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Preparation and properties of $MoSi_2$ based composites reinforced by carbon nanotubes

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Abstract

Molybdenum disilicide ($MoSi_2$) based composites with various contents of carbon nanotubes (CNTs) were made by sintering in vacuum at 1500 °C for 1 h. Mechanical properties of these composites at room temperature revealed the addition of CNTs to have good hardening and toughening effect on the matrix. Especially when adding 6.0% CNTs by volume, the hardness and fracture toughness were improved respectively by about 25.3% and 45.7% compared to pure $MoSi_2$. Phase identification and microstructure of the samples were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HTEM). Multi-walled CNTs were found in the powders synthesized by self-propagating high temperature synthesis (SHS) and SiC phase existed in the sintering samples. Fine grain and the favorable effect of dispersed SiC particles resulted in a high hardness of the CNTs/$MoSi_2$ composite. The toughening mechanisms for the CNTs/$MoSi_2$ composites included crack deflection, crack micro-bridging, crack branching, crack bowing and fine-grain pullout.

Keywords: B. Microstructure; C. Mechanical property; Molybdenum disilicide; Carbon Nanotube

1. Introduction

Molybdenum disilicide ($MoSi_2$) is one of the intermetallic compounds with a potential for being used as advanced high temperature structural materials because of its lower density, high melting point, high thermal conductivity and elevated oxidation resistance [1]. However, its C_{11b} crystal structure and the brittle grain boundary of SiO_2 glass phase formed as a result of oxygen contamination during processing leads to room-temperature brittleness of $MoSi_2$ [2,3]. Extensive research from the literature indicates several possible approaches for improving its mechanical properties, involving introduction and microstructural control of a second phase and by means of adding, for instance, Ta, Nb, W, ZrO_2, SiC, Si_3N_4, WSi_2, Mo_5Si_3, TiB_2, Al_2O_3, etc. to enhance the properties of the matrix [3–5]. Nevertheless, the unique structure endows carbon nanotubes (CNTs) with excellent properties, which makes them a promising reinforcement for composites [6–8]. It has been reported that adding CNTs to Cu [9,10], AZ91D magnesium alloy [11], Al_2O_3 [12], Fe_3Al [13], significantly improved their mechanical properties. In the present study, CNTs/$MoSi_2$ composites were made by self-propagating high temperature synthesis and sintering in vacuum. The mechanical properties of $MoSi_2$ reinforced with CNTs at room temperature were also investigated.

2. Experiment

CNTs were suspended and refluxed at 120 °C in 16 M HNO_3 solution for 3 h, and then separated from the suspension by filtering until pH was neutral. After drying at 80 °C in vacuum, the surface-modified CNTs were dispersed in deionized water and sonicated for 30 min for use.

The elemental materials used in this study were 99.9% pure Mo powder with a particle size of 2–4 μm and 99.9% pure Si powder with a particle size less than 43 um. Firstly, powder

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mixtures of Mo and Si were prepared for the desired composition of $MoSi_2$. Modified CNTs with contents of 1.5 vol%, 3.0 vol%, 4.5 vol%, 6.0 vol% and 8.0 vol% were then added to the mixed powders, respectively. After being milled for 5 h in deionized water using a planetary ball miller with a weight ratio of refractory alloy ball to powder of 5:1 and a rotation speed of the milling vial of 200 rpm, the mixed powders were dried off in a vacuum drying oven at 90 °C for 2 h. The mixture was then synthesized in argon by self-propagating high temperature synthesis (SHS). Finally, the resulting powders were sintered in vacuum at 1500 °C for 1 h. For comparison, pure $MoSi_2$ samples were also made using the same technique.

Hardness of the CNTs/$MoSi_2$ composites was measured by a Vickers hardness tester at 49.8 N for 10 s. The indentation fracture toughness (K_{IC}) was then calculated by using the equation given in Ref. [14]. Each of the data was the average of five measured values. Phase identification and microstructure of the samples were analyzed by X'pert PRO X-ray diffraction (XRD) and S-4800 scanning electron microscopy (SEM) and JEM-2100F high resolution transmission electron microscopy (HTEM).

