

RESEARCH ARTICLE | DECEMBER 09 2002

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Appl. Phys. Lett. 81, 4739–4741 (2002)

<https://doi.org/10.1063/1.1530371>



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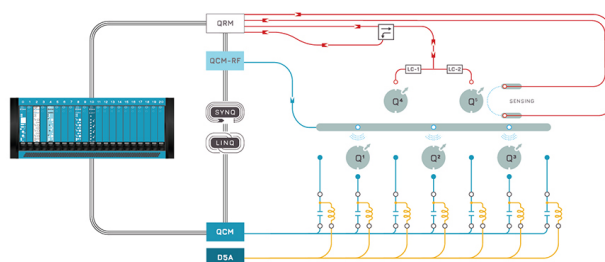
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Carbon-nanotube-reinforced $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ bulk metallic glass composites

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(Received 15 March 2002; accepted 22 October 2002)

Carbon-nanotube (CNT) reinforced Zr-based bulk metallic glass composites are prepared by the conventional die cast method. A large amount of CNTs still keep their seamless cylindrical morphology in the glassy matrix, even though some CNTs react with Zr, resulting in the formation of ZrC phase. Investigation shows that the elastic moduli, Vicker's hardness, density, and Debye temperature of the composite are markedly changed by introducing CNTs into the glass. Our results suggest that CNTs are promising materials for preparing reinforced, lightweight bulk metallic glass composites with improved mechanical and physical properties relative to the undoped glass.

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Recently, the preparation of bulk metallic glass (BMG) matrix composites has received great attention.^{1–8} Metals or metal fibers,^{1–4} as well as ceramic particles,^{1,5,6} are introduced successfully into Zr-based BMGs to improve their mechanical properties. More recently, BMGs reinforced with carbon fibers have also been successfully processed,⁹ and the glass state of the matrix can be retained after processing. Carbon nanotubes (CNTs), possessing excellent mechanical properties and chemical stability (e.g., extremely high elastic modulus and good plasticity^{10,11} originating from their cylindrical graphitic structure), might act as a material for preparing BMG composites. The composites reinforced with CNTs might have properties such as high strength, good ductility, light weight, and stiffness. In this letter, we report the preparation of the CNT-reinforced BMG composites. A $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ alloy is used as a matrix material, which is one of the best glass-forming alloys developed so far. It will be shown that under the proper processing condition the CNTs can be dispersed in the BMG matrix and keep their good multiwalled structure, and the properties of the glass have been improved.

Ingots with a nominal composition of $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ were prepared by arc-melting a mixture of high purity Zr, Al, Ni, Cu, and Ti under a Ti-gettered, purified Ar atmosphere. The prealloyed ingots were ground mechanically into fine powder with a particle size of about 200 μm . The CNT powder with a density of 1.8 g/cm^3 was cleaned in acetone and dehydrated at 473 K before mixing. The ingot powder was mixed homogeneously with CNTs and dried immediately in a vacuum furnace for 5 h. The mixed powder was compressed into cylinders in steel dies (diameter=8 mm). The cylinders were melted in a quartz tube rapidly by induction under a high, pure-Ar atmosphere, and then cast into a copper mold to produce rods with a diameter of 5 mm. The composite was analyzed by x-ray diffraction (XRD) using a MAC M03 XHF diffractometer with $\text{Cu K}\alpha$ radiation, differential scanning calorimetry (DSC) and high resolution transmission electron microscopy

(HRTEM) in a JEM-200cx operating at 200 kV. The composite sample was mixed with $\text{CH}_3\text{CH}_2\text{OH}$ and mechanically ground into very fine powder; the powder was put on the copper grid covered with carbon thin film and observed by HRTEM. DSC measurements were carried out under a purified argon atmosphere in a Perkin Elmer DSC-7. The composite rods were cut into pellets with a length of 8 mm. The ends of the pellets were carefully polished flat and parallel. An acoustic measurement was done by using a pulse-echo overlap method. The travel time of ultrasonic waves propagating through the pellet with a 10 MHz frequency was measured using a MATEC 6600 ultrasonic system. The density was measured by the Archimedeian technique and the accuracy lies within 1%. The Vicker's hardness (H_V) is measured by using a Polyvar MetTM microhardness tester with a 200 g load. Elastic constants (e.g., Young's modulus E , shear modulus G , bulk modulus K), Poisson's ratio ν and Debye temperature θ_D of the BMG and the composite were derived from the acoustic velocities and the density.

Figure 1 shows XRD patterns of the undoped BMG, 3 vol % CNT-reinforced BMG composite, and pure CNT powder. The curve of the composite exhibits a superimposition of broad maximum from the amorphous phase and several sharp peaks characteristic for a crystalline phase, suggesting

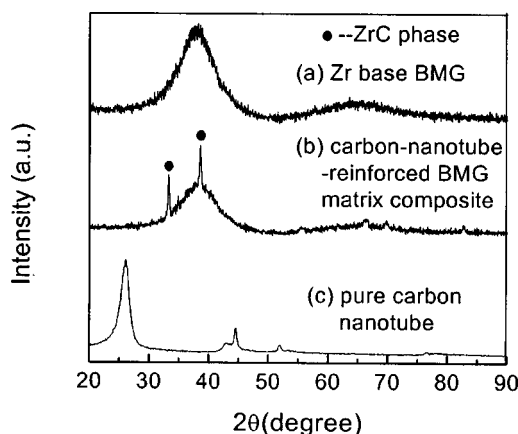


FIG. 1. XRD patterns of the undoped BMG, 3 vol % CNT-reinforced BMG composite and pure CNTs.

