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Heat treatment investigations on the laser synthesized amorphous Si/C/N nanocomposite powders

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Changes of chemical composition, crystallization, and morphology of laser synthesized amorphous Si/C/N nanocomposite powders during heat treatment under nitrogen and argon were investigated. The influence of nitrogen and argon on the chemical composition and crystallization of the powders were different. When the temperature exceeded 1750 °C, however, the amorphous Si/C/N nanocomposite powders were transformed into pure crystalline β-SiC powders under either nitrogen or argon. The particle sizes of the nanometric powders increased abruptly as increasing the annealing temperature and reached micrometer scale above 1750 °C.

1. Introduction

Laser synthesis of powders, which was developed by Haggerty *et al.* [1, 2], offers several advantages over conventional methods. The reactions are conducted in a confined, well-defined, wall-less zone with rapid heating and cooling rates and with fast reaction times (1–10 ms). Laser synthesis can yield powders whose elements are homogeneously mixed at atomic scale via *in situ* deposition from a homogeneous gas phase. The laser synthesized powders are spherical and very small with a very narrow range of sizes and loose agglomeration. For all of these reasons, the laser method is one of the best methods to obtain ultrafine particles that are very pure and uniform in composition and particle size. Ultrafine particles of Si [1, 2], SiC [1–5], Si_3N_4 [1, 2, 6, 7], Si/C/N [8–11] and TiO_2 [12] have been synthesized by a laser-induced gas-phase reaction.

Si_3N_4-SiC nanocomposite ceramics have been attracting the attention of many researchers because of their better properties than monolithic ceramics. One successful example of such attractive materials has been studied and developed by Niihara *et al.* [13]. They showed that the Si_3N_4-SiC nanocomposite fabricated by hot-pressing of the amorphous Si/C/N powder produced by chemical vapor deposition of $[Si(CH_3)_3]_2NH$-NH_3-N_2 system revealed superplasticity. This fact strongly stimulates the studies on the preparations and the relative properties of Si/C/N nanocomposite powders in the world.

In the case of laser synthesized Si/C/N powders, a few works [8–11] have been reported. Rice and Woodin [8, 9] synthesized amorphous Si/C/N nanometric powders from hexamethyldisilane ($[Si(CH_3)_3]_2NH$, HMDS) and studied the reaction kinetics. Suzuki *et al.* [10] reported the synthesis of amorphous and partial crystalline Si/C/N fine particles from SiH_4-C_2H_2-NH_3 system. Cauchetier *et al.* [11] prepared nanocomposite Si/C/N powders by laser-HMDS aerosol interaction and simply studied the powder changes such as crystallization during heat treatment (1000–1600 °C) under nitrogen. In fact, although the particle size, the composition and the structure of starting powders have a great influence on the properties of composite ceramics [14], the changes of the above characteristics during heat treatment or sintering also greatly affect the properties of composite ceramics. So, it is necessary to systematically investigate the changes of the laser synthesized Si/C/N nanocomposite powders during heat treatment under nitrogen or argon at a wide range of temperature.

In a previous report [15], we synthesized amorphous Si/C/N nanocomposite powders from HMDS by laser-induced gas phase reaction. In this paper, we have focused our interest on the studies of changes of chemical composition, crystallization, and morphology of these Si/C/N powders during heat treatment under nitrogen (1250–1850 °C) and argon (1350–1750 °C).

2. Experimental

The Si/C/N nanocomposite powders were prepared by irradiating HMDS with a 5 kW CO_2 laser (Rofin-Sinar 850 model). The preparation method has been described in detail in [15]. The Si/C/N powder prepared was an amorphous mixture of Si-C and Si-N bonds homogeneously mixed with some excess carbon. The chemical composition of the Si/C/N powder was 51.3 wt % for silicon, 30.6 wt % for carbon, 13.6 wt % for nitrogen and 3.6 wt % for oxygen. The particle size was in the range of 50–80 nm. The specific surface area of the as-formed powders was 102.5 m^2/g.

The heat treatment experiments were conducted in a high-temperature graphite furnace under nitrogen or argon at atmospheric pressure with a heating rate of 600 °C/h and a plateau duration of 1 h. The temperature ranges under nitrogen and argon were of 1250–1850 °C and 1350–1750 °C, respectively.

