled for up to 24 h or attrition-milled for up to 4 h, in alcohol.^{23,24} Our data of US and BM in nitrogen/pyridine up to 24 h were in the high end of this temperature range. For β -Si₃N₄, Bellosi and Babini⁷ observed that the ultrasonically milled powders (β -Si₃N₄ with Y₂O₃ and La₂O₃) had a higher T_1 (1640°C) than its attrition-milled counterpart (1600°C), which also supports our observations.

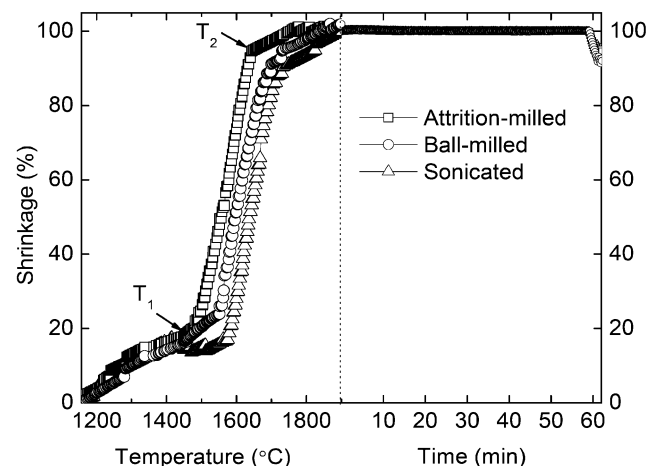


Fig. 1. Densification curves of α -SiAlON prepared from powders milled by different methods (sample # 5, 10, 15, see Table I).

(3) Phase Compositions in Hot-Pressed Ceramics

Although oxidation of nitride powders in the case of β - $\text{Si}_3\text{N}_4/\text{SiAlON}$ typically only affects the ratio of β - $\text{Si}_3\text{N}_4/\text{glass}$ and the composition of the glass, in the case of α - SiAlON it may push the overall composition outside the single-phase α - SiAlON region resulting in β - SiAlON , AlN polytypes, and other unintended phases as shown in Table I. This is because of the fact that, unlike β - $\text{Si}_3\text{N}_4/\text{SiAlON}$, α - SiAlON must contain a certain fraction of Al-N bonds in its structure to be stable, and, therefore, is sensitive to AlN hydrolysis, while β - $\text{Si}_3\text{N}_4/\text{SiAlON}$ is not. Oxidation during AM in water for only 4 h (sample #1) completely destabilized α - SiAlON in favor of β - SiAlON . Unintended water may also be introduced by atmospheric moisture when mixing is conducted in air, as both isopropanol and pyridine are fully miscible with water. Oxygen from air readily participates in the reaction as well. As a result, AM in air for 24 h in either alcohol (sample #2) or pyridine (#3) also significantly destabilized α - SiAlON and caused the formation of β - SiAlON as the major phase. A nitrogen atmosphere limited oxidation during AM, restoring a large α - SiAlON content (sample #4–6). Yet, mechanochemical reaction with alcohol still led to considerable β - SiAlON (XRD peak-height ratio of α : β \approx 1:1 in sample #4), which was greatly reduced (#6), even eliminated (#5), when AM was conducted in pyridine in a nitrogen atmosphere (#5–6).

