

Thermal Behaviors of Chemical Vapor Deposited Bulk Si-C-N Ceramic

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Abstract: The amorphous bulk Si-C-N ceramic was prepared by chemical vapor deposition (CVD). The thermal behaviors of as-prepared Si-C-N ceramic were investigated using TG/DSC, XRD, SEM and TEM. The phase separation firstly occurred in amorphous Si-C-N during the heat treatment, and one of separating phases appeared granular. β -SiC was formed in the granular separating phase. The amorphous Si-C-N began to crystallize at about 1200°C when the ceramic exposed to the heat treatment. The crystallization temperature was about 1372.6°C, which was determined by DSC under the condition of continuous heating at a heating rate of 20°C/min. β -SiC was found at 1200°C, while β -Si₃N₄ and α -SiC were formed at about 1500°C. A laminate-like structure appears in the heat-treated Si-C-N. This kind of structure was proved to be the highly crystallized Si-C-N.

Key words: amorphous; Si-C-N ceramic; thermal behavior; crystallization

Si-C-N ceramics have attracted growing attention of researchers recently, because of their high hardness, wide energy gap, high thermal conductivity and outstanding high temperature properties^[1-7]. It is difficult to produce such ceramics by the conventional solid state sintering, as resulted from the covalent bonding between the atoms in the materials. However, thermolysis of polymer precursors^[8-9] and chemical vapor deposition^[1, 10-11] can be applied to prepare the Si-C-N ceramics at the temperature of lower than 1000°C in recent years. Generally, both the polymer derived Si-C-N ceramics and the chemical vapor deposited Si-C-N ceramics (CVD Si-C-N) were proved to be amorphous. Because of metastability of amorphous substance, the structural change of these materials will take place as they are exposed to the high temperature.

Various characterization apparatus were used including thermogravimetry (TG), nuclear magnetic resonance (NMR), fourier-transform infrared spectroscopy (FT-IR), X-ray diffractometry (XRD), and high-resolution transmission electron microscope (HRTEM), to reveal the structural evolution. It was found that the escape of some gases could contribute to small weight loss at lower temperature^[12-13], at the same time, the amorphous Si-C-N ceramics could separate into an amorphous carbon and an amorphous domain, called am-SiCN phase^[14-19]. However, at high temperature, the weight loss was significant which was associated with the release of nitrogen and oxide species^[13], and the SiC and Si₃N₄ precipitated in the amor-

phous Si-C-N^[8, 13-14, 20]. At temperature between 1757K and 2114K, Si₃N₄ reacted with carbon and SiC formed. Above 2114K, Si₃N₄ decomposed^[12]. Moreover, the thermal behaviors of the amorphous Si-C-N are related with composition and the atmosphere^[9, 12-13, 19]. Although these studies have outline the thermal behaviors of the amorphous Si-C-N, many phenomena during the heat treatment are still unknown. In addition, previous investigations mainly focused on the polymer derived Si-C-N ceramics, but the thermal behaviors of the amorphous CVD Si-C-N ceramics have seldom been investigated.

Therefore, the aim of the present work is to determine the thermal behaviors of amorphous CVD Si-C-N by TG/DSC, XRD, SEM and TEM.

1 Experimental details

1.1 Materials

Bulk Si-C-N ceramic was prepared by a chemical vapor deposition method at 900°C for 10h using single hexamethyldisilazane (HMDS) as precursor, and the Si-C-N was deposited on a graphite plate. HMDS was bubbled by N₂ carrier gas at room temperature and the mixed gases were introduced to the chamber at a flow rate of 5cm³/min through a stainless-steel tube. The chamber pressure during the deposition was maintained at atmospheric pressure. The Si-C-N was deposited in argon atmosphere. The composition of Si-C-N ceramic was determined to be ap-

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proximately $\text{Si}_{43}\text{C}_{45}\text{N}_{12}$ by X-ray Fluorescence (XRF: Model S4 PIONEER, Bruker, Germany). After preparation, the graphite plate was removed by oxidation at 600°C , and then the bulk Si-C-N ceramic is gotten.

1.2 Sample characterization

Thermal behaviors of the CVD Si-C-N in flowing argon (flow rate: 100mL/min, heating rate: $20^\circ\text{C}/\text{min}$) was investigated by DSC/TG (Model: Q600, TA, USA) analyzer.

