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THE CRITERION OF FORMING THE CARBON LAYER ON THE INTERFACE OF THE SiC FIBER REINFORCED LITHIUM ALUMINOSILICATE(LAS) COMPOSITE
Thermodynamic and mass spectrometric thermal analysis

Changwei Lu, Yufeng Zhang, Xuehua Yang, Yunxian Chen, Tonggeng Xi and Jingkun Guo

Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

Abstract

The criterion of forming the carbon layer on the interface of the SiC fiber reinforced lithium alumino-silicate(LAS) composite studied by thermodynamic and mass spectrometric thermal analysis was presented for the first time in this paper.

Keywords: carbon layer, mass spectrometric, SiC fiber/LAS composite, thermal analysis, thermodynamic

Introduction

The SiC fiber reinforced lithium alumino-silicate(LAS) composite has high strength and breaking toughness and can keep this superiority up to 1000°C [1–4]. There were only a few papers relating to its thermal decomposition mechanism seen in literature. It has been pointed by some researchers that the carbon layer may be formed on the interface between fiber and the matrix, meanwhile due to its lower shearing stress, and that the carbon layer should be considered as the key of maintaning the high breaking toughness and demage-resisting for the SiC fiber/LAS composite [5, 6]. Benson *et al.* characterized the balanced diffusion of the Nicalon SiC fiber by an ideal interface model [7]. R. Chain *et al.* studied the micro-structure of the SiC fiber reinforced glass matrix composite by scanning electron microscope [5], but no carbon layer on the interface was detected. We studied the thermal decomposition processes of the SiC/LAS composite from room temperature to 1530°C by thermodynamic calculation and mass spectrometric analysis (TG-DTA-MS) and presented for the first time the criterion of forming the carbon layer on the interface of the composite.

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Experimental

Sample preparation

The Nicalon SiC fiber (produced by Japan Carbon Company) with 15 μm diameter, 200 Gpa elasticity modulus and 3 Gpa tensile strength was homogeneously distributed in the slurry of the lithium aluminum silicate micro crystal glass through melting and supersonic mixing. The resulting block green mass was sintered by hot-press sintering.

Mass spectrometric thermal analysis (TG-DTA-MS)

The 120 mg powdered uncrystallized and crystallized SiC/LAS samples were weighed in alumina crucibles separately. The Netzsch-STA 429 Simultaneous Thermal Analyzer coupled with Balzers QMG-511 Quadrupole Mass Spectrometer was used. The TG and DTA full scales were 25 mg and 0.2 mV respectively. The heating rate was 10 deg·min^{-1}. The chart speed was 240 mm/h. The atmosphere was air. The proposed parameters for quadrupole mass spectroscopy analysis are shown in Table 1.

Table 1 Parameters for quadrupole mass spectroscopy analysis

Proposed channel	1	2	3	4
Positive ion	C^+	C^+	CO_2^+	CO_2^+
M/Z	12	12	44	44
Intensity, *A*	10^{-11}	10^{-11}	10^{-11}	10^{-9}
Amplifying rate	×10	×1	×1	×10

Channels 5 and 6 were proposed as the curves of the P and the temperature T, separately. The Faraday cup was used for detecting signals. The mass scanning speed was 1 amu.s^{-1}. The time for mass filtering was 0.03 s. The vacuum for the system was 2×10^{-5} Torr.

Results and discussion

TG-DTA-MS results

The TG-DTA-MS results for the SiC/LAS composite powder were shown in Fig. 1 (noncrystalline powder) and in Fig. 3 (crystalline powder). There was about 1 mg mass loss at 382–500°C in the TG curve of noncrystalline powder in Fig. 1, and there was about 0.5 mg mass loss at 570–710°C in the TG curve in Fig. 3. In Fig. 1, the corresponding DTA endothermic peak of noncrystalline

