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The effect of heat treatment on mechanical properties of carbon nanofiber reinforced copper matrix composites

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Abstract The effect of heat treatment of carbon nanofibers (CNFs) on the mechanical properties of CNF (Ni/Y)–Cu composites was investigated. CNF (Ni/Y)–Cu composite powder mixtures were prepared by a combination of in situ chemical vapor deposition (CVD) and co-deposition processes. The in situ CNF (Ni/Y)–Cu powder synthesized by CVD was subject to heat treatment at temperatures ranging from 700 to 1,000 °C. The morphology and quality of CNFs were characterized by transmission electron microscope, scanning electron microscope, and Raman spectroscopy. Heat treatment can improve the CNFs by eliminating the amorphous carbon and disordered graphite. Bulk composites containing various fractions of CNFs were fabricated from the powder by cold pressing and sintering followed by repressing. With the same fraction of CNFs (2.5 wt%), the strengthening efficiency of the CNFs heat treated at 800 °C is 88% higher than that of as-synthesized CNFs. The strengthening mechanism of CNFs in the composites is discussed in detail.

Introduction

Due to their singular mechanical, electrical, and thermal properties, carbon nanotubes (CNTs) and carbon nanofibers (CNFs) can be very useful materials in composites to improve a particular property for specific applications. Most of the reported composites have been made focusing on their mechanical properties, but the electrical and thermal properties of the composites have also received more attention recently [1, 2]. In order to exploit the potential of these composites, there are two important processing issues in the fabrication of CNT (or CNFs) composites: a homogeneous distribution of CNTs and a high interfacial strength between the CNTs and the matrix. Work on CNTs or CNFs in metals and ceramics with improved properties have been reported [3, 4]. However, unlike CNT/polymer nanocomposites [1, 5], for which a homogeneous distribution and the load transfer through good bonding between the polymer matrix and CNTs has been observed, a detailed investigation of the CNT(or CNFs)/metal nanocomposites to establish the origin or nature of the enhanced mechanical properties has not been performed to date.

In this work, we fabricated CNF–Cu composites using a novel process, consisting of in situ synthesis of CNFs on the Cu powder followed by mixing Cu ions with the in situ CNF (Ni/Y)–Cu composite powders in a solvent. A high dispersion of CNFs in the matrix has been successfully achieved [6]. At the same time, the investigation of the interfacial bonding properties between the nanofibers and matrix is of great interest, since this ensures a good stress transfer between the nanofiber and matrix in composite structures. There are three main load transfer mechanisms that control the full operation of the stress transfer, including micro-mechanical interlock, chemical bonding (interaction), and a weak van der Waals attractive force. As

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Cu cannot react with untreated CNFs directly, chemical bonding between CNFs and Cu is impossible. In order to enhance the interfacial strength, many approaches have been made, e.g., coating CNFs or CNTs with some active materials (such as Ni, Cu) to form a transient interlayer [7] or roughening the surface of CNFs to enhance the micro-mechanical interlock [8]. Recently, Kim et al. [9] reported that chemically bonded oxygen atoms present at the CNT/Cu interface in the nanocomposite can also play an important role as atomic transition agents accommodating the load transfer between the CNT and the Cu matrix. However, degradation of some functional properties such as thermal and electrical conductivities could not be avoided because of electron or phonon dissipation by interfacial oxygen atoms. In our experiments [10], CNTs and CNFs were in situ synthesized on copper powders by CVD at low temperature, during which some impurities such as amorphous carbon and catalyst were inevitably co-produced. The existence of the impurities tends to influence the final properties of the composites. It is accepted that heat treatment at proper temperature can enhance the graphitization and purities of CNTs and CNFs. A number of results have been reported on the effect of heat treatment of carbon nanofibers on polymer nanocomposite properties [11]. However, there are no publications dealing with this in metal matrix composites as far as we know. In this article, CNF–Cu composite powders were subjected to heat treatment temperatures ranging from 700 to 1,000 °C to alter the physical interactions between the CNFs and the Cu matrix. The strength of adhesion between the fiber and Cu matrix was characterized by the compressive yield strength.

