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Synthesis and microstructural characterization of silicon carbide nanofibers from different carbon templates in a solid-vapor reaction

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Silicon carbide (SiC) nanofibers have been synthesized by a solid-vapor reaction (SVR) between carbon nanofibers (CNFs) and SiO vapor, the CNFs being grown using alloys of Ni-Fe, Fe-Al, and Ni-Fe-Al as catalysts by thermal decomposition of C_2H_4 in the temperature range of 550-650 °C. After removal of the catalysts in the as-synthesized CNFs with 2 mol// HNO₃, the SVR process occurred between the CNFs and the SiO vapor in the temperature range of 1200-1450 °C for a fixed dwell time of 5 h, with a heating rate of 5 °C·minute⁻¹ under an Ar/H₂ (160 : 40) flow of 200 cm² (m//minute). The SiC nanofibers consisted of β -SiC and α -SiC and have a thicker diameter than that of the mother CNFs. The effects of catalyst composition and synthesis temperature on the microstructural evolution of the SiC nanofibers are discussed based on the quantitative and qualitative results obtained.

Key words: Carbon nanofiber, Silicon carbide, Nanostructure, Catalyst, Solid-vapor reaction.

Introduction

Nanostructured materials such as nanotubes, nanofibers, and nanowhiskers have been extensively studied since the discovery of carbon nanotubes (CNTs) in 1991 [1]. Recently, silicon carbide (SiC) nanofibers and nanotubes have been synthesized by the reaction of SiO vapor or Si with CNTs, after the report of the preparation of SiC nanotubes using a shape memory synthesis (SMS) method by Dai et al. in 1995 [2-5]. The SiC nanostructured materials with a fiber or tubular form have attracted attention because of their particular properties, such as electronic and mechanical properties and excellent resistance to oxidation, for use in electrical devices, semiconductors, and structural applications [6-8]. However, the SMS technique indicates a limited thickness owing to the diffraction distance or diffusion barrier. To overcome these problems, there are still challenging technical problems in preparing SiC materials.

Most SiC nanofibers and nanotubes have been synthesized from CNTs and/or carbon nanofibers (CNFs), which are very expensive materials. Carbon nanostructured materials (CNMs) can be easily prepared by the decomposition of various carbon-containing gases on metallic catalysts of iron [9], nickel [10], cobalt [11], molybdenum [12], bimetallic compounds [13-15], or trimetallic compounds [16], indicating that the method has a high selectivity. Using the same catalysts, the effects of the hydrocarbon (CH₄, C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , *etc.*) as a carboncontaining gas on the morphology and degree of graphitization have been investigated, showing different morphologies, microstructures, crystallinities, and activities [17]. The heterogeneous catalyst systems are very useful to synthesize CNMs, which will enhance the conversion of CNMs to SiC nanofibers. Furthermore, to the best of our knowledge, a comparison of the growth of SiC nanofibers using different catalyst species has not been reported in the open literature. In our previous studies, SiC microtubes were successfully synthesized by the reaction of SiO vapor with a carbon template and carbon microfibers [18, 19]. Therefore, the same process was adopted to synthesize nanostructured SiC materials with fiber or tubular forms.

In this study, CNFs were prepared by thermal decomposition of C_2H_4 using Ni-Fe, Fe-Al, and Ni-Fe-Al catalysts. The effects of catalyst species and temperature on the microstructural evolution of SiC nanostructured materials were investigated through microstructural observations and characterizations of the synthesized SiC materials by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and field emission transmission electron microscopy (TEM).

