A NOVEL CATALYTIC METHOD TO PREPARE SILICON CARBIDE NANOMETER WHISKERS FROM SiO_2-Mg^*-CH_4 SYSTEM

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Introduction

Silicon carbide whiskers (SiC_w) exhibit high chemical and thermal stability and excellent mechanical properties. SiC_w may be used as reinforcements for the high performance composite materials of both metals and ceramics. At present, there are nearly ten kinds of methods to prepare SiC_w or silicon carbide fibers (SiC_f), such as direct carbonization, chemical vapor deposition, sol-gel, carbothermal reduction, pyrolysis of organic precursor, and chemical catalysis, etc. The reaction temperatures are usually higher than 1000 ℃ and the diameters of SiC_w are micron size in most of the methods reported in the literatures.

In this work we investigated the reactions of preparation of SiC_w from the SiO_2-Mg^*-CH_4 system by catalytic method at 800 ℃, where Mg^* is the highly reactive nanometer magnesium powder. TEM, XRD, EDS, and FT-IR were used to characterize the reaction products.

Experimental

Reagent-grade SiO_2 (purity>98.2%) was dried at 120 ℃ for 4 hours beforehand. Mg^* was prepared and the transition metal catalyst was doped according to the reference [1]. CH_4 (purity>99.99%) and H_2 (purity>99.9%) were used without further purification.

SiO_2 and Mg^* were ground in a mortar for 5 minutes and then transferred into a basket which is made of the stainless steel net. The basket was hang into the middle of a vertical quartz reactor. All these operations were carried out under the N_2 atmosphere. The mixed samples were reduced in-situ by H_2 for 2 hours at 600℃ and then CH_4 was passed in at a chosen ratio of CH_4 to H_2. The reactor was heated to 800 ℃ to carry out the reactions. The reactions were quenched by replacing CH_4-H_2 with Ar (purity>99.99%). TEM measurements were performed using JEOL JEM-100C X II. XRD measurements were performed using Rigaku 2038. EDS measurements were performed using JEM-2010F. FT-IR measurements were performed using FTS3000.

Results and Discussion

Characterization of the reaction products Figure 1 shows the morphology of several whiskers of the reaction products, the diameters of two straight ones are about 38 nm and that of the zigzag one is about 28 nm, and the length are larger than 2 μm. The dark short nanorod shown by an arrow at the end of the zigzag whisker contains the catalyst, which may assist the whisker growth. The EDS spectra (Figure 2) shows that C, O, Mg, and Si elements exist in the whiskers. In the XRD pattern of the reaction products (Figure 3a), two new strong peaks appeared and the SiO_2 peaks strength was reduced sharply, as compared with that of the reactant SiO_2. (Figure 3b). This means that a certain amount of SiO_2 was transferred into a new phase. However, the belongings of two new strong peaks could not be determined by our indexing the Powder Diffraction Files of the known inorganic compounds. But, the peak at about 42.6 degree is close to α-SiC peak reported in the reference [2], in which the 2θ region given is only from 15 to 50 degrees. The FT-IR spectra of the reaction products (Figure 4a) are very similar with those of the commercial SiC (purity 98.5%) (Figure 4b). The peak at about 800 cm^{-1} is corresponding to the Si-C stretching [3] and the strong broad peak between 400-600 cm^{-1} is consistent with that of the IR spectra of MgO.

Investigation of the effect of the reaction conditions on preparation of SiC_w Table 1 shows the effect of the some conditions on the reactions. It is known from No. 1 to No. 6 that H_2 plays some important role in the formation of SiC_w. This may be due to that H_2 could accelerate the reduction of Mg^* on SiO_2 and prevent the catalyzed pyrolytic carbon from sintering. The experiments of No. 7 to No. 9 show that increasing the ratio of Mg^* to SiO_2, the flow rate of CH_4, and the reduction temperature can obviously im-prove the results of the reactions.