Experimental

Preparation of the catalyst precursor

The catalyst precursor was prepared by means of a deposition–precipitation process [12, 13]. Appropriate amounts of $Ni(NO_3)_2{\cdot}6H_2O$ (4.954 g, 98.0% purity), $Y(NO_3)_3{\cdot}6H_2O$ (2.154 g, 98.0% purity), and 400 mesh electrolytic copper powder (48.5 g, 99.9% purity) with a mass ratio of 2:1:97 (Ni:Y:Cu) were mixed in 500 mL distilled water. NaOH (2.038 g, 97% purity) was dissolved in 300 mL distilled water and added to the previous mixture with constant stirring to obtain the ternary colloid ($(Ni(OH)_2/Y(OH)_3/$Cu). The colloid was washed with distilled water until a neutral pH was reached and then dried at 100 °C in a N_2 atmosphere. Finally, the dry colloid was calcined in a N_2 atmosphere at 250 and 400 °C consecutively for 2 h each time to form the catalyst precursor supported on Cu particles.

Production of CNF (Ni/Y)–Cu composite powders

Carbon nanofibers were in situ synthesized on the Cu powders by chemical vapor deposition (CVD). The as-prepared catalyst precursor was reduced at 450 °C for 3 h in a hydrogen (99.9% purity, 100 mL) atmosphere. Then, CNF growth was performed with a mixture of gases, i.e., 100 mL/min CH_4 and 300 mL/min N_2, at 500 °C for a certain time, which determined the quantity of CNFs produced [6]. In order to modify the properties of the CNFs, the composite powders obtained by CVD were annealed at different temperatures (700–1,000 °C) for 1 h and then cooled to room temperature under a nitrogen atmosphere.

The second step is to coat the CNFs with copper by a co-deposition process. 2.5 g of the in situ CNF (Ni/Y)–Cu composite powders and 9.157 g of $Cu(NO_3)_2{\cdot}2.5H_2O$ were added into 100 mL ethanol. Then, the solution was vaporized with magnetic stirring at 80 °C and the dried powders were calcined at 300 °C in air. The calcined powders were reduced at 250 °C for 3 h under a hydrogen atmosphere. As the new Cu added is equal to the amount of in situ CNF (Ni/Y)–Cu composite powders, the weight percent of CNTs in the composite can be calculated as follows:

$$\mathrm{C_{composite}}(\mathrm{wt\%}) = \frac{\mathrm{C_{in\ situ\ composite}}(\mathrm{wt\%})}{2} = (\mathrm{mg/mg}) = \frac{M_1\,(\mathrm{mg}) - M_2\,(\mathrm{mg})}{2 \times M_1\,(\mathrm{mg})} \times 100\%$$

where M_1 (mg) is the weight of the in situ CNF (Ni/Y)–Cu composite powders (original or heat treated) and M_2 (mg) is the weight of the composite catalyst powders (Ni/Y/Cu) after reducing for 3 h in a H_2 atmosphere.

Fabrication of CNF (Ni/Y)–Cu composites

The final CNF (Ni/Y)–Cu composite powders were pressed in a tool steel mold, 13 mm in diameter, under a pressure of 600 MPa. Then, the compact obtained was sintered at 650 °C for 1.5 h in a vacuum sintering furnace, and the sample was repressed again in the mold under a pressure of 800 MPa to obtain the final CNF (Ni/Y)–Cu composite.

Characterization

Microstructural characterization of the composite powders and composites was carried out using a transmission electron microscope (TEM, PHILIPS TECHAI G2 F20) and a scanning electron microscope (SEM, JEOL JSM-T330). Raman spectroscopy of the composite powders was performed by using the 514-nm line of an Ar+ laser as the excitation source to validate the quality of the CNFs. Compressive tests were performed using an Instron 5583 with a loading speed of 22 kN/min. The compression samples were cylindrical and about 2 mm in height and 13 mm in diameter.