After the heat treatment, the annealed powders were subsequently analyzed by X-ray diffractometry (XRD) using CuK_α radiation for the crystalline phase. The silicon content was determined by chemical analysis method. Standard LECO combustion analysis systems were used for accurate measurements of C, N, and O contents of the annealed powders. The morphology of the annealed powders was examined by a transmission electron microscopy (TEM). The specific surface area of the annealed powders was measured by the Brenauer-Emmett-Teller method.

3. Results and discussion

Tables I and II show the evolution of elemental composition under nitrogen and argon, respectively. From Table I it can be seen that under the case of nitrogen atmosphere the nitrogen content first increases as the temperature is increased, and reaches a maximum at 1350 °C to probably form Si_3N_4. Above 1550 °C, the nitrogen content dramatically decreases and the chemical composition of the powders is very close to SiC. In Table I the excess carbon content is calculated (neglecting possible Si_2N_2O) by assuming oxygen, nitrogen and carbon combined with silicon to form SiO_2, Si_3N_4 and SiC, respectively. It can be seen from Table I that, as the temperature increasing from room temperature to 1850 °C, the excess carbon content decreases from 18.7 to 0.9 wt %, whereas the Si_3N_4 content decreases from 34.3 to 2 wt %, and, at the same time, the SiC content increases from 39.6 to 96.5 wt %.

Under argon, the nitrogen content of the powder continuously decreases as increasing the annealing temperature, which is different from that under nitrogen. Above 1450 °C, the chemical composition of the powders is very close to that of SiC. Comparing Table I with Table II, it can be found that at the same annealing temperature nitrogen in the powders is easier to loss under argon atmosphere than under nitrogen atmosphere.

The XRD spectra recorded for the as-formed and the annealed powders under nitrogen and argon are shown in Figs 1 and 2, respectively. Fig. 3 shows the crystallinity of the powder at various temperature under nitrogen and argon calculated by the computer attached to the X-ray diffractometry by assuming that the as-formed powder is completely amorphous and the powder treated at 1850 °C is completely crystalline. From Fig. 1 it can be found that the as-formed powder is amorphous with featureless spectrum. Under nitrogen at 1250 °C, the powder remains amorphous. At 1350 °C, the spectrum already presents many small peaks which can be attributed to Si_3N_4 and trace of SiC; the crystallinity at 1350 °C is about 20.5% (Fig. 3). This clearly indicates that the amorphous to crystalline transformation is initiated during the heat treatment at 1350 °C for 1 h under nitrogen. After the 1450 °C treatment, most of the above Si_3N_4 peaks disappear and the SiC peaks get stronger; the crystallinity of the powder at 1450 °C slightly increases. The results at 1350 and 1450 °C under nitrogen indicate that the nitrogen content of the powders increases at 1350 °C and decreases at 1450 °C, which is agreement with the chemical analysis results (Table I). Heating at 1550 °C leads mainly

TABLE I Evolution of powders during annealing under nitrogen

Temperature (°C)	Chemical analysis (wt %) Si	C	N	O	Chemical composition (wt %) SiC	Si_3N_4	SiO_2	Excess-C	Empirical formula
As-formed	51.3	30.6	13.6	3.6	39.6	34.3	6.7	18.7	$SiC_{1.39}N_{0.53}O_{0.12}$
1250	53.2	28.6	15.9	2.4	39.8	38.9	4.5	16.9	$SiC_{1.31}N_{0.56}O_{0.08}$
1350	53.4	26.1	18.8	1.9	33.6	47	3.6	16	$SiC_{1.14}N_{0.71}O_{0.06}$
1450	58.4	28.5	11.4	1.7	56.9	28.5	3.2	11.4	$SiC_{1.14}N_{0.39}O_{0.05}$
1550	62.7	28.7	7.3	1.3	72.3	18.3	2.4	7	$SiC_{1.07}N_{0.23}O_{0.04}$
1650	67.4	29.2	2.5	0.9	89.8	6.3	1.7	2.4	$SiC_{1.01}N_{0.07}O_{0.02}$
1750	68.6	29.3	1.4	0.7	94.1	3.5	1.3	1.1	$SiC_{0.99}N_{0.04}O_{0.02}$
1850	69.1	29.7	0.8	0.4	96.5	2	0.7	0.9	$SiC_{1.00}N_{0.02}O_{0.01}$