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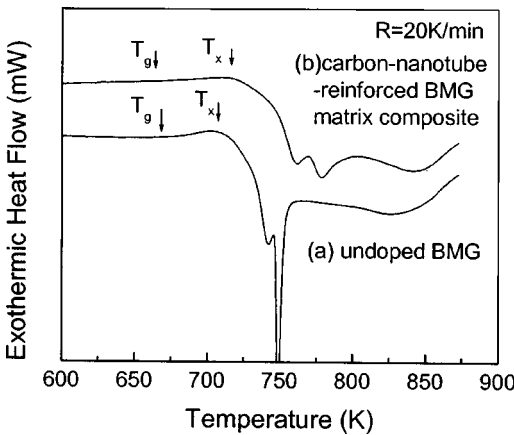


FIG. 2. DSC traces of the undoped BMG and 3 vol % CNT-reinforced BMG composite.

that a mixture of the amorphous and some crystalline phases is formed. The position and the intensity of the crystalline peaks match exactly with that of ZrC phase, as shown in Fig. 1. No other phases are detected within the sensitivity limit of XRD. The result indicates that CNTs have reacted partially with Zr and have formed crystalline ZrC. Zr element has a much larger negative heat of mixing (109 KJ/mol)¹² with C than that of other constituents (Al, Cu, or Ni), meaning that Zr and C have the largest driving force for the interfacial reaction. Thus, the C and Zr reaction is favored during the melting and casting processes, and leads to the formation of ZrC. Kim *et al.*⁹ and Wang *et al.*^{6,13} have also reported similar results by introducing carbon fibers or carbon element into BMG matrix.

Figure 2 presents DSC traces of the undoped BMG and CNT-reinforced composite ($R=20$ K/min). DSC traces show that the composite exhibits an endothermic heat characteristic of the glass transition followed by three exothermic heat events, indicating the successive stepwise transformations from supercooled liquid state to crystalline phases. The crystallization behavior is much different from that of the BMG. Glass transition temperature T_g of both samples has no obvious difference, but the onset temperature T_x of all the crystallization peaks of the composite shift to higher temperature. The results indicate that the composite containing a CNT addition has a different crystallization behavior compared to the BMG. The possible reasons for this difference are due to the variation of the matrix composition in the composite resulting from the following process: (i) some carbon atoms dissolve into the amorphous matrix of the composite and increase the packing density of the amorphous matrix and (ii) the formation of ZrC at the interfaces between the amorphous matrix and CNTs leads to a depletion of Zr in the matrix.

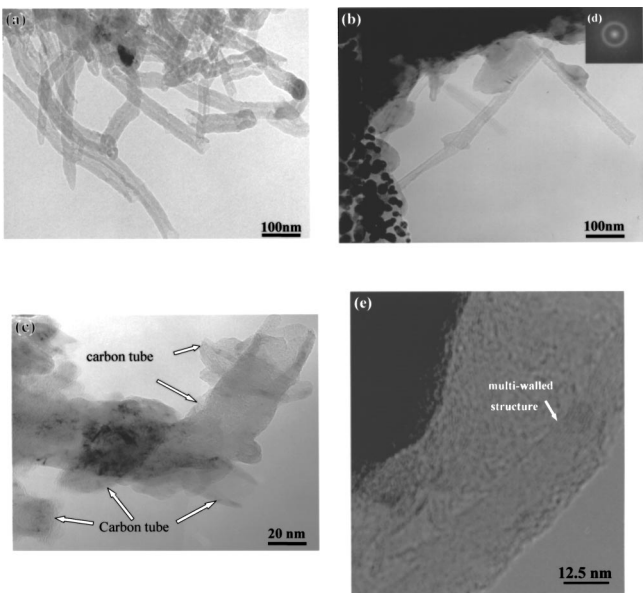


FIG. 3. TEM image of as-prepared CNTs shows their typical tubular morphology. (a), TEM morphology of CNTs after distributing into the BMG matrix still displays their tubular structure (b), (c), the selected area diffraction pattern in the matrix of the composite shows the glass state of the matrix (d), and HRTEM image displays the multiwalled structure of carbon nanotubes after adding into the BMG (e).