Results and discussion

In this experiment, the carbon fraction of the original in situ CNF–Cu composite powders obtained by CVD at 500 °C for 1.5 h is 7.6 wt%. Figure 1 shows the TEM image of the composite powders. It can be seen that the main product obtained by CVD is herringbone CNFs with an average diameter of 40 nm. The catalyst particles were located on one side of the CNFs. From the TEM observation, we can also observe some impurities, such as amorphous carbon. Figure 1b displays a typical high-magnification TEM image of the CNFs. There exists a disordered carbon layer on the surface of both CNFs and catalyst. It is known that the thermal stability of various carbon phases is different. CNTs are structurally stable up to 2,000 °C [14]; however, the CNTs and CNFs, especially obtained by CVD, usually have some defects, which affects their properties. Theoretical studies indicate that the multi-walled CNT layers start to deform at 727 °C [15]. Yi et al. [16] reported that heat treatment (500–800 °C) can make the CNTs thinner and enhance the electrochemical properties for CNT–$LaNi_5$ electrodes. In this experiment, the in situ CNF (Ni/Y)–Cu composite powders were subjected to thermal treatment between 700 and 1,000 °C for 1 h. Figure 2b–e shows the SEM images of the composite powders after heat treatment at different temperatures. When the heating temperature is 700 °C, the diameters of the CNFs have no obvious changes from the SEM observations (Fig. 2b), compared with the original CNFs (Fig. 2a). The weight loss of the composites is due to the elimination of amorphous carbon. At 800 °C, the diameters of the CNFs decrease obviously (Fig. 2c). Figure 3 shows the TEM images of the CNFs heat treated at 800 °C, it can be seen that the average diameter has become about 25 nm. From the high resolution TEM image (Fig. 3b), it is observed that the graphite layers become more regular and the amorphous carbon coated on the surface of catalyst and CNFs disappears. It is also interesting that some layers seem to extrude from the CNF surface (indicated by arrows in Fig. 3b), which increases the surface roughness. When the heating temperature is increased to 1,000 °C, some bead-like particles with diameters of several hundred nanometers appear among or above the CNFs, as shown in Fig. 2d, e. These bead-like particles were identified from energy dispersive X-ray analysis as Ni–Cu alloy. The formation of these Ni–Cu alloy beads is due to the diffusion between the catalyst (Ni) and substrate (Cu) and this causes the separation of catalyst nanoparticles from the CNF tips. It is known that Cu has little solubility in carbon. It is impossible for Cu to diffuse through carbon, which implies that all the disordered graphite or amorphous carbon on the surface of the catalyst has been removed. However, the beads were not formed directly on the surface of the Cu (Fig. 2d, e), suggesting that the catalyst nanoparticles have separated from the surface of Cu after the CNF growth. Combining with the TEM observations, we can conclude that the growth mechanism of CNFs in the experiments is the tip-growth. The reaction between Cu and Ni may be due to Cu atoms vaporizing at high temperature and diffusing into Ni particles to form Ni–Cu alloy. It is also interesting that the weight loss of the composite powders is

