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High temperature evaporation characteristics of amorphous Si_3N_4–C composite prepared by chemical vapour deposition

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Evaporation characteristics of amorphous Si_3N_4 and amorphous Si_3N_4–C composite (6 wt% C) prepared by the chemical vapour deposition (CVD) were investigated in the temperature range of 1400 to 1650° C in a vacuum of about 10^{-6} torr. The weight loss due to the evaporation was linear with time for all the samples tested. Evaporation rate of the amorphous CVD-(Si_3N_4–C) composite was 50 to 70% of that for the amorphous CVD-Si_3N_4. The activation energy for evaporation, calculated from the temperature dependence of the evaporation rates, was about 160 kcal mol^{-1} for both samples. The carbon dispersed in the amorphous CVD-(Si_3N_4–C) composite reacted at the time of heat-treatment with the amorphous Si_3N_4 matrix and formed β-SiC particles. The β-SiC particles were found to be about 100 nm in diameter and connected each other to form a three-dimensional network structure.

1. Introduction

Materials with a low atomic number (Low-Z) have a potential use as limiters (the part of a fusion reactor nearest the plasma) because of the small probability of contamination by the plasma. The ideal material for a limiter would have a high resistance to thermal shock, a low susceptibility to radiation damage, a low vapour pressure and would be chemically compatible with hydrogen [1]. Recent studies [2] indicate that silicon and titanium compounds (e.g. SiC, Si_3N_4, TiB_2 and TiC) are some of the most promising materials for this use. In particular, Si_3N_4 has the superior thermal shock resistance and a good compatibility with hydrogen. Unfortunately it has the disadvantage of being volatile at high temperatures and thus having a high vapour pressure. In order to depress the high temperature evaporation of Si_3N_4, the authors have added carbon on Si_3N_4 and prepared Si_3N_4 composite (Si_3N_4–C composites) by chemical vapour deposition.

This paper presents the results of measurements of the evaporation rates of the CVD-(Si_3N_4–C) composite at high temperatures, and describes the effect of the carbon on the evaporation rates. In addition, the relationship between the present state of the carbon in the CVD-(Si_3N_4–C) composite and the evaporation characteristics are also examined.

2. Experimental procedures

2.1. Sample preparation

The Si_3N_4–C composite was prepared by chemical vapour deposition on electrically heated graphite substrates using a mixture of the gases $SiCl_4$, H_2, NH_3 and C_3H_8. A detailed preparation procedure is reported elsewhere [3]. The samples used in the present work were prepared at a deposition temperature (T_{dep}) of 1300° C and total gas pressure (P_{tot}) of 30 torr. Carbon content in the resulting Si_3N_4–C composite was 6 wt % and its structure was amorphous. The carbon-free amorphous CVD-Si_3N_4 was also prepared at the same T_{dep} and P_{tot} for a comparative measurement.

Plate-like sample deposits were cut to a size of about 5 mm by 10 mm using a diamond cutter. The graphite substrate attached to the deposits was completely removed by use of SiC abrasive, and the sample was thinned down to about 1 mm in thickness with a diamond grinder. Both sides of this sample were polished to a mirror surface with an alumina paste (0.03 μm), then ultrasonically cleaned in acetone to obtain a specimen for the measurements.

2.2. Measurements

The specimen was placed in a graphite crucible and suspended by a tungsten wire from an electrobalance (Cahn R-100) at the centre of the vacuum furnace. The furnace was evacuated to about 10^{-6} torr using a diffusion oil pump and the specimen was heated to the temperature of 1400 to 1650° C. A Penning gauge (Daia CT-2P) and an ion gauge (Daia IT-10P) were used for the vacuum pressure measurements. A WRe 5%–WRe 25% thermocouple and a two-colour pyrometer (ChinoPyroscope-Q) were used for the temperature measurements. The specimen was heated at a rate of 20° C min^{-1}, and the weight change of the specimen was continuously recorded at a specified temperature interval. The maximum sensitivity of the electrobalance was about 0.5 μg.

