Fabrication of Carbon Nanotube-TiC Nanocomposites by Spark Plasma Sintering

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1 Introduction

Carbon nanotubes have attracted a lot of interest because of their unique structure and unprecedented properties such as less than one nanometer in diameter for a single-walled nanotube with the elastic modulus and tensile strength as large as 5 TPa and 0.8 TPa, respectively[1~4].The exceptional mechanical and physical properties of carbon nanotubes, combined with their low density, make this new form of carbon an excellent candidate for composite reinforcement. Preliminary studies have been carried out on carbon nanotube composites with polymer, metal and ceramic to improve their mechanical and electrical properties[5~9]. To successfully achieve the outstanding mechanical performances of these new advanced composite materials, the issue of the structural integrity and the interfacial bonding between the nanotubes and matrix is important. Titanium carbide is a good potential material used in high temperature environment for its good strength, erosion resistance and thermal stability at high temperatures. Unfortunately, the low fracture toughness is a well-known obstacle to its application as structure components. TiC ceramics can be toughened and strengthened with the addition of particles, whiskers and fibers[10,11]. In our work, Carbon nanotubes were selected to reinforce TiC ceramics.

In recent years, innovative powder densification technology known as spark plasma sintering (SPS) has been an active method for fabricating metals, ceramics and composites[12~14]. Compared with other sintering process, such as hot-pressing, the SPS allows sintering and sinter-bonding possible at low temperature and short periods. These are obtained by charging the intervals between powder particles with electrical energy and effectively applying high-temperature spark plasma generated instantaneously. Thus, the SPS method is considered to be appropriate for fabricating fine-grained ceramics and nanocomposites. It is also promising to improve the interfacial bonding between nanotubes and matrix through active surface and rapid heat-transfer and mass-transfer in the SPS process.

The present work investigated a new process for fabricating Carbon Nanotue-TiC Nanocomposites by SPS in vacuum with Ni as additive. The characteristics and mechanical behavior of the Carbon Nanotue-TiC composites composites with

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different content have been investigated.

MWCNTs produced through catalytic vapour decomposition were supplied by the Chengdu Insititute of Organic Chemistry of CAS, China. The diameter and length distribution of the nanotubes that were used for the present study was about 10 nm-100nm and 50nm-3μm, as seen in figure 1. Commercially available pure TiC powder(average size of 20μm, purity>99%) and Ni powder(average size of 3.1μm, purity>99.5%) were used in this investigation.

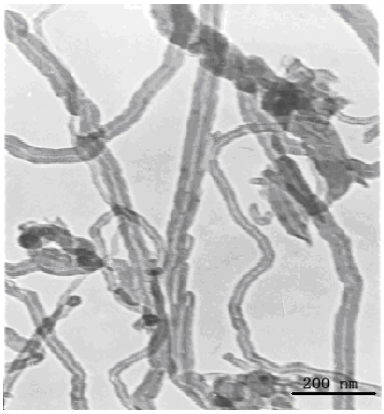


Fig.1 TEM image of carbon nanotubes powder before sintering

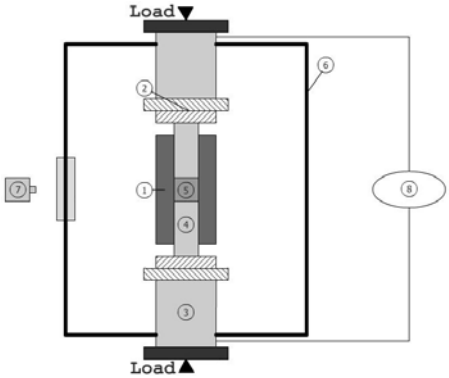


Fig. 2. Schematic diagram of the apparatus for spark plasma sintering (1, graphite die; 2, graphite plates; 3, ram; 4, graphite punch; 5, sample; 6, vacuum chamber; 7, optical pyrometer; 8, SPS pulsed generator).

The nanotube composites were firstly prepared by mixing nanotube/ethanol solutions with different nanotube weight fractions into TiC-Ni powder mixtures pretreated by ball-milling 4 hours. The mixtures were then sonicated for several hours and kept in 30℃ to allow evaporation of the solvent. Dried powders were milled again and sieved through a 150μm mesh screen. The mixed powders were put into a graphite die with diameter of 25mm and vibrated for homogeneous packing. Then carbon nanotube-TiC-Ni nanocomposites with different carbon nanotube contents(0,0.5wt% and 2wt%) were sintered by spark plasma sintering(SPS), which was carried out in vacuum using Dr Sintering 1020 SPS apparatus(Sumitomo Coal Mining Co., Ltd., Japan).The schematic diagram of SPS apparatus is shown in figure 2. The samples were sintered at 1400℃ with a heating rate of 600℃/min and a holding time of 3min. A pressure of approximately 40MPa was applied from the beginning of sintering and also held for 3 min. Then the sintering sample was fast cooled to 600℃ within 2-3 min. Samples of pure carbon nanotubes were also fabricated under the same conditions. The temperature was measured by means of an optical pyrometer focused on the graphite die surface.