To confirm the existence of CNTs in the composite, bright-field TEM and HRTEM observations are made, and images are shown in Fig. 3. Figure 3(a) shows typical tubular morphology of as-prepared CNTs. Figures 3(b) and 3(c) show typical morphology of CNTs after adding into the BMG matrix. From Figs. 3(b) and 3(c), some whole CNTs with obviously tubular structure can be observed, which suggests that CNTs have been distributed into the BMG matrix. The selected area diffraction pattern [shown in Fig. 3(d)] in the matrix of the composite shows that the glass state is still retained after processing. To further investigate the structural variation of CNTs after distributing into BMG, HRTEM observation was also carried out [shown in Fig. 3(e)]. It is clearly seen that some CNTs still keep their cylindrical graphitic structure, and their multiwalled structure can also be observed clearly. The above results demonstrate that some CNTs have been introduced into the BMG matrix and still keep their multiwalled structure. The glass state of the matrix is still retained. The reason for the distribution of CNTs in the glass matrix is due to high thermal stability and the chemical stability of the CNTs,^{14–16} and the low melting point (about 1100 K) and the strong glass-forming ability of the $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ alloy.

The variation of the physical properties caused by dispersing CNTs in BMG matrix is also studied by ultrasonic method. Table I lists the variation of the density ρ , the lon-

TABLE I. The ρ , v_l , v_t , E , K , G , H_V , ν , and θ_D for the undoped BMG and 3 vol % CNT-reinforced BMG composite, and their relative changes ($(Y - Y_a)/Y_a$).

Alloy	ρ (g/cm ³)	v_l (Km/s)	v_t (Km/s)	E (GPa)	K (GPa)	G (GPa)	H_V	ν	θ_D (K)
BMG	6.73	4.833	2.191	88.6	114.1	32.3	579	0.371	280.8
Composite	6.61	5.130	2.281	94.7	128.0	34.4	626	0.377	290.8
$(Y - Y_a)/Y_a$ (%)	-1.83	6.2	4.1	6.9	12.2	6.4	8.1	1.7	3.6

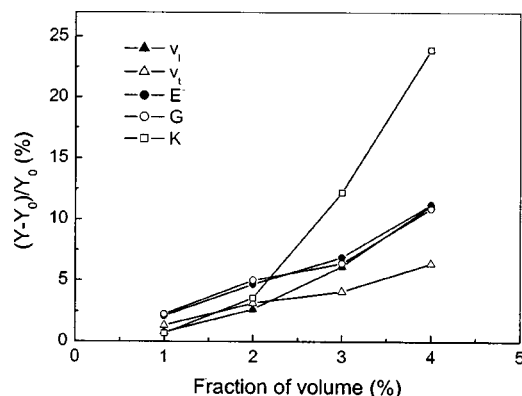


FIG. 4. Relative changes in v_l , v_t , E , K , and G as function of volume fraction of CNT addition.

gitudinal and transverse acoustic velocities (v_l and v_t), E , K , G , H_V , ν , and θ_D of the composite containing 3 vol % CNT addition. All the parameters increase except the density. The relative changes $(Y - Y_a)/Y_a$ (Y_a is the parameters of the BMG; Y are the parameters of the composites) in v_l , v_t , E , K , G , H_V , and θ_D are 6.2%, 4.1%, 6.9%, 12.2%, 6.4%, 8.1%, and 3.56%, respectively. The density has decreased by about 1.83%. Large relative changes are observed on v_l , E , K , G , and H_V . The relative changes in v_l , v_t , E , K , and G as function of volume fraction of CNT addition are also shown in Fig. 4. It can be seen that the relative changes increase with the increase of CNT content. The results suggest that the addition of CNTs into the BMG matrix has an effective strengthening role. Chen *et al.*¹⁷ have reported that the mixed structure of nanocrystalline phase and ZrC phase dispersing randomly in the glass matrix has a higher hardness than the glass matrix and improves mechanical properties significantly. The microstructure of the composite with CNT addition is similar to that of the composites with carbon powder addition after annealing,¹⁷ which consists of the glass matrix, CNTs, and ZrC phase. The CNT is one of the stiffest structures ever made.^{11,18} The residual CNTs and the formed ZrC dispersing in the BMG matrix have made a significant contribution toward improving mechanical properties of the composite. The value of E of CNTs has been reported to be 1.8 TPa,^{10,11} which is much larger than that of the Zr-based BMG. Even if only 1 vol % CNTs are kept and distributed

homogeneously into the BMG matrix, according to the simple rule of mixtures,⁵ the theoretical value of E of the present composite is estimated to be 110 GPa. This value is roughly close to our experimental value (about 94.6 GPa). More CNT addition could greatly improve the mechanical properties of the Zr-based BMG.

In conclusion, the CNT-reinforced, Zr-based BMG composite was processed successfully. The composite consists of the glass matrix, ZrC phase, and CNTs that still keep their tubular and multiwalled structure. The addition of CNTs results in the increase of elastic constants and decrease of density, which suggests that the dispersing of CNTs in the BMG matrix is promising for preparing lightweight BMG composites with improved mechanical and physical properties relative to undoped BMG.

The authors are grateful to the financial support of the Natural Science Foundation of China (Grant Nos. 50201019, 50031010, and 59925101), and to Dr. C. L. Xu for providing the carbon nanotubes.

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