The as-received Si-C-N ceramic was cut into $10\text{mm}\times 10\text{mm}\times 5\text{mm}$ samples. The samples were heat-treated in temperature range from 1200°C to 1800°C in argon. The heating rate was $20^\circ\text{C}/\text{min}$. After heat treatment, the samples were grounded into powder in a mortar. The investigations with XRD were carried out by an χ 'Pert MPD PRO diffractometer in the $\theta/2\theta$ modus using $\text{CuK}\alpha$ radiation (40kV, 35mA) on powdery samples.

Parts of heat-treated samples were cut off along the growth direction of the Si-C-N ceramic. The microstructure on the polished samples was investigated by a scanning electron microscope (SEM: Model S-4700, Hitachi, Japan) and XRD. The microstructure was also investigated by transmission electron microscope (TEM: Model JEM-200CX, JEOL, Japan) equipped with an EDX system. The TEM foil preparation followed standard techniques, which involve diamond cutting, ultrasound drilling, mechanical grinding, dimpling, argon-ion thinning to perforation and subsequent light carbon coating.

2 Results and discussion

2.1 Analyses of DSC/TG

Figure 1 shows the DSC/TG curves for the CVD Si-C-N from room temperature to 1500°C . It can be seen that the mass of the Si-C-N ceramic decreases with increasing temperature. The weight loss rate increases at about 1310°C , significantly, gets a maximum at about 1370°C , and then the weight loss rate slows down. The weight loss of 0.215% account for 40% of total weight loss between 1310°C and 1500°C . Simultaneously a sharp

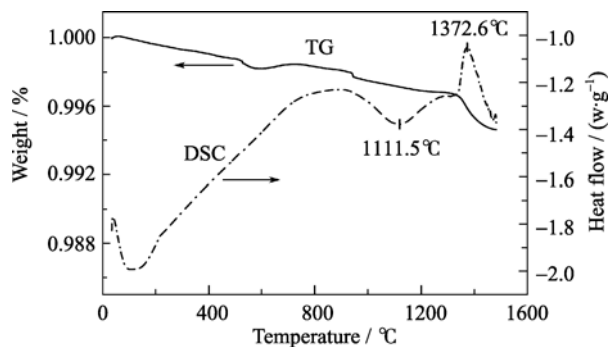
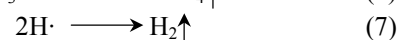
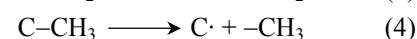
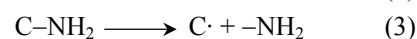
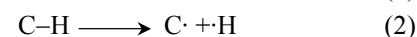
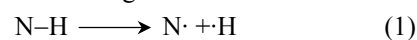


Fig. 1 TG-DSC curves of CVD Si-C-N

exothermic peak is found at 1372.6°C by DSC. These results mentioned above indicate that the crystallization of the Si-C-N sample initiated at about 1372.6°C . This temperature is about 300°C lower than polymer derived Si-C-N^[12]. In addition, the DSC profile also shows an endothermic peak at about 1111.5°C .

The prepared Si-C-N contains some free gases. During the heating process, the escapement of the stored gases leads to the continuous mass loss of amorphous Si-C-N, even the temperature is lower than the processing temperature. In addition, a small amount of organic groups, such as CH_3 , CH_2 , CH , NH_2 , NH and so on^[1, 13, 21], exist in the amorphous Si-C-N materials prepared by CVD. When the ceramic was exposed to the higher temperature, further pyrolysis and combination of the organic groups could occur according to the following reactions:



These pyrolysis and combination reactions could contribute to the appearance of the endothermic peak at about 1111.5°C . However, the exothermic peak at 1372.6°C and the weight loss in the temperature range of $1310\text{--}1500^\circ\text{C}$ could result from the reaction between amorphous Si-C-N and carbon, showed in Ref [13].

2.2 Analyses of XRD

XRD patterns of the untreated sample are shown in Fig. 2. There is no diffraction peak, indicating the amorphous nature of the Si-C-N.