Experimental Procedure

Reagent grade iron (III) nitrate [Fe(NO₃)₃·9H₂O], nickel nitrate [Ni(NO₃)₂·6H₂O], and aluminum nitrate [Al(NO₃)₃] were used to prepare the catalysts. Three catalyst compositions of Ni-Fe, Fe-Al, and Ni-Fe-Al were prepared by dissolving their nitrates in ethanol with a mole ratio of 1 : 1 for Ni-Fe, 1 : 1 : 1 for Ni-Fe-Al, and for Ni-Fe, a mole ratio of 4 : 1 [20]. The mixed solutions were dried at 70 °C after sonication for 5 minute, and then the dried powders were heated at 110 °C for 8 h. The resulting powders were used as catalysts after grinding. CNFs were

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prepared by thermal decomposition of C₂H₄ at a reaction temperature of 550-650 °C. After removal of the catalyst with 2 mol/l HNO₃, the CNFs were kept in an alumina crucible, and then heated in the temperature range from 1200-1450 °C for 5 h with a heating rate of 5°C minute⁻¹ in an Ar/H₂ (160 : 40) flow of 200 cm² (ml/min). A solid-vapor reaction (SVR) occurred between CNFs and SiO vapor. The pack composition for Si and SiO₂ was adjusted to a 1:1 mole ratio, which was used as a precursor for the SiO vapor. Details of the generation method for the SiO vapor and control method for the dilution of carrier gases have been given previously [18, 19]. The microstructure of the synthesized materials was observed using SEM (JEOL Model JMS-840, Tokyo, Japan) and FE-TEM (JEM 2100F, Tokyo, Japan). Elemental analysis of SiC products converted from CNMs was conducted using an energy-dispersive X-ray spectrometer (EDS, S2700, Hitach, Japan).

Results and Discussion

An overall view of CNFs synthesized at 600 °C with different catalysts is illustrated by the SEM images in Fig. 1(a-c). SEM micrographs show the dramatic changes that take place with the use of different catalysts, independent of temperature, in the synthesis of CNFs. Fig. 1(a) indicates that the Ni-Fe catalyst gave entangled assemblies of carbon nanoproducts, because Ni and Fe particles promote the formation of nanogrowths with a larger size. When the mole ratio of Fe in the bimetallic Ni-Fe catalyst was increased and decreased to 1:1 and 1:4, respectively, it was difficult to get CNTs or CNFs (data not shown here). Therefore, the optimum mole ratio of Ni-Fe catalyst for preparing CNFs was determined as 1:1, which is in good agreement with a previous report [14]. Fig. 1(b) shows the continuous formation of CNFs with a change of catalyst from Ni-Fe to Fe-Al, whereas the Ni-Fe-Al catalyst was useful for the growth of uniform and continuous nanofibers, as can be seen by Fig. 1(c). The as-synthesized nanofibers were not straight, but entangled together and coiled with each other to form bird nests, exhibiting many nodes along their axes. The diameter of the CNFs was below 100 nm.

Fig. 2 illustrates SEM features of the SiC products synthesized at 1300 °C with different catalysts, using the CNFs synthesized at 600 °C. Fig. 2(a) shows that the Ni-Fe catalyst was not very helpful for the growth of SiC nanofibers. It gave a blunt type of feature and the diameter of SiC nanofibers was in the range of 45-180 nm. Addition of the Al component in Ni and Fe catalysts promoted the growth and formation of SiC nanofibers, as can be seen by comparing Fig. 2(b) and (c). The diameter of the SiC nanofibers was slightly thicker than the mother CNFs, showing an entangled microstructure in both SiC nanofibers prepared by Fe-Al and Ni-Fe-Al catalysts. The diameters of each SiC nanofiber prepared at 1300 °C from Fe-Al and Ni-Fe-Al catalysts are in the range of 80-120 nm and 60-110 nm, respectively.



Fig. 1. SEM micrographs of as-synthesized carbon products at 600 °C with different catalysts: (a) Ni-Fe, (b) Fe-Al, and (c) Ni-Fe-Al.