The surface and cross-section of the specimen after heat-treatment were observed by a scanning electron microscope (SEM) (Hitachi-Akashi MSM-4), and structural change due to the heat treatment was studied by an X-ray diffractometer (Ni filtered, Cu$K\alpha$,

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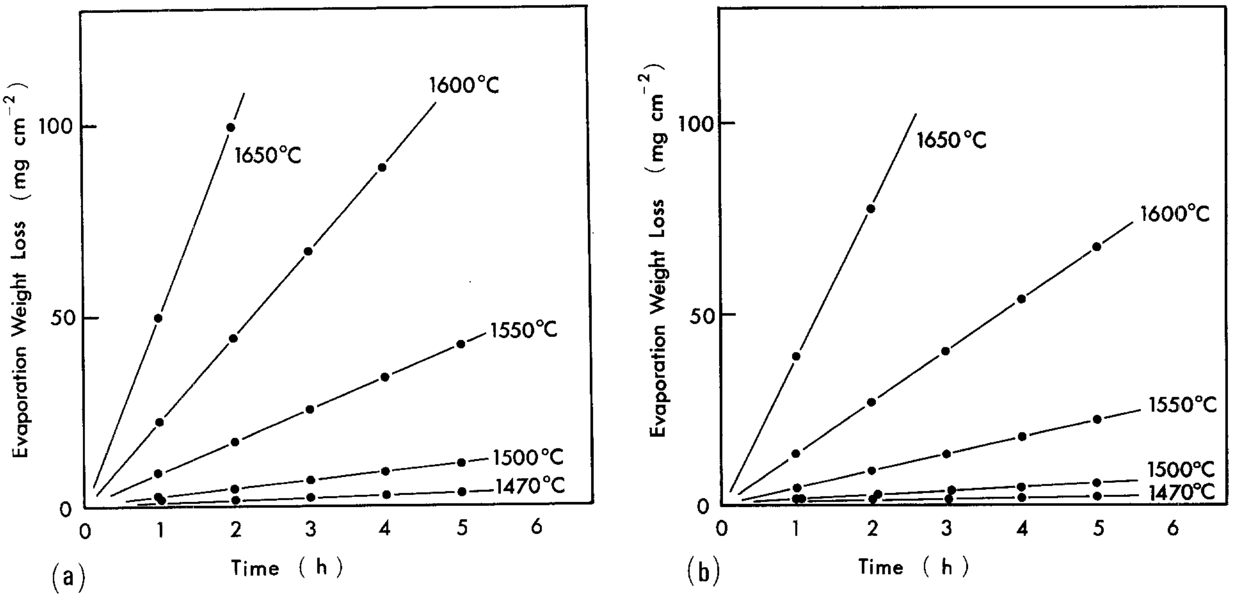

Figure 1 Relationship between heat-treatment time and weight loss by evaporation of (a) amorphous CVD-Si_3N_4 and (b) amorphous CVD-(Si_3N_4–C) composite, 6 wt % C.

JEOL DX-GO-S) and a transmission electron microscope (TEM) (Hitachi HU-10DS).

3. Results and discussion

Figs 1a and b show the relationship between weight loss by evaporation and heat-treatment time for the amorphous CVD-Si_3N_4 and the amorphous CVD-(Si_3N_4–C) composite, respectively, in the temperature range of 1470 to 1650° C. Below the temperature of 1400° C no weight loss has been observed. Both specimens showed a linear decrease of weight with time within this temperature range. The evaporation rate was calculated from the slope of these lines. Figs 1a and b clearly show that the evaporation rate of the amorphous CVD-(Si_3N_4–C) composite is 50 to 70% of that for the amorphous CVD–Si_3N_4. The weight change of both the graphite crucible and tungsten wire during the measurements was found to be negligibly small.

Figs 2a and b are the results of surface observations by an SEM of the amorphous CVD-Si_3N_4 and the amorphous CVD-(Si_3N_4-C) composite, respectively. Those samples were both heat-treated at 1400° C for about 3 h. The surface of the amorphous CVD-Si_3N_4 is nearly flat, but occasional cracks are also observed. These cracks seem to be caused by volume contraction occurred during the crystallization process. On the other hand, β-SiC particles with a diameter of about 100 nm were observed on the surface of the amorphous CVD-(Si_3N_4–C) composite giving the appearance of an emerald-coloured powder spread over the surface. The SEM observation shows that they are actually connected to each other to form a network structure. One of the typical colours of SiC is blue-green. Fig. 3 shows the surface of the amorphous CVD-(Si_3N_4–C) composite which is heat-treated at 1650° C for about 3 h until the decomposition had completed so that no further weight loss is observed. The surface consists of a three-dimensional network structure formed by each SiC particle. The outer size of the porous specimen after the heat-treatment was almost the same as that of pre-treatment. However, when the amorphous CVD-Si_3N_4 is heat-treated under similar conditions no observable substance remained due to the total evaporation of the composite. Fig. 4 presents a TEM observation of the particles which were showed in Fig. 3. These particles are identified to be β-SiC by electron and X-ray diffractions. The TEM observation shows that larger β-SiC particles result as both heat-treatment time and

