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Thermochemical studies of the reactions between silicon nitride and carbon

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Abstract

The reactions between silicon nitride and carbon were studied using thermogravimetric analysis and X-ray diffraction. A two-stage mass loss process was observed during the interaction. The first beginning at around 1130°C is related to the reaction between carbon and the surface silica of the silicon nitride powder; the second starting at about 1280°C corresponds to the silicon nitride and carbon interaction. The majority of the silicon carbide was formed during the second stage without the assistance of the silica on the silicon nitride powder surfaces — a reaction mechanism for the Si_3N_4–C system which is different from that suggested by other researchers.

INTRODUCTION

Silicon nitride as a potential high temperature engineering material has attracted much attention during the past two decades because of its superior high temperature properties, such as high strength, high chemical stability and good thermal shock resistance at high temperatures. Recently we have reported that through the partial carbothermal reduction of silicon nitride, silicon carbide whiskers can be synthesized in situ in silicon nitride powders [1]. The resultant chemically mixed silicon nitride powders and silicon carbide whiskers can be subsequently made into silicon carbide whisker reinforced silicon nitride matrix composites [2]. Such a so-called chemical mixing process has certain advantages compared with the conventional physical mixing process, such as improving the homogeneity of the whisker–powder mixture and minimizing the individual handling of SiC whiskers which are considered potentially harmful to human health [3].

As we have demonstrated in our previous study [1], the phase evolution in the Si_3N_4–C system is a strongly thermally activated process, and we have suggested that the formation of silicon carbide through the interaction

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of silicon nitride and carbon is primarily related to the decomposition of silicon nitride, and the reaction of the resulting silicon with carbon. Another well-known model for the reactions in the Si_3N_4–C system was proposed by Colquhoun et al. [4]. They suggested that the reactions involved the volatilization of the surface silica of silicon nitride powder to form silicon monoxide which reacted with carbon to produce carbon monoxide; the latter, in turn, carburized the silicon nitride to form silicon carbide.

The objectives of the present study, therefore, were to investigate further the thermochemical activities during the silicon nitride and carbon interaction primarily by thermoanalytical techniques, and to reveal the mechanism of the reactions between silicon nitride and carbon.

EXPERIMENTAL

The silicon nitride used in this study was SN-E 10 Si_3N_4 powder produced by Ube Industries Ltd. of Japan. The surface area of the powder is 11.5 $m^2\ g^{-1}$ and the particle size is about 0.2 μm. The oxygen impurity content is 1.26 mass% and the powder consists of more than 95% α-Si_3N_4. The carbon-source material was Monarch 900 carbon black produced by Cabot Corporation of the USA; its surface area is 230 $m^2\ g^{-1}$ and particle size 15 nm. The carbon black has a 2.0 mass% volatile content.

The silicon nitride and carbon black powders were mixed (molar ratio $Si_3N_4 : C = 1:6$) in propanol by ball milling for 24 h using silicon nitride milling media. The slurry was then heated in an open container under a flame hood to evaporate the propanol quickly and prevent segregation. The mixture was further dried at 120°C for 8 h and then sieved through a 100 mesh screen before being used for thermal analysis.

Thermogravimetric analysis (TGA) was conducted on a Setaram TAG 24 thermoanalyzer (Setaram, France) with a controlled flow of carrier gases at a rate of approximately 40 ml min^{-1}. Samples were evenly distributed in a covered graphite crucible (diameter 10 mm and height 7 mm) with sample masses kept at about 20 mg for all the tests. To compensate for the buoyancy effect, a blank run using calcined graphite powders was conducted following each of the TGA runs. The thermoanalytical data were collected and analyzed on a microcomputer.

After TGA measurement, the samples were examined by X-ray diffraction (XRD) for phase identification using Cu K_α radiation on a NORELCO wide range goniometer (Philips Electronic Instruments, USA).