Densities were measured by immersion in distilled water using Alchimedes principle. Sintered samples were cut and ground into bar specimens with 4×3×18mm.Bending strength was measured with polished bars using three-point bending test and fracture toughness was measured through SENB(Single-edge notched beam) method with a span length of 10mm and crosshead speed of 0.5mm/min in Shimadzu DCS-5000. TEM and SEM observations were carried out using a Jeol 200CX Transmission Electron Microscope and a Philips XL20 Scanning Electron Microscope, respectively.

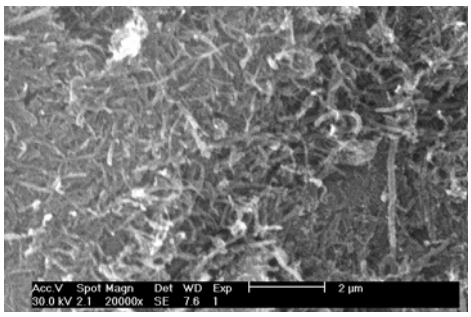
2 RESULTS & DISCUSSION

The results of porosity and mechanical properties versus carbon nanotube content are shown in Table 1. It shows that the porosity is minimized first with 0.5wt% carbon nanotubes additive and then takes a rise with 2wt% carbon nanotubes additive. The bending strength of carbon nanotube –TiC-Ni composites increases to 810MPa with However, the strength values of the samples fabricated by SPS are generally markedly lower than those of carbon nanotube-free TiC-Ni composites fabricated by other methods reported[15,16]. The fracture toughness values show the same trend as the bending strength versus carbon nanotubes contents. The fracture toughness of the samples with 0.5wt% carbon nanotubes additives are higher than that of the carbon nanotube-free TiC-Ni composites and has got the mean maximum of 13.6MPa • $m^{1/2}$. The bending strength and fracture toughness decrease at 2wt% carbon nanotubes content may be due to the lower relative density.

Table1 Carbon nanotubes contents and some properties of the SPS samples

Carbon nanotubes contents(wt%)	0	0.5	2
Porosity(%)	11.2	11	16.8
Bending strength(Mpa)	760	810	545
Fracture toughness(MPa•m1/2)	11.5	13.6	8.0

SEM observations of sample surfaces of pure carbon nanotubes reveal that most carbon nanotubes still retain tube-like images and take on random state after SPS process(seen in Fig.3a) , which means that carbon nanotubes have not been greatly damaged by SPS treatment and SPS is appropriate to fabricate carbon nanotubes composites. But the sample is too loose to characterize its mechanical properties. Fig.3.b,3.c.and3.d shows the surface morphologies of the SPS samples of composites. The diameter of TiC particles is from 3μm to 10μm. Ni locates evenly on the boundaries of TiC particles in all samples. The grain size of TiC tends to decrease and becomes unevenly as the CNT content increases. All samples are not very dense. The pores may be induced by the high fusion and precipitation of Ni in the SPS procedure and poor cohesion between the entangled CNTs group and TiC-Ni grains. Some graphite particles are present in the composites and the sample of pure carbon nanotubes after SPS process, which may be produced by the local high temperature and activated nanotubes surface in SPS procedure. These particles may weaken the mechanical properties. The weakened bending strength is chiefly related with these causes.



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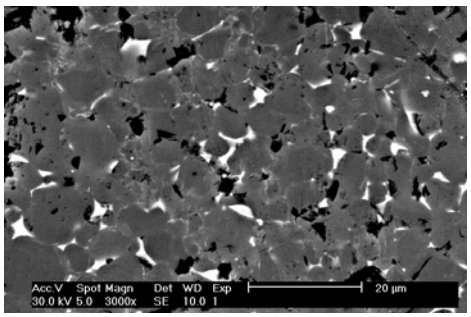

