SYNTHESIS OF SiC-AlN CERAMIC ALLOY BY THE COMBINATION OF REACTION SINTERING AND HIP

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ABSTRACT
Ceramic alloys were synthesized by the combination of reaction sintering and hot isostatic pressing (HIP) in this work. The starting powders were commercial silicon nitride and aluminium nitride and graphite powders. A small amount of calcia was added in the form of $Ca(NO_3)_2 \cdot 4H_2O$, and the reaction sintering was performed in a nitrogen atmosphere in a temperature range of 1670 to 2170K. The reaction process was well investigated and found to be as following: at first, α-sialon forms from 1770K to 1870K, then at above 1973K, graphite reduce α-sialon to produce SiC-AlN solid solution. When AlN content was less than 35mol%, a fine-grained uniform 2HSiC-AlN solid solution was synthesized, and its grain size was three times finer than that of the starting powders. On the other hand, when an excess amount of AlN was added, two-phase composite was formed. After HIP-sintered at 2070 to 2120K under a pressure of 200MPa, porous SiC-AlN ceramic alloy specimens were fully densified.

INTRODUCTION

It is well known that silicon carbide is a strong candidate for high temperature structure ceramics due to its excellent high temperature strength, but its fracture toughness is too low. Alloying has been proved to be an effective method to improve the mechanical property of metal materials, so it is also necessary to attempt alloying SiC ceramics.

A solid solution forms in 2H-SiC and AlN system in a wide range of composition because both have the same structure and their lattice parameters are very close.[1] So SiC can be alloyed with AlN, and a little of work about the synthesis of SiC-AlN solid solutions has been done, for example, Ruh et al. hot pressed SiC and AlN powder mixtures at 2173 to 2473K and obtained solid solutions of the hexagonal 2H structure, but their bending strength values were much low, due to inhomogeneous mixing.[2] SiC-AlN alloys were also prepared by the carbothermal reduction of silica and alumina or their mixture.[3,4]

Recently, it was reported that SiC-AlN solid solutions can be formed by the reaction of Si_3N_4, AlN, CaO and Carbon, but the reaction process is not clear and only porous specimen was obtained.[5] In the present work, it is the objective to synthesize uniform SiC-AlN alloys by this method and clarify the reaction process. And in order to obtain dense specimens, densification condition of HIP-sintering was also investigated.

EXPERIMENTAL

Commercial Si_3N_4#, AlN$, graphite powders* were mixed in ethylalcohol according to the composition ratio given in Table 1, 4mol% CaO was added in the form of $Ca(NO_3)_2 \cdot 4H_2O$+ which is dissolvable in ethylalcohol. After ball milled and dried, the mixtures were heated at 1073K for 15 minutes in the flow of high-purity H_2 gas to decompose $Ca(NO_3)_2 \cdot 4H_2O$ to CaO, then compacted to a columnar green body of 10mm in diameter, using a metal die (100MPa) and a cold isostatic pressing machine (200MPa). The sintering was performed in a nitrogen atmosphere at 1673K to 2173K.

The synthesized specimens with high porosity were coated with BN powders to prevent the reaction between specimen and glass capsule, and encapsulated in a vacuum ($<10^{-4}$ Torr.) into a vycor glass tube, then HIP-sintered at 2070 to 2120K under a pressure of 200MPa, using the equipment made by Nippon Steel Corporation (Model HIP2000S).

In order to investigate the reaction process, X-ray diffraction analysis was done on the reaction products sintered at various

#α-Type Si_3N_4,99.0% pure, major impurity: free C(1.0w/o),by Toshiba Co.
$TOYALNITE, 99.0% pure, major impurity: oxygen (1.0w/o),by Toyo Aluminium Co.,Ltd.
*Graphite, flake shape, special grade, by Junsei Chemical Co.,Ltd.,
+Calcium Nitrate Tetrahydrate, 99.9%, by Wako Pure Chemical Industries Co.,Ltd.

temperature using the commercial X-ray diffractometer made by Rigaku Denki Co.,Ltd., which is equipped with a personal computer for data processing. In all case, Ni-filtered CuKα radiation was used. The microstructure was observed using the scanning electronic microscope (SEM) made by Hitachi Corporation (Model S-530).

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the specimens sintered at different temperature are shown in Fig.1. After the sample was sintered at 1873K for 90 minutes, a new compound which can be indexed on the basis of α-sialon (according to ASTM card No.33-260) was formed, and added graphite existed as unreacted. But after it was sintered at 1973K, almost only the peaks of 2H-SiC were detected out, and a small quantity of β-SiC coexisted. Furthermore, the sample was sintered for various times at the same temperature of 1973K: after sintered for 5 minutes the major phase was α-sialon, but for 15 minutes almost only 2H-SiC solid solution were obtained,