Due to the structural instability of the amorphous materials, the amorphous Si-C-N will transform into crystalline state at higher temperature through nucleation and growth. XRD patterns of the heat-treated sample are also shown in

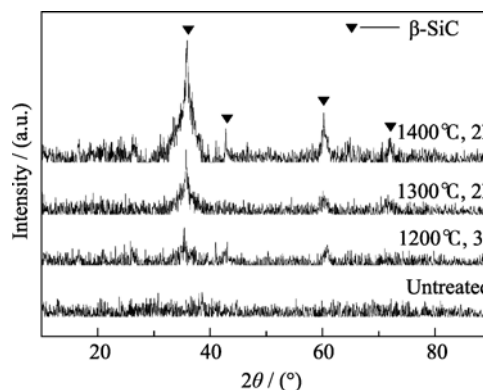


Fig. 2 XRD patterns of untreated and heat-treated CVD Si-C-N

Fig. 2. The small peaks of β -SiC are detected in the sample annealed at 1200°C for 3h. It indicates that the crystallization of the amorphous CVD Si-C-N might initiate at 1200°C, and the primary phase is β -SiC, which is in agreement with Du's results^[10]. However, the crystallization temperature was about 300°C lower than that of amorphous polymer derived Si-C-N according to Ref [8] and Ref [12]. The reason why the crystallization temperature of amorphous CVD Si-C-N decreases is that the short range ordering of Si-N and Si-C can be formed during preparation of CVD Si-C-N. Compared with the results of DSC/TG analyse, it could be found that the crystallization temperature determined by XRD was lower than that detected by DSC/TG. This shift of the crystallization temperature could be explained by kinetic hindrance. Because of the rapid heating rate (20°C/min) and the sluggishness of the crystallization reaction it cannot be detected exactly by thermal analysis using a defined heating rate at this temperature.

Figure 3 shows the XRD patterns of the samples heat-treated above 1400°C for 2h. The XRD pattern of the sample annealed at 1500°C reveals obvious diffraction

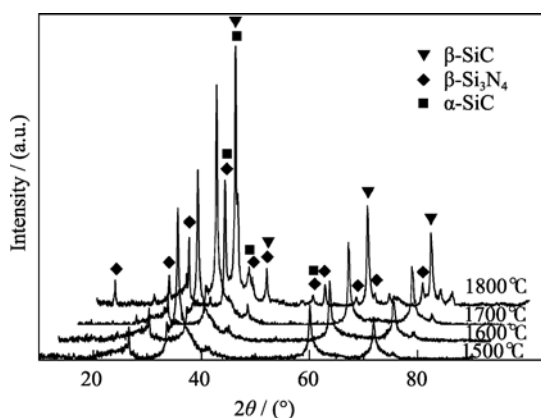


Fig. 3 XRD patterns of CVD Si-C-N heat-treated at different temperatures for 2h

peaks of β -SiC. Also, β -Si₃N₄ and α -SiC can be detected in the sample annealed at 1600°C. The stronger diffraction peaks at higher temperatures of these three phases indicates that the crystallization degree increases with the temperature. β -Si₃N₄ and α -SiC can be clearly distinguished in sample heat-treated at 1800°C for 2h.

2.3 TEM and HRTEM investigation

As shown in Fig. 4(a), untreated CVD Si-C-N is amorphous, which is in concordance with the XRD results. The granular materials can be found in the TEM image of the CVD Si-C-N after heat treatment at 1700°C for 0.5h (Fig. 4(b)). Both the granular structure and intergranular structure are amorphous, implying that the phase separation may occurs in amorphous CVD Si-C-N, as well as amorphous polymer derived Si-C-N during heat treatment. The phase separation of the amorphous Si-C-N was always determined by the NMR^[14, 18-19] and FT-IR^[18]. Seldom evidence in manner of TEM can be found in the previous investigation. With the duration of the time, β -SiC was observed in some granular materials (Fig. 5). The granular materials might be considered as the so-called “am-SiCN” named in some previous studies^[22]. The phase between the granules will be the amorphous carbon. The crystallized materials in Si-C-N are mainly consist of β -SiC after heat-treatment at 1700°C for 2h (Fig. 6), which also consists with XRD analyses. In this sample, the granular materials have almost completely become the crystalline materials, while the materials between granules basically remain amorphous (Fig. 7).

