Growing SiC nanowires on modified SiC fibers surface via a chemical vapor deposition route

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Abstract: SiC nanowires were grown successfully on the surface of SiC fibers via an in situ chemical vapor deposition (CVD) route with Fe(NO$_3$)$_3$ as catalyst. Ethylenediaminetetraacetic acid (EDTA) and dimethylformamide (DMF) were mixed to prepare surface modification agent which was used for surface grafting treatment of SiC fibers. The changes of surface chemical groups between modified and non-modified SiC fibers were analyzed by fourier transform infrared spectroscopy. The as grown products were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results show that the surface modification could bring COOH groups onto the surface of SiC fibers, which could strongly improve the interfacial adhesion strength between fibers surface and catalyst particles. In addition, the surface modification can also make the catalytic particles distribute uniformly throughout the fiber surface which provided a good surface condition for the growth of SiC nanowires.

1. Introduction

One-dimensional (1D) nanostructures such as nanowires (NWs) and nanotubes are expected to have excellent mechanical, optical and electronic properties compared to their bulk or thin film counterpart [1], which have attracted extensive attention due to their potential applications in kinds of functional nanodevices and composite reinforcement [2,3]. It is reported that SiC nanorods exhibited an elastic modulus of over 50 GPa and ultimate bending strengths of over 600 GPa, which make SiCNWs an ideal nanoreinforcement to improve the strength and toughness of composites [4]. For fiber reinforced polymer derived ceramic (PDC), the deposition of SiCNWs on the fiber surface is an effective reinforcement in ceramic composites [5] which result in an obvious improvement of the mechanical properties. There are some efforts to fabricate SiC/SiC composites by introducing SiCNWs into the surface of SiC fabrics before chemical vapor infiltration (CVI) of the SiC matrix [5,6]. This is an efficient approach to shorten the CVI time by growing higher density SiCNWs in SiC fabric homogeneously due to the SiCNWs increasing the surface area at which the SiC deposition can take place.

There are many methods for the growth of SiCNWs using catalysts with the vapor-liquid-solid (VLS) growth mechanism. Jin-Seok Lee et al.[7] has reported the growth of SiCNWs by carbothermal reduction using a mixture of carbon and low-purity SiO$_2$ containing iron component as raw material. The iron riched component of the low-purity SiO$_2$ material forms iron-rich droplets acting as the role
of catalyst for the growth of SiCNWs. Bharat Krishnan et al. [8] deposited Au, Ni, or NiSi catalyst layer on the 4H-SiC substrate by physical vapor deposition (PVD), and then grew SiCNWs on the substrate. Li et al. [9] synthesized long SiCNWs in large areas on graphite substrate which had been first immersed in ethanol solution of Fe(NO$_3$)$_3$ (0.1 mol/L), and dried naturally. Comparing to vapor-solid (VS) growth mechanism, it is very important to obtain a lay of uniform catalyst particles in the surface of substrate in VLS growth mechanism. In most previous works, the catalysts were loaded directly on the substrate by immersing solution or PVD methods. For fiber fabrics, it is often difficult to obtain a metal catalyst layer by PVD or a surface with uniformly distributed catalysts by immersing solution.

In present work, we have demonstrated that the EDTA/DMF modified SiC fibers absorbs iron from the catalyst solution, providing the surface of the fibers homogeneous deposition of iron catalyst and then homogeneous growth of SiCNWs.

2. Experiments

Three dimensional four-step (3D 4 step) SiC fiber fiber preform was prepared with the KD-Ⅱ SiC fiber which was provided by National University of Defense Technology (Changsha, China). Polycarbosilane (PCS, Mw = 2000, Tm = 180°C) in this work was also provided by National University of Defense Technology. In order to prepare the surface modification agent, DMF was mixed with EDTA to form a suspended solution which has been reported elsewhere [10]. The preform had been firstly immersed in the suspended solution at 110°C and held for 6h, then rinsed with deionized water and dried in the air at room temperature. The preform with/without modification then dipped in the aqueous solution of Fe(NO$_3$)$_3$ (0.1 mol/L) at 60°C and held for 4h, rinsed with deionized water then dried naturally or dried naturally without rinse. In a typical CVD synthesis process, about 5g PCS was placed in a corundum crucible. The corundum crucible together with four differently treated preforms at the downstream was placed in a quartz boat. After that, the quartz boat was moved into the middle of a tube corundum furnace. The furnace was heated to 1300°C at an average heating rate of 5°C/min with a flowing ultra-high purity N$_2$ atmosphere at a flow rate of 10 sccm. Holding for 1 h, the furnace was cooled to room temperature naturally. Infrared spectroscopy (FTIR) measurements were used to character the chemically modified surfaces of SiC fibers. The loaded catalysts on the preform surface and microstructures of the SiC nanowires was examined using a scanning electron microscope (SEM, Hitachi S-4800) equipped with an energy dispersive X-ray spectroscopy (EDS), and a high resolution transmission electron microscope (HRTEM, JEOL JEM-3010).