TABLE II Evolution of powders during annealing under argon

Temperature (°C)	Chemical analysis (wt %) Si	C	N	O	Chemical composition (wt %) SiC	Si_3N_4	SiO_2	Excess-C	Empirical formula
As-formed	51.3	30.6	13.6	3.6	39.6	34.3	6.7	18.7	$SiC_{1.39}N_{0.53}O_{0.12}$
1350	57.5	30.1	10.3	2.1	57.4	25.8	3.9	12.8	$SiC_{1.22}N_{0.36}O_{0.06}$
1450	61.8	28.9	7.8	1.5	69.6	19.5	2.8	8.1	$SiC_{1.09}N_{0.25}O_{0.04}$
1550	65.5	28.6	4.6	1.4	82.1	11.5	2.6	3.9	$SiC_{1.02}N_{0.04}O_{0.04}$
1650	68.7	29.3	1.2	0.8	94.5	3.1	1.5	0.9	$SiC_{1.00}N_{0.03}O_{0.02}$
1750	69.5	29.7	0.3	0.5	98	0.8	0.9	0.3	$SiC_{0.99}N_{0.01}\ O_{0.01}$

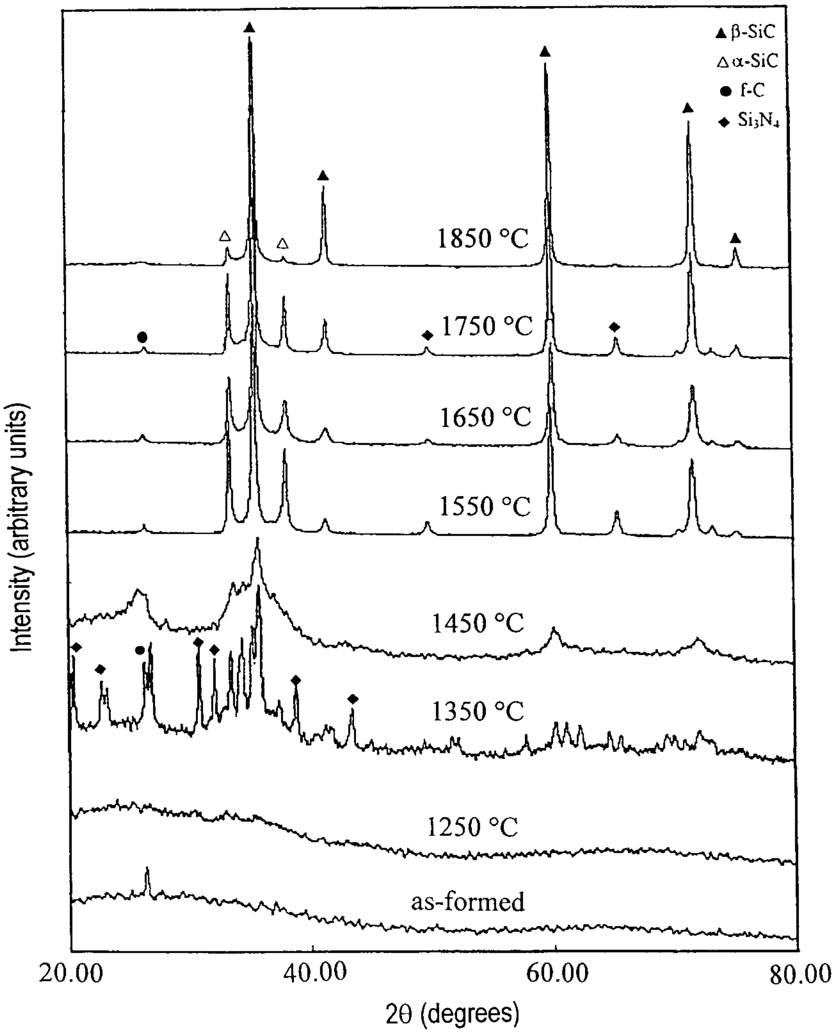

Figure 1 XRD patterns of the as-formed powders and powders treated at 1250–1850 °C under nitrogen for 1 h.

