SYNTHESIS OF TANTALUM CARBIDE NANOFIBRES IN MOLTEN SALTS USING CARBON NANOTUBES AS A REACTIVE TEMPLATE

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Abstract

Tantalum carbide nanofibres of varying morphologies were synthesised using multi-walled carbon nanotubes (MWNTs) of different morphologies as reactive templates in a mixture of molten salts composed of potassium chloride, lithium chloride and potassium fluoride along with pure tantalum powder at 950°C. The product was characterised by scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and electron energy loss spectroscopy (EELS) analyses. Tantalum carbide nanofibres with polycrystalline structures were formed. The polycrystalline tantalum carbide nanofibres are either entangled or straight and have a similar morphology to their precursor MWNTs. This novel method presents possibilities for the controllable preparation of tantalum carbide materials with various morphologies, sizes and microstuctures using a variety of carbon sources.

Keywords: 1. Carbide nanofibres 2. Carbon nanotubes 3. Chemically modified carbons

Introduction

Transition metal carbides of groups IV and V have unusual physical and chemical properties which make them targets for basic research and several technological applications. Tantalum carbide (TaC) is a very promising material among transition metal carbides, being characterised by a very high melting point (>3500°C), high hardness, high resistance to chemical attack and thermal shock (Stroms, 1967 and Chan & Kauzlarich, 1997), excellent electronic conductivity (Chen, Li & Zhai, 2001 and Khyzhun, 1997) and catalytic activity (Choi, 1999 and Kojima, Miyazaki, Inoue & Yasumori, 1982). These make it useful for high-temperature, wear-resistant and electronic applications (Stroms, 1967 and Rubinshtein, Shneck, Kanon, Hayon, Nathan & Raveh, 2001). It is also expected to be useful as a catalyst for ammonia decomposition and hydrogen dissociation (Choi, 1999, Kojima et al., 1982, Claridge, York, Brungs & Green, 2000 and Li, Hernberg & Mantyla, 1998). Some reports have revealed that nanoscale materials can in some cases give rise to unique new catalytic activity (Valden, Lai & Goodman, 1998 and Narayanan & El-Sayed, 2004). For catalytic applications it is imperative to control the morphology and size of TaC nanofibres.

In this work, a novel method of synthesising nanostructured TaC fibres in molten salts is reported. This method uses pure tantalum powder as a Ta source and carbon nanotubes (prepared by a catalytic CVD method) as both carbon source and template to prepare TaC nanofibres in a molten salt system composed of LiCl, KCl and KF salts.

Experimental

Carbon nanotubes, prepared by a CCVD method over a NiO/SiO_2 binary aerogel or by a floating catalytic method, were used as both carbon source and template for the synthesis of TaC in a molten salt mixture composed of KCl, LiCl, KF and pure tantalum powder. The carbon nanotubes were dispersed in trichloromethane by ultrasonic vibration for 15 minutes before grinding together with the mixture of salts and Ta powder and drying for several hours in an oven at 120°C. The carbon nanotubes and Ta powder were mixed in a molar ratio of 1.1:1. The salt mixture, when molten, is believed to facilitate dissolution and transport of the tantalum. This mixture was placed in a covered alumina crucible and heat-treated at 960°C for 5 hours under a flowing argon atmosphere.

After cooling, the crucible was boiled in water to remove the salts and the carbide product was then separated in a centrifuge. Finally, the resulting samples were washed to neutrality in de-ionised water and dried at 110°C for 5h. In some cases, the washing cycle was repeated.

In order to provide information on product microstructure and elemental composition, HRTEM and SAED analyses were conducted on representative areas / fibres. TEM samples were prepared by ultrasonic dispersion of the powder products in alcohol, dropping the dispersion onto a standard TEM holey carbon support film (ex Agar Scientific) and then drying in air. 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). HRTEM and SAED were used to probe the microstructure and crystallinity of the product. The d-spacings measured by electron diffraction patterns were compared with the International Centre for Diffraction Data (ICDD) inorganic compound powder diffraction file (PDF) database to identify the crystalline phases present.