Conclusions

α-SiC_W may be prepared from the SiO_2-Mg^*-CH_4 system. The reactions may be summarized as the following formulas

$$SiO_2 + Mg^* \xrightarrow[\Delta]{H_2} Si + MgO \quad (1)$$

$$CH_4 \xrightarrow[\Delta]{\text{catalyst}} C + H_2 \quad (2)$$

$$Si + C \xrightarrow[800\ ℃]{} \alpha\text{-}SiC_w \text{ or } SiC_f \quad (3)$$

Acknowledgments

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References

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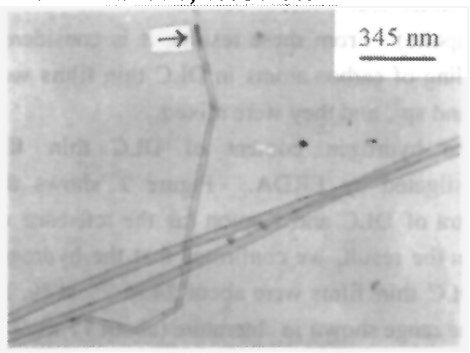

Figure 1. TEM micrograph of the whiskers in the reaction products. The dark short nanorod pointed by an arrow contains the catalyst which may assist the whisker growth. Reaction conditions:800 ℃,CH_4:H_2=100:50(ml min^{-1}), 3h.

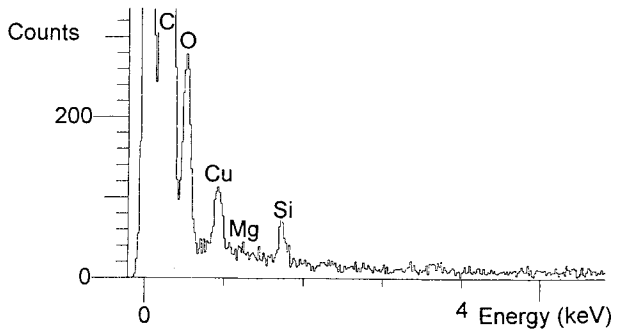

Figure 2. EDS spectra of one straight whisker in the reaction products. (Cu signal occurs from the Cu grid.)

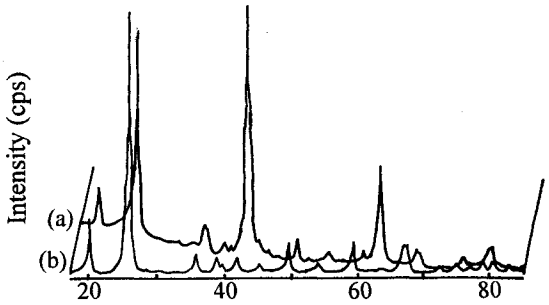

Figure 3. XRD patterns of (a) the reaction products and (b) reactant SiO_2. (a) 30 kV, 25 mA; (b) 25 kV, 5 mA.

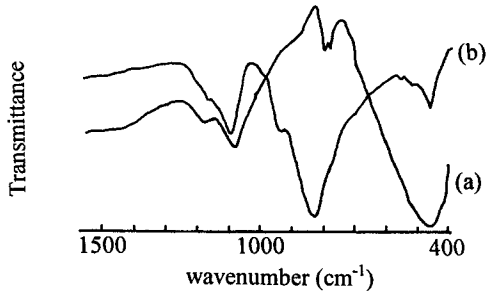

Figure 4. FT-IR spectra of (a) the reaction products and (b) the commercial SiC.

Table 1. The effect of the reaction conditions on preparation of SiC_w

No.[a]	Reduction conditions			Reaction conditions			Results[c]
	H_2 (ml min^{-1})	temperature (℃)	time (h)	CH_4:H_2 (ml min^{-1})	temperature (℃)	time (h)	
1[b]	0	—	0	100:0	800	0.5	nanometer particles
2[b]	0	—	0	100:50	800	0.5	very few whiskers
3	50	600	2	100:50	800	0.5	certain whiskers
4	50	600	2	100:50	800	2	many whiskers
5	100	600	4	100:50	800	2	many whiskers
6	100	600	4	100:100	800	2	many whiskers
7	100	600	4	100:100	800	2	many whiskers
8	100	600	4	200:100	800	2	many whiskers
9	100	700	2	200:100	800	2	many whiskers

a: The weight ratio of Mg^* to SiO_2 is 1:1 from No. 1 to No. 6 and 2:1 from No. 7 to No. 9. b: The reactants were heated to 800 ℃ under Ar atmosphere.
c: The TEM micrograph and XRD patterns are omitted here.