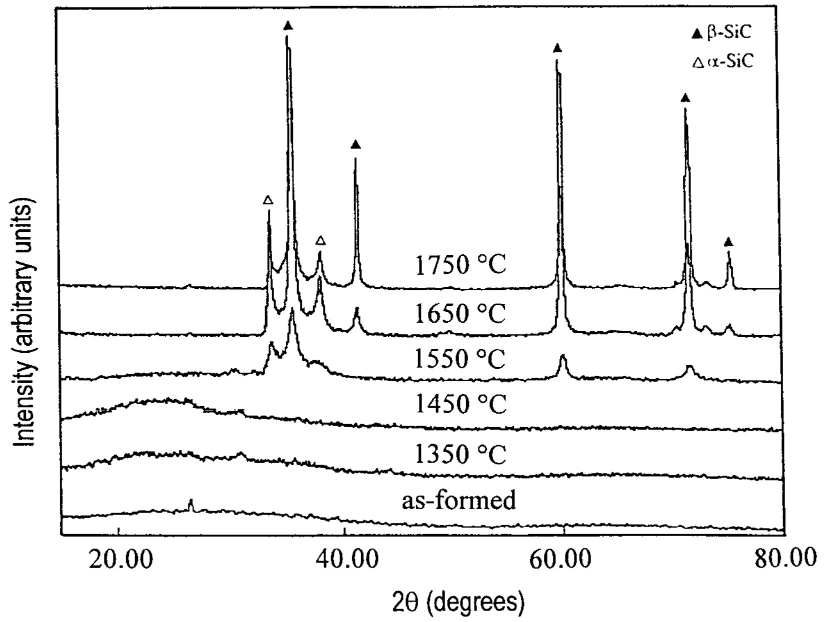

Figure 2 XRD patterns of the as-formed powders and powders treated at 1350–1750 °C under argon for 1 h.

to the formation of SiC (including α-SiC and β-SiC), and the powder is already very well crystallized with crystallinity of about 85%. Then, as the temperature increasing, the crystallinity slightly increases and the amorphous to crystalline transformation nearly completes at 1750 °C. At 1850 °C, only SiC peaks exist in the spectrum, which indicates that after heat treatment at 1850 °C under nitrogen, the amorphous Si/C/N powder turns into crystalline SiC (mainly β-SiC) powder.

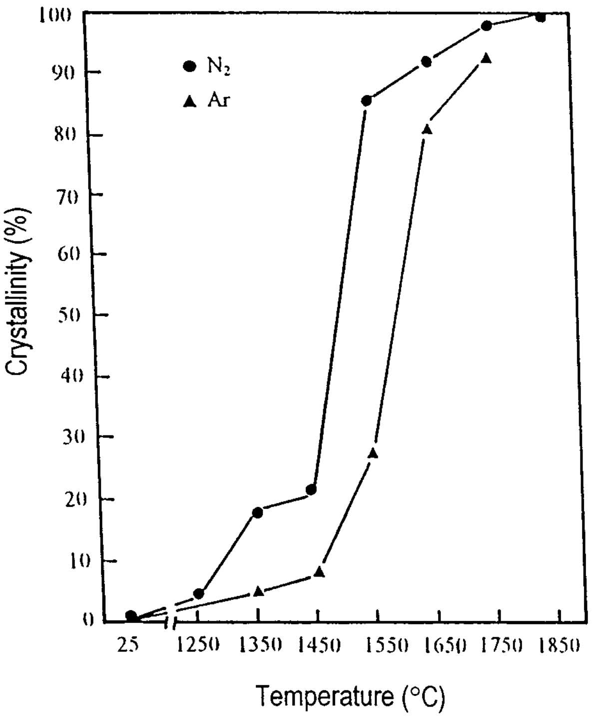

Figure 3 The crystallinity of the annealed powders at various temperature under nitrogen and argon.