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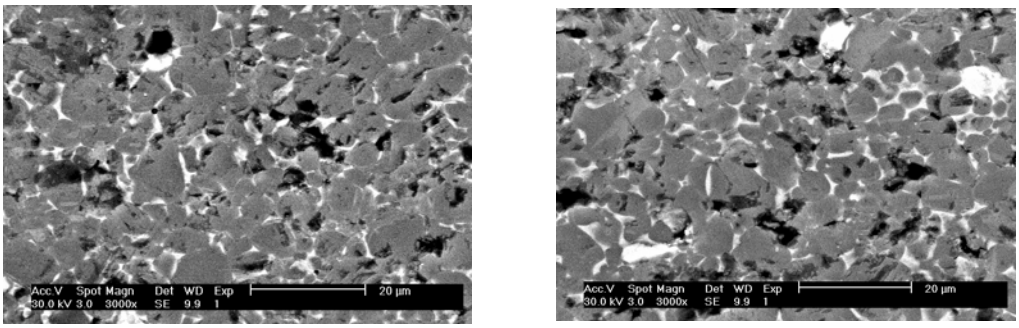
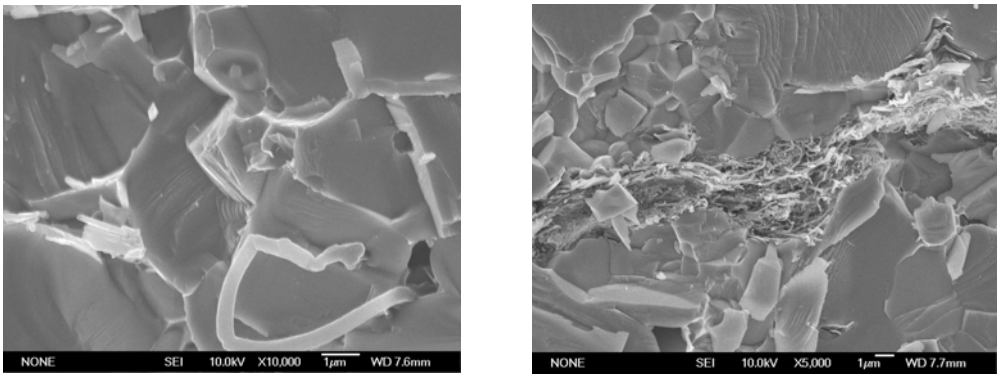


c d

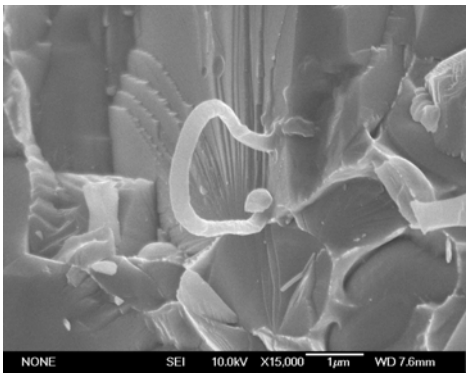
Fig.3 SEM image of surface of sintered sample: a. pure carbon nanotubes; b. TiC-Ni composite; c. TiC-Ni-0.5wt%CNT composite; d. TiC-Ni-2wt%CNT composite



a b

Fig.4. SEM images of the fractured surface of samples: a TiC-Ni-0.5wt%CNT composite; b. TiC-Ni-2wt%CNT composite

The SEM observations of the fractured surface of the specimens(as shown in Fig.4) display typical brittle fracture of intergranular yupture. However, there are nanotubes pull-out and bridge existing in the fracture surface, which could dissipate some fracture energy and improve the fracture toughness. The observations of composite show carbon nanotubes were distributed well in the sample of 0.5wt% carbon nanotube content, but some carbon nanotubes were aggregated in composites of 2wt% carbon nanotubes content. It seems that CNT and TiC may form a strong interface in SPS procedure when CNT distributed well, as seen in Fig.5a, detailed study on the interface will be shown in another paper. In Fig.5b and 5c,Striations are clearly observed over the large area of the fracture surface in carbon nanotube composites. It was found that striations are formed mainly at the immediate vicinity of the carbon nanotubes, which may also do contribution to the fracture toughness. The present results indicate that with appropriate addition of carbon nanotubes and spark plasma sintering process, the fracture toughness of TiC-Ni composites can be improved.



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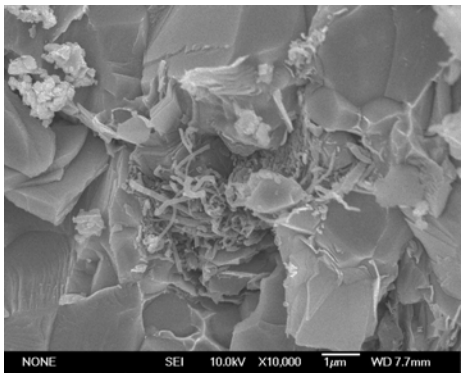