RESULTS AND DISCUSSION

Although the system under study consists of two components, silicon nitride and carbon, the higher free energy of formation of silica will cause

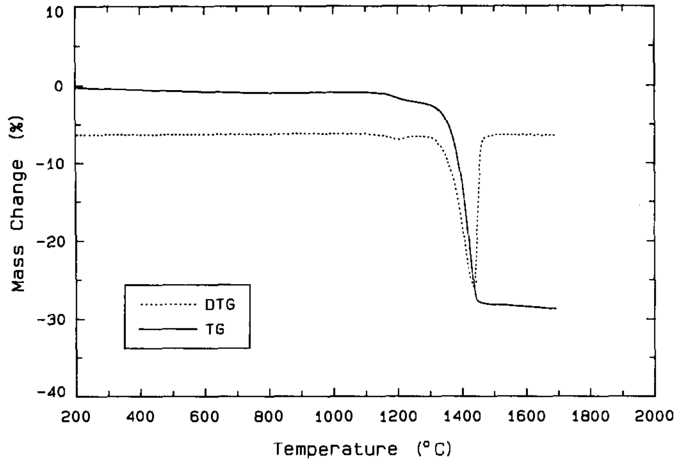

Fig. 1. TG and DTG traces of a silicon nitride and carbon black mixture heated at 10°C min^{-1} in flowing helium.

oxidation of silicon nitride to form a silica surface layer in the presence of an oxygen or a water-containing atmosphere [4–6]. Therefore the system we were studying was actually a Si_3N_4–C–SiO_2 three-component system, the silica surface layer serving as a barrier between the silicon nitride and carbon particles. In the following calculations of theoretical mass losses, we assumed the total oxygen impurity content to be in the form of silica existing on the surfaces of silicon nitride particles.

Figure 1 is a TGA graph showing the thermogravimetric (TG) and derivative thermogravimetric (DTG) traces of a silicon nitride and carbon black mixture. The sample was heated at 10°C min^{-1} in flowing helium (research grade, minimum purity 99.9995%). A two-stage mass loss process is clearly seen. The first stage, starting at about 1130°C, had a mass loss of about 1.4% at 1280°C when the second stage started. During the second stage the sample lost about 26.3% of its mass. The peak of the DTG trace of the second stage was at 1425°C, and the mass loss process was complete at 1480°C.

Using the same TGA conditions as those for the experiment shown in Fig. 1, a TGA run was done on the pure starting silicon nitride powder, and the result is shown in Fig. 2. The mass loss process in Fig. 2 corresponds to the decomposition of silicon nitride in a nitrogen-free atmosphere. The minor mass loss starting at 1130°C as observed in Fig. 1 was absent in Fig. 2, which indicates that this first-stage mass loss cannot be attributed to the volatilization of the surface silica of the silicon nitride. In addition, although the carbon black used in this study contains 2 mass% volatile content, the volatilization of impurities is finished before 900°C, which accounts for part of the low temperature gradual mass loss as seen in Fig. 1.

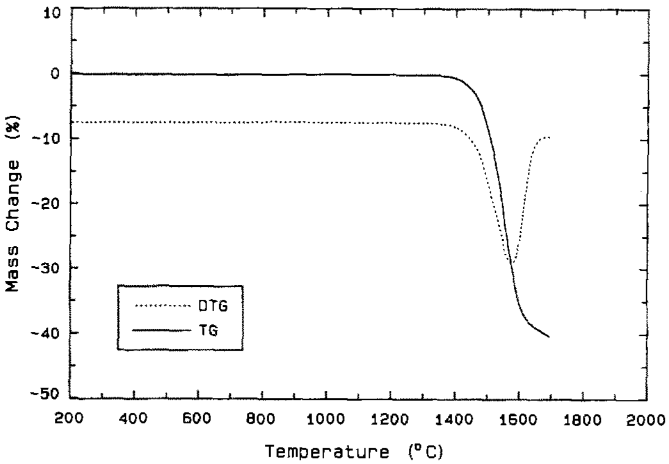

Fig. 2. TG and DTG traces of the pure starting silicon nitride powder tested under the same conditions as in Fig. 1.