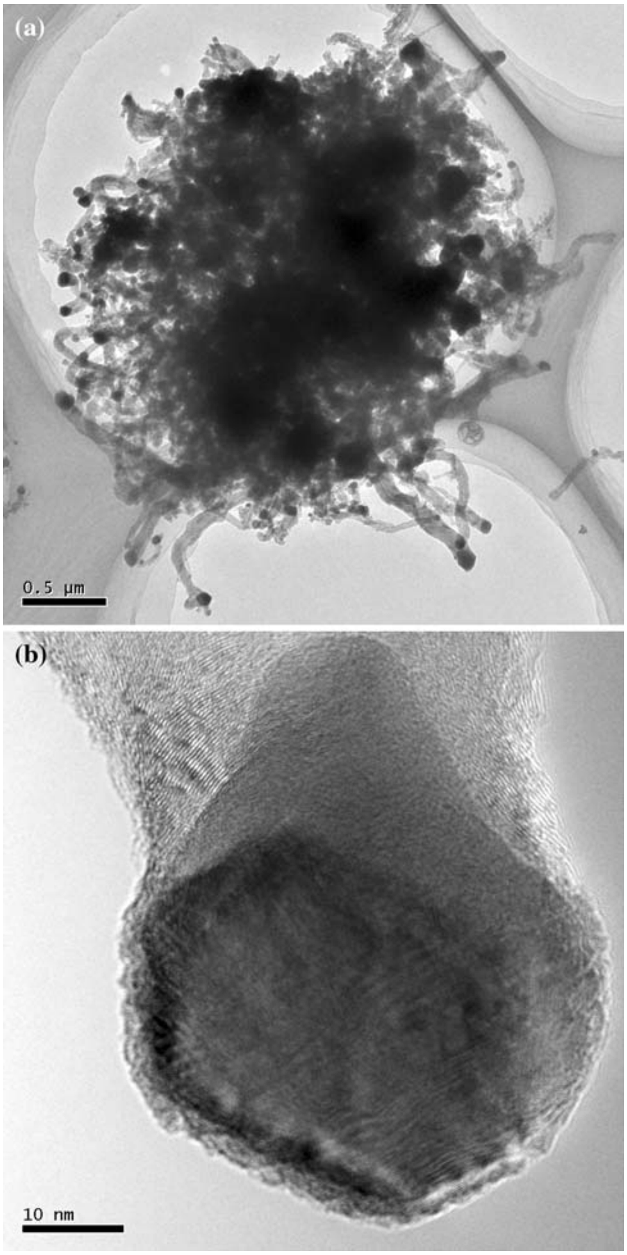

Fig. 1 TEM images of the products obtained by CVD

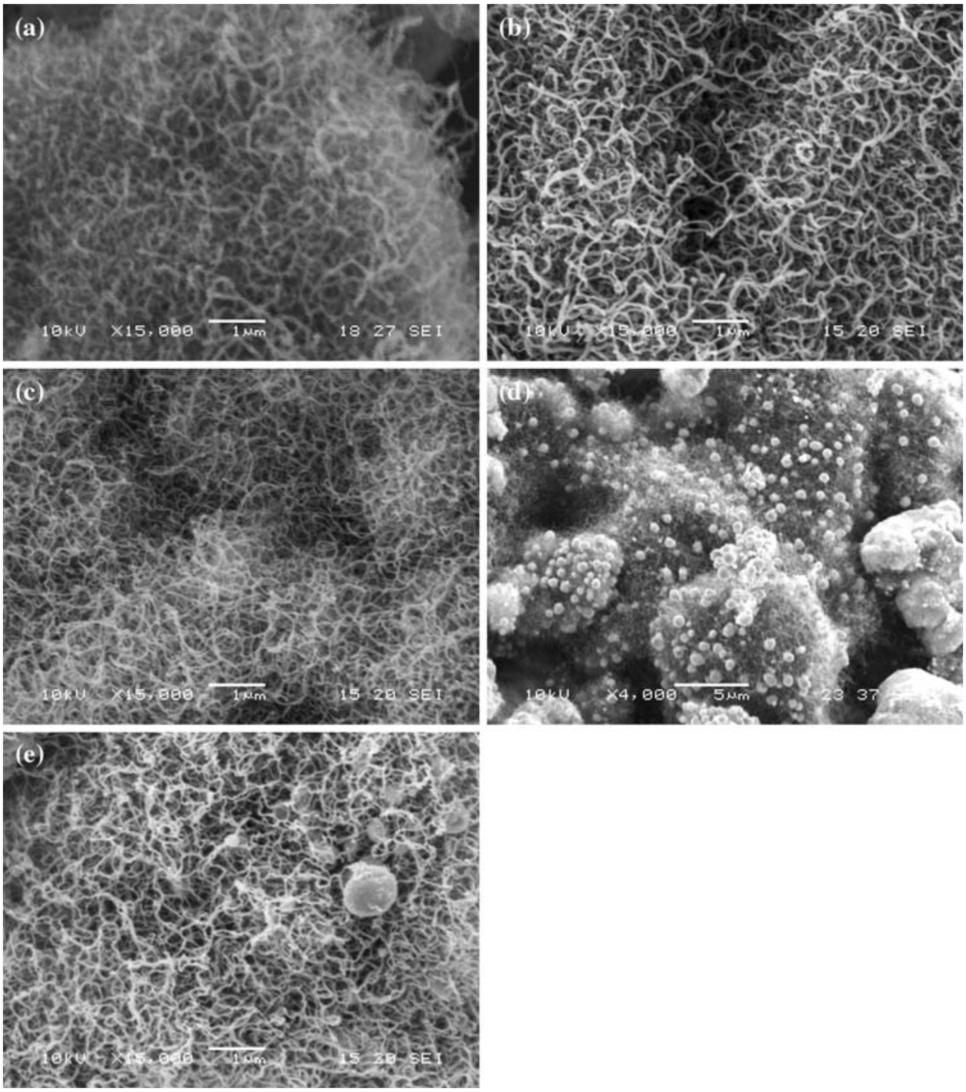

Fig. 2 SEM images of the original (**a**) and heat treated in situ CNF (Ni/Y)–Cu composite powders at 700 °C (**b**), 800 °C (**c**), and 1,000 °C (**d**, **e**)

very small when the heating temperature is increased from 800 to 1,000 °C (Table 1), indicating that almost all disordered graphite and amorphous carbon has been eliminated at 800 °C. The similar diameters of the CNFs treated at 800 °C and 1,000 °C also testify to this (Fig. 2c, e).

