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STUDIES ON THE THERMAL STABILITY OF NANO-SiC POWDER WITH EXCESSIVE FREE CARBON BY TG-DTA-MS, XRD AND TEM

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We studied the removal process of excessive free carbon in the nano-SiC powder by TG-DTA-MS, XRD and TEM three methods. The studies showed that the temperature of removing excessive free carbon in the nano-SiC powder should be about 750 °C in air.

Keywords: *nano-SiC powder, TEM, TG-DTA-MS, thermal stability, XRD*

Introduction

SiC is one of the important high temperature structural materials which have widely been used to prepare sintering SiC warm gear [1–3]. In recent years, the processing of using nano-powder as raw materials for the preparation of SiC ceramics with high mechanical strength, high thermal conductive coefficient and good chemical stability has widely been used. However, in the process of preparing nano-SiC powder, the materials containing excessive free carbon were often added in the precursors in order to decrease the oxidation on the surface of the powder and resulted in the formation of the excessive free carbon. The excessive free carbon caused great effect on the dispersing behavior of the SiC powder in the solvent. It leads the particles to adhere each other and to deposit and to hinder the sintering process of SiC. Therefore, it is necessary to remove the excessive free carbon before the sintering of the nano-SiC powder.

Tartaj *et al.* [4] used DTA and TG techniques to characterize the excessive free carbon in the nano-SiC powder. Their research results showed that the excessive free carbon could be removed in air at about 650°C. Using DTA and TG methods, only the changes of mass losses and thermal effects were obtained, while the evolved gases during heating process were not characterized. Therefore, the whole process of removing the excessive free carbon could not be reflected completely. In this work, TG-DTA-MS [5–9], XRD and TEM are combined to study the removal of the excessive free carbon in the nano-SiC powder before and after thermal treatment. The discussion for the results given by TG-DTA-MS, XRD and TEM is also done in this paper.

Experimental

SiH_4 and C_2H_4 were used as the precursors. The nano-SiC powder with excessive free carbon was prepared by laser vapor method. The amount of C and Si in the sample was 1:1 (atomic scale).

Netzsch STA 449C TG-DTA thermal analyzer coupled with Balzers Thermostar^{TM} quadruple mass spectrometer was used in the experiments. The sample mass was about 4 mg. The air of 20 mL min^{-1} was used as the carrying gases. The measuring region was from room temperature to 800°C. The heating rate was 10 K min^{-1}. The vacuum of the quadruple mass spectrometer was 10^{-4} Pa. The multiple ion detection (MID) mode was used for the MS measuring. The first channel was proposed for m/z=12. The second channel was proposed for m/z=28. The third channel was proposed for m/z=44. The filtering time of mass was 1 s. The mass resolution was 50. The mass scanning speed was 1 s.

Japan Regaku RAX-10 rotating X-ray diffraction analyzer was used to characterize the solid phase components of the prepared sample. Cu Kα radiation was used. The voltage was 40 KV. The electric current was 60 mA. JEM2010 high resolution scanning TEM was used to observe the particle size of nano-SiC powder before and after thermal treatment at 650°C in air.

Results and discussion

XRD results

The X-ray diffraction pattern of the nano-SiC powder is shown in Fig. 1. The XRD profile of the nano-SiC

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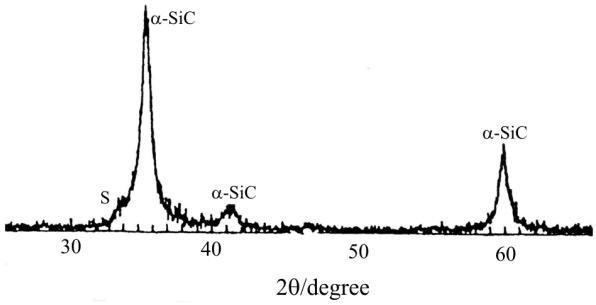

Fig.1 X-ray diffraction pattern of the nano-SiC powder

powder shows three peaks on the basis of the crystal structure of α-SiC (cubic). In the X-ray diffraction pattern, a weak peak (symbolized with s) appeared at $2\theta=33.7^{o}$. Through the research, the shoulder peak may be caused by the existence of the stacking faults of β-SiC [4].

TEM results

The TEM results for the untreated nano-SiC powder with excessive free carbon are shown in Fig. 2. Through TEM and energy dispersive spectrometry (EDS) analysis, we observed that the average particle size of SiC was about 20 nm and the average particle size of the free carbon was about 6 nm. The Fig. 3 shows the TEM picture of the nano-SiC powder after thermal treatment at 650°C in air. The TEM results only show the nano-SiC powder particles, not the free carbon particles.