Results and Discussion

The morphology and crystalline structure of the carbon nanotubes and nanofibre products were characterised by SEM, TEM and SAED as shown below. Figures 1a and 1b show FESEM images of the curved carbon nanotubes the straight carbon nanotubes, prepared by a CCVD method over a NiO/SiO_2 binary aerogel and by a floating catalytic method, respectively. The diameter and length of the curved carbon nanotubes are around 15-40 nm and a few micrometers, respectively. The straight carbon nanotubes possess the diameter and length of about 5-60 nm and a few micrometers, respectively.

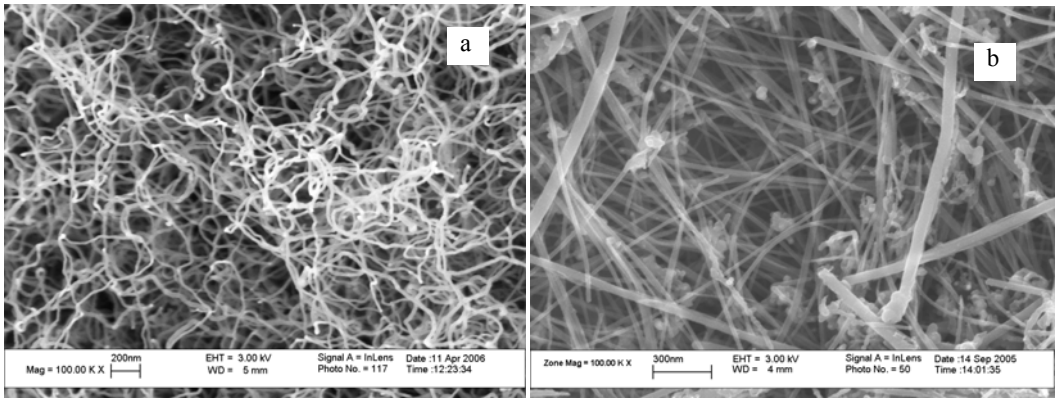

Figure 1. Field-emission scanning electron microscope (FESEM) images of (a) curved carbon nanotubes prepared by the catalytic decomposition of methane over a NiO/SiO_2 binary aerogel and (b) straight carbon nanotubes synthesised by a floating catalytic method.

Figure 2a illustrates, in an SEM image, the typical morphology of curved nanofibres prepared in the molten salts. It can be seen that these fibres are curved and tangled together. The diameter of these fibres is about 40-90nm, i.e. larger than their carbon nanotube source but their morphology is similar to that of the curved carbon nanotubes. A higher magnification TEM image of these curved fibrillar materials is shown in Figure 2b. From this figure, it can also be seen that the curved fibres are composed of many grains. The inset in Figure 2b shows the selected-area electron diffraction (SAED) pattern obtained from the curved fibres in Figure 2b. The relative intensities of the rings in the SAED pattern are similar to the standard XRD intensities for bulk TaC.

The SEM micrograph in Figure 2c illustrates the typical morphology of the straight nanofibres obtained following reaction of the straight carbon nanotubes with tantalum in molten salts. These products show morphology and length characteristics similar to those of the straight carbon nanotube source. Figure 2d shows a low magnification TEM image of the straight nanofibres. Inset in Figure 2d is the corresponding selected-area electron diffraction (SAED) pattern of these nanofibres. The d-spacings and relative intensities of the diffraction rings in the SAED pattern can be correlated with the standard XRD diffraction data for bulk cubic TaC, revealing that the straight nanofibres consist of a polycrystalline cubic TaC.

The carbon K-edge EEL spectra (not shown) for both curved and straight nanofibres are consistent in shape, peak position and relative intensity with a near-stoichiometric tantalum carbide phase. The carbon and tantalum compositions of these two nanofibres were also measured by semi-quantitative TEM-EDX analysis on ultrathin sample areas, and indicated that the atomic ratio of C/Ta was about 1:1.