The in situ CNF (Ni/Y)–Cu composite powders were also characterized in detail by Raman spectroscopy to validate the quality of CNFs (Fig. 4). The Raman spectrum of all the composite powders exhibits two peaks (near 1,350 and 1,580 cm^{-1}), which are associated with the vibrations of carbon atoms with dangling bonds for the in-plane termination of disordered graphite (D) and the vibrations in all sp2-bonded carbon atoms in a 2D hexagonal lattice (G), respectively [17]. It can be seen that the intensity ratio of the D band to the G band decreases with increasing heating temperature (ID/IG: $a(1.145) > b(1.076) > c(1.046) > d(1.045)$). However, the value of ID/IG is still large, inferring that the herringbone structure of CNFs, even heat treated at 1,000 °C, does not change. The small reduction of ID/IG value is due to the elimination of amorphous carbon and coalescence of dangling bonds of graphite.

The in situ CNF (Ni/Y)–Cu composite powders both treated and untreated were subject to the next step to cover CNFs with Cu using a co-deposition method. SEM studies of the final composite powders found that there was little visual difference between the powders using treated and untreated in situ composite powders. Almost all the CNFs were covered with Cu and homogeneously dispersed in the matrix. It is inferred that the heat treatment of in situ CNF (Ni/Y)–Cu composite powders does not weaken the bonding between CNFs and Cu substrate. Figure 5 shows the final reduced composite powders with CNFs heat treated at 1,000 °C. There are no obvious aggregations of CNFs observed. A high-magnification SEM image of the composite powders (Fig. 5b) confirms the presence of a fine network structure of the CNFs covered with Cu particles.