2.4 Structure evolution

Figure 8(a) is SEM image of polished untreated sample. The regions around the pores and microcracks show no difference from that far from the pores and microcracks, suggesting homogeneous amorphous structure through the materials. After heat treatment, obvious difference in the structure can be seen (Fig. 8(b)). The structure far from the

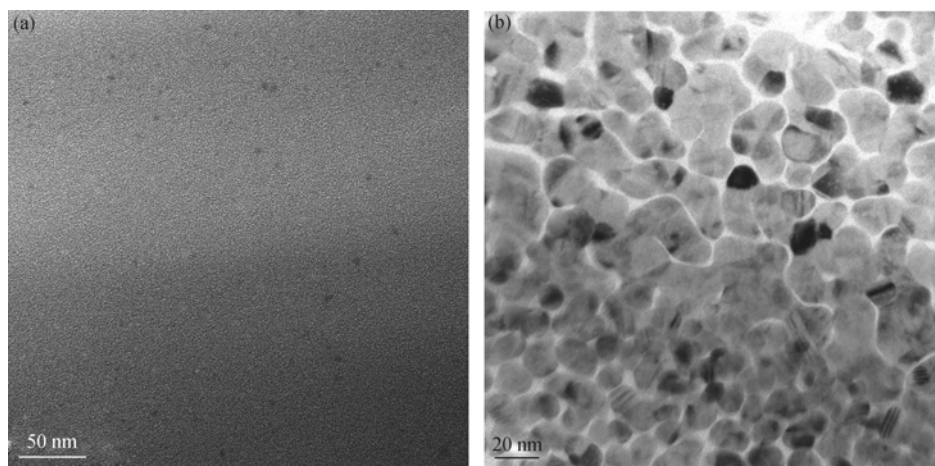


Fig. 4 TEM image of untreated Si-C-N (a) and heat-treated Si-C-N at 1700°C (b) for 0.5h

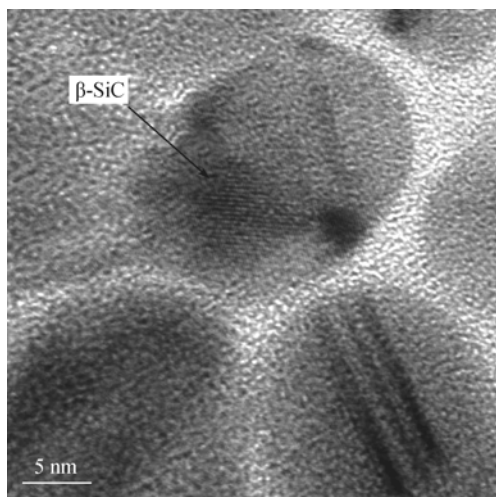


Fig. 5 The crystallization of the am-SiCN after annealing at 1700°C for 1h

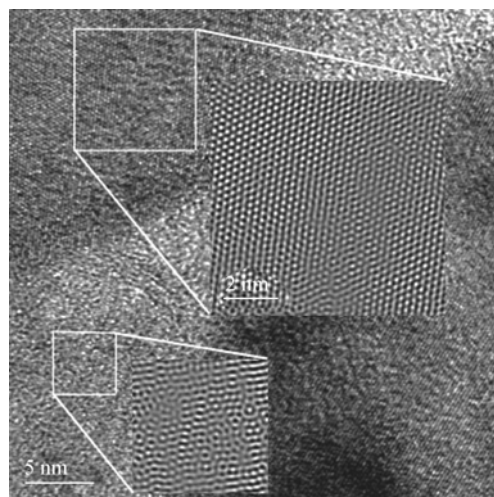


Fig. 7 HRTEM image of the CVD Si-C-N after heat-treated at 1700°C for 2h

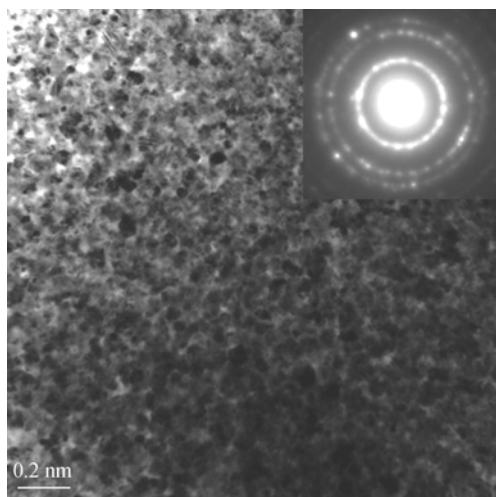


Fig. 6 TEM image and corresponding EDP of the Si-C-N after heat-treated at 1700°C for 2h