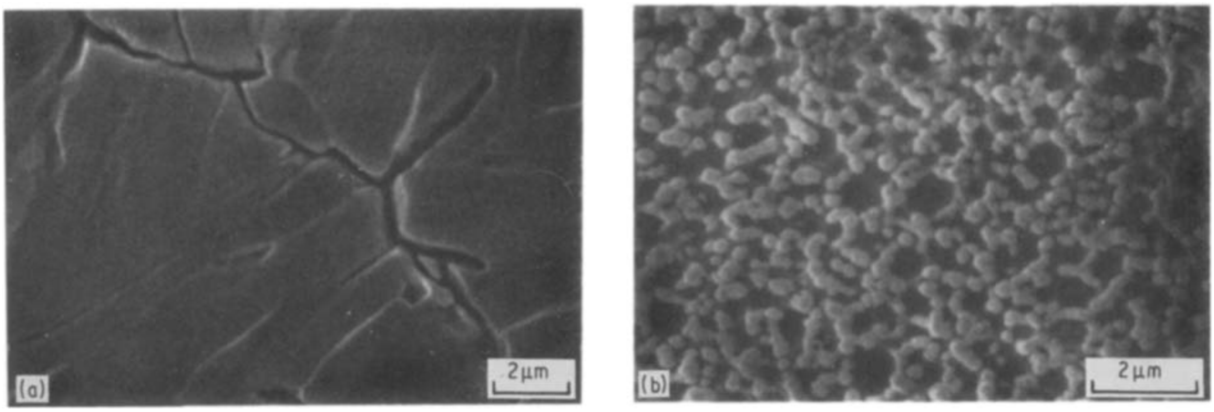

Figure 2 SEM observation of the surfaces of (a) amorphous CVD-Si_3N_4 and (b) amorphous CVD-(Si_3N_4–C) after a heat-treatment at 1400° C for 3 h.

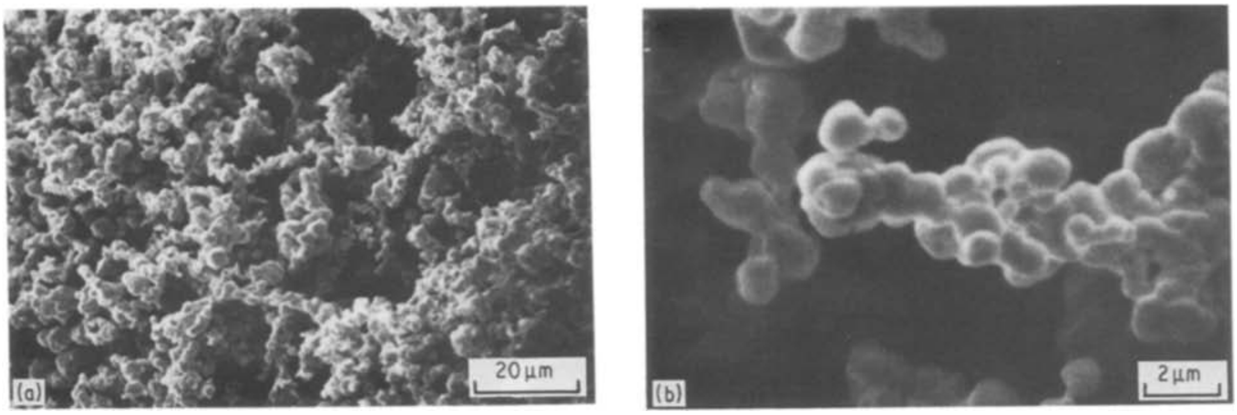

Figure 3 SEM observation of the surface of amorphous CVD-(Si_3N_4–C) composite after a heat-treatment at 1650° C for 3 h: (b) is a higher magnification of (a).