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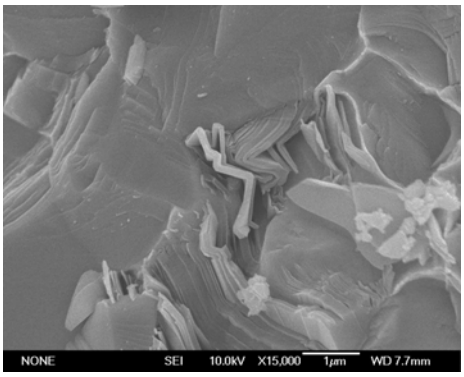

c

Fig.5 SEM images of the fractured morphology: a. the flexible CNT embedded in TiC particle; b fracture surface near CNTs region; c enlarged image of striations at the vicinity of the carbon nanotubes

3 CONCLUSIONS

Carbon nanotube-TiC-Ni nanocomposites with different carbon nanotube contents(0,0.5wt% and 2wt%) were sintered by spark plasma sintering, the porosity is minimized first with 0.5wt% carbon nanotubes additive and then takes a rise with 2wt% carbon nanotubes additive. The bending strength and the fracture toughness values show the same trend as the density versus carbon nanotubes contents. These samples have ordinary bending strength and high fracture toughness when compared with samples fabricated by other methods. The fracture toughness of the samples with 0.5wt% carbon nanotubes additives has got the mean maximum of 13.6MPa • $m^{1/2}$. The presence of carbon particles and the high fusion and precipitation of Ni in the SPS procedure weaken the samples, but the nanotubes pull-out and bridge and striations exist in the fracture surface dissipate some fracture energy and improve the fracture toughness. The results proved that SPS is a potential method for fabrication carbon nanotube-TiC composites and CNT can improve the mechanical properties of composites, but more work on CNT dispersion and CNT-base interface should be done to optimize microstructures and properties of the carbon nanotube nanocomposites.

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References:

[1] Iijima,S. “Helical microtubules of graphitic carbon”, Nature, 354(1991),56-58

[2]Saito,R., Dresselhaus, G. and Dresselhaus, M.S., Physial Properties of Carbon Nanotubes, Singapore:Imperial College Press,1998

[3]Qian,D.,Wagner,G.J., et al., “Mechanics of carbon nanotubes”, Applied Mechanics Review, 55(2002),495-533

[4] Yu,M.F., Lourie,O., et al., “Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load”, Science, 287(2000),637-640

[5] Thostenson, E.T., Ren, Z.F.and Chou,T.W., “Advances in the science and technology of carbon nanotubes and their composites: a review”,Comp.Sci.Tech., 61(2001),1899-1912

[6] Cs. Bala´zsi, Z. Ko´nya, F. We´ber, L.P. Biro´c, P. Arato´, “Preparation and characterization of carbon nanotube reinforced silicon nitride composites”, Materials Science and Engineering C, 231(2003),1133-1137

[7] Nikhil A. Koratkar, Bingqing Wei, Pulickel M. Ajayan, “Multifunctional structural reinforcement featuring carbon nanotube films”, Composites Science and Technology 63(2003), 1525-1531

[8] H.W. Goh, S.H. Goh, G.Q. Xu, K.P. Pramoda , W.D. Zhang, “Dynamic mechanical behavior of in situ functionalized multi-walled carbon nanotube/phenoxy resin composite”, Chemical Physics Letters, 373(2003),277-283

[9] E.Flahaut, A.Peigney, Ch.Laurent,et al., “Carbon nanotube-metal-oxide nanocomposites: Microstructure, electrical conductivity and mechanical properties”. Acta Mater., 48(2000),3803-3812

[10] Durlu N. “Titanium carbide based composites for high temperature applications”. J Eur Ceram Soc 19(1999),2415-2419

[11] Gui-Ming Song , Yu Zhou , Suk Joong L Kang. “Experimental description of thermomechanical properties of carbon fiber reinforced TiC matrix composites”. Materials and Design 24 (2003) 639-646

[12] Sirirat Rattanachan, Yukio Miyashita, Yoshiharu Mutoh, “Microstructure and fracture toughness of a spark plasma sintered Al_2O_3-based composite with $BaTiO_3$ particulates”. J.Eur.Ceram.Soc., 23(2003),1269-1276

[13] Seung I. Cha, Soon H. Hong, Byung K. Kim. “Spark plasma sintering behavior of anocrystalline WC_/10Co cemented carbide powders”. Materials Science and Engineering A351 (2003) 31-38

[14] Mats Nygren , Zhijian Shen. “On the preparation of bio-, nano- and structural ceramics and composites by spark plasma sintering”. Solid State Sciences 5 (2003) 125-131

[15] Han Jie-Cai, Xing-Hong Zhang, J.V. Wood. “In-situ combustion synthesis and densification of TiC–xNi cermets”. Materials Science and Engineering A280 (2000) 328–333

[16] Yumin Zhang, Jiecai Han, Xinghong Zhang, ,et al. “Rapid prototyping and combustion synthesis of TiC:Ni functionally gradient materials”. Materials Science and Engineering A299 (2001) 218–224