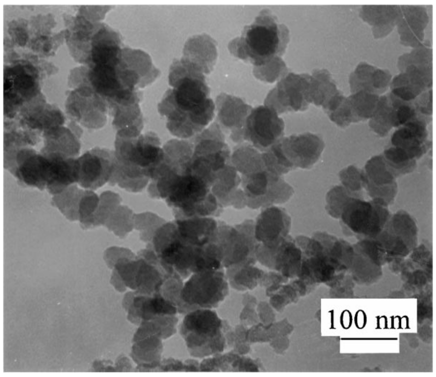

Figure 4 TEM micrograph of the as-formed powders.

The crystalline characteristic of the amorphous Si/C/N powder under argon (Fig. 2) is different from that under nitrogen. Up to 1450 °C, no peak presents in the XRD spectrum. At 1550 °C, some small peaks attributed to α- and β-SiC present, but the crystallinity of 28.4% is much lower than that of 85% under nitrogen at the same annealing temperature. This result indicates that under argon the crystallization occurs near 1550 °C, which is higher than that of 1350 °C under nitrogen. Then, as the temperature is further increased, the crystallinity increases rapidly and reaches to 92% at 1750 °C. Heating under argon leads only to the formation of SiC.

From Fig. 3 it can be found that, at the same annealing temperature, the crystallinity under argon is lower than that under nitrogen (especially at 1550 °C), which indicates that argon hinders the crystallization process compared to nitrogen. This is because under nitrogen atmosphere, nitrogen reacts with Si/C/N powder to form crystalline Si_3N_4 at lower temperature (such as at 1350 °C) (Fig. 1), these crystalline Si_3N_4 may promote further crystallization at higher temperature.

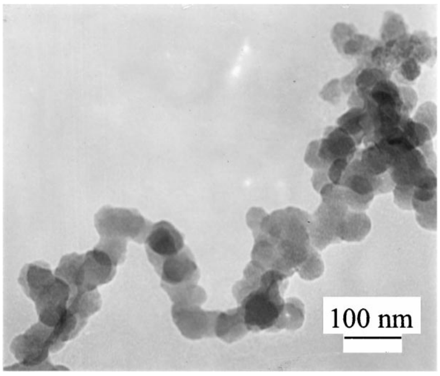

Figure 5 TEM micrograph of the powders treated at 1250 °C for 1 h in nitrogen atmosphere.

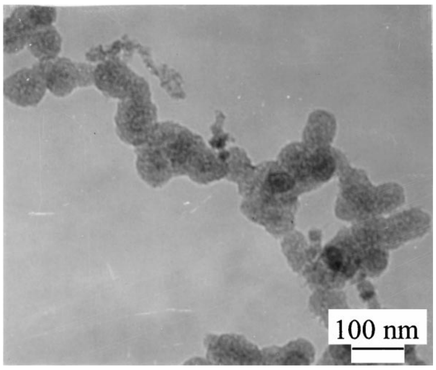

Figure 6 TEM micrograph of the powders treated at 1350 °C for 1 h in nitrogen atmosphere.

Changes in the chemical composition and crystallization can be explained from the reactions that occur in the Si-C-N-O system [16, 17] either in the solid or in the gaseous phase. The main reactions involving the evolution of nitrogen and CO_2 (or CO) with the presence of excess carbon under nitrogen are listed below:

$$Si_3N_4 + 3C = 3SiC + 2N_2 \tag{1}$$

$$SiO_2 + C = SiO + CO \tag{2}$$

$$SiO + 3CO = SiC + 2CO_2 \tag{3}$$

$$CO_2 + C = 2CO \tag{4}$$

$$SiC + 2SiO + 2N_2 = Si_3N_4 + C + O_2 \tag{5}$$

The thermodynamics calculation [18] of the above reactions show that under nitrogen Si_3N_4 forms preferentially below 1374 °C, while for SiC above 1374 °C. This can explain well the experimental results (shown in Table I and Fig. 1).

Changes in morphology of the powders under both nitrogen and argon have the similar characteristics. Thus, here we only give the results obtained under nitrogen case.