temperature are increased. This fact suggests that the growth or consolidation of the β-SiC particles has been accelerated due to the enhanced mass transport of SiC by surface diffusion and/or volatilization–condensation mechanisms at the high temperatures. As previously reported, the amorphous CVD-(Si_3N_4–C) composite is highly electrically conductive, its d.c. conductivity at the room temperature ranged from 10^{-3} to $10^{-1}\,\Omega^{-1}\,cm^{-1}$, and the activation energy for electrical conduction is reported to be 0.02 to 0.06 eV [4]. This high conductivity is considered to be a result of the current flow through the three-dimensional carbon networks shown in Fig. 3. The value of the activation energy agrees well with that of an amorphous carbon [5]. Previous studies by EPMA [3], ESCA [6] and HF (hydrofluoric acid) treatment [7] revealed that the amorphous CVD-(Si_3N_4–C) composite is a mixture of amorphous Si_3N_4 matrix and amorphous carbon dispersion.

When the mixture of Si_3N_4 and carbon is heated to high temperatures, the following chemical reaction will take place.

$$Si_3N_4(s) + 3C(s) \rightarrow 3SiC(s) + 2N_2(g) \qquad (1)$$

Fig. 5 indicates the calculated temperature dependence of the Gibbs standard free energy change and also that of the equilibrium N_2 partial pressure in Equation 1 using the JANAF table [8]. The highest vacuum used in the present work was about 10^{-6} torr, and the vacuum tends to decrease with the increased evaporation rate but even at 1650° C it is below 10^{-4} torr. Thus the chemical reaction as indicated by Equation 1 is thermodynamically feasible in all measurements. Hirai *et al.* [9] investigated the reaction between α-, β-Si_3N_4 and carbon powders in the temperature range of 1320 to 1760° C at N_2 pressure of 1 atm, and reported that the starting temperature of Equation 1 is more than 1490° C. However the reaction between the Si_3N_4 matrix and the carbon dispersion in the amorphous CVD-(Si_3N_4–C) composite took place at 1400° C. The difference in the reaction temperature of Equation 1 between the work of Hirai *et al.* and the present work may be caused by the difference of the N_2 partial pressure. Based on the stoichiometric relationship shown in Equation 1 the weight loss by the evaporation of the amorphous CVD-(Si_3N_4–C) composite containing 6 wt % carbon is calculated to be 80% of that for the carbon-free amorphous CVD-Si_3N_4. It was pointed out earlier in this paper that the experimentally found evaporation rate of the amorphous CVD-(Si_3N_4–C) composite is about 50 to 70% of that for the amorphous Si_3N_4; thus the experimental result agrees well with the above calculated value.

There are two well known methods in investigating the evaporation behaviour of solids. One is the Knudsen method in which the evaporation rate at an equilibrium condition is measured, and the other is the Langumuir method in which the evaporation rate at a non-equilibrium condition is measured [10]. The method used in the present work is the Langumuir method and the evaporation found by this method is called Langumuir free evaporation. The evaporation rate for the Langumuir free evaporation (J) is given

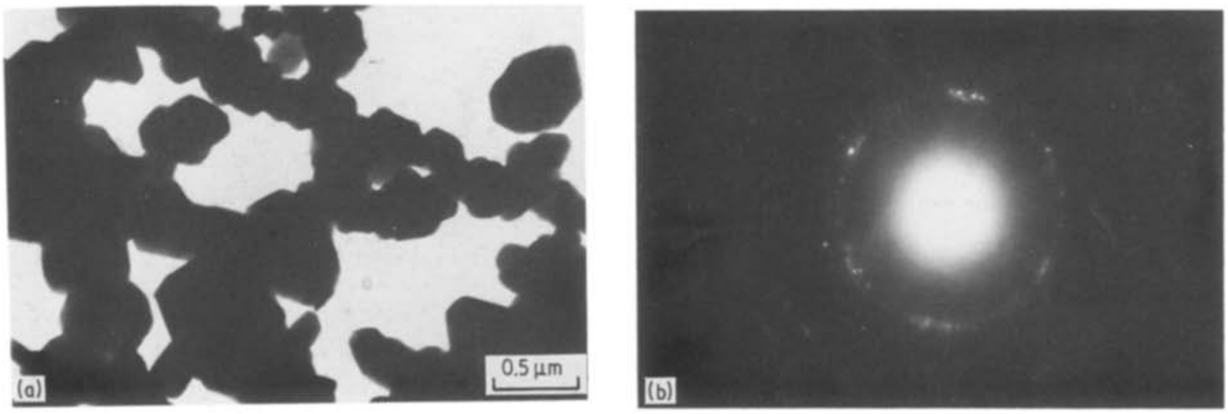

Figure 4 TEM observation of β-SiC particles, (a) electron micrograph and (b) electron diffraction pattern.