pores and microcracks keeps unchangeable, while the structure around the pores and microcracks seems laminated, and the bedding planes of this laminate-like structure are approximately vertical to the growth direction of the CVD Si-C-N (Fig. 8(b)) and its interlayer spacing is

about 2–3 μm (Fig. 9). The laminate-like structure also can be seen at the vicinity of surface. This result suggests that the hardness of the laminate-like structure varies periodically along the growth direction considering that the surface of this sample underwent the polishing treatment. The periodic variation of the hardness may results from the fluctuation of the composition along the growth direction. Previous investigations indicated that the C/Si atomic ratio of CVD Si-C-N was determined by the preparation temperature^[11]. The temperature fluctuation during the preparation may results in the compositional fluctuation along the growth direction. The difference in the chemical composition leads to the periodical variation of the hardness.

When this sample was observed by an optical microscope, the laminate-like structure corresponds to the light regions around the microcracks and pores (Fig. 10). The results of micro-area X-ray diffraction show that the crystallization degree in the light regions is obviously higher than that in the dark regions, which indicates that amorphous Si-C-N around the pores and microcracks can be crystallized more easily than that far from the pores and microcracks. Based on the above phenomena, it is thought

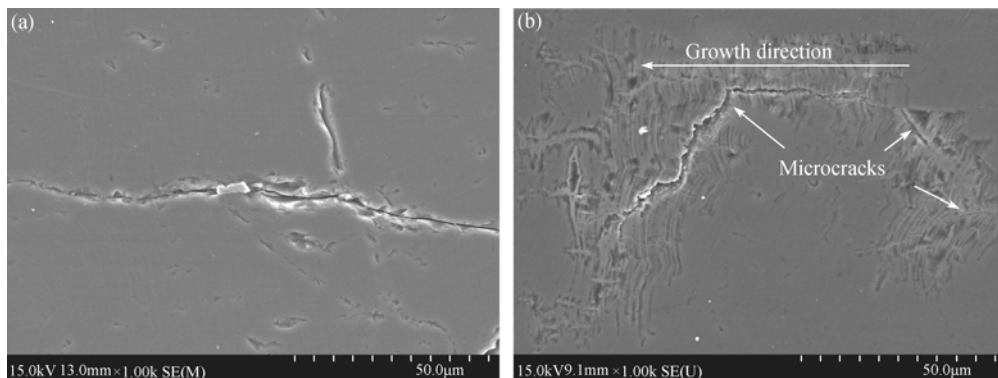


Fig. 8 SEM image of untreated Si-C-N (a) and the Si-C-N after heat-treated at 1700°C for 2h (b)

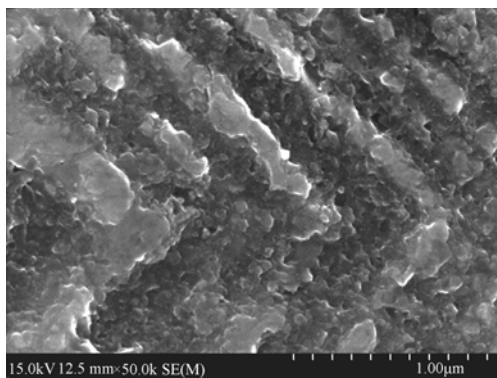


Fig. 9 SEM image of the laminate-like structure in the heat-treated Si-C-N

that crystallization occurred in the region around the microcracks at first, which consists with Kleebe's work^[9]. A lot of gases are released from the Si-C-N ceramic during heat treatment. The unsteadiness of the amorphous Si-C-N around the pores and microcracks may relate with the fact that the gases in this region diffused out the ceramic more easily.

3 Conclusions

The mass of the CVD Si-C-N ceramic decreases with increasing temperature, and the weight loss rate shows an increase above 1310°C. The crystallization of the CVD Si-C-N initiates at about 1372.6°C under the condition of continuous heating at a heating rate of 20°C/min. The

primary phase is β -SiC at 1200°C under the condition of heat treatment. β -Si₃N₄ and α -SiC are formed at 1500°C. The phase separation firstly occurs in amorphous CVD Si-C-N during heat treatment, and one of separating phases appears granular. With the duration of the time, β -SiC is formed in the granular phase. After annealing at 1700°C for 2h, the granular structure transformed into crystal SiC. A laminate-like structure, proved to be the highly crystallized Si-C-N, appears in the heat-treated Si-C-N and mainly locates around the microcracks and pores.