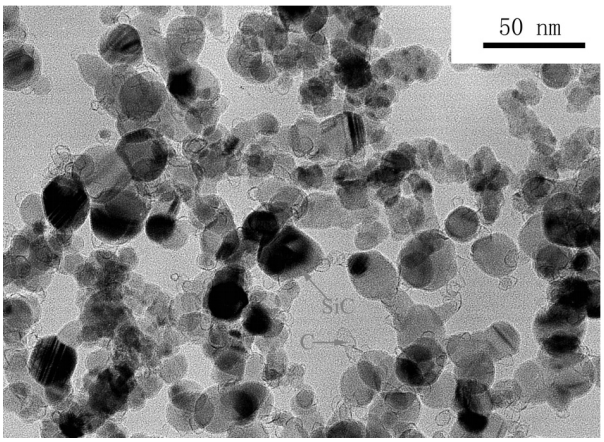

Fig. 2 TEM graph of the nano-SiC powder with excessive free carbon

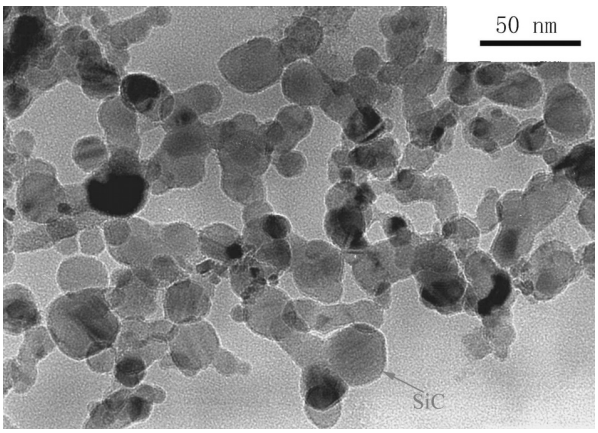

Fig. 3 TEM graph of the nano-SiC powder after thermal treatment at 650°C

TG-DTA-MS results

The TG-DTA curves for the nano-SiC powder with excessive free carbon are shown in Fig. 4. The TG curve shows the mass losses of 2.59% at 40–150°C, the mass losses of 3.36% from 150 to 550°C and the mass losses of 3.19% from 550 to 750°C. There was no mass losses appeared above 750°C. It shows that the excessive free carbon in the nano-SiC powder was removed out at about 750°C. The DTA curve shows the endothermic effect at 40–150°C and three exothermic peaks at 510.6, 609.5 and 668.4°C separately. In Fig. 5, the MS curve shows the C^{+} (m/z=12) positive ion mass spectrometric peaks at 150–700°C. An obvious C^{+} (m/z=12) positive ion mass spectrometric peak appears at 646°C. In Fig. 6, the MS curve shows the