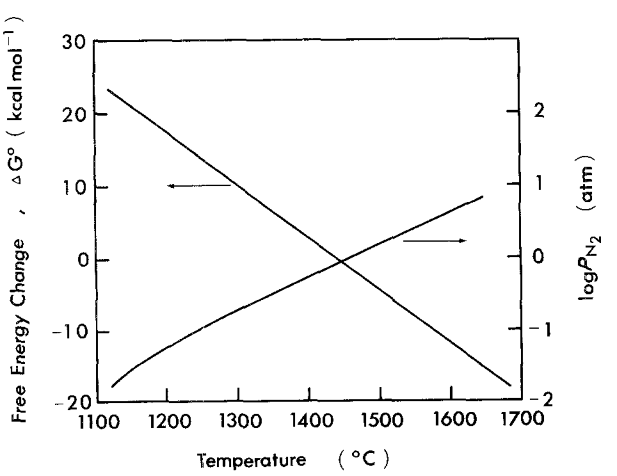

Figure 5 Temperature dependence of the standard Gibbs free energy change and equilibrium partial pressure of N_2.

by the following equation [11],

$$J = \alpha P/(2\pi MRT)^{1/2} \qquad (2)$$

where α is the evaporation coefficient, P is the equilibrium pressure of evaporating species, M is the molecular weight of evaporating species, R is the gas constant, T is the absolute temperature. The equilibrium pressure of evaporating species (P) can now be calculated using Equation 2 by knowing the evaporation rate. Wolff and Alcock [12] investigated the evaporation of a porous Si_3N_4 in the temperature range of 650 to 1400° C by the Langumuir method. The N_2 partial pressure calculated by Equation 2 using $\alpha = 1$ and $M = 28$ is found to be several orders smaller than the theoretical value. They reported that their samples contained a large amount of oxygen, and the evaporation of SiO gas controlled the rate-determining step for the evaporation of the Si_3N_4. Ryklis *et al.* [13] studied the evaporation of Si_3N_4 powder by using both the Langumuir and Knudsen methods in the temperature range of 1415 to 1500° C, and reported that the Si_3N_4 powder decomposed to solid or liquid silicon and N_2 gas which subsequently evaporated. The evaporation coefficient (α) for the Langumuir free evaporation was found to be less than 10^{-4}. Batha and Whitney [14] measured the evaporation rate of Si_3N_4 powder in the temperature range of 1490 to 1750° C under a constant volume condition. They found that the initial stage of the evaporation process is a first-ordered kinetic and its activation energy is 93 kcal mol^{-1}. This value is very close to the binding energy of 104 kcal mol^{-1} between silicon and nitrogen [15]. The later period of the evaporation is Jander's kinetic and its activation energy is 186 Kcal mol^{-1}. Liquid silicon was formed over the surface of the Si_3N_4 powder. They considered that the diffusion of nitrogen atom in the Si_3N_4 is the rate-determining step of the evaporation.

Previously reported results on the evaporation of Si_3N_4 all belong to the "incongruent" evaporation described by the following equation,

$$Si_3N_4(s) \rightarrow 3Si(s, l)\downarrow + 2N_2(g)\uparrow \qquad (3)$$

In the present work, free silicon was not detected within the specimen after its heat-treatment and condensed silicon was found in the low temperature regions of the furnace i.e. the observation port. These facts lead us to conclude that the "congruent" evaporation given by Equation 4 had taken place.

$$Si_3N_4(s) \rightarrow 3Si(g)\uparrow + 2N_2(g)\uparrow \qquad (4)$$

The reason that the free silicon has been observed in the past reports, is that the partial pressure of Si(g) in the furnace is higher, and/or evaporation temperature is lower, than those used in the present work, therefore it is difficult for silicon to evaporate.