Fig. 4 shows a typical morphology of the as-formed powders. It can be seen that the as-formed particles are spherical, loosely agglomerates with the particle size in the range of 50–80 nm. After heat treatment at 1250 °C, the particles agglomerated to clusters (Fig. 5) due to surface diffusion, but the particles within these clusters

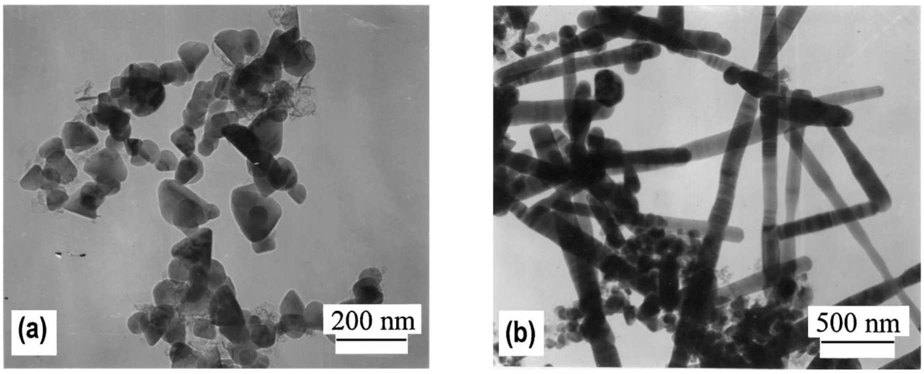

Figure 7 TEM micrograph of the powders treated at 1550 °C for 1 h in nitrogen atmosphere showing (a) particles and (b) SiC whiskers.

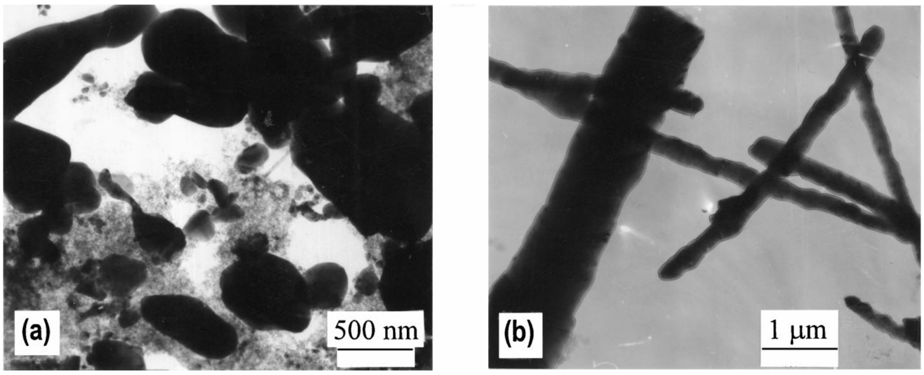

Figure 8 TEM micrograph of the powders treated at 1750 °C for 1 h in nitrogen atmosphere showing (a) particles and (b) SiC whiskers.

are distinguished and have the same sizes as that of the as-formed particles. Selected area electron diffraction (SAED) reveals that the particles annealed at 1250 °C are mainly amorphous.

At 1350 °C, the particles began to grow (Fig. 6). The particles within the clusters are difficult to be distinguished, which indicates that the bulk diffusion between particles occurred. SAED analysis shows that the particles treated at 1350 °C are partial crystalline.

After heat treatment at 1550 °C, the morphology of the particles changes greatly. On the one hand, the spherical small starting particles grow to irregular large particles with size of 50–150 nm (Fig. 7a). On the other hand, many whiskers with diameters of 100–200 nm and length of 0.5–5 μm present in the annealed powders (Fig. 7b). SAED studies reveal that both the irregular particles and the whiskers are pure β-SiC, which is agreement with the XRD results (Fig. 1). It can be seen clearly from Fig. 7b that there exists large quantities of sub-structures in these SiC whiskers. The morphology, microstructure and formation mechanism of the SiC whiskers will be discussed in detail elsewhere.

At 1750 °C, the particle sizes increase dramatically and reach about 0.2–1 μm (Fig. 8a). The whisker diameters increase apparently with a wide distribution in the range of 0.2–1 μm (Fig. 8b). It can be seen clearly from Fig. 8 that after heat treatment at 1750 °C, the Si/C/N nanocomposite powders appear to be sintered severely and the particle sizes reach micrometer scale. SAED of the annealed powders shows that at 1750 °C the powders are already well crystallized.