From the X-ray diffraction results, the reaction process is thought to be as shown in the model of Fig.2, at first, the liquid phase appeared on the powders surface due to the existence of oxides, then α-sialon formed with increasing temperature or sintering time, but graphite powders remained in an unreacted state, when the sintering temperature was higher than 1873K, graphite reduced sialon to produce SiC-AlN solid solution. So α-sialon whose molecular formula can be written as $CaSi_{12-x}Al_xO_yN_{16-y}$ was a transient phase. The reaction formulae can be written as following:

$$Si_3N_4+xAlN+CaO \rightarrow CaSi_{12-x}Al_xO_yN_{16-y}$$

$$CaSi_{12-x}Al_xO_yN_{16-y}+C \rightarrow 3SiC{:}xAlN+Ca\uparrow+CO\uparrow+N_2\uparrow$$

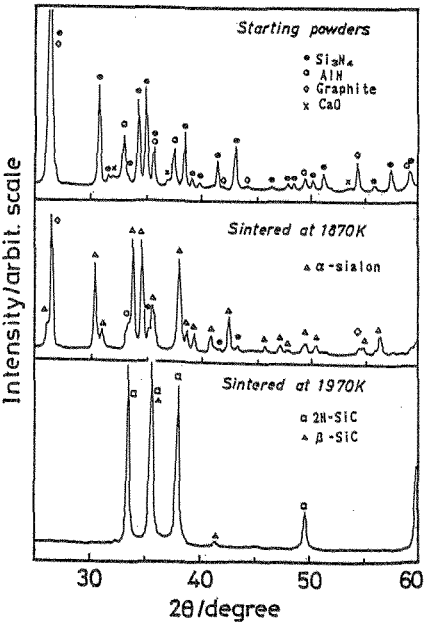

Fig.1 The X-ray diffraction profiles of starting powders and reaction products

Table 1 The composition of starting powders and designed reaction products.

sample	composition/mol%					
	starting powders				reaction products	
	Si_3N_4	AlN	C	CaO	SiC	AlN
SNAN01	18	6	72	4	90	10
SNAN02	16	16	64	4	75	25
SNAN03	14.5	23.4	58.1	4	65	35
SNAN04	12	36	48	4	50	50
SNAN05	8	56	32	4	30	70

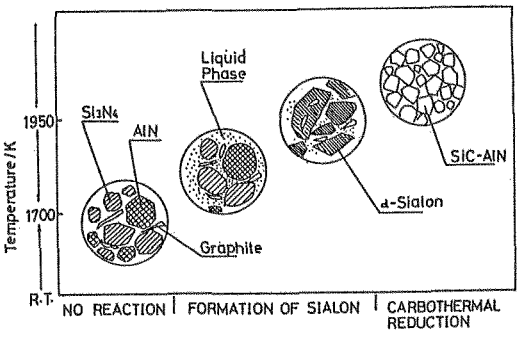

Fig.2 The schematic drawing of reaction process.

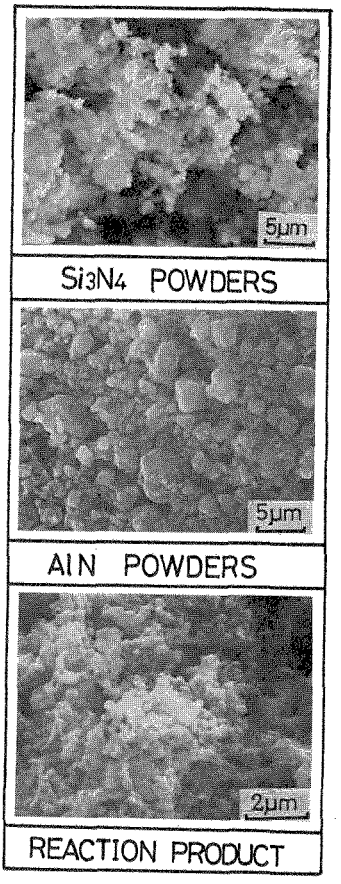

Fig.3 The SEM photographs of the starting powders and the reaction products of sample SNAN02.

But at a few place where no liquid phase existed, Si_3N_4 reacted directly with graphite powders, so that a small quantity of β-SiC was formed, as shown in Fig.1.

The SEM photographs of the starting powders and one sintered specimen are shown in Fig.3. It should be noticed that the grain size of SiC-AlN solid solution is three times smaller than that of the starting powders. It is very meaningful that ultrafine SiC-AlN alloy can be synthesized by reaction sintering.

Because 2H-SiC and AlN have the same crystalline structure and their lattice parameters are close, their X-ray diffraction peaks are too near to decide whether SiC-AlN solid solution was exactly formed or not by the ordinary operation of X-ray diffraction, so more careful diffraction was done on the (002) plane. As shown in Fig.4, only one peak was detected out when less than 35mol% AlN was added, this indicates that the single phase was formed below 35mol% AlN content, but the two phase of SiC-AlN solid solution and AlN (or AlN-SiC solid solution) coexisted when 50mol% or 70mol% AlN was added. This result coincides with the phase diagram presented in reference(5).