Fig. 6 shows the temperature dependence of the evaporation rate for the amorphous CVD-Si_3N_4 and the amorphous CVD-(Si_3N_4–C) composite. The linear relationship exists between the logarithm of the evaporation rate and the reciprocal of the temperature for both specimens. The values of activation energy obtained from the slopes of these lines were both about 160 kcal mol^{-1}. The theoretical values calculated from Equation 2 are also shown by a broken line in Fig. 6. In calculating these values P is substituted by the decomposition pressure of Si_3N_4 obtained from JANAF table [8] and α is chosen to be 1. The activation energy calculated from the slope of the broken line is about 100 kcal mol^{-1} which is smaller than the present experimental value. It is well known that an evaporation coefficient (α) increases with increase of the temperature and reaches 1 at the melting point or sublimation temperature [16]. The evaporation coefficient (α) of the amorphous CVD-Si_3N_4 can be estimated by using the measured evaporation rate after Equation 2, and it was found that at the temperature of 1527° C, $\alpha = 0.21$ and at 1627° C, $\alpha = 0.46$. These values of α for the amorphous CVD-

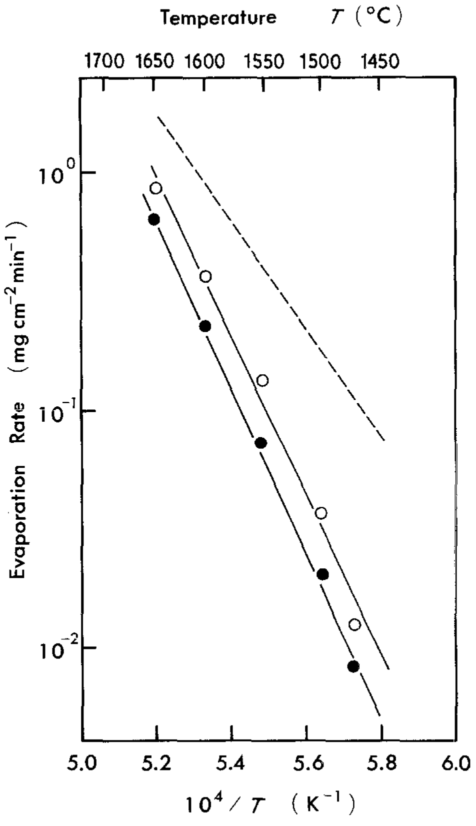

Figure 6 Temperature dependence of evaporation rates: A broken line is calculated from Equation 2 (○) Am. CVD-Si_3N_4, (●) Am. CVD-(Si_3N_4–C) 6 wt % C.

Si_3N_4 agree well with those reported for oxides such as Cr_2O_3 and Y_2O_3 in the same temperature range [16]. The larger values of the activation energy measured in the present experiment compared to the theoretically calculated values, may be caused by the increase of evaporation coefficient α with the increase of the temperature.

4. Conclusion

The amorphous CVD-Si_3N_4 and the amorphous CVD-(Si_3N_4–C) composite containing 6 wt % carbon were heat-treated in the temperature range of 1400 to 1650° C in a vacuum of about 10^{-6} torr. The weight of these specimens decreased linearly with time for all temperatures. The evaporation rate of the amorphous CVD-(Si_3N_4–C) composite is 50 to 70% of that for the amorphous CVD-Si_3N_4. The decrease of the evaporation rate for the carbon containing specimen is caused by the formation of β-SiC by the chemical reaction of the carbon in the amorphous CVD-(Si_3N_4–C) composite and the amorphous Si_3N_4 matrix. The values of activation energy for evaporation of these specimens are both about 160 kcal mol^{-1}. This value is greater than the previously reported values as well as that calculated from thermodynamic data (about 100 kcal mol^{-1}). This difference may be caused by the increase of the evaporation coefficient with increasing temperature. A network of β-SiC particles was observed on the surface of the amorphous CVD-(Si_3N_4–C) composite as the evaporation proceeded. Thus β-SiC particles are formed by the reaction between the carbon in the amorphous CVD-(Si_3N_4–C) composite and the Si_3N_4 matrix. The amorphous CVD-(Si_3N_4–C) composite seems to have an excellent resistance to high temperature evaporation.

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