

FORMATION OF OXIDATION-RESISTANT CARBON COMPOSITES FROM EXFOLIATED GRAPHITE AND SILICONE

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Introduction

Exfoliated graphite is known to have very high sorption capacity for oils. Taking advantage of this property, we prepared the precursors composed of exfoliated graphite (EG) and metal organic complexes or silicone. By heating these precursors in inert atmospheres, a variety of carbon composites containing metals, metal oxides, and/or ceramics are possible to synthesize. In the present work, the results with EG containing silicone are reported. It produces oxidation-resistant C/Si/O composites and β -SiC depending on the heat treatment temperature (HTT).

Experimental

Two types of low molecular weight silicone, VC-4: $\{\text{CH}_3(\text{CH}=\text{CH}_2)\text{Si}\}_n$ ($n=3-7$) and KF-99B: $(\text{CH}_3)_3\text{Si-O}\{\text{CH}_3(\text{H})\text{SiO}\}_m\text{Si}(\text{CH}_3)_3$ ($m\approx 20$), were used by courtesy of Shin-Etsu Chemical Co. Ltd. The 43g of VC-4 and 31g of KF-99B were dissolved into 100 cm³ of toluene with 0.5g of Pt catalyst (Shin-Etsu Chemical PL-8) and 0.5g of catalyst regulator (Shin-Etsu Chemical PLR-31), then 2.05-4.4 g of EG were added. Sorption of the mixture by EG completed within a few minutes. After drying in a vacuum oven at 100°C for 30 min, silicone compounds were polymerized at 300°C for 1 h in air. The precursors thus obtained were flakes of a few millimeters in size. The precursors were treated at various HTTs up to 1600°C in a stream of argon using graphite boats. Characterization of the products was done by XRD (Cu K α), TG-DTA, SEM, OM, and MAS-NMR.

Results and Discussion

The yields and XRD patterns of the products by 1 h at various HTTs are shown in Figs. 1 and 2. Chemical composition of the precursor and the products at 1300 and 1600°C is shown in Table 1. Carbon 002 peak from EG remains up to 1400°C and peaks from β -SiC starts to appear at this temperature. Above 1400°C, products are a single phase of β -SiC by XRD. A small peak on the left side of β -SiC 111 peak observed for 1600°C product is probably due to stacking faults. The chemical composition of the product at 1600°C in Table I corresponds to $\text{Si}_{0.93}\text{C}_{1.00}\text{O}_{0.05}$, indicating fairly pure silicon carbide. This was confirmed also by MAS-NMR as shown in Fig. 3. The peak is sharp and narrow, indicating that the product is well crystallized β -SiC in consistent with XRD pattern, though a very weak peak due

to SiO_2 is observed. SEM observation revealed that the products were powder of sub-micrometers in size. The same XRD pattern was obtained by 10 h heating at 1500°C as shown in Fig. 4, and the yield was 39 mass%, which was higher than that at 1600°C in Fig. 1. Further, the product by 10 h heating at 1400°C (Fig. 4) showed very similar XRD pattern to that by 1 h heating at 1500°C (Fig. 1). Thus it was that the present process can produce fine powder of β -SiC at relatively low temperatures with high yield.

The products by $\text{HTT}\leq 1300^\circ\text{C}$ were black flakes which resemble the precursors. Many particles smaller than ca. 100 nm were observed on the flakes by SEM but no SiO_2 peaks are observed by XRD as shown in Fig. 2. MAS-NMR of the 1300°C products showed the presence of Si species bonding to both C and O and those bonding only to O. Therefore, there may be some silicon oxides but no crystallized ones. These results imply that the products by $\text{HTT}\leq 1300^\circ\text{C}$ were not simple mixtures of EG and SiO_2 .

Oxidation tests of the products were carried out in pure O_2 . An example for the product at 1000°C is shown in Fig. 5. The samples were heated at 10 K min⁻¹ in Ar up to 1000°C then the atmosphere was changed to O_2 , and they were kept at that temperature. Just after changing atmosphere, a sudden mass loss took place and it was around 7.5 mass% for 1000°C products (Fig. 5) and around 6.5 mass% for 1300°C products. No mass changes were observed for 1 h after the initial ones as can be seen in Fig. 5. Based on these results, pre-oxidation of the sample was carried out, which was heating at 10 K min⁻¹ up to 1000°C in O_2 then cooling to room temperature. The samples thus treated showed no mass loss or a small mass gain (Fig. 5) by the same oxidation tests. All the samples remained black and no SiO_2 peaks were observed by XRD after the oxidation tests. To sum up, the present process is useful to produce C/Si/O composites and SiC. Commonly used silicone oils are easily taken into EG by sorption but they are not useful to the present method because they evaporate at relatively low temperatures.