As described above, SiC-AlN solid solution or composite was able to be synthesized by the reaction sintering method, but because a large amount of gas formed due to the reaction mentioned above, no densification occurred during the reaction sintering. To measure the mechanical property of this new material, dense specimens are required, so the specimens were HIP-sintered.

Fig.5 shows the change of bulk density, because weight loss occurred during the reaction, the density of reaction product was small than green density, but after HIP-sintered for two hours at 2070K, the specimens containing more than 25mol% AlN were fully densified, on the

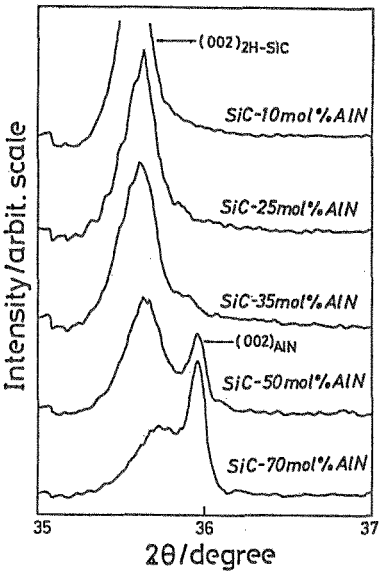

Fig.4 The X-ray diffraction results on (002) plane.

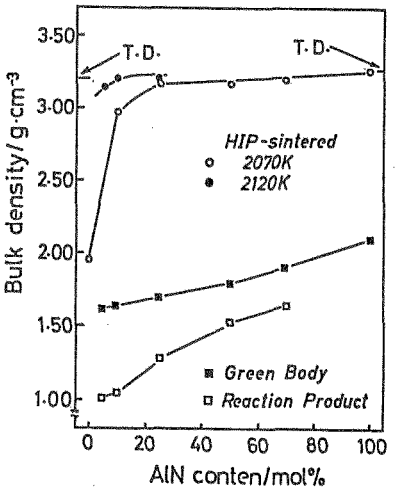

Fig.5 The change of bulk density.

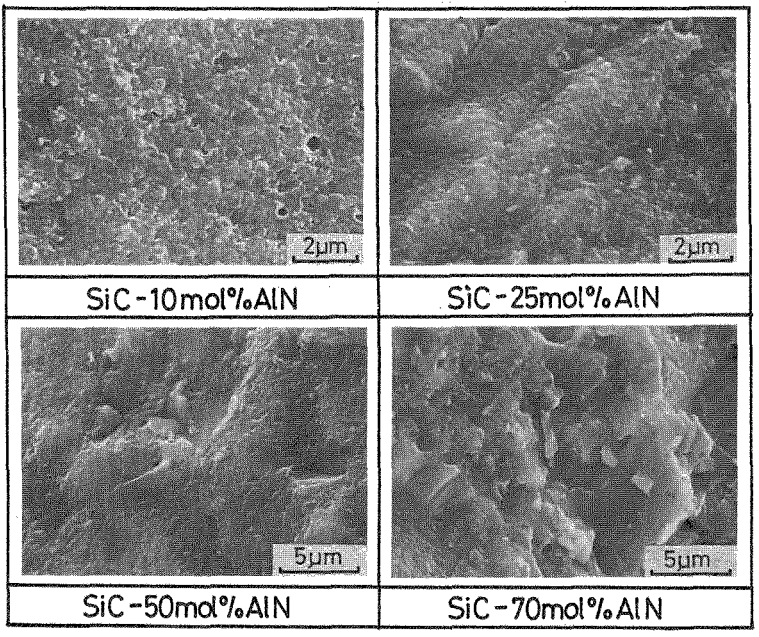

Fig.6 The fractography of SiC-AlN alloys.

contrary, relative density of pour SiC powders was about 60%. It can be concluded that addition of AlN effectively accelerates the densification of SiC.

The SEM photographs of the fractured surfaces were shown in Fig.6. the ultrafine grains are SiC-AlN solid solution, and the larger grains are AlN (or AlN-SiC solid solution). there is only one single phase in the specimens containing 10mol% and 25mol% AlN,but two phases exist in those containing 50mol% and 70mol% AlN.

CONCLUSION

SiC-AlN ceramic alloys were synthesized by the reaction sintering at rather low temperature. When AlN content was less than 35mol%, a fine-grained uniform solid solution was formed. On the other hand, when an excess amount of AlN was added, two-phase composite was obtained. The reaction process includes two steps: the formation of α-sialon and the carbothermal reduction. It can be described by the following reaction formulae.

$$Si_3N_4+AlN+CaO \rightarrow CaSi_{12-x}Al_xO_yN_{16-y}$$

$$CaSi_{12-x}Al_xO_yN_{16-y}+C \rightarrow 3SiC\text{-}xAlN+Ca\uparrow+CO\uparrow+N_2\uparrow$$

The synthesized SiC-AlN alloy specimen with high porosity was fully densified after HIP-sintered at 2070 to 2120K under a pressure of 200MPa.

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