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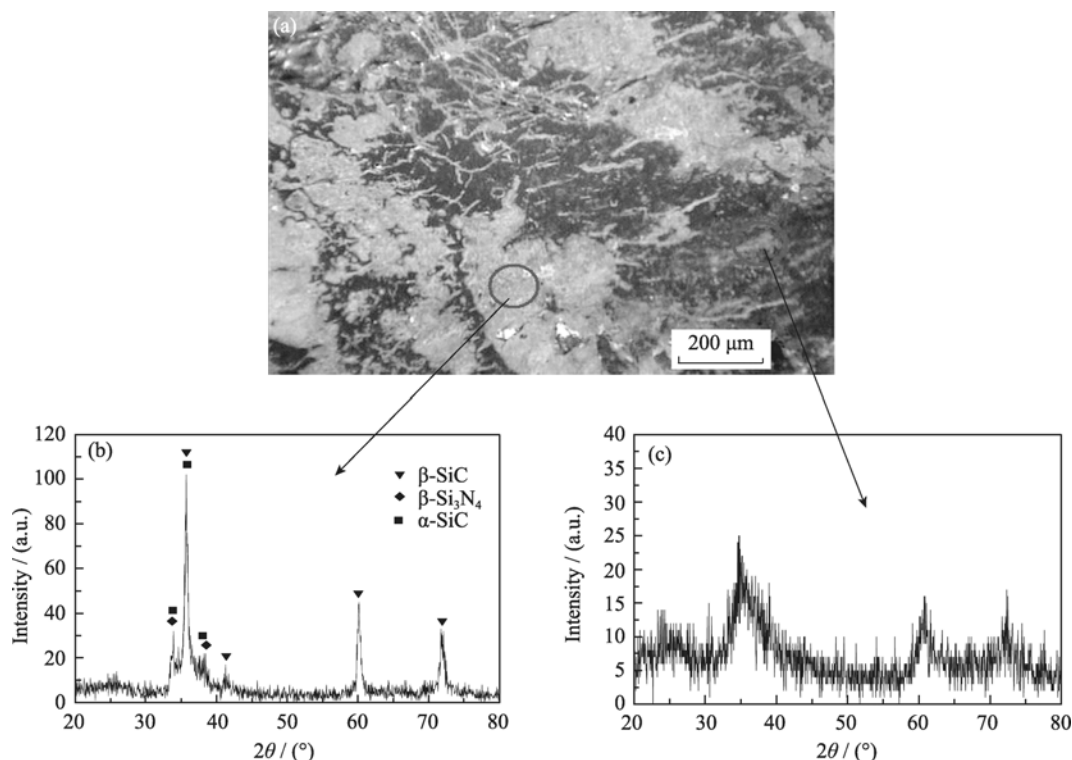


Fig. 10 The photograph and corresponding Micro-area XRD patterns of the heat-treated Si-C-N

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化学气相沉积法制备的块体 Si-C-N 陶瓷的热行为

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摘要: 采用化学气相沉积法制备了块体非晶态 Si-C-N 陶瓷. 用 TG/DSC、XRD、SEM 和 TEM 等技术方法研究了所制备的 Si-C-N 陶瓷的热行为. 研究结果表明: 在热处理过程中, 非晶态 Si-C-N 首先发生相分离, 分离后的一种相呈颗粒状; β -SiC 就是从这种颗粒状的分离相中形成. 在热处理条件下, 非晶 Si-C-N 的晶化温度约为 1200°C; 在加热速率为 20°C/min 的连续加热条件下, 其晶化温度为 1372.6°C. β -SiC 在 1200°C 首先形成, β - Si_3N_4 和 α -SiC 则在 1500°C 形成. 在扫描电镜观察中, 热处理后的 Si-C-N 中出现一种类似于层状的组织, 这种组织的晶化程度较高.

关键词: 非晶态; Si-C-N 陶瓷; 热行为; 晶化

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