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RESEARCH PAPER

Synthesis of tantalum carbide from multiwall carbon nanotubes in a molten salt medium

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Abstract: Tantalum carbide (TaC) nanofibers and coatings were synthesized using multiwall carbon nanotubes (MWCNTs) with different structures as templates and the carbon source in a KCl-LiCl molten salt mixture (41.2/58.8 mol/mol). The TaC and MWCNTs were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction and selected area electron diffraction. Results indicate that the microstructure of the MWCNTs has a distinct influence on the formation of a TaC coating on the MWCNTs. MWCNTs heat-treated at 2 900 ^{o}C have a higher crystallinity and are harder to react with Ta to form TaC than those without the heat-treatment. The formation of TaC nanofibers or TaC coatings on MWCNTs is dependent on the molar ratio of tantalum to carbon nanotubes. The morphology of the polycrystalline cubic TaC nanofibers and the TaC coating is similar to that of MWCNTs. The reaction time and temperature have a great influence on the conversion of carbon to TaC and its crystallite size.

Key Words: Carbon nanotubes; Tantalum Carbide; Carbide coatings

1 Introduction

Carbon nanotubes (CNTs) are attracting increasing scientific and technological interest owing to their novel properties and potential applications[1]. The morphology and size of carbon nanotubes suggest that they could be used as supports for heterogeneous catalysis, reinforcing agents for metallic and ceramic matrix materials or as templates for creating nano wires or tubular structures[2]. Despite their uniquely superior properties, the interface compatibility problems between carbon nanotubes and most matrices have limited their industrial applications in carbon nanotube-reinforced metallic and ceramic matrix composites[3]. It means that, if carbon nanotubes are used as reinforcing fibers for metal-matrix composites or as catalyst supports without any surface treatments, it will be difficult to achieve high strength interfacial adhesion or to anchor effectively catalyst particles on carbon nanotubes[4, 5]. Moreover, the applications of carbon nanotubes as composite reinforcement are also limited since carbon reacts with many metallic and ceramic matrix materials[6, 7].

Tantalum carbide (TaC) is a promising ceramic coating material owing to its very high melting point (>3 500 °C), high hardness, high resistance to chemical attack and thermal shock[8-10], and excellent electronic conductivity[11, 12]. It has been reported that TiC, SiC, NbC and TaC nanorods could be obtained in vapor-solid reactions using carbon nanotubes as a template[13, 14], or in chemical vapor infiltration in carbon fiber composites reinforced with layer-structured PyC and TaC phases[15, 16], or in spark plasma sintering by reaction of carbon materials such as CNTs with transition metals[17, 18]. All the carbon materials reinforced with carbides such as TaC show an improved mechanical strength and stability in high temperature. However, these syntheses are difficult to realize applications as they require high temperatures and / or rigorous handling of volatile / highly-reactive reagents, which results in a high cost.

In our previous work, we have developed a simple process for coating carbon fibers with thickness-controllable TiC and TaC layers and for producing carbide nanofibers from carbon nanotubes in a liquid phase KCl-LiCl-KF molten salt medium[19-22]. This approach also provides the possibility for the controllable preparation of TaC products with various morphologies. However, the influence of crystal structure and morphology of carbon sources on the formation of tantalum carbide coating is still not very clear.

In this work, we report that the various morphologies and crystal structures of multi-walled carbon nanotubes (MWCNTs) influenced the morphology of TaC in synthesis of TaC in molten salt reaction medium using MWCNTs as carbon sources and templates. The carbide products were

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characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and selected area electron diffraction (SAED).

2 Experimental

Three carbon nanotubes as both carbon sources and templates were employed: one set was the curved MWCNTs prepared by the catalytic decomposition of methane[23, 24], while the other two were the straight MWCNTs prepared by a floating catalytic method[25] and their heat treated products at 2 900 ºC.

The carbon nanotubes were dispersed in trichloromethane by ultrasonication for 15 min and then mixed with the reaction medium of a salt mixture composed of LiCl-KCl eutectic (LiCl:KCl = 58.8:41.2, mol%) and Ta powder. The mass ratio of molten salt (Ms) and reactants (tantalum and MWCNTs) (Mr) is about 11:1. For three different sets, the molar ratio of the MWCNTs/Ta is 1:1, 2:1 and 3:1 in synthesis of TaC nanofibers and TaC-coated carbon nanofibers. This mixture was placed in a covered alumina crucible and reacted at the required temperature for various time under an argon flow. After cooling, the crucible was repeatedly boiled in water to remove the salts. The remaining product was dried at about 100 °C for 5 h. In order to provide information on microstructure and elemental composition of the products, XRD, SEM, high resolution TEM (HRTEM) and SAED characterizations were conducted on representative sample areas. The powder products were ultrasonic dispersed in alcohol before dropped onto a standard TEM holey carbon support (Agar Scientific). The specimens were examined with a Philips CM200 FEG-TEM operating at 197 kV and fitted with a Gatan imaging filter (GIF 200) and an Oxford Instruments UTW ISIS X-ray detector (EDS). The *d*-spacings measured by electron diffraction patterns were compared with the International Centre for Diffraction Data (ICDD) of inorganic compound powder diffraction file (PDF) database in order to identify the crystalline structure and phases.