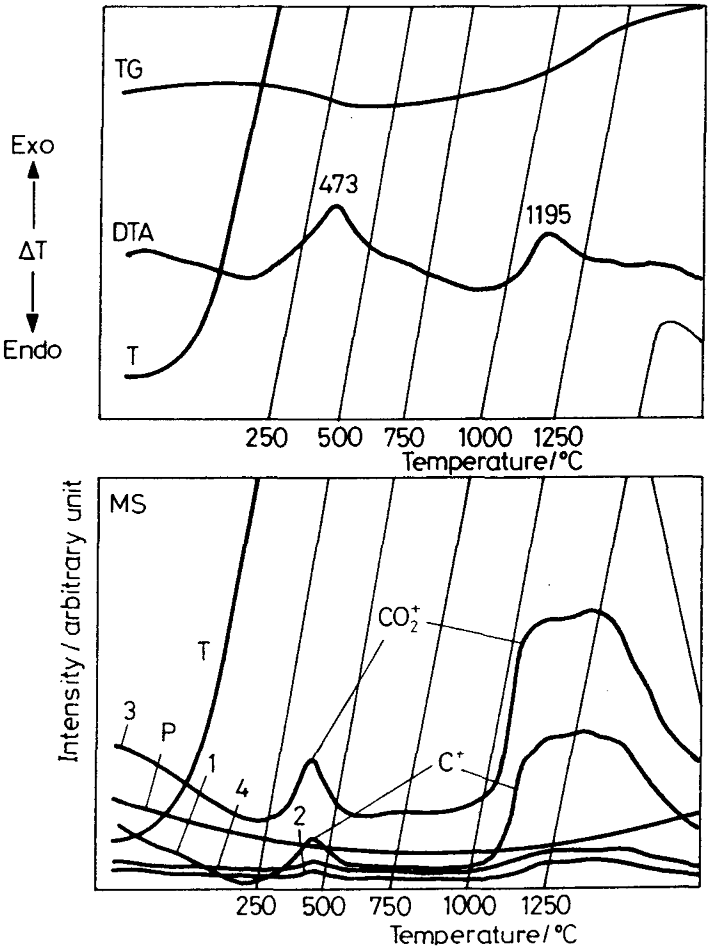

Fig. 1 The TG-DTA-MS curves for the uncrystallized SiC fiber/LAS composite powder

powder appeared at 473°C, and that of the crystalline powder appeared at 670°C in Fig. 3. The corresponding MS peaks CO_2^+ (m/z,44) of noncrystalline powder appeared at 473°C in the channel 3 and the channel 4 in Fig. 1. The corresponding MS peak CO_2^+ (m/z,44) of crystallized powder appeared at 670°C in channels 3 and 4 in Fig. 3. The corresponding smaller peaks C^+ (m/z,12) also appeared in the channels 1 and 2 at 473°C (noncrystalline powder, in Fig. 1) and 670°C (crystalline powder, in Fig. 3) separately. All these results show that the CO_2(g) and the smaller amount of dissociated carbon were released in the first step of the thermal decomposition of the SiC/LAS composite.

There was about 2 mg mass increase at 582–1145°C in the TG curve of noncrystalline powder in Fig. 1. For the crystalline powder, there was about 5 mg mass increase at 1120–1210°C in the TG curve in Fig. 3. It can be considered as SiO_2 and CO_2(g) formed by the reaction between the SiC and the excess oxygen. The other DTA endothermic peaks appeared at 1195°C (noncrystalline powder, in Fig. 1) and 1186°C (crystalline powder, in Fig. 3) separately. The corresponding MS peaks CO_2^+ (*m*/*z*,44) of noncrystalline powder and crystalline powder appeared at 1200°C in the channels 3 and 4 (Figs 1 and 3). Both corresponding MS peaks C^+ (*m*/*z*,12) also appeared at 1200°C in the channels 1 and 2 (Figs 1 and 3). The mass increase appeared at 1145–1530°C shows that the SiO_2 were produced steadily during the reaction.

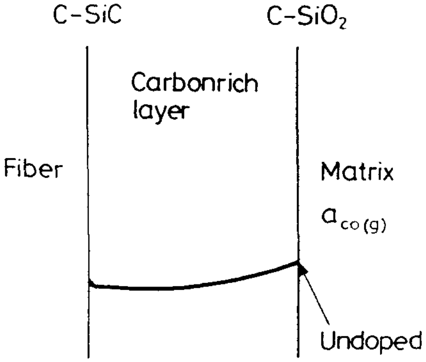

Fig. 2 Idealized interfacial model for Nicalon SiC/glass matrix

Benson *et al.* presented a model for characterizing the interface of the glass matrix. They pointed out that due to the Nicalon SiC is a kind of C–Si–O compound with non-stereochemistry, at a high temperature, the excess oxygen in fiber reacts with the dissociated carbon and to form CO(g). The proposed equation for the reaction is the follows:

$$2C + O_2 \text{ (excess oxygen in fiber)} \rightarrow 2CO(g) \tag{1}$$

The resulting CO in fiber reached the interface between the fiber and the matrix. At the interface, the SiC in the fiber was oxidized by the CO. At last, the SiO_2 and C were produced. The reaction equation can be proposed as follows:

$$SiC + 2CO \rightarrow SiO_2 + 3C \tag{2}$$

The interface model for characterizing the balanced diffusion was shown in Fig. 2. The model indicates that if a carbon layer was formed (the proposed carbon layer was continuous), two new interfaces would exist. On the C–SiO_2 interface, the excess oxygen from the glass matrix reacts with the carbon to form CO which in term reacts with the SiC as follows:

$$2C + O_2 \text{ (excess oxygen in the glass matrix)} \rightarrow 2CO(g) \tag{3}$$

$$SiC + 2CO \rightarrow 3C + SiO_2 \; (P_{CO} > 0.25 \text{ atm}) \tag{4}$$

As a result, the C and the SiO_2 were kept in a balanced state on the C–SiO_2 interface. The TG-DTA-MS results show that the C^+ (m/z,12) at 1200°C should be the one criterion for forming the carbon layer at the interface due to the reaction between SiC and CO. The MS peaks CO_2^+ (m/z,44) may be produced by the further oxidation of the carbon or the reaction between SiC and the excess oxygen [8].