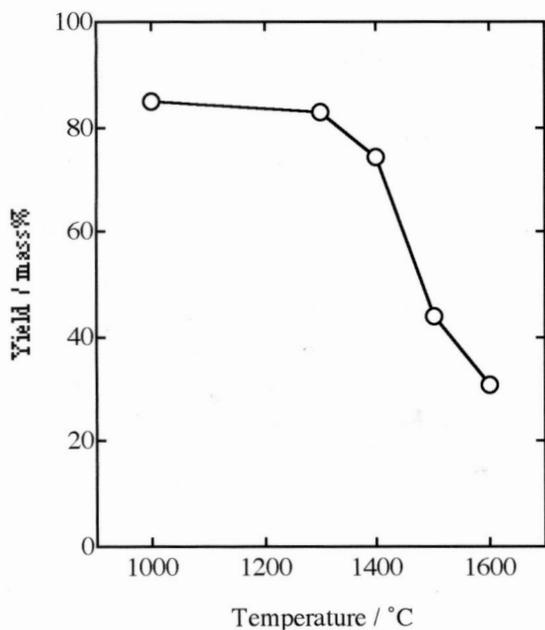


Fig. 1 Yield after 1 h HTT in Ar.

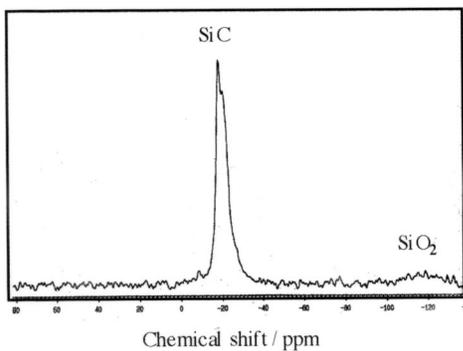


Fig. 3 NMR spectrum of 1600°C product.

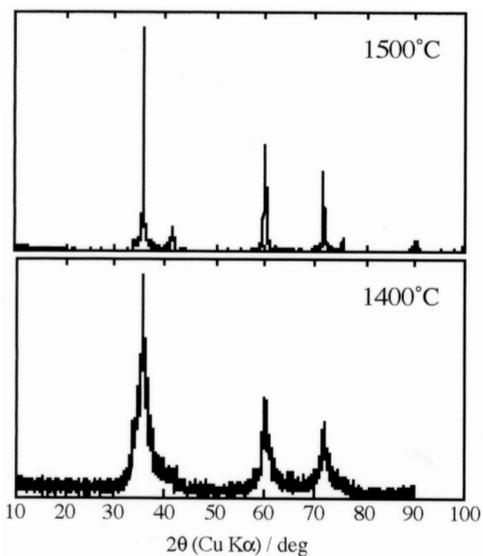


Fig. 4 XRD patterns of the products by 10 h HTT.

Table 1 Chemical composition (mass%)

	C	Si	O	H
Precursor	27	38	*	6.1
1300°C product	30	38	*	<0.1
1600°C product	30	65	2	<0.1

* reproducible data were not obtained so far.

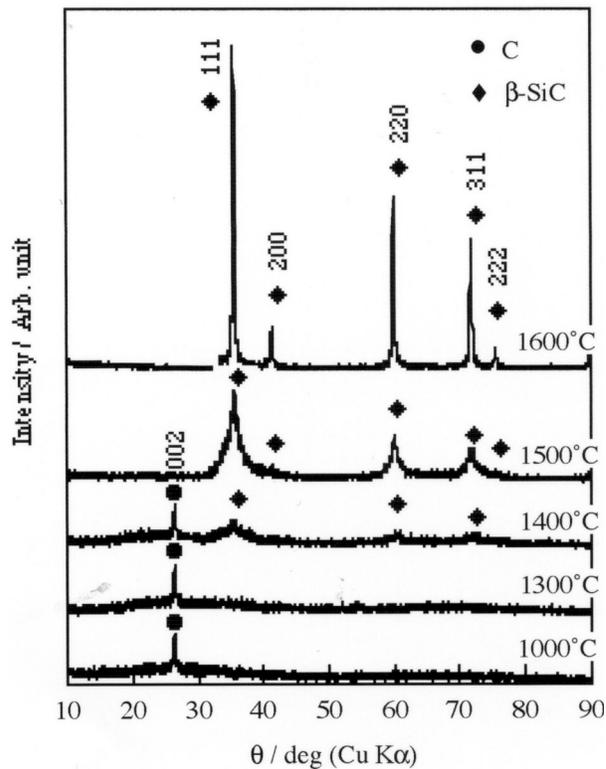


Fig. 2 XRD patterns of the products by 1 h HTT.

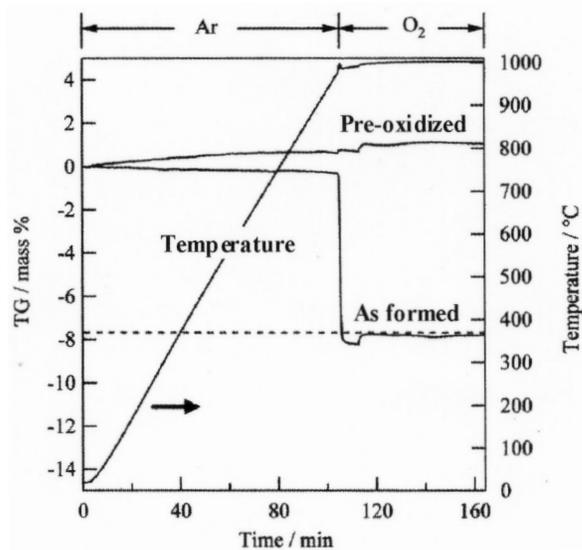


Fig. 5 Oxidation tests of 1300°C product.