

PREPARATION OF SiC-AlN COMPOSITE POWDERS BY INORGANIC SOL-GEL PROCESSING^①

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ABSTRACT SiC-AlN composite powders were prepared with silica sol, alumina sol and carbon black by sol-gel processing. The particle size of the powders usually ranged in 50~100 nm and showed a slight increase with the increase of AlN content. In the carbothermal carbide/nitride process of Si-Al-O-C-N system, an intermediate product $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ (sialon) appeared at 1300 °C and gradually decomposed into SiC and AlN at higher temperatures. However, Si_3N_4 was not observed during the synthesizing process. SiC was obviously dissolved into AlN and resulted in the formation of SiC-AlN solid solution over 1500 °C.

Key words silicon carbide aluminium nitride sol-gel

1 INTRODUCTION

SiC particles strengthened AlN or Si_3N_4 composite reveals high-strength, -toughness and -hardness, good wear and oxidation resistance, especially that the strength and toughness of the composite are improved obviously^[1-5]. The study of advanced ceramics has being directed to develop nanometer powder and composite. In order to dig potential properties of composite, one of the most effective methods is to prepare composite powders. Cutle *et al*^[6] prepared SiC-AlN composite powders by carbothermal carbide/nitride process using SiO_2 and Al_2O_3 . Mitomo *et al*^[7] also synthesized SiC-AlN powders by sol-gel processing using organometallic precursors. The powder could be sintered at lower temperature and the sintering material reveals better properties. Xiao and colleagues^[8-11] investigated the preparation of SiC and the composite powders by carbothermal carbide/nitride reactions with an inorganic sol-gel processing. In this paper, SiC-AlN composite powders were prepared by sol-gel processing. The characteristics of carbothermal process and synthesizing conditions are discussed.

2 EXPERIMENTAL

Silica sol, carbon black and alumina sol were used as original materials in this work. The silica sol and alumina sol were mixed with carbon black by ball milling for 2 h. The carbon was added into the mixture with molar ratio of C/Si = 3.1 and C/Al = 1.6. Some agents for dispersing and gelling were also added in the process. The well mixed precursor was gelled at 80 °C in air, then dried up to 150 °C. The precursor was placed in a graphite pot and annealed at 1300~1600 °C for carbothermal carbide/nitride reactions in a flowing nitrogen atmosphere. Synthesized powders were heated at 600 °C in air for removing residual carbon.

The powders were analyzed using X-ray diffraction (XRD) for phases composition, transmission electron microscopy (TEM) for primary crystal size and shape, Stokes particle analyzer (SKC-2000) for agglomerate size.

3 RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of Si-Al-O-C gel (with a molar ratio of Si:Al = 1:1) annealed

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at different temperatures in nitrogen atmosphere for 60 min. It is found that the gel at 300 °C is an amorphous precursor, γ - Al_2O_3 and θ - Al_2O_3 appears at 900 °C, a complex phase composition composed of α - Al_2O_3 , $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ (sialon), AlN and SiC comes out at 1300 °C. With the increase of temperature, the contents of α - Al_2O_3 and $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ gradually decrease accompanying the increase of AlN and SiC. At 1600 °C, only AlN and SiC are observed and the peaks of AlN become stronger than those of SiC. It is considered that SiC dissolving into AlN resulted in the formation of SiC-AlN solid solution^[7].

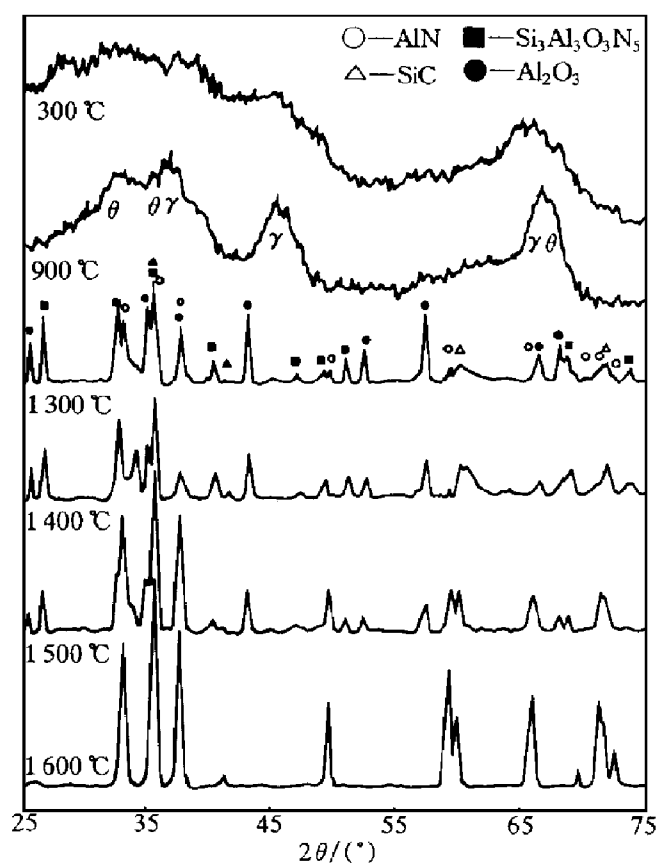


Fig. 1 XRD patterns of powders synthesized at various temperatures (CuK α)