It has been reported that in the presence of carbon, silica will react with carbon at high temperature through the following reactions [7–10]:

$$SiO_2(s) + C(s) = SiO(g) + CO(g) \tag{1}$$

$$SiO(g) + 2C(s) = SiC(s) + CO(g) \tag{2}$$

or through a global reaction

$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g) \tag{3}$$

According to reaction (3) the theoretical mass loss due to the evolution of CO is 58.28%. This is converted to 1.46% for the sample used in the TGA of Fig. 1 (molar ratio $Si_3N_4 : C = 1:6$, and 1.26 mass% oxygen content in Si_3N_4), which is in good agreement with the first-stage mass loss as observed in Fig. 1.

Once the surface silica of the silicon nitride powder was extracted through reaction (3), silicon nitride was exposed directly to carbon black. As seen in Fig. 2, under a helium atmosphere, silicon nitride started to decompose at around 1300°C yielding silicon and N_2 [11,12]:

$$Si_3N_4(s) = 3Si(s, l) + 2N_2(g) \tag{4}$$

In the presence of carbon black, the residual silicon will react with carbon to form silicon carbide [1,7,13,14]. At temperatures below 1410°C, the silicon is in solid form, and it reacts with carbon by diffusion:

$$Si(s) + C(s) = SiC(s) \tag{5}$$

Reaction (5) can proceed at a measurable rate at 1200°C [13,14]. With melted zinc–aluminum alloy containing silicon and carbon, Baumann [13]

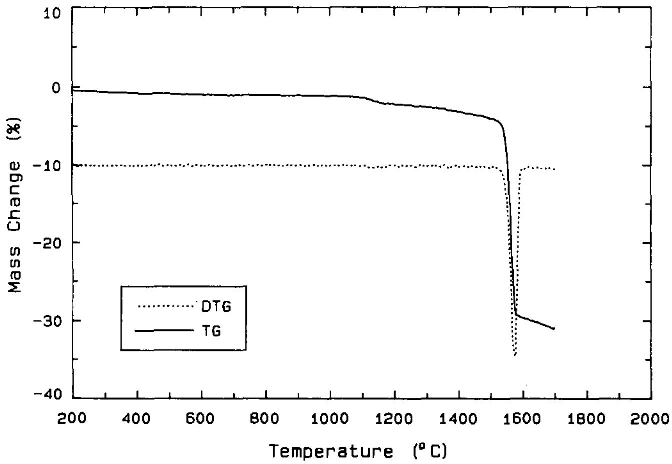

Fig. 3. TG and DTG traces of a silicon nitride and carbon black mixture heated in N_2 and under conditions otherwise identical with those of Fig. 1.

has observed the reaction of silicon with carbon to form silicon carbide at a temperature as low as 525°C.

From the second stage of mass loss shown in Fig. 1, we can see that as the temperature increased, the rate of reaction increased and reached its maximum at 1425°C as illustrated by the DTG peak, which was right above the melting point of silicon, 1410°C. In the presence of liquid silicon the reaction between silicon and carbon is facilitated and becomes strongly thermodynamically favorable:

$$\mathrm{Si(l)} + \mathrm{C(s)} = \mathrm{SiC(s)} \tag{6}$$

$$\Delta G^\circ = -113.930 + 0.036T \quad (\mathrm{kJ\ mol^{-1}})\ [7]$$

The resulting overall reaction during the second stage can be represented by

$$\mathrm{Si_3N_4(s)} + 3\mathrm{C(s)} = 3\mathrm{SiC(s)} + 2\mathrm{N_2(g)} \tag{7}$$

with a theoretical mass loss of 31.78%. For the sample used for the TGA in Fig. 1, this theoretical mass loss is converted to 26.42%, which is in excellent agreement with the experimental measurement of the second-stage mass loss in Fig. 1.