3 Results and discussion

Fig. 1a presents the X-ray diffraction (XRD) profiles of the curved, straight and heat-treated straight MWCNTs at 2 900 ºC. The pattern of the curved MWCNTs shows one broad and one weak peaks at about 2θ = 25.9° and 42.9° corresponding to the (002) and (100) crystal planes of graphite, respectively. One broad peak at about 2θ = 25.8° can also be seen in XRD profile of the straight MWCNTs. The (002) *d*-spacings of the curved and the straight MWCNTs are about 0.343 nm and 0.345 nm, corresponding to 2θ = 25.9° and 25.8°, respectively. Two weak peaks in the XRD profiles of the curved MWCNTs at about 2θ = 44.4° and the straight MWCNTs at about 2θ = 44.6° correspond to (111) and (110) crystal planes of cubic nickel and iron from a few nickel and iron catalyst particles encapsulated in carbon nanotubes, respectively. In comparison with the straight MWCNTs, the curved MWCNTs shows a stronger (002) crystal plane reflection at 2θ = 25.9°. This indicates that the crystal structure of the curved MWCNTs is more ordered than that of the straight ones. The XRD profile of the heat-treated straight MWCNTs at 2 900 ºC shows a sharp diffraction peak at about 2θ = 26.4° and two weak and broad peaks at about 2θ = 54.4° and 77.6°, corresponding to (002), (004) and (110) crystal planes of a hexagonal graphite, respectively. The disappearance of iron catalyst diffraction peak at about 2θ = 44.6° (shown in profile of the straight MWCNTs in Fig. 1a) suggests that the catalyst in the graphitized straight MWCNTs has been removed. In comparison to the curved MWCNTs and the straight MWCNTs, a broader (100) diffraction peak at 2θ = 41.6° can be observed in the graphitized straight MWCNTs. In addition, the strong and sharp peak at about 2θ = 26.4° corresponding to (002) plane of graphite also indicates that the crystal structure of the graphitized straight MWCNTs become more perfect.

Fig. 1b-i show the typical field emission scanning electron microscope (FESEM), transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) images of the curved, straight and heat-treated straight MWCNTs at 2 900 ºC. Images from FESEM (Fig. 1b) and HRTEM (Fig. 1c) clearly present the abundant entangled morphology of the curved carbon nanotubes, which is composed of entangled MWCNTs with a fish-bone structure. The diameter and length of the curved carbon nanotubes are mainly around 15-40 nm and a few micrometers, respectively. The HRTEM image of the straight carbon nanotubes shown in Fig. 1f displays the misorientation of their graphene planes. The straight carbon nanotubes possess a turbostratic structure and are composed of some straight nanofibers and a few hollow spheres. The diameter and length of the straight carbon nanotubes are mainly about 10-70 nm and a few micrometers, respectively. It shows that the graphene orientation of the curved carbon nanotubes is better than that of the straight carbon nanotubes. The morphology of the straight MWCNTs does not show an obvious difference before (Fig. 1d) and after (Fig. 1g) heat-treatment at 2 900 ºC. In comparison to the turbostratic structure of the primary straight MWCNTs, the HRTEM image (Fig. 1i) of the straight MWCNTs treated at 2 900 ºC shows a distinct concentric nanotube morphology. The graphene planes of the graphitized MWCNTs in Fig. 1i have become straighter and more ordered, suggesting that the graphitization treatment effectively promotes the crystal growth of the graphitic walls of the MWCNTs and carbon spheres, and obviously improves their layer orientation degree. These results are consistent with the analysis of the XRD profiles shown in Fig. 1a. And the pristine straight MWCNT products with a turbostratic structure are converted to the highly oriented and concentric carbon nanotubes after heat-treatment at 2 900 ºC. As a result, the (100) plane diffraction peak of the latter becomes boarder and shifts to 2θ = 41.6° owing to the decrease of the graphene curvature radius