FE-TEM micrographs of the as-synthesized SiC products with the Ni-Fe catalyst at different temperatures using CNFs synthesized at 600 °C are shown in Fig. 3. It is seen that the CNFs are transferred to SiC nanostructures in a laminar form, if the temperature is 1200 °C. However, with an increase of the temperature from 1200 °C to 1300 °C, the CNFs are converted to a fiber form. Because the SiC layer formed on the surface of a CNF behaves as a barrier against diffusion of SiO (gas) and CO (gas),



Fig. 2. SEM micrographs of as-synthesized SiC products at 1300 °C using carbon products synthesized at 600 °C with different catalysts : (a) Ni-Fe, (b) Fe-Al, and (c) Ni-Fe-Al.

the resultant rate of SiC formation decreases. The outside thickness of the SiC phase converted is about 10 nm. Rapid formation of SiC layers is attributed to a relatively high synthesizing temperature at which diffusion of SiO (gas) is possible. From the above results, the SiC nanofibers can be synthesized at and above 1300 °C, indicating that a higher reaction temperature is favorable in forming a



Fig. 3. FE-TEM micrographs of as-synthesized SiC products at different temperatures using carbon products synthesized at 600 °C with the Ni-Fe catalyst : (a) 1200 °C, (b) 1300 °C, and (c) high magnification of SiC product synthesized at 1300 °C.

thicker layer. An image of a SiC nanofiber is clearly illustrated at high magnification in Fig. 3(c).

SEM and TEM micrographs of the as-synthesized SiC nanofibers at 1450 °C using CNFs synthesized at 550 °C with the Ni-Fe catalyst are illustrated in Fig. 4(a-c). The SEM micrograph indicates a clear image of SiC nanofibers, as shown in Fig. 4(a). More detailed information concerning the structural complexity of the synthesized SiC nanofiber can be obtained by TEM (Fig. 4(b-c)), showing a high density of stacking faults and an amorphous Si layer in Fig. 4(c). Characteristic diffraction peaks for Si, β -SiC, and α -SiC (with 2θ) were observed in the XRD results



Fig. 4. SEM and FE-TEM micrographs of as-synthesized SiC products at 1450 °C using carbon products synthesized at 550 °C with the Ni-Fe catalyst : (a) SEM micrograph, (b) FE-TEM at low magnification, and (c) FE-TEM at high magnification.

(data not shown here). The diameter of SiC nanofibers prepared at $1450 \,^{\circ}$ C is in the range of $50-150 \,\text{nm}$. The nominal thickness of the amorphous Si layer is 2.5 nm, as shown in Fig. 4(c).

Fig. 5 shows SEM and Fe-SEM micrographs of SiC nanofibers prepared at 1450 °C using CNFs synthesized at 650 °C, with the Ni-Fe catalyst showing a similar morphology with the SiC nanofibers prepared using CNFs synthesized at 550 °C. The high density of stacking faults and the amorphous Si layer observed in Fig. 4 are also seen in Fig. 5(c). The diameter is in the range of 80-160 nm and the nominal thickness of the amorphous Si



Fig. 5. SEM and FE-TEM micrographs of as-synthesized SiC products at 1450 °C using carbon products synthesized at 650 °C with the Ni-Fe catalyst : (a) SEM micrograph, (b) FE-TEM at low magnification, and (c) FE-TEM at high magnification.

layer is 4.8 nm, as shown in Fig. 5(c). Therefore, the reaction temperature for preparing CNFs affected the activity of the catalyst and increased the yield, indicating that the higher temperature for preparing CNFs increases the diameter of SiC nanofibers and enhances the formation of the Si amorphous layer. The EDS results of SiC products synthesized using different CNFs prepared with Ni-Fe and Ni-Fe-Al catalysts are shown in Fig. 6. The EDS analysis reveals that the element Al promotes the formation of SiC nanofibers, which can be obtained at the relatively low temperature of 1300 °C. The bimetallic catalyst without the element Al, the Ni-Fe catalyst can give



Fig. 6. EDS analysis of SiC products synthesized using different carbon products: (a) Ni-Fe-Al at 1300 °C and (b) Ni-Fe at 1450 °C.

a similar EDS result at the relatively high temperature of 1450 °C, indicating that the conversion of CNFs to SiC nanofibers is terminated at a higher temperature.

