

Effects of Sintering Additives on the Microstructure Development in Silicon Oxynitride Ceramics

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Using a small amount of additives and amorphous $\text{Si}_2\text{N}_2\text{O}$ powders, O'-SiAlON ceramics have been hot-pressed and its microstructure and mechanical properties were investigated. Scandium oxide was demonstrated to be an effective densification additive for O'-SiAlON. Amorphous $\text{Si}_2\text{N}_2\text{O}$ was densified at relatively low temperatures and a microstructure with acicular grains was developed. Fine grains found in materials obtained from amorphous powders suggest that nucleation and crystallization of O'-SiAlON is relatively easy compared with the $\text{Si}_3\text{N}_4\text{-SiO}_2$ reaction.

Key words: O'-SiAlON, Amorphous, Microstructure, Scandium oxide

I. Introduction

The phase $\text{Si}_2\text{N}_2\text{O}$, denoted as the O'-SiAlON phase of silicon nitride ceramics, forms from an equi-molar mixture of SiO_2 and Si_3N_4 . Like several other phases in the silicon nitride family, $\text{Si}_2\text{N}_2\text{O}$ can also be extended into a solid solution by incorporating Al and O in the network structure, $\text{Si}_{2-x}\text{Al}_x\text{N}_{2-x}\text{O}_{1+x}$, namely O'-SiAlON.¹⁾ The stoichiometric compound is believed to be stable until it melts at 2200°C.²⁾ It is also more oxidation resistant than all the other nitrogen-rich compounds in the silicon nitride family.³⁻⁵⁾ In addition, the presence of a large amount of SiO_2 could offer an advantage in processing, since a liquid phase may readily form to aid sintering. For these reasons, O'-SiAlON has been investigated by various researchers in the past. Most of the published work, however, involved the use of a large amount of sintering additives, especially rare earth oxides and silica.⁶⁻⁸⁾

Instead, the present work is focused on O'-SiAlON with a small amount of additives. In particular, the use of Sc_2O_3 , a lightweight substitute of rare earth oxides, was investigated and compared with other additives. Such work is facilitated by the use of amorphous $\text{Si}_2\text{N}_2\text{O}$ powders. The processing, microstructure, and properties of dense crystalline $\text{Si}_2\text{N}_2\text{O}$ with Sc_2O_3 additive are reported with the results of other efforts in the $\text{Si}_2\text{N}_2\text{O}$ family.

II. Experimental Procedures

Starting powders of $\text{Si}_2\text{N}_2\text{O}$ (Amorphous, Ube Ind., Japan), Y_2O_3 , Sc_2O_3 , MgO , SiO_2 (Crystalline, 99.9%, Aldrich Chem. Co., WI), Al_2O_3 (TM-DAR, 99.99% Taimei Chem. Co.,

Japan), and Si_3N_4 (crystalline, SN-E10, Ube Ind., Japan) were used to achieve the desired composition. Powder mixtures, in batches of 20 g, were attrition milled in isopropyl alcohol for 1 h with high purity Si_3N_4 milling media in a TeflonTM-coated jar. The powder slurry was subsequently dried at 80°C under a lamp while being stirred. The dried mixture was then sieved for later use. Hot pressing was conducted at various temperatures for 1 h using a graphite furnace in a nitrogen atmosphere, with a typical heating rate of 10°C/min and a uniaxial pressure of 30 MPa. Approximately 10 g of the powder mixtures was used in each run. During hot pressing, the shrinkage of the powder compacts was continuously monitored by an LVDT (Linear Variable-Differential Transformer) with an accuracy of 0.1 mm. The extension of the load train, due to thermal expansion, was obtained separately and subtracted from the obtained travel data.

Phase analysis of the sintered specimens was performed by X-ray diffraction (XRD) using pulverized powders to avoid the texture effect caused by hot pressing. Silicon powders were used as the internal standard. Microstructure was observed, using scanning electron microscopy (SEM) on polished sections after etching in molten NaOH at 500°C for about 10 s. Fracture toughness and hardness were determined by indentation techniques using 10 kg Vickers indentation at room temperature.