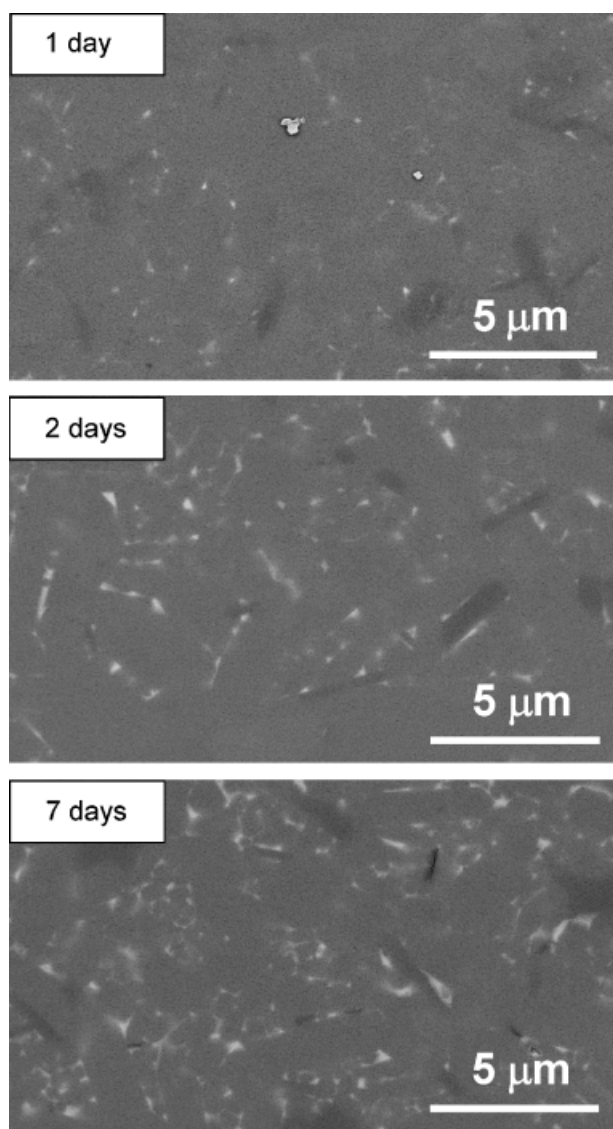


Fig. 2. Scanning electron microscope (backscattered electron) micrographs of α - SiAlON fabricated from powders ball-milled for 1, 2, and 7 days in pyridine/nitrogen showing increasing amount of residual glass as white regions (samples #10, 11, 13).

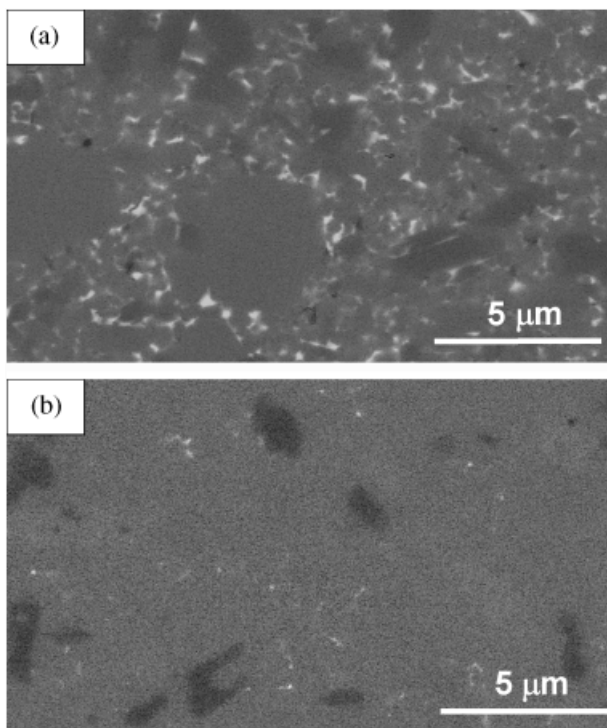


Fig. 3. Scanning electron micrographs of α - SiAlON fabricated from powders (a) attrition-milled for 1 day in pyridine/nitrogen, showing more residual glass (sample #6), and (b) sonicated for 1 h in alcohol/air, showing less residual glass (sample #14). Dark areas in (b) are 27R AlN polytype.

Less energetic BM apparently caused less oxidation as no β - SiAlON remained in the final ceramics (sample #7–13), although transient β - SiAlON might have formed during hot pressing at intermediate temperatures but later disappeared.^{12,23,25,26} This is because α - SiAlON is less stable at lower temperatures, so the oxygen-rich composition that is a single-phase α - SiAlON at higher temperature may actually lie in a two-phase region at lower temperatures.¹⁹ In comparison, sonicated powders had least oxidation as the hot-pressed ceramics showed the least amount of second phase. Comparing sonication with other milling methods, we note that as oxidation increased the AlN-polytype composition changed from 27R (8AlN:SiO₂), observed in sonicated materials, to 21R (6AlN:SiO₂) to even 15R (4AlN:SiO₂), found in ball-milled and attrition-milled ones.

(4) Amount of Residual Glass

Visualization of the oxygen content in differently mixed powders was afforded by backscattered electron SEM images of hot-pressed ceramics. The amount of oxygen-rich glass, which appears as white regions in Fig. 2 because of their high Y concentration, increased in the order of sample #10, #11, and #13 corresponding to increasing BM time (1–7 days in nitrogen/pyridine). More glass was evident if powders were attrition milled for 1 day in the same environment (sample #6, Fig. 3(a)), while less glass resulted if ultrasonically milled, even in air and alcohol (#14, Fig. 3(b)).

IV. Conclusions

1. Compared with β - $\text{Si}_3\text{N}_4/\text{SiAlON}$, α - SiAlON processing is much more oxidation sensitive. Direct evidence of mixing-induced powder oxidation can be found in the densification kinetics and phase assemblage as well as the amount of residual glass in the final ceramics.
2. Powder oxidation is more severe when more energetic milling is practiced. This results in lower densification temper-

atures, higher amounts of residual glass, and destabilization of α -SiAlON in favor of β -SiAlON and other O-rich phases.

3. Powder oxidation can be minimized by using a water-free non-oxidizing environment and by reducing the mixing energy and time. Nitrogen and pyridine (which exhibits good dispersibility for nitride powders) are recommended for this purpose.

4. Practical mixing methods that affect densification with minimal oxidation are AM in nitrogen/pyridine for 2 h, BM in nitrogen/pyridine for 1 day, or US for several hours in pyridine or alcohol, in nitrogen or air.

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