3. Results and discussion

3.1. Mechanical properties

All relative densities of the CNTs/$MoSi_2$ composites were more than 95% in this study. Fig. 1 shows their properties for the various CNTs contents. With increasing CNTs contents, hardness and fracture toughness increase until 6.0 vol% CNTs. The sample with 6.0 vol% CNTs has the highest hardness and toughness in all samples. The hardness and fracture toughness of this composite are improved respectively by 25.3% and 45.7% than pure $MoSi_2$ sample. Therefore, this investigation shows that the addition of CNTs has good integrative strengthening and toughening effect on the matrix and the optimal content of CNTs is 6.0 vol%.

3.2. Phase and microstructure

Fig. 2(a) shows the X-ray diffraction patterns of CNTs modified by HNO_3, in which the only broader weak C peak exists. Microstructure of CNTs in Fig. 2(b) indicates

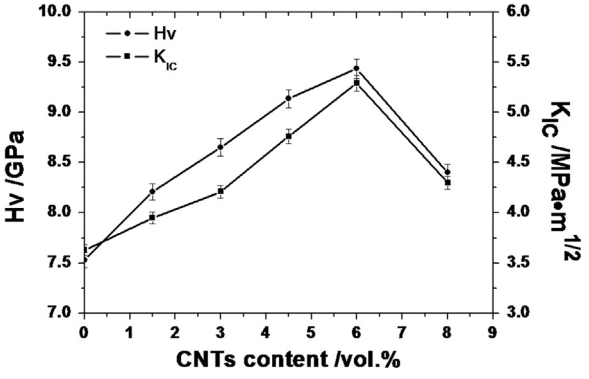

Fig. 1. Mechanical properties of the $MoSi_2$ based composites reinforced by various contents of CNTs.

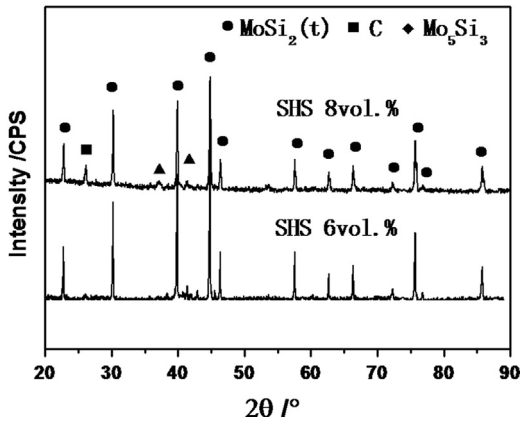

Fig. 3. XRD of the Mo–Si-CNTs mixed powders synthesized by SHS.

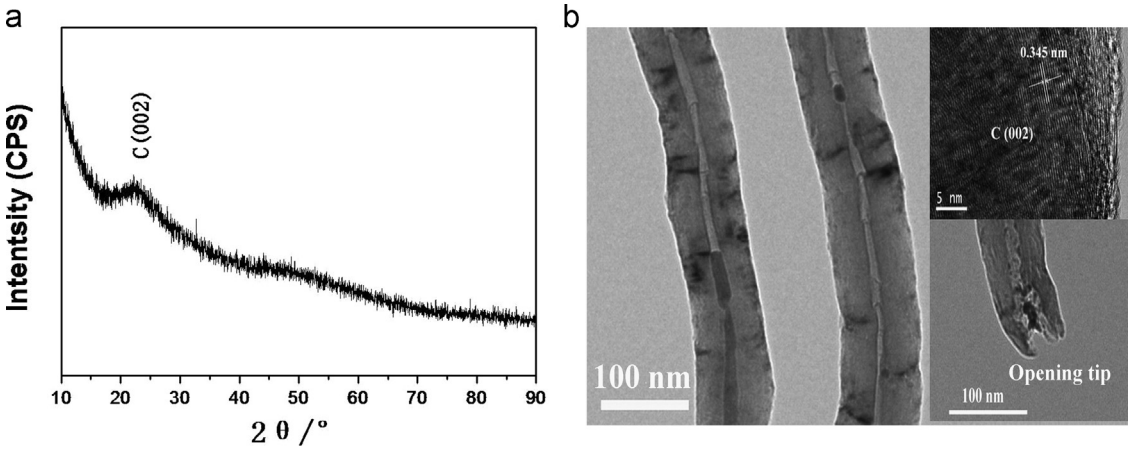

Fig. 2. Phase (a) and microstructure (b) of modified CNTs.

that the CNT is a multi-walled carbon nanotube, and the thickness of nanotube wall is about 35–40 nm and the external diameter is about 80–90 nm. Investigation using HTEM shows that the carbon atoms on surface of carbon nanotubes are located at (002) crystal face with 0.345 nm of the interplanar crystal spacing, which is the same result as described in Fig. 2(a), and the tip of CNT is open due to the modification of HNO_3, which is beneficial to disperse carbon nanotubes.