III. Results and Discussion

In forming and densifying O'-SiAlON, amorphous $\text{Si}_2\text{N}_2\text{O}$ powders generally showed much more shrinkage in hot pressing than their counterparts of equimolar mixtures of

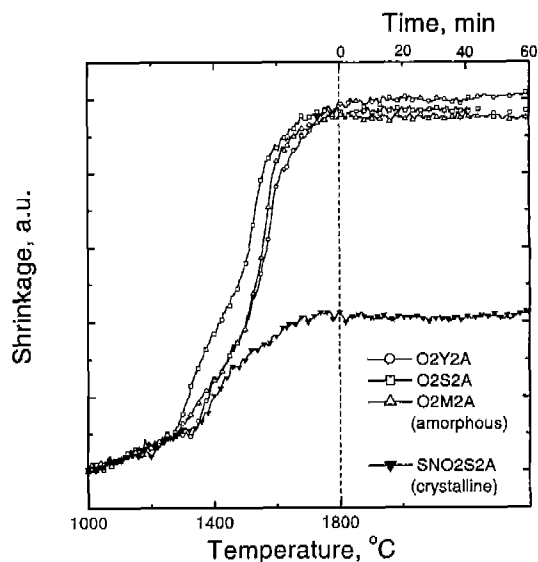


Fig. 1. Shrinkage curves of various $\text{Si}_2\text{N}_2\text{O}$ specimens hot-pressed at 1800°C for 1 h. O₂Y₂A denotes 2 wt% Y_2O_3 and 2 wt% Al_2O_3 added $\text{Si}_2\text{N}_2\text{O}$ and S, M and SNO denote Sc_2O_3 , MgO and $\text{Si}_3\text{N}_4+\text{SiO}_2$ respectively.

crystalline SiO_2 and Si_3N_4 powders. Fig. 1 shows three shrinkage curves of various specimens using amorphous starting powders to contrast with that of equi-molar crystalline powder mixtures. Roughly twice as much shrinkage was observed in the former case regardless of additive type. The hot-pressed specimens have been examined on polished sections and verified that they had all achieved full density. Thus, the much larger shrinkage of the specimen starting from amorphous powders was confirmed. Obviously, part of the larger shrinkage can be attributed to crystallization. In addition, since the amorphous powders have a very fine particle size, the packing density in the compact is lower than that of crystalline powder. This also contributes to the observed larger shrinkage.

The efficiency of a small amount of additives in densification was confirmed for both amorphous starting powders and crystalline powders. As shown in Fig. 1, the shapes of the densification curves are similar for all the curves, even though they have different onset temperatures of fast densi-

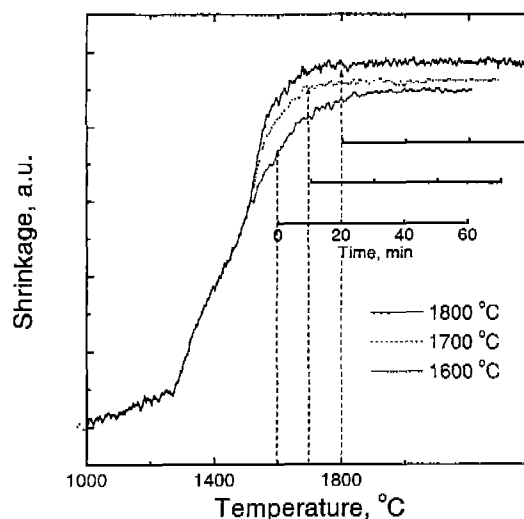


Fig. 2. Shrinkage curves of 2 wt% Sc_2O_3 and 2 wt% Al_2O_3 added $\text{Si}_2\text{N}_2\text{O}$ specimens hot-pressed at various temperature for 1 h. Arrows indicate the start point 1h holding at each temperature.

fication. Not surprisingly, shrinkage curve of the specimen starting from equimolar SiO_2 and Si_3N_4 powders with 2 wt% Sc_2O_3 and 2 wt% Al_2O_3 additives shows the highest onset temperature for initial densification. For amorphous powders, three sets of additives, 2 wt% Sc_2O_3+2 wt% Al_2O_3 , 2 wt% MgO+2 wt% Al_2O_3 , and 2 wt% Y_2O_3+2 wt% Al_2O_3 , have been investigated. The first additive composition gave the best results for promoting densification.