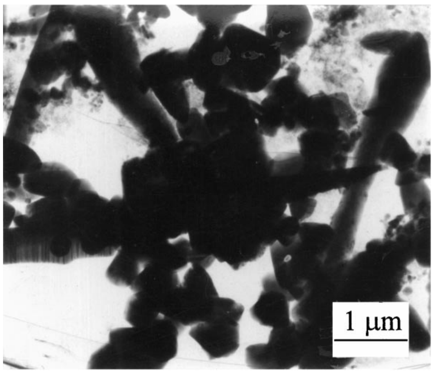

Figure 9 TEM micrograph of the powders treated at 1850 °C for 1 h in nitrogen atmosphere.

At 1850 °C, the powders appear to be sintered more severely than that at 1750 °C. The sizes of the particles is in the range of 0.5–2 μm (Fig. 9). Meanwhile, the whiskers are shorten with lower aspect ratio than that at 1750 and 1550 °C. Since the whiskers are sintered together with the particles, it is difficult for us to find an individual whisker under the TEM observations.

Fig. 10 shows the specific surface area of the powders changed with the temperature under nitrogen atmosphere. It can be seen that the values of specific surface area decrease rapidly as increasing the annealing temperature due to the particle agglomeration and grain growth described above. The values of specific surface area decrease from 102.5 m^2/g at room temperature to 8.7 m^2/g at 1850 °C.

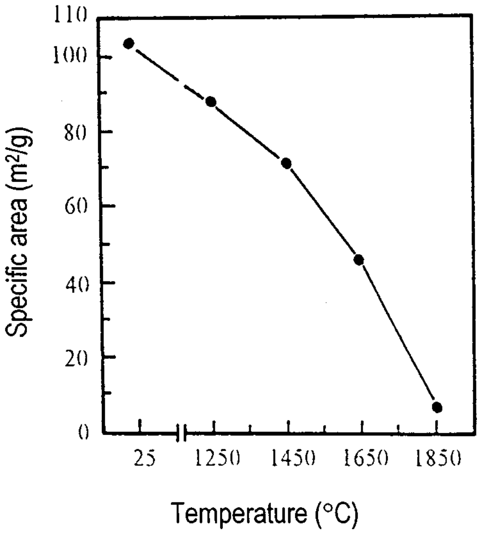

Figure 10 The specific surface area of the powders changed with temperature under nitrogen.

4. Conclusion

The following conclusions may be made from above results.

1. Under either nitrogen or argon, the composition of the laser synthesized Si/C/N nanocomposite powders changed greatly. At low temperature ($\leq$1350 °C) under nitrogen, the Si_3N_4 content of the powders increased slightly and reached maximum at 1350 °C. But when the temperature exceeded 1450 °C, the content of Si_3N_4, SiO_2 and free-carbon of the powders decreased abruptly, whereas the SiC content increased greatly. At 1750 °C, the stoichiometry of the powders was very close to pure β-SiC. At the same annealing temperature, nitrogen in the powders is easier to loss under argon atmosphere than under nitrogen atmosphere.
2. The initiating crystalline temperature of the amorphous Si/C/N powders under nitrogen and argon atmosphere was $\sim$1350 and $\sim$1550 °C, respectively. Argon hindered the crystallization process compared to nitrogen. Up to 1750 °C, the amorphous Si/C/N powders was nearly transformed into crystalline β-SiC powders.
3. The particle sizes increased greatly as increasing the annealing temperature. The range of the particle sizes increased from 50–80 nm of the starting powders to 50–150 nm at 1550 °C, 0.2–1 μm at 1750 °C, and 0.5–2 μm at 1850 °C. The Si/C/N nanometric powders appeared to be sintered severely above 1750 °C. From 1550 °C, a lot of SiC whiskers appeared in the annealed powders. The diameters of the SiC whiskers increased with the annealing temperature.
4. The specific surface area of the powders decreased abruptly with increasing the annealing temperature. The specific surface area decreased from 102.5 m^2/g at room temperature to 8.7 m^2/g at 1850 °C.
5. From above results listed, it can be conclude that for obtaining nanometric SiC ceramic, the sintering temperature should below 1750 °C.

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