Silicon Carbide Films Prepared by Silicon Nitride Evaporation

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Abstract: Silicon carbide (SiC) films were synthesized on graphite substrates using silicon nitride (Si₃N₄) as silicon source at 1850°C, 1950°C, 2050°C, and 2150°C, respectively. The characteristics of the synthesized films were analyzed by X-ray diffraction and scanning electron microscopy. The results show that the synthesis reaction can take place above 1850°C, and the SiC films were β-SiC. With the increase of temperature, the size of SiC particles increases, and when the soaking time is too short, the SiC particles are connected in a large area. Through the analysis of the films synthesis process, it is inferred that the growth of the SiC films belongs to the gas-solid growth mechanism.

1. Introduction
The graphite materials have good high-temperature mechanical properties and are widely used in metallurgy, aerospace and chemical industry. However, oxidation at high temperature limits its application. SiC ceramics have excellent oxidation resistance, low thermal expansion, chemical compatibility, and corrosion resistance. Therefore, it has advantages in the application of graphite surface coating and improves the high-temperature oxidation resistance of graphite materials [1-3]. SiC film prepared by chemical vapor deposition [4,5] (CVD) have good oxidation resistance, but the deposition time is long, the deposition rate is slow and the deposition area is small. SiC film prepared by dipping method [6-8] has many crack defects on the surface. Oxygen diffuses through the crack to the interior of the composite, resulting in oxidative damage of the composite. Up to now, the research on the conversion of Si₃N₄ [9,10] mainly focuses on the preparation of SiC whiskers, and the research on the SiC films is less. This method has fast deposition rate and large deposition area. The graphite coated with silicon carbide film is suitable for applications with low surface requirements.

In this study, SiC films were prepared by using Si₃N₄ powder as a silicon source and graphite as a carbon source in the argon atmosphere at 1950-2100°C. Thermodynamic analysis of the synthesis process was carried out, and the influence of the synthesis temperature on the SiC film was studied. The growth mechanism of the SiC film synthesized by the conversion method of Si₃N₄ was also discussed.
2. Material and methods
The raw materials used in this work are commercial Si$_3$N$_4$ powder (purity >98.5%; 0.5μm; Shuitian Material Technology Co. Ltd., Shanghai, China), Graphite sagger (purity >99%; Jinglong Special Carbon Technology Co., Ltd., Beijing, China). Weighing 6g Si$_3$N$_4$ powder, these powders were mixed absolutely with ethyl alcohol in an agate mortar. After dried at 90 °C for 2 h, the powder was placed in graphite sagger. Then the graphite sagger was sintered in SiC vacuum sintering furnace in the argon atmosphere at 1850 °C, 1950 °C and 2050 °C, respectively for 1 h. As a control group, one sample was sintered at 1950 °C for 0.5 h. The phase composition of the sintered specimens was determined by X-ray diffractometry (XRD, D/MAX-IIIB, Rigaku, Osaka, Japan) with CuKα radiation. The microstructure and morphology of SiC film were observed by scanning electron microscope (SEM, JEOL JSM-5610LV, Tokyo, Japan).

3. Results and discussion

3.1. Phase and microstructure
The XRD patterns of Si$_3$N$_4$ evaporated into SiC films at different temperatures were illustrated in Figure 1. When the sintering temperature is 1850°C, the phase includes SiC and Si, which indicates that Si$_3$N$_4$ is completely decomposed into nitrogen and silicon vapor. Then, silicon vapor reacts with graphite to form SiC. However, the sintering temperature is too low and Si cannot react with graphite completely, so some Si still exists. When the sintering temperature rises to 1950°C and 2050°C, all the peaks of Si disappeared and the main phase is 3C-SiC. It shows that increasing the sintering temperature is helpful to the decomposition of Si$_3$N$_4$ and the formation of SiC.

Figure 1. XRD patterns of the samples sintered at different temperatures.

Figure 2 presented the SEM micrographs of the film surfaces of the samples sintered at various sintering temperatures. It can be seen that the particle size is large and uneven at 1850°C ([Figure 2(a)], which is about 3-21 μm. There is a large area of bridging between particles with distinct edges and corners. Combined with XRD images, indicates that the phenomenon is caused by the presence of liquid silicon. With the increase of sintering temperature, the surface of particles tends to be smooth and round, and the size of particles tends to be uniform. At 1950°C [Figure 2 (b)], the diameter of the particles is about 2.5-6 um, and the sintering neck between the particles is well developed. At 2050°C [Figure 2 (c)], the particles grow up slightly, and the bridging is more obvious, which may be related
to the recrystallization of SiC. The effect of holding time on the product was studied at the reaction temperature of 1950°C. Figure 2 (d) is an SEM image of SiC film formed at 1950°C for 0.5 h. Compared with the holding temperature for 1 h [Figure 2(b)], SiC particles are bridged in a large area, with high density, sharp edges and large size.