To determine the temperature effect on densification, we used the 2 wt% Sc_2O_3+2 wt% Al_2O_3 composition as additive and hot pressed with amorphous starting powder from 1600 to 1800°C . Fully dense specimens were again obtained in all three cases after holding for 1 h and their shrinkage curves are shown in Fig. 2. These experiments also verified that the onset temperature for densification of the 2 wt% Sc_2O_3+2 wt% Al_2O_3 added specimen is near 1280°C , which is 50 degree lower than other additive used specimens. The minimum temperature required for full densification in hot pressing is probably around 1500°C , judging from the shape of the shrinkage curves in Fig. 2. These experiments showed that Sc_2O_3 could substitute for Y_2O_3 as an effective densifi-

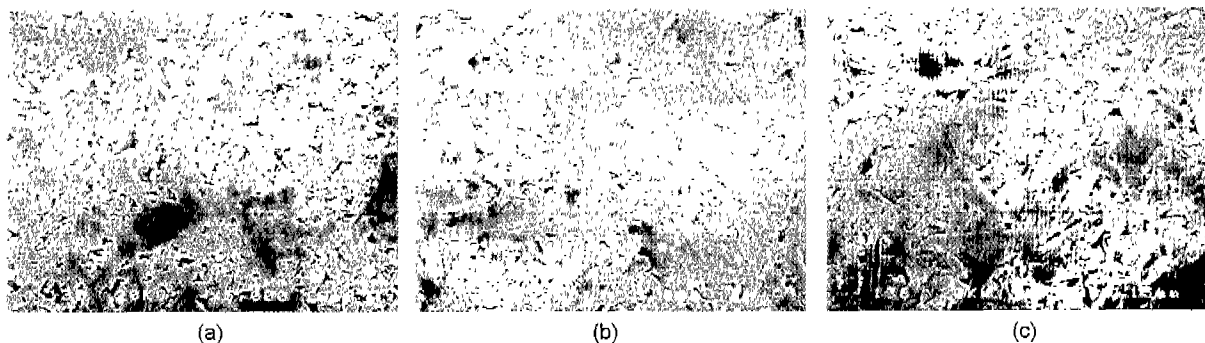


Fig. 3. SEM micrographs of (a) 2 wt% Y_2O_3 and 2 wt% Al_2O_3 , (b) 2 wt% MgO and 2 wt% Al_2O_3 and (c) 2 wt% Sc_2O_3 and 2 wt% Al_2O_3 , added amorphous $\text{Si}_2\text{N}_2\text{O}$ specimens hot-pressed at 1800°C for 1 h, 30 MPa.



Fig. 4. SEM micrograph of 2 wt% Sc_2O_3 and 2 wt% Al_2O_3 added amorphous $\text{Si}_2\text{N}_2\text{O}$ specimen hot-pressed at 1600°C for 1 h, 30 MPa.

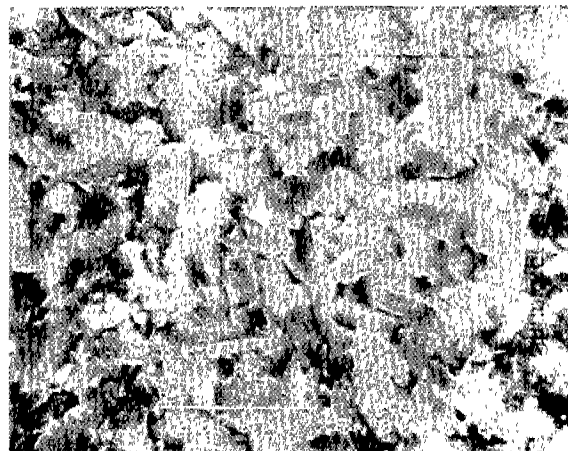


Fig. 5. SEM micrograph of 2 wt% Sc_2O_3 and 2 wt% Al_2O_3 added $\text{Si}_3\text{N}_4+\text{SiO}_2$ specimen hot-pressed at 1800°C for 1 h, 30 MPa.

cation aids. In addition, on an equal-weight basis, this substitution allows a higher molar fraction of Sc_2O_3 to be introduced because it is lighter than Y_2O_3 . This is probably the main reason why 2 wt% Sc_2O_3+2 wt% Al_2O_3 is the best additive composition in Fig. 1.

In case of pressureless sintering of O'-SiAlON by using SiO_2 and Si_3N_4 as starting powders, it has been reported that the reaction to form $\text{Si}_2\text{N}_2\text{O}$ starts at about 1750°C , but the product later starts to decompose at above 1800°C .⁸⁻¹⁰ Thus, the processing window for sintering $\text{Si}_2\text{N}_2\text{O}$ is quite narrow. As a result, a large amount of liquid forming additives, such as Y_2O_3 and Al_2O_3 , are required. Our results demonstrated that such a large amount of liquid need not to be the case. In particular, the amorphous powders with a small amount of Sc_2O_3 and Al_2O_3 can be readily densified by hot pressing at relatively low temperatures. With amorphous starting powders, the densified O'-SiAlON shows a microstructure with acicular grains, as shown in Fig. 3, when the specimens were hot-pressed at 1800°C for 1 h. When the specimen was hot-pressed at 1600°C , a microstructure of fine equiaxed grains was obtained, as shown in Fig. 4.