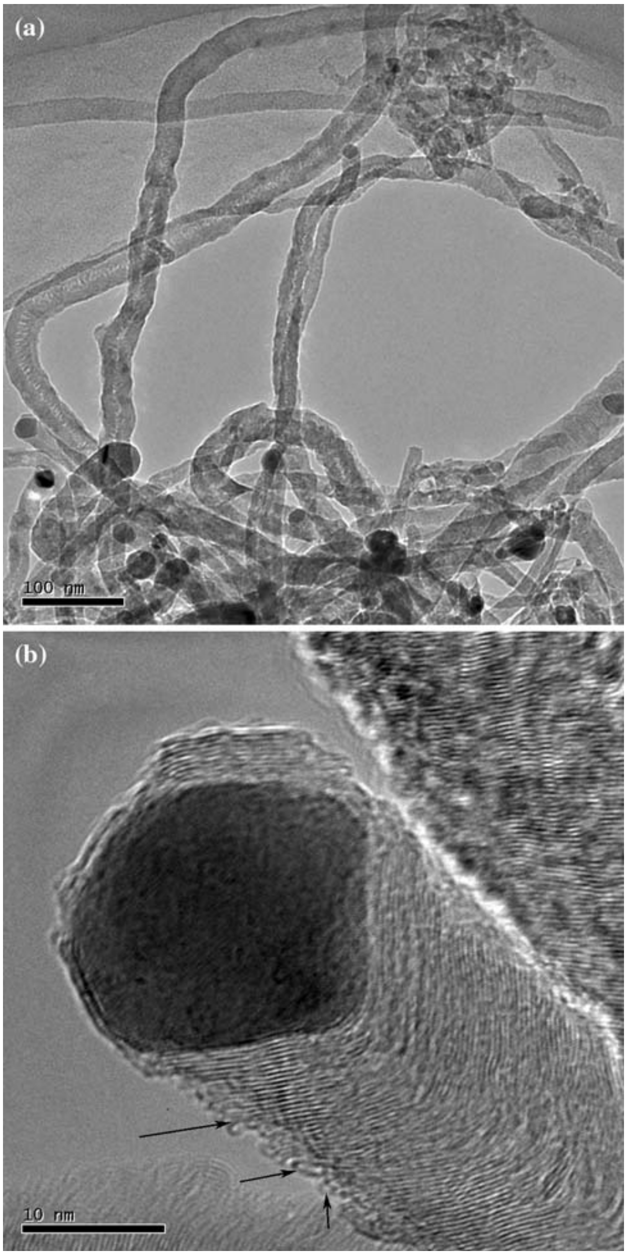

Fig. 3 TEM images of the in situ CNF (Ni/Y)–Cu composite powders heat treated at 800 °C

Table 1 Comparative study of the composites with original and heat-treated CNFs

Material	Heating temperature (°C)	Carbon content (%)	Yield strength (MPa)
CNFs (Ni/Y)–Cu composite	–	3.8	470
	700	3.2	611
	800	2.5	632
	1,000	2.4	514

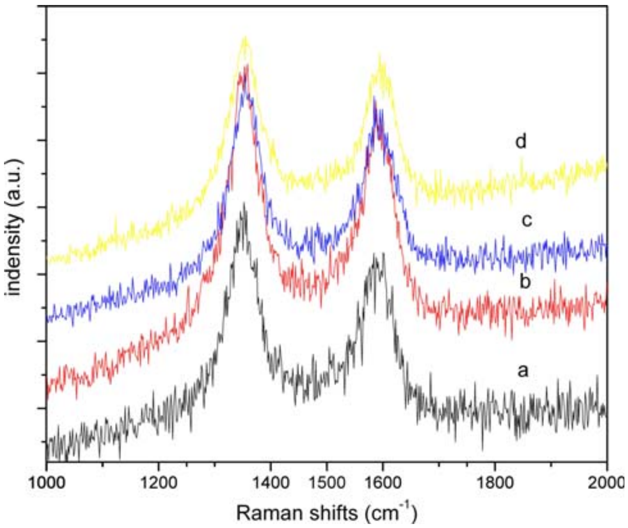

Fig. 4 Raman spectrum of the original (a) and heat treated in situ CNF (Ni/Y)–Cu composite powders at 700 °C (b), 800 °C (c), and 1,000 °C (d)

The mechanical properties of the CNF (Ni/Y)–Cu composites, obtained by pressing and sintering the final CNF (Ni/Y)–Cu composite powders, were characterized using compression tests. As shown in Fig. 6, the compressive yield strengths of the composites with original CNFs increased with the carbon fraction until the value of the yield strength reached a maximum at 3.4 wt% and then decreased. When the fraction of original CNFs is 3.4 wt%, the yield strength is 501 MPa, almost 2.3 times higher than that of the Cu matrix (221 MPa).

As discussed above, the states of CNFs and catalyst changed after heat treatment, consequently affecting the properties of the final composites. Table 1 presents a comparative study of compressive yield strength values of the composites processed from CNFs heat treated under different temperatures. All the samples use the same original in situ CNF (Ni/Y)–Cu composite powders. It can be seen that yield strength of the composites with heat-treated CNFs increases significantly. Below 800 °C, the effect of heat treatment of CNFs on the composite property increases with the heating temperature increasing. However, when the CNFs were heated at 1,000 °C or higher, the strength of the composite was reduced. As shown in Table 1, the carbon fraction in the composites was reduced with increasing heating temperature of the CNFs, due to the elimination of disordered graphite and amorphous carbon, which caused the CNFs to become thinner (Fig. 2). From Fig. 6, the yield strength of the composite increased until the carbon fraction reached 3.4 wt%. Thus, considering the effect of CNF fraction, the strengthening effect of heat-treated CNFs is even greater. With the same fraction of CNFs (2.5 wt%), the strengthening efficiency of the