3. Results and discussion

As depicted in Fig. 1(a), the modified preform has intensive absorption bands at about 3400 cm$^{-1}$ and 1650 cm$^{-1}$ compared to the non-modified preform. The bands are attributed to the H−O−H stretching vibration and deformation vibration of H$_2$O, respectively. This indicates that the water content increases in the modified preform. On the other hand, the two bands broaden obviously with shoulder peaks at 3250 cm$^{-1}$ (−OH stretching from −COOH) and 1750 cm$^{-1}$ (C=O stretching from −COOH), which demonstrates that the surface modification in DMF/EDTA mixed solution can efficient bring COOH active sites onto the preform surface. During modification, the increasing of molecular water may be attributed to the additional COOH groups, which are polar and easy to absorb water. As shown in Fig. 1(b), the particles distribute uniformly throughout the surface of the modified preform. Fig. 1(c) shows EDX spectrum of the particle in Fig. 1(b), Fe element was detected. After immersing the modified preform in aqueous solution of Fe(NO$_3$)$_3$, the surfaces of the preform was successfully obtained Fe catalyst particles homogeneously which was bonded to the COOH groups introduced by the EDTA/DMF surface modification. Preform loaded with catalysts by different treatment were showed in Fig. 2. It can be seen in the Fig. 2 that both preform (a) and preform (b) have an equally distributed Fe catalyst particles layer. The Fe catalyst particles have not been wiped off during
deionized water rinsing. The non-modified preforms are showed in Fig. 2(c) and Fig. 2(d). A few particles distributed unequally in the non-modified preform surface (Fig. 2(c)). After rinsing with deionized water, the particles were almost removed entirely due to the absence of chemical interaction with the surface (Fig. 2(d)).

The corresponding CVD growth products are shown in Fig. 3. It can be seen that the surface of the preform (a) and (b) are covered with randomly oriented SiCNWs. The NWs are very dense and almost coat the entire surface of the fiber. While, a non-uniform SiCNWs layer is observed in the non-modified preform (c). The non-modified preform (d) without catalysts has no products. As we known, the catalyst is the key factor for growth of NWs by VLS mechanism. In our works, the SiC fibers preform was activated with COOH groups by an EDTA/DMF suspension. Then, the Fe acts as catalyst for the following growth of SiCNWs. The modified preform has an intensive absorption of catalysts than non-modified preform thus got a well distribution growth of SiCNWs.

The detailed structure of the as-grown SiCNWs is shown in Fig. 4. Some spherical droplets can be seen clearly at the NWs tips (in Fig. 4(b)). The EDX spectrum of the spherical droplet (inset of Fig. 4(b)) shows that the Fe element is involved besides Si and C, indicating that the SiCNWs grow through VLS mechanism. At high temperature the Fe liquid nanoclusters were formed, at the same time the PCS decomposed and released gases containing Si and C elements. Then the gaseous Si and C dissolved into the Fe nanoclusters and formed the SiC phase [11]. The morphologies of SiCNWs were further observed in detail by TEM. Stacking faults can be seen in Fig. 4(c). Fig. 4(d) show that the SiCNW grew along the <111> direction, exhibiting a single crystal β-SiC structure in which the distance of {111} planes is 0.25 nm.

Figure 1. (a) FTIR spectra of preforms, (b) modified preform covered with particles, (c) EDS pattern of the particles in (b).
Figure 2. SiC fiber preforms covered with particles (a) modified preform dipped with Fe(NO$_3$)$_3$ solution and dried naturally without rinse, (b) modified preform dipped with Fe(NO$_3$)$_3$ solution, rinsed with deionized water and dried naturally, (c) non-modified preform dipped with Fe(NO$_3$)$_3$ solution and dried naturally without rinse, (d) non-modified preform dipped with Fe(NO$_3$)$_3$ solution, rinsed with deionized water and dried naturally.

Figure 3. SiCNWs on the differently treated SiC fiber preforms with or without modified by catalyst corresponding to Fig. 2(a)-(d).
Figure 4. (a) SiCNWs grow along the SiC fiber, (b) the SiCNWs tips and the EDX pattern of the SiCNWs tips, (c) TEM image of a single SiCNW, (d) HRTEM image of the SiCNW.

4. Conclusions
The novel catalyst introducing methods has been studied to grow SiCNWs on the surface of SiC fibers. It is analyzed that the SiC fibers modified by an EDTA/DMF suspension has more strong adhesion to Fe particles due to the COOH groups on the fibers surface. With the Fe particles dispersed homogeneously throughout the fiber surface, the SiCNWs on the SiC fibers layers were synthesized by the decomposition of PCS through a CVD route with VLS growth mechanism. The present work provides a novel route to introduce Fe catalyst for synthetizing SiCNWs on the SiC fabrics, which will be applied in SiCNWs-reinforced SiC/SiC composites in the future.

Acknowledgments
This work was financially supported by the National Natural Science Foundation of China (Grant No. 51372274). The authors declare that there is no conflict of interest regarding the publication of this paper.

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