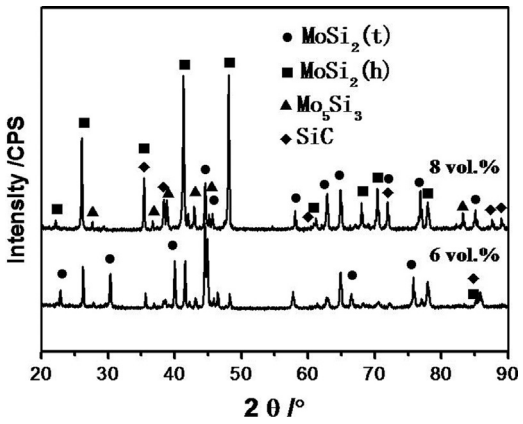

Fig. 4. XRD of the sintering CNTs/$MoSi_2$ composites.

All Mo–Si-CNTs mixed powders synthesized by SHS show the similar X-ray diffraction patterns as described in Fig. 3. The tetragonal $MoSi_2$ phase ($MoSi_2$ (t)) is dominant, and a few Mo_5Si_3 and C phases are also found in the powders. X-ray diffraction patterns of the sintering CNTs/$MoSi_2$ composites are shown in Fig. 4. It is shown that $MoSi_2$ is the primary phase, together with secondary phases of Mo_5Si_3 and SiC. However, if the content of CNTs is not higher than 6.0 vol%, the peak intensity of tetragonal $MoSi_2$ phase is higher than that of hexagonal $MoSi_2$ phase ($MoSi_2$ (h)). This indicates that the $MoSi_2$ (t) phase becomes weak and the $MoSi_2$ (h) phase becomes strong with increasing CNTs content. No C phase is shown in Fig. 4 due to the formation of SiC by the reaction between CNTs and Si. The formation results in the excess Mo to form Mo_5Si_3 phase with Si. Therefore, the peak intensity of SiC and Mo_5Si_3 improves with increasing CNTs content.

Fig. 5 shows the fracture surface of $MoSi_2$ based composites with various contents of CNTs. The fracture surface of pure $MoSi_2$ is indicated mostly by transgranular cleavage of the coarse-grain. With increasing CNTs content, the grain size of $MoSi_2$ based composite becomes gradually refined, and the fracture surface changes from a mainly transgranular cleavage for coarse grain of pure $MoSi_2$ to a predominantly intergranular fracture for fine grain of 6.0 vol% CNTs/$MoSi_2$ composites. However,