In contrast, the specimen prepared with equi-molar Si_3N_4 and SiO_2 powders showed a coarse microstructure after hot pressing at 1800°C ; moreover, some acicular grains are mixed with equiaxed grains, as shown in Fig. 5. The above results demonstrate that the development of acicular grains is much favored by the use of amorphous powders, even though the grain size in such materials remains small. The

large grain size in the samples with Si_3N_4 and SiO_2 starting powders suggests that the grain size, in this case, is controlled by the nucleation of O'-SiAlON crystals during the $\text{Si}_3\text{N}_4\text{-SiO}_2$ reaction. If nucleation is difficult, as expected from the high reaction temperature quoted above, then relatively few grains form and they can grow to a large grain. In comparison, in case of the specimen prepared with amorphous $\text{Si}_2\text{N}_2\text{O}$ powder, the nucleation of O'-SiAlON is expected to be relatively easy so that the grain size at 1600°C is very fine. Such a fine-grained microstructure, furthermore, is known to favor the onset of abnormal grain growth result in anisotropic growth of acicular grains.¹¹⁻¹⁵

Microstructures with elongated grain have a potential to enhance fracture toughness.¹² However, as shown in Table 1, fracture toughness and hardness of the specimens prepared from the amorphous powders are relatively similar, regardless of their microstructure. In fact, we have tried various post-hot-pressing heat treatments such as 1350°C for 20 h, 1500°C for 24 h, and 1700°C for 4 h. We did not observe a significant change in mechanical properties. It should be noted that the hardness of these materials is relatively high compared to silicates. Thus, the low toughness values may not an indication of intrinsically weak bonds of the $\text{Si}_2\text{N}_2\text{O}$ ceramics. It may rather be due to the inability to trigger interface debonding. This suggests that the debonding strength of the grain boundaries of these ceramics is quite high. High fracture toughness, however, has been reported for O'-SiAlON with acicular grains.³ Compared to the compositions of the materials studied here, high tough-

Table 1. Mechanical Properties of Various O'-SiAlON

Raw Materials	Additives	Heat Treatment	Hardness (GPa)	K_{1C} ($\text{MPa}\cdot\text{m}^{1/2}$)
Amorphous $\text{Si}_2\text{N}_2\text{O}$	$\text{Y}_2\text{O}_3, \text{Al}_2\text{O}_3$	$1800^\circ\text{C}, 1$ h	14.5 ± 0.3	1.6 ± 0.2
	$\text{MgO}, \text{Al}_2\text{O}_3$	"	14.0 ± 0.3	1.7 ± 0.3
	$\text{Sc}_2\text{O}_3, \text{Al}_2\text{O}_3$	$1600^\circ\text{C}, 1$ h	15.0 ± 0.3	1.6 ± 0.1
	"	$1700^\circ\text{C}, 1$ h	14.6 ± 0.5	1.6 ± 0.1
	"	$1800^\circ\text{C}, 1$ h	14.2 ± 0.3	1.7 ± 0.2
$\text{Si}_3\text{N}_4, \text{SiO}_2$	$\text{Sc}_2\text{O}_3, \text{Al}_2\text{O}_3$	$1800^\circ\text{C}, 1$ h	17.7 ± 0.1	2.0 ± 0.1

ness O'-SiAlON used a much large amount of additives; therefore it might have been easier to realize a weak interface by crystallization or impurity segregation. Higher hardness and fracture toughness have been found in our specimen prepared with Si_3N_4 and SiO_2 powders, as shown in Table 1. We believe these higher values are due to the unreacted $\beta\text{-Si}_3\text{N}_4$. During sintering, a large fraction of $\alpha\text{-Si}_3\text{N}_4$ in the starting powders probably transforms to $\beta\text{-Si}_3\text{N}_4$, at relatively low temperatures, say 1550°C . Because of slow kinetic reaction between $\beta\text{-Si}_3\text{N}_4$ and SiO_2 , unreacted product, such as large amount of silicate phase with $\beta\text{-Si}_3\text{N}_4$, would be remained at the grain boundaries even after the high temperature sintering. This is supported by XRD in which $\beta\text{-Si}_3\text{N}_4$ was detected. The crystallization of the silicate phase could also facilitate interface debonding and hence contribute to higher toughness.