Figure 3 shows the TGA traces of a sample of silicon nitride and carbon mixture run in a nitrogen atmosphere (ultra high purity, minimum 99.999%) and under conditions otherwise identical with those of Fig. 1. The sample exhibited a two-stage mass loss, but the onset temperatures were different from those observed in Fig. 1. The first stage of mass loss in N_2 started at 1080°C and the second stage at 1510°C. The presence of nitrogen suppressed the second stage mass loss to higher temperature, which can be easily understood if the reaction proceeded according to reaction (7). The

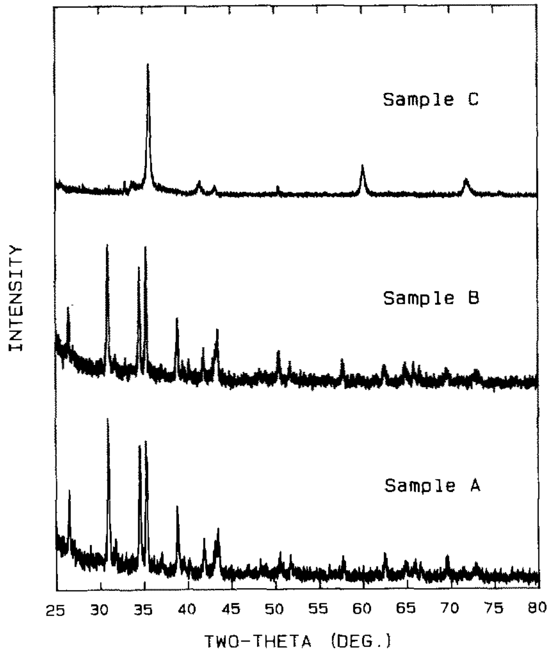

Fig. 4. XRD patterns of samples: sample A, raw powder mixture of silicon nitride and carbon; sample B, quenched from 1160°C after a hold of 1 h in helium; sample C, quenched from 1350°C after a hold of 2 h in helium.

lowering of the onset temperature of the first-stage mass loss is other evidence that this mass loss process is related to the reaction between silica and carbon, because with the participation of nitrogen, silica will react with carbon to form silicon nitride

$$3SiO_2(s) + 6C(s) + 2N_2(g) = Si_3N_4(s) + 6CO(g) \tag{8}$$

and this reaction takes place at a lower temperature than reaction (3) as concluded by other researchers on the basis of both experimental and thermodynamic considerations [15–18]. It has been discovered that in the system of SiO_2–C–N_2, silicon nitride is a low temperature product, whereas silicon carbide is a high temperature product.

Figure 4 presents the XRD patterns of three samples: sample A is the raw powder mixture, sample B was quenched from 1160°C after a hold of 1 h in helium, and sample C was quenched from 1350°C after a hold of 2 h in helium. As predicted from the above reaction mechanism, the sample quenched from 1160°C after the first-stage reaction was completed did not show any significant phase change as compared with the raw powder. The amount of SiC thus far formed, according to reaction (3), was about 1.05 mass% of the sample used for XRD. This was difficult to detect by XRD. The bulk of silicon nitride powders remained unreacted. By the end of the second-stage reaction, however, the silicon nitride has been totally converted to β-SiC according to reaction (7) as shown by the XRD pattern of sample C.

CONCLUSIONS

Both the TGA measurement and XRD analysis confirm that the solid state reactions between silicon nitride and carbon take place in two stages. The first stage corresponds to the reaction between the surface silica of silicon nitride powder and carbon (reaction (3)) while the bulk of the silicon nitride remains unreacted. The amount of silicon carbide formed during the first stage is too small to be detected by XRD. The majority of the silicon carbide is formed during the second stage through direct interaction between silicon nitride and carbon without the aid of surface silica of the silicon nitride, as opposed to the mechanism proposed by Colquhoun et al. [4]. The overall reaction can be expressed by reaction (7).

The predicted theoretical mass losses according to reactions (3) and (7) agree very well with the experimental measurements of TGA. In the presence of sufficient carbon, complete conversion of silicon nitride to silicon carbide will occur by carbothermal reduction of silicon nitride.

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