$$SiC + 2O_2 \rightarrow SiO_2 + CO_2(g) \tag{5}$$

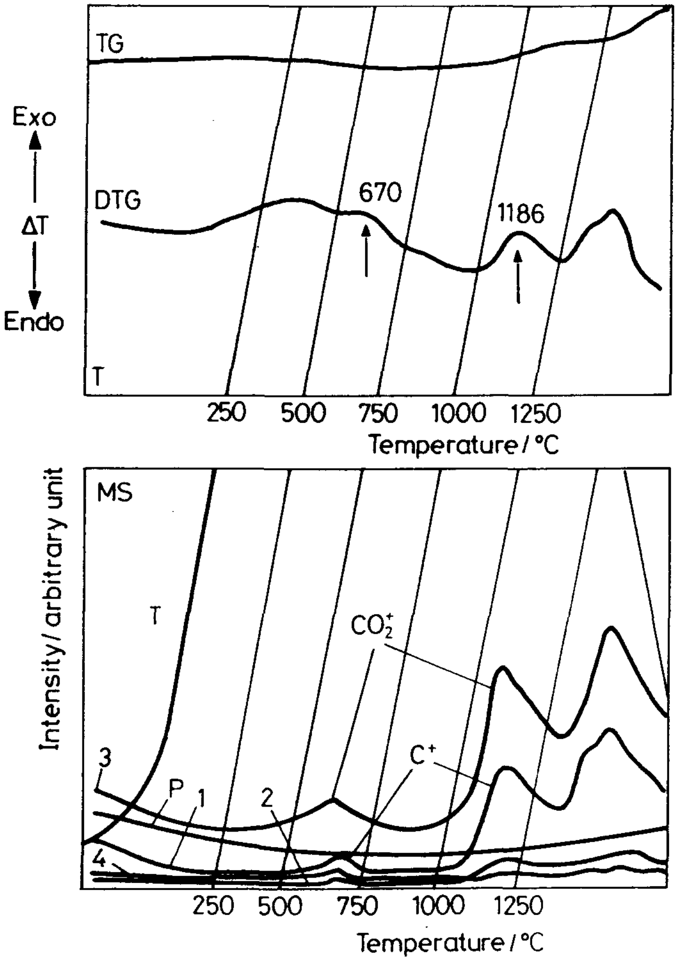

Fig. 3 The TG-DTA-MS curve for the crystallized SiC fiber/LAS composite powder

The thermodynamic calculation and the mass spectrometric analysis

Under the standard state, the appropriate relationship between the free enthalpy of the reaction and the temperature for SiC and CO (Eq. 2) should be:

$$\Delta G_i^\circ = -147360 + 84.54\,T \tag{6}$$

According to thermodynamics, the reaction for the SiC and the CO should be possible when the temperature is lower than 1470°C. However, the chemical reaction may be limited by the other conditions such as the dynamic conditions, for example, the amount of CO formed. Firstly, CO would not form and diffuse to the interface at lower temperatures. Secondly, the reaction can only be enhanced only at a certain temperature. It can be seen from the MS results that carbon and CO_2 would form over 1100°C. Therefore, the reaction between SiC and CO can only be carried out at that temperature. Besides the carbon reacting with the excess oxygen in SiC to form CO, the reaction between carbon and excess oxygen in the LAS matrix also produces CO. Based on the Bensons' interface model, it can be seen that the partial pressures of CO on both interfaces were the same [7].

Conclusions

During the thermal decomposition process of the SiC fiber/LAS composite, for the noncrystalline powder, the first release of the CO_2 and small amount of dissociated carbon took place at 473°C; for the crystalline powder, the first step of thermal decomposition temperature was 673°C. When the temperature was increased near to 1200°C, CO_2 and much more dissociated carbon were released secondly. Through the thermodynamic calculation and by mass spectrometric analysis, the carbon layer formed at the interface of SiC fiber/LAS reinforced glass-ceramic matrix composite.

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Zusammenfassung — Vorliegend wird erstmals über das mittels thermodynamischer und massenspektrometrischer Thermoanalyse bestimmte Kriterium für die Bildung der Kohlenstoffschicht am Übergang des Verbundwerkstoffes SiC-fiberverstärktes Lithiumaluminosilikat berichtet.