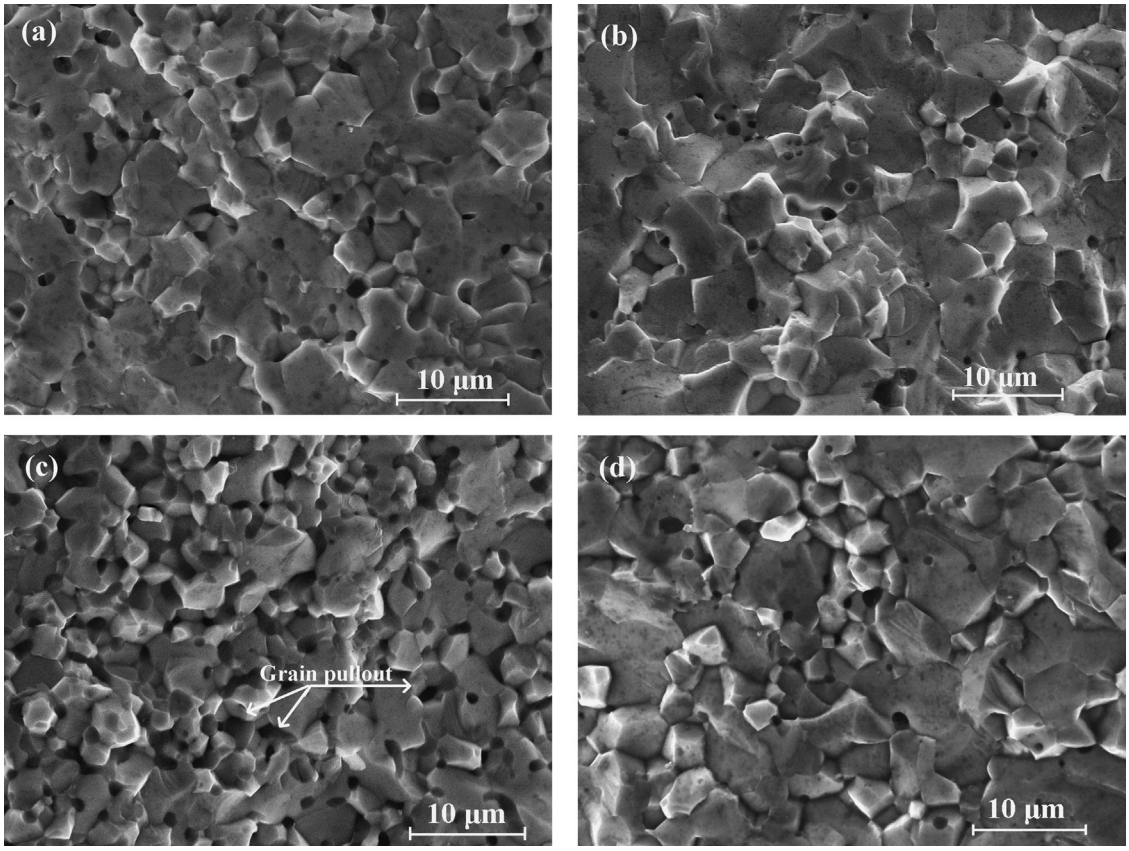

Fig. 5. SEM images of fracture surface in the $MoSi_2$ based composites with various contents of CNTs. (a) pure $MoSi_2$; (b) 3.0 vol% CNTs/$MoSi_2$; (c) 6.0 vol% CNTs/$MoSi_2$ and (d) 8.0 vol% CNTs/$MoSi_2$.