The XRD pattern obtained from specimens prepared with amorphous $\text{Si}_2\text{N}_2\text{O}$ powders show that the second phase of $\beta\text{-Si}_3\text{N}_4$ was formed after the hot-pressing at 1800°C for 1 h, regardless of the sintering additives used. Such an observation is common for processing $\text{Si}_2\text{N}_2\text{O}$ when Si_3N_4 and SiO_2 are used as raw materials, and is usually taken as the evidence of un-reacted $\beta\text{-Si}_3\text{N}_4$.¹⁶⁾ In the case of amorphous $\text{Si}_2\text{N}_2\text{O}$ powders, however, the $\beta\text{-Si}_3\text{N}_4$ observed could not come from the starting powders. Instead, we found that it resulted most likely from the decomposition of $\text{Si}_2\text{N}_2\text{O}$ because of off-stoichiometry. In the specimens hot pressed at 1600°C and 1700°C , sharp reflections of O'-SiAlON were found in XRD without any trace of those of $\beta\text{-Si}_3\text{N}_4$. (Fig. 6) Thus, a $\beta\text{-Si}_3\text{N}_4$ forms only at higher temperatures and thus

to be the result of decomposition.

In order to suppress the decomposition, we added excess 2 wt% SiO_2 to the starting powders and repeated the hot pressing experiment at 1800°C . The XRD of the specimen showed only O'-SiAlON and no $\beta\text{-Si}_3\text{N}_4$. Thus, it seems that the decomposition is a result of off-stoichiometry, due to the loss of SiO_2 from the remaining amorphous phase or even the crystalline $\text{Si}_2\text{N}_2\text{O}$ itself. Because a crystallization of amorphous $\text{Si}_2\text{N}_2\text{O}$ cannot be completed during sintering, the decomposed product may originate from either the crystalline $\text{Si}_2\text{N}_2\text{O}$ or the remaining amorphous $\text{Si}_2\text{N}_2\text{O}$. A more detailed investigation and judicious modification of these phases may be required to improve the fracture properties of $\text{Si}_2\text{N}_2\text{O}$ with small amounts of additives.

IV. Conclusions

Scandium oxide was demonstrated to be an effective densification additive for O'-SiAlON. Amorphous $\text{Si}_2\text{N}_2\text{O}$ would be densified at relatively low temperatures and a microstructure with acicular grains was developed. The relatively fine grains found in materials obtained from amorphous powders suggest that nucleation and crystallization of O is relatively easy compared with the $\text{Si}_3\text{N}_4\text{-SiO}_2$ reaction. As a remedy, excess SiO_2 may be added to maintain stoichiometry. Even with the well-developed acicular grains in microstructure, no enhancement in fracture toughness was observed. A weaker grain boundary was suggested to be necessary to realize in-situ toughening.

Acknowledgement

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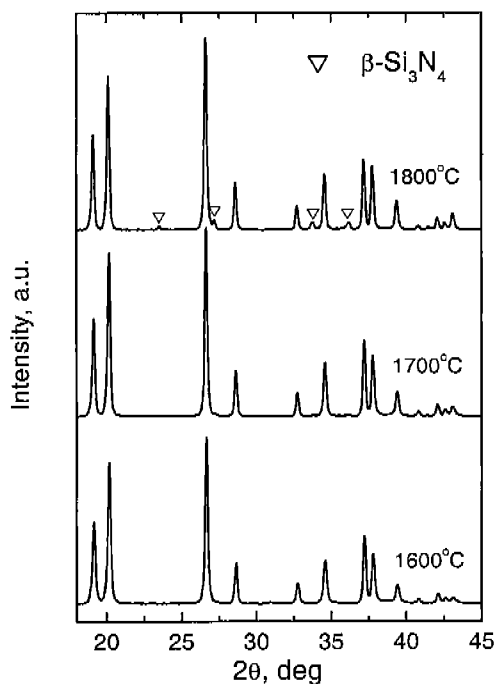


Fig. 6. X-ray diffraction patterns of 2 wt% Sc_2O_3 and 2 wt% Al_2O_3 added $\text{Si}_2\text{N}_2\text{O}$ specimens hot-pressed at various temperature for 1 h, 30 MPa.

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