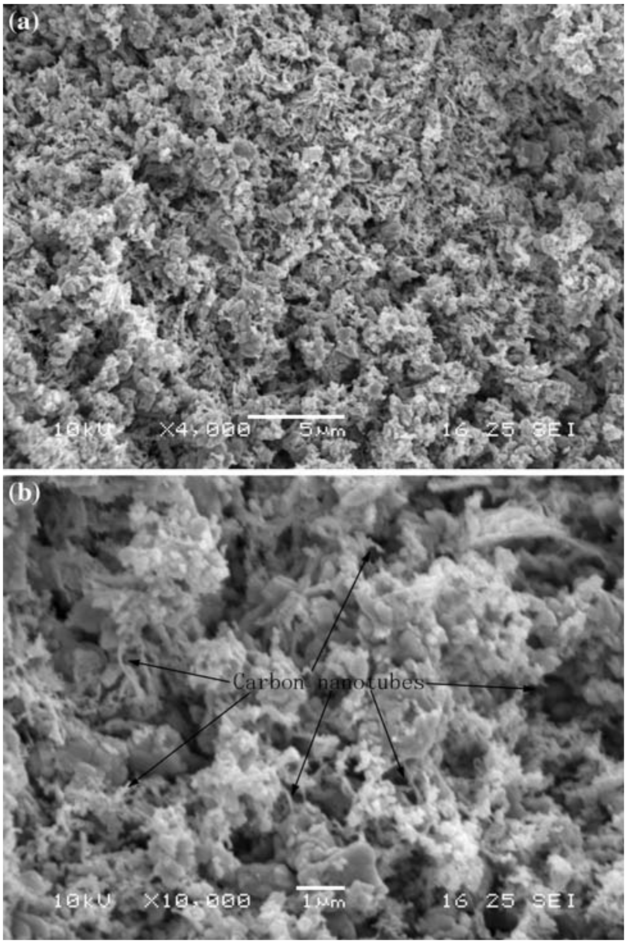

Fig. 5 SEM images of the final reduced composite powders with CNFs heat treated at 1,000 °C

CNFs heat treated at 800 °C is 88% higher than that of the original CNFs.

Such remarkable strengthening by CNF reinforcement was due to the high load-transfer efficiency of CNFs in the metal matrix. High load-transfer efficiency was caused by strong interfacial bonding between CNFs and Cu. As is known, the Cu–C system does not form any intermetallic compounds and the solubility of C in Cu is almost zero. The chemical bond strength is extremely low. Therefore, the extraordinary strengthening effect of CNFs must mainly originate from the very homogeneous dispersion of CNFs in the Cu matrix and micro-mechanical interlocking bonds formed by molecular-level contact between CNFs and Cu. It is noted that all of the composites were fabricated by the same process and the distributions were the same for both original and heat-treated CNFs. Therefore, the authors believe that the improvement of mechanical strength of the composites with heat-treated CNFs is due to the enhancement of the interfacial bonding between the CNFs and Cu. As mentioned above, the surface of vapor-grown CNFs and some catalyst nanoparticles were covered by a layer of disordered graphite and amorphous carbon. Thus, Cu atoms cannot react with the CNFs directly. In another words, it forms a transition interlayer between the CNFs and the Cu matrix. The transition layer cannot enhance the interfacial bonds because it does not react with CNFs or Cu. On the contrary, it may promote the relative displacement between the CNFs and Cu during the load transfer, due to the lubricity of carbon and weak bonding between the CNFs and transition layer. After heat treatment, the disordered graphite and amorphous carbon were removed. Cu atoms can directly react with dangling bonds of the graphite plane of the CNFs and catalyst nanoparticles, which are located at the top of the CNFs. The rough and irregular surface of the CNFs easily forms micro-mechanical interlocks with the Cu matrix, which enhances the interfacial bonds between CNFs and Cu and thus improves the mechanical properties of the composites. Figure 7 shows the TEM images of the composite with annealed CNFs at 800 °C. It can be seen that a CNF penetrates through several Cu grains (Fig. 7a), although some parts of the CNF are embedded in Cu matrix. From the high resolution TEM observations, it is seen that the graphite layers have been partially destroyed by ion milling and bombardment during sample preparation and TEM observation. However, we can still observe some black particles on the surface of the CNF (Fig. 7b), which are confirmed as Cu by EDS and interplanar distance. This infers that the bonding between CNF and Cu is very strong. It is also interesting that a trace of extruded graphite layers inserted in Cu can be observed on the interface region of Cu and CNF (indicated by arrows in Fig. 7c), which is consistent with the structure of the CNFs annealed at 800 °C. These special structures further enhanced the interfacial bond between CNFs and Cu, thus causing a higher strength. In a study of carbon fiber reinforced copper