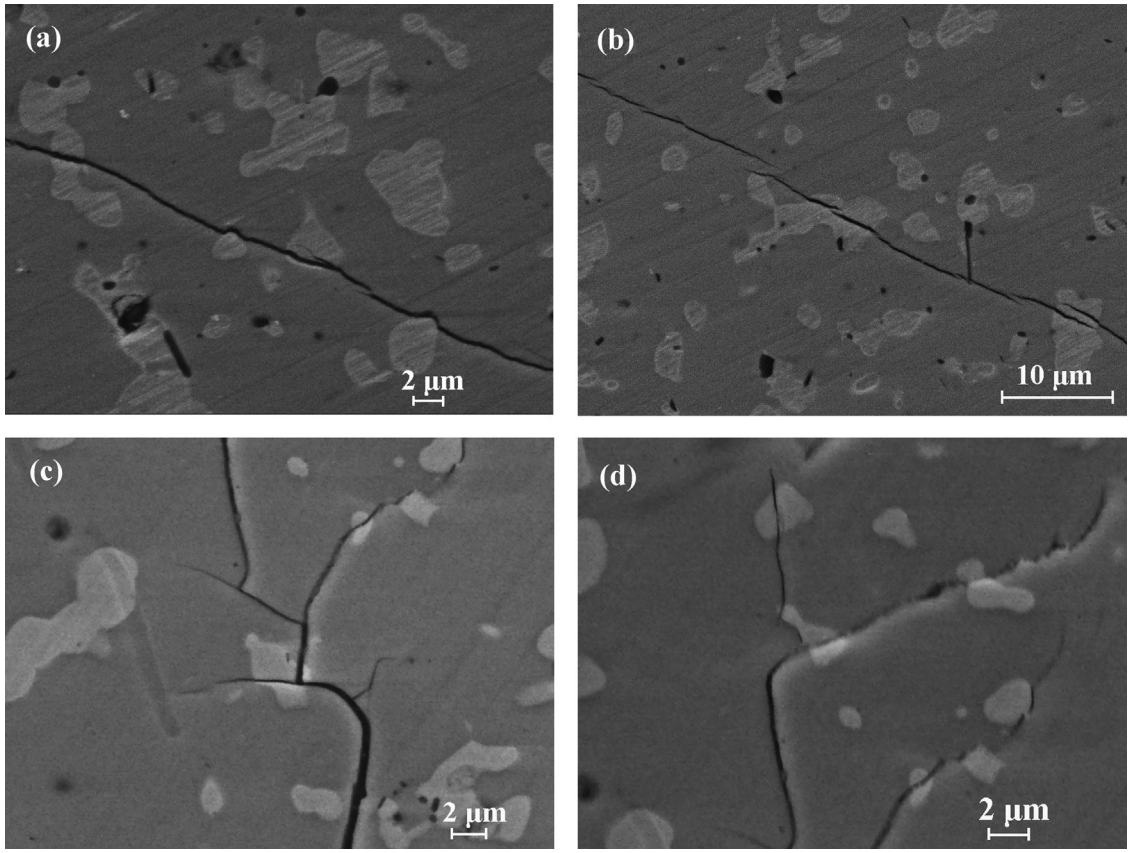

Fig. 6. SEM images illustrating the crack propagating behavior in the CNTs/$MoSi_2$ composite, (a) crack deflection, (b) crack microbridging, (c) crack branching and (d) crack bowing.

when the content of CNTs is 8.0 vol%, the coarsening grain and mainly transgranular cleavage are formed again, as shown in Fig. 5(d). The $MoSi_2$ based composite with 6.0 vol% CNTs has the smallest grain together with the favorable effect of the dispersed SiC particles, which results in the highest hardness as shown in Fig. 1. Similar results were also found in other $MoSi_2$ matrix composites reinforced by SiC [15] and carbon [16].

Crack propagation behavior in the CNTs/$MoSi_2$ composite is illustrated in Fig. 6. Fig. 6(a), (b), (c) and (d) shows crack deflection, crack microbridging, crack branching and crack bowing in the composite, respectively. Rice [17,18] reviewed the mechanisms that could toughen ceramic composites. These mechanisms include matrix microcracking, crack branching, crack deflection, crack bowing and fiber pullout. Carter and Hurley [19] suggested crack deflection be an important toughening mechanism in SiC-whisker-reinforced $MoSi_2$. Bhattacharya and Petrovic [20] provided evidence for crack-interface grain bridging (crack micro-bridging) in 20 vol% SiC/$MoSi_2$ composite and crack branching in 40 vol% SiC/$MoSi_2$ composite. In the present study, crack deflection and micro-bridging are present in all CTNs/$MoSi_2$ samples. Fine grain pullout only appears in the $MoSi_2$ based composite with 6.0 vol% CNTs, as shown in WSi_2/$MoSi_2$ composites [21], while crack branching and crack bowing are found in the $MoSi_2$ based composite with 8.0 vol% CNTs. Such behavior is due to the presence of a complex residual stress field [22] and the high resistance to crack propagation because of the addition of CNTs, where more energy can be absorbed, leading to a higher fracture toughness value.

4. Conclusions

$MoSi_2$ based composites with various contents of carbon nanotubes were prepared by sintering in vacuum at 1500 °C for 1 h. Microstructure and mechanical properties were investigated. Conclusions can be drawn from the present study as follows:

(1) The $MoSi_2$ based composite with 6.0 vol% CNTs has the highest hardness and fracture toughness which are improved respectively by about 25.3% and 45.7% compared to pure $MoSi_2$. It means that the addition of CNTs can significantly improve hardness and toughness of the composite and its optimal content is 6.0 vol%.
(2) High hardness of the CNTs/$MoSi_2$ composite is attributed to the strengthening effect of fine-grain and dispersion of SiC particles. The toughening mechanisms for the CNTs/$MoSi_2$ composites include crack deflection, crack micro-bridging, crack branching, crack bowing and fine-grain pullout.

Acknowledgments

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