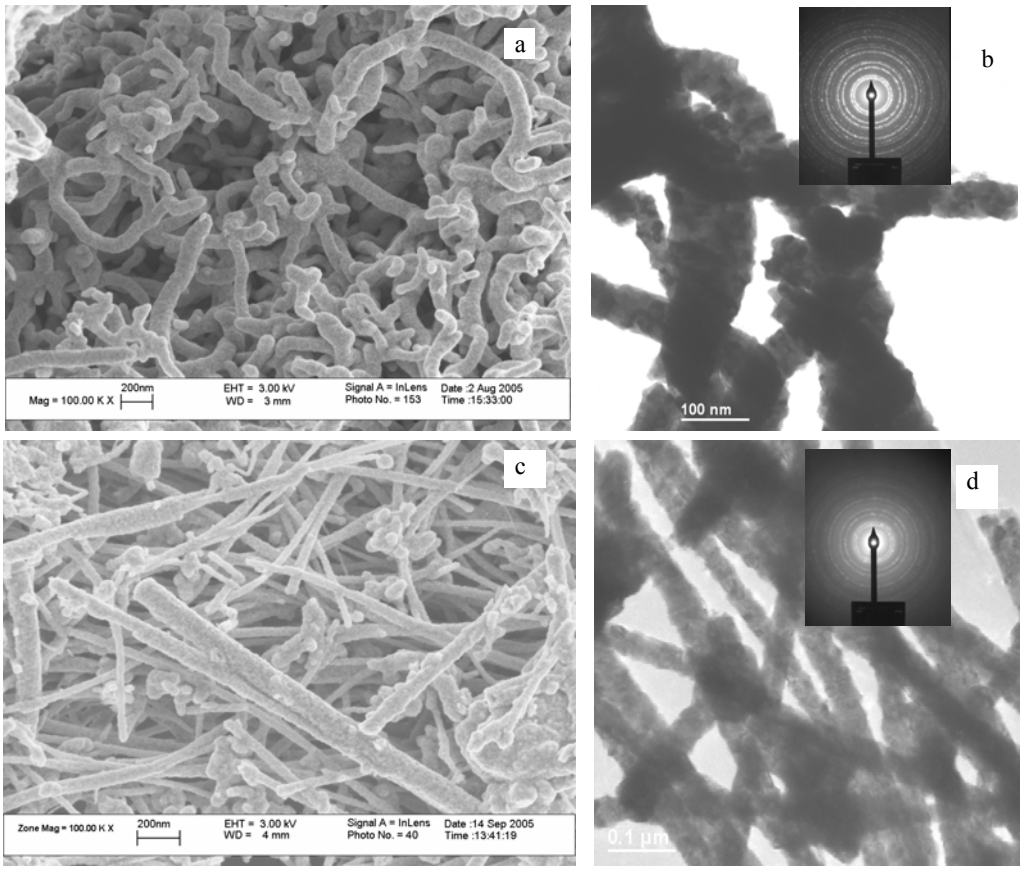

Figure 2. SEM image (a) and bright-field TEM image (b) of the nanofibres prepared from curved carbon nanotubes in molten salts; inset in (b) is the corresponding SAED pattern.

SEM image (c) and bright-field TEM image (d) of the straight nanofibres prepared from straight carbon nanotubes in molten salts; inset in (d) is the corresponding SAED pattern.

Conclusions

This work has demonstrated that molten salt synthesis provides a facile and general synthetic route to useful tantalum carbide materials with controlled morphology. The molten salt route enables controlled syntheses to be accomplished using easily handled reactants at relatively low temperatures and with simple and effective purification steps. A significant feature of the molten salt route is that the carbide products appear to be templated on the carbon source used. In the work described here, curved and straight carbide nanofibres were produced from curved and straight MWNTs, respectively. However, it can be envisaged that other carbide morphologies will be produced depending upon the morphology of the carbon source, e.g. carbide coatings from reaction on carbon fibres or carbide sheets from reaction on a carbon substrate.

Acknowledgements

The authors acknowledge the financial support of the National Natural Science Foundation of China (grant No. 50672070) and the Leeds Nanomanufacturing Institute.

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