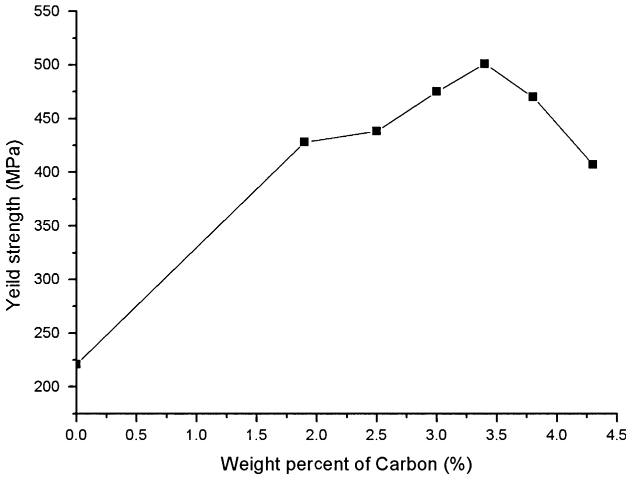

Fig. 6 Variation of composite yield strength with carbon weight content

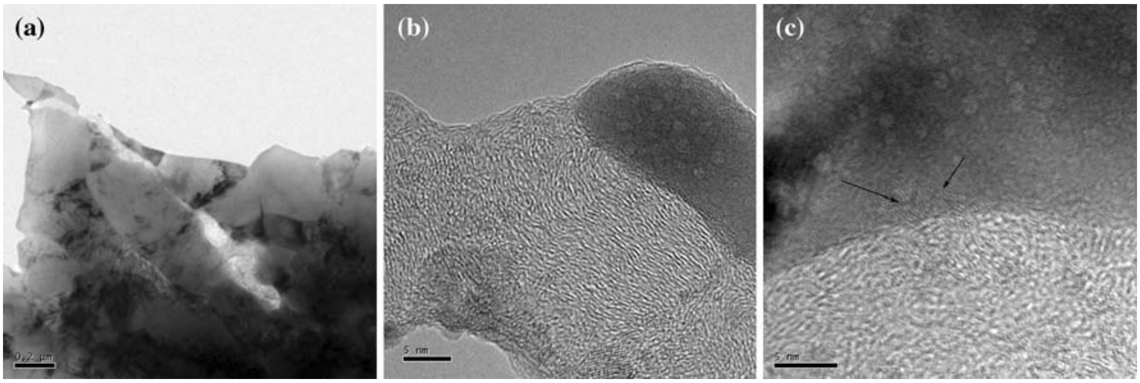

Fig. 7 TEM images of the composite with the CNFs heat treated at 800 °C

matrix composites [18], the copper–nickel duplex coating of carbon fibers was converted to a non-brittle, continuous layer of face-centered cubic copper–nickel solid solution during the hot-pressing process, causing continuous transition from carbon fiber to the interface zone. The bare catalyst (Ni/Y) on the top of the CNFs may also have some diffusion with the matrix to form an interface zone and thus improve the strength of the composites. When the heating temperature reached 1,000 °C, the catalyst aggregated and alloyed with Cu to form bead-like particles with a diameter of several hundred nanometers. The bead-like particles may aggregate during the co-deposition process and cannot enhance the interfacial bonds between CNFs and Cu. Therefore, the mechanical properties of the composite are reduced.

Conclusion

The effect of heat treatment of CNFs on the mechanical properties of CNF (Ni/Y)–Cu composites was investigated. CNF (Ni/Y)–Cu composite powder mixtures were prepared by a combination of in situ CVD and co-deposition process. The in situ CNF (Ni/Y)–Cu powders synthesized by CVD were subject to heat treatment at temperatures ranging from 700 to 1,000 °C. Heat treatment can clean away the amorphous carbon and disordered graphite located on the surface of the CNFs and catalyst, which causes the CNFs to become thinner. Considering the same fraction of CNFs (2.5 wt%), the strengthening efficiency of the CNFs heat treated at 800 °C is 88% higher than that of the original CNFs. However, when the in situ CNF (Ni/Y)–Cu powders were heated above 1,000 °C, the catalyst alloyed with Cu and formed larger bead-like particles (several hundred nanometers in diameter). The yield strength of the composite was then reduced.

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