Conclusions

SiC nanofibers have been synthesized at and above 1300 °C through the reaction of CNFs and SiO vapor using the SVR process. The Ni-Fe catalyst is not helpful in preparing the CNFs, whereas the presence of Al in the catalyst promotes the growth and formation of CNFs, showing an entangled and coiled microstructure with diameters below 100 nm. The CNFs synthesized with catalysts including the element Al are fully converted to SiC nanofibers at the relatively low temperature of 1300 °C, showing a slightly thicker diameter than the mother CNFs. The diameter of SiC nanofibers converted at 1300 °C is not dependent on the CNF species, showing a range of 45-180 nm for the Ni-Fe catalyst, 80-120 nm for the Fe-Al catalyst, and 60-110 nm for the Ni-Fe-Al catalyst. However, CNFs synthesized without the element Al start to synthesize SiC nanofibers at 1300 °C, and are fully converted at 1450 °C, showing a diameter of 50-150 nm for CNFs prepared at 550 °C and 80-160 nm at 650 °C. An amorphous Si layer can be obtained for both SiC nanofibers converted at 1450 °C with a thicker layer of 4.8 nm in the SiC nanofibers converted from CNFs prepared at 650 °C. Consequently, the element Al in the catalyst plays an important role in synthesizing SiC nanofibers, decreasing the synthesis temperature to 1300 °C.

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References

- 1. S. Iijima, Nature 354 (1991) 56-58.
- 2. C. Phan-Huu, N. Keller, G. Ehret and M.J. Ledous, J. Catalysis 200 (2001) 400-410.
- 3. T. Taguchi, N. Igawa and H. Yamamoto, J. Am. Ceram. Soc. 88 (2005) 459-461.
- D.P. Yu, Y.J. Xing, M. Tence, H.Y. Pan and Y. Leprince-Wang, Physica E 15 (2002) 1-5.
- H. Dai, E.W. Wong, Y.Z. Lu, S. Fan and C.M. Lieber, Nature 375 (1995) 769-772.
- A. Fissel, B. Schroter and W. Richter, Appl. Phys. Lett. 66 (1995) 3182-3184.
- Y. Morisada, M. Maeda, T. Shibayanagi and Y. Miyamoto, J. Am. Ceram. Soc. 87 (2004) 804-808.
- R.Z. Ma, J. Wu, B.Q. Wie, J. Liang and D.H. Wu, J. Mater. Sci. 33 (1998) 5243-5246.
- J. Kong, A.M. Cassell and H.J. Dai, Chem. Phys. Lett. 292 (1998) 567-574.
- F.H. Kaatz, M.P. Siegal, D.L. Overmyer, P.P. Provencio and J.L. Jackson JL, Mater. Sci. Eng. C 23 (2003) 141-144.
- 11. C.J. Lee and J. Park, Carbon 39 (2001) 1891-1896.
- H. Dai H, A.G. Rinzler, P. Nikolaev, A. Thess, D.T. Colbert and R.E. Smalley, Chem. Phys. Lett. 260 (1996) 471-475.
- C. He, N. Zhao, C. Shi, X. Du and J. Li, Mater. Chem. Phys. 97 (2006) 109-115.
- S. Lim, S.H. Yoon, Y. Korai and I. Mochida, Carbon 42 (2004) 1765-1781.
- M. Maruyama, T. Fukasawa, S. Suenaga and Y. Goto, J. Euro. Ceram. Soc. 24 (2004) 463-468.
- N. Zhao, C. He, Z. Jiang, J. Li and Y. Li, Mater. Lett. 60 (2006) 159-163.
- 17. J.H. Zhou, Z.J. Sui, P. Li, D. Chen, Y.C. Dai and W.K. Yuan, Carbon 44 (2006) 3255-3262.
- J.W. Kim, S.W. Myung, H.C. Kim, J.H Lee, Y.G. Jung and C.Y. Jo, Mater. Sci. Eng. A 434 (2006) 171-177.
- J.W. Kim, S.S. Lee, Y.G. Jung, B.G. Choi, C.Y. Jo and U. Paik, J. Mater. Res. 20 (2005) 409-416.
- 20. S. Lim, S.H. Yoon and Y. Korai, I. Mochida, Carbon 42 (2004) 1765-1781.