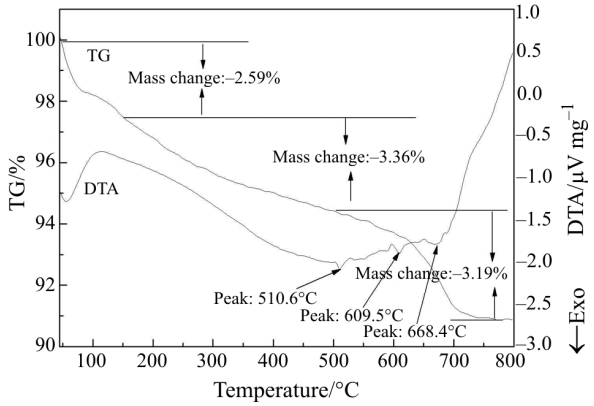

Fig. 4 TG-DTA curves of the nano-SiC powder

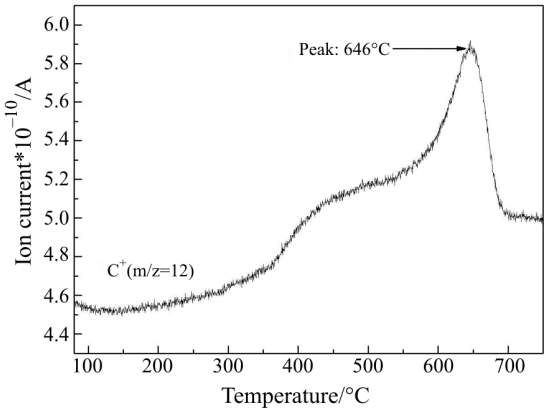

Fig. 5 MS curve of C^{+} (m/z=12) for the nano-SiC powder

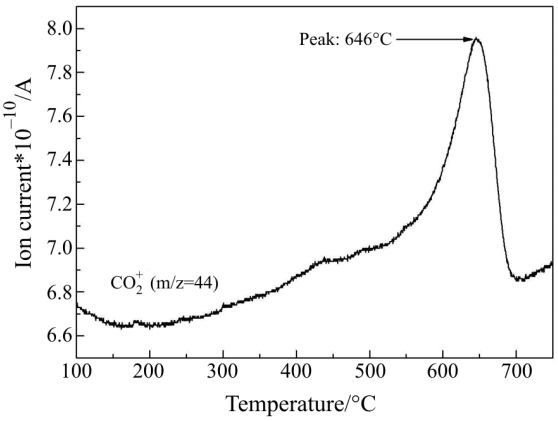

Fig. 6 MS curve of CO_2^+ (m/z=44) for the nano-SiC powder

CO_2^+ (m/z=44) positive ion mass spectrometric peaks at about 150–700°C. An obvious CO_2^+ (m/z=44) positive ion mass spectrometric peak appears at 646°C. However, there was no the CO^+ (m/z=28) positive ion mass spectrometric peak appeared in the MS curves.

From the XRD results of the nano-SiC powder, the carbon phase was not detected. The XRD results were accorded with that given by FTIR in [10]. The FTIR spectra showed a strong absorption due to the vibration of SiC at 820 cm^{-1} with a shoulder at ca. 900 cm^{-1}. There were no peaks of carbon appeared in the FTIR spectra. Because XRD has the limitation of the measuring sensitivity, in the case of carbon phase was too low, the carbon would not be detected by XRD. Consequently, we cannot make conclusions that the carbon is not existed on the basis of XRD studies alone [10]. Thus, without the carbon phase in the X-ray diffraction pattern, it does not mean the excessive free carbon has been removed completely.

From the TEM results of the nano-SiC powder after treatment at 650°C, we only found the particles of the nano-SiC powder of 20 nm and not the particles of free carbon. But the statistics of TEM for the characterization of the system is not good enough. Taking into account the difficulties, a combination of various complementary structural and thermal analysis methods was used in the present work.

The DTA-TG coupling techniques were used by Tartaj *et al*. to characterize the process of removing excessive free carbon in the nano-SiC powder [4]. Their research results showed that the excessive free carbon could be removed in air at about 650°C. While the evolved gases during heating process were not characterized. In order to fetch up the deficiency of DTA-TG, we used TG-DTA-MS coupling techniques in this work. Based on the results given by TG-DTA-MS, we can see that the whole process of the excessive free carbons of the nano-SiC powder was completed in the three steps. In the first step, the TG curve shows the mass losses of 2.59% at 40–150°C. The corresponding DTA curve showed a small endothermic effect at 40–150°C. It indicated that the adsorbed water on the surfaces of the nano-SiC powder were released at 40–150°C. In the second step, the TG curve shows mass losses of 3.36% at 150–550°C. The corresponding DTA curve shows a slowness exothermic effect with a small exothermic peak at 510.6°C. The corresponding MS curves showed the shouldered peaks of C^+ (m/z=12) and CO_2^+ (m/z=44) in Figs 5 and 6 separately. It indicated that the part of the excessive free carbons of the nano-SiC powder was released in the form of the dissociated carbon at 150–550°C. At the same time, the part of the excessive free carbon was oxidized by the oxygen in air at 150–550°C and evolved in the form of the CO_2. In the third step, the TG curve shows mass losses of 3.19% at 550–750°C. The corresponding DTA curve showed two exothermic peaks at 609.5 and 668.4°C. The corresponding MS curves showed two strong peaks of C^+ (m/z=12) and CO_2^+ (m/z=44) at 646°C in Figs 5 and 6 separately. It indicated that the excessive free carbons of the nano-SiC powder were combusted at 550–750°C. The free carbons were also released in the form of the dissociated carbon and the CO_2. In the experiment, we did not detect the proposed CO^+ (m/z=28), it may be related to the complete oxidation of the excessive free carbon by the oxygen in air. In this case the combustion product of free carbon should be CO_2.

Conclusions

Combined the results measured by XRD, TEM and TG-DTA-MS techniques, we can see that for the complete removal of the free carbons, the thermal treatment temperature of the nano-SiC powder should be at about 750°C in air.

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