According to our previous work^[11], SiO_2 is possible to produce Si_3N_4 above 1300 °C in nitrogen atmosphere. However, $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ in the product instead of Si_3N_4 was observed. Fig. 2 shows the effect of the partial pressure of p_{N_2} and p_{CO} on the products of Si-O-C-N system. When $p_{\text{N}_2} \leq 0.1$ MPa, Si_3N_4 is stable below

1450 °C in thermal dynamics, and it can exist at 1327 °C only when the p_{CO} is less than 0.01 MPa. Therefore, the reason for Si_3N_4 not appearing may be: (a) Si_3N_4 reacted with Al_2O_3 and AlN to form $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$, (b) Si_3N_4 tended to convert into SiC above 1450 °C when carbon exists, and (c) the partial pressure of product CO was not low enough because the flow of nitrogen was only 1 L/min, which restrained the formation of Si_3N_4 . Anyhow, $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ is just an intermediate material, it can be decomposed into SiC and AlN at temperatures above 1300 °C in the existence of carbon. Following reactions are thought to be existed in the system of Si-Al-O-C-N at temperatures ranged from 1300 °C to 1600 °C:

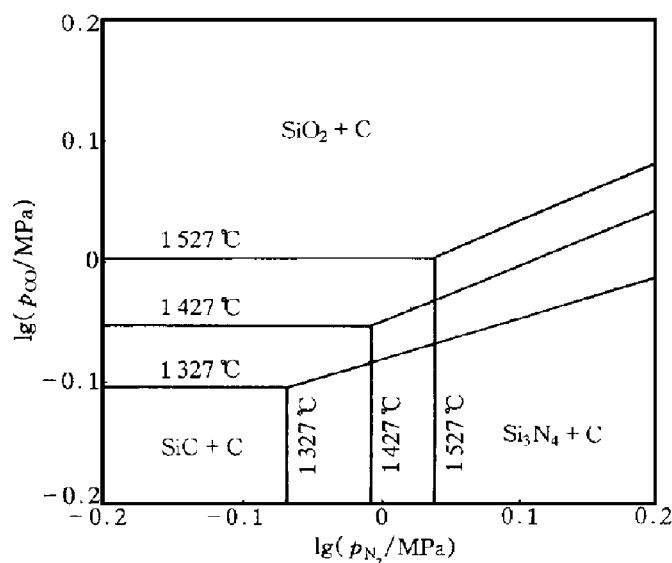
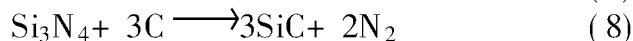
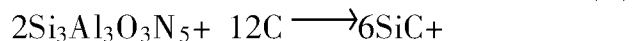
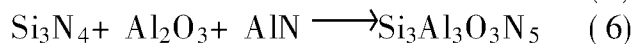
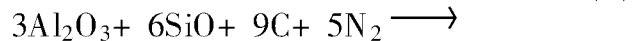
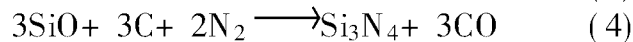
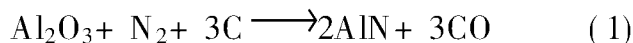


Fig. 2 Effect of p_{N_2} and p_{CO} on products of Si-O-C-N system



Particle sizes of the composite powders

synthesized at different temperatures and Si/Al ratio are listed in Table 1. All powders were prepared at given temperature for 60 min at a nitrogen flow of 1 L/min. The higher the content of silicon, the smaller the particle size. This means that the grain growth of AlN is faster than that of SiC. The grain prepared at 1 300 °C was coarser than that at 1 500 °C, which was blamed for unreacted precursor. With the reactions of carbonation and nitration went on, the grain size became smaller and then increased with the increase of temperature.

Table 1 Effect of composition and temperature on particle size of powder

Run No.	Si: Al (Molar ratio)	Temperature / °C	Primary size/ nm	Agglomerate size/ μm
1	100: 0	1 500	30~ 60	0. 25
2	100: 0	1 600	50~ 80	0. 32
3	75: 25	1 500	30~ 80	0. 24
4	75: 25	1 600	50~ 100	0. 29
5	50: 50	1 300	30~ 200	0. 40
6	50: 50	1 400	30~ 100	0. 37
7	50: 50	1 500	50~ 80	0. 47
8	50: 50	1 600	50~ 100	0. 55
9	25: 75	1 500	50~ 100	0. 52
10	25: 75	1 600	80~ 150	0. 50
11	0: 100	1 500	80~ 100	0. 49
12	0: 100	1 600	100~ 200	0. 52

Fig. 3 is a TEM micrograph of SiC-AlN composite powder prepared at 1 600 °C for 60 min with a molar ratio of Si: Al= 1: 1. The figure illustrates the particle size ranged from 50 to 100 nm and connected each other, and the soft agglomerated structure can be broken by ball milling.

4 CONCLUSIONS

Nanosized SiC-AlN composite powder was prepared at 1 500~ 1 600 °C using silica sol and alumina sol by sol-gel processing. In the carbothermal carbide/nitride process of Si-Al-O-C-N system, an intermediate product $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ appeared at 1 300 °C and gradually decomposed into SiC and AlN at higher temperature, but

Si_3N_4 was not observed during the synthesizing process. SiC-AlN solid solution was obviously formed over 1 500 °C by the solving of SiC into AlN.

Fig. 3 TEM micrograph of SiC-AlN powder reacted at 1 600 °C for 60 min

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