![Figure 2](image)

**Figure 2** SEM micrographs of the film surfaces of the samples sintered at various temperatures. (a) 1850 °C for 1h, (b) 1950 °C for 1h, (c) 2050 °C for 1h, (d) 1950 °C for 0.5h.

### 3.2. The Growth mechanism of SiC film with evaporation temperature

SiC films were synthesized by the evaporation-conversion method of Si₃N₄. The following reactions occurred during the heating process:

\[
\text{Si}_3\text{N}_4 + 3\text{C} \rightarrow 3\text{SiC} + 2\text{N}_2
\]  

(1)

Reaction equation (1) will be decomposed into two steps. The first step is the decomposition of \( \text{Si}_3\text{N}_4 \) into silicon vapor and nitrogen, and the second step is the reaction of silicon with carbon. Concrete reaction equations such as (2) and (3).

\[
\text{SiN}_4 \rightarrow 3\text{Si} + \text{N}_2
\]

(2)

\[
\text{Si} + \text{C} \rightarrow \text{SiC}
\]

(3)

According to the theory of reaction thermodynamics and using the relevant thermodynamic data [11], the formula (2) can spontaneously react when the temperature is higher than 1889°C. Hincke [12] and Batha [13] have studied the decomposition of Si₃N₄. They believe that there is a relationship between decomposition temperature (Td) and nitrogen pressure (Pd) at corresponding temperature conditions as follows:

\[
2.3\log P_d = 19.75 - 44500/T_d
\]

(4)

\[
2.3\log P_d = 20.85 - 44500/T_d
\]

(5)

According to the above formula, as shown in Table 1, it can be seen that the lower the pressure of nitrogen, the lower the temperature at which Si₃N₄ begins to decompose. In this study, Si₃N₄ was decomposed in the argon atmosphere at about 1500 °C. When the gaseous silicon atom meets the high temperature activated carbon atom on the graphite surface, SiC forms on the graphite surface. A
supersaturated solution of SiC is formed to produce a SiC crystal nucleus. At this low temperature, the SiC is mainly the $\beta$ phase.

| Pressure / kPa | Decomposition temperature / $^\circ$C |
|---------------|--------------------------------------|
|               | Formula (4)                          |
| 100           | 1 980                                |
| 10            | 1 745                                |
| 1             | 1 555                                |
| 0.1           | 1 397                                |
| 0.01          | 1 264                                |
|               | Formula (5)                          |
| 100           | 1 861                                |
| 10            | 1 649                                |
| 1             | 1 476                                |
| 0.1           | 1 331                                |
| 0.01          | 1 208                                |

It is speculated that the growth mechanism of SiC film is gas-solid. When the sintering temperature is 1850$^\circ$C, because Si$_3$N$_4$ begins to decompose gradually at 1500$^\circ$C, and some silicon vapor does not react with graphite at 1850$^\circ$C. As a result, the SiC formed is bridged in a large area, and the grain edges and corners are clear, as shown in Figure 2 (a). When the temperature rises to about 2 000$^\circ$C, the recrystallization of SiC occurs. Evaporation occurs at the sharp corners of SiC grains and condensation occurs at concave and flat places, which make SiC grains smoother and rounder, as shown in Figure 2 (b), (c).

When the sintering temperature is 1950$^\circ$C and the holding time is 0.5 h, the gaseous silicon atom meets the high temperature activated carbon atom on the graphite surface, forming the supersaturated solution of SiC. The SiC film particles are larger and the grain boundary between particles is not obvious, because the holding time is too short and the number of precipitated SiC crystal nuclei is less. As shown in Figure 2 (d). With the holding time prolonged to 1 h, silicon and graphite react fully. SiC nuclei are continuously precipitated from the supersaturated solution of SiC, and recrystallization occurs. It makes the SiC particles smooth and round, as shown in Figure 2 (b).

4. Conclusions
(1) Using Si$_3$N$_4$ and graphite as main raw materials, $\beta$-SiC films were prepared by evaporation and conversion of Si$_3$N$_4$. The sintering temperature is 1950-2050$^\circ$C, which is beneficial to the formation of SiC film.
(2) According to the experiment and thermodynamic analysis, the mechanism of Si$_3$N$_4$ reacting with graphite to convert into $\beta$-SiC at 1950-2050$^\circ$C is complicated. The main mechanisms are the gas-solid reaction between silicon vapor and graphite, the direct solid-solid reaction between graphite and Si$_3$N$_4$, and the recrystallization of SiC at high temperature.
(3) When holding time is 1 h, the morphology of SiC film is better. SiC particles with holding time of 0.5 h are not fully developed and sphericity is low.

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