Excellent ultrasonic absorption ability of carbon-nanotube-reinforced bulk metallic glass composites

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$Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ bulk metallic glass composites (BMGCs) containing carbon nanotubes (CNTs) are found to have a strong ultrasonic wave absorption ability. Ultrasonic attenuation coefficients of Zr-based BMGCs increase dramatically with increasing volume fraction of CNTs. The excellent ultrasonic wave absorption ability is attributed mainly to the multiscattering caused by the CNTs and ZrC phase dispersing randomly in the glass matrix. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1570938]

Recently, ultrasonic measurement has been applied extensively to investigate the structural variation and vibration characteristics of the bulk metallic glasses (BMGs).[1–5] Measurements of acoustic velocities and attenuation in BMGs become much easier than in thin amorphous ribbons because of their larger geometry and higher thermal stability. More recently, Zr-based BMGs reinforced with carbon nanotubes (CNTs) have been processed.[6] The CNTs dispersing in the BMG matrix still keep their tubular and multiwalled structure. The CNT-reinforced BMG composites are lightweight and have improved mechanical and physical properties compared to the BMG itself. In this letter, we report an ultrasonic attenuation study of the CNT-reinforced $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ bulk metallic glass composites (BMGCs). Investigation shows that the BMGCs have strong ultrasonic attenuation characteristics and show excellent wave absorption ability, which implies that BMGs may have significantly potential application in the field of shielding against acoustic sound or environmental noise.

The preparation of the composites containing different volume fractions of CNT addition was described in detail in Ref. 6. The composite rods were cut into cylinders with a length of 8 mm. The ends of cylinders were carefully polished flat and parallel. The acoustic attenuation of the specimens at room temperature was measured by using a pulse-echo overlap technique using a MATEC 6600 ultrasonic system with a 10-MHz carrier frequency.[1,7] This method has been described in detail in Ref. 1. Ultrasonic attenuation was obtained from the measurements of the amplitude decay of successive echoes. The attenuation coefficient (α, dB/cm) of a sample is calculated according to the relation[8]

$$\alpha = \frac{20}{2nl}\log\left(\frac{A_i}{A_{i+n}}\right),$$

where A_i and A_{i+n} indicate the amplitudes of the ith and $(i+n)$th echoes, respectively; l is the length of the sample. The measuring sensitivity of attenuation was about 5%.

X-ray diffraction patterns and high resolution transmission electron microscopy (HRTEM) observations show that the BMGCs containing different volume fractions (vol %) of CNT addition have the mixed structure of residual CNTs and ZrC phase dispersing randomly in the glassy matrix.[6] The ZrC phase comes from the interfacial reaction between the added CNTs and the amorphous matrix. Although the added CNTs have reacted partially with the glass matrix, HRTEM observations show that the most residual CNTs still keep their multiwalled and tubular structure.[6] The effect of the addition of CNTs on acoustic wave attenuation of BMGCs is shown in Table I and Fig. 1. The longitudinal ultrasonic attenuation coefficient (α_l) and the transverse ultrasonic attenuation coefficient (α_t) increase dramatically with increasing volume fractions of CNT addition. Even a 1.0-vol % CNT addition can cause a very large relative change in α_l and α_t (440% and 255%, respectively). Compared with carbon addition, the ultrasonic attenuation induced by CNT addition is much larger,[4] indicating that ultrasonic attenuation is very sensitive to CNT addition, and CNT addition can markedly enhance the ultrasonic absorption ability of the composites. With further increase of the addition, the relative changes in α_l and α_t increase significantly. The relative changes in α_l and α_t for the composites containing 2.0-, 3.0-, and 4.0-vol % CNT addition are 560%, 640%, 900%, and 391%, 482%, 536%, respectively. For a 4.0-vol % CNT addition, α_l and α_t are about 10 and 7 times larger than that of the undoped BMG, respectively. With more than a 5.0-vol % CNT addition, the reflected acoustic velocities of the BMGCs could not be detected because ultrasonic attenuations are too strong, so that no pulse echo was observed on oscilloscope screen under applying experiment conditions. These results demonstrate that the addition of CNTs into Zr-based BMG matrix causes strong ultrasonic wave absorption.

It is known that the anharmonicity in a homogeneous glass solid gives rise to wave absorption via the so-called Akhieser effect.[9–11] The loss originates from the absorbed energy as the phonons of an anharmonic solid shift to a new nonequilibrium distribution under stress. For multiphase solids, acoustic attenuation originates from multiple scattering of multiple scatterers dispersed randomly in an elastically isotropic matrix. After adding CNTs into the BMG matrix, the tubular shape of CNTs is basically kept.[6] These CNTs dispersing randomly in the glassy matrix supply large

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TABLE I. The longitudinal and transverse ultrasonic attenuation (α_l and α_s) for the undoped BMG and the BMGCs containing different vol % CNT additions.

	BMG	1.0 vol %	2.0 vol %	3.0 vol %	4.0 vol %	5.0 vol %	7.0 vol %	10.0 vol %
ρ (g/cm^3)	6.73	6.701	6.643	6.607	6.549	6.502	6.345	6.161
α_l (dB/cm)	0.5	2.7	3.3	3.7	5.0	⋯	⋯	⋯
α_s (dB/cm)	1.1	3.9	5.4	6.4	7.0	⋯	⋯	⋯

amounts of nanoscale tubes embedded randomly in the glassy matrix. The interfacial reaction between the glassy matrix and the adding CNTs also leads to the formation of an amount of new interfaces and ZrC phase.[6] The mixed structure, which consists of nanoscale tubes, the interfaces and ZrC phase, can act as multiple scatterers. Morse has reported that the scattered wave spreads isotropically in all directions at low frequencies when the wavelength of an incident wave (λ) is much greater than the particle radius D.[12] For an ultrasonic wave with a frequency of 10 MHz, its wavelength is much larger than the mean size of CNTs. When ultrasonic waves transmit across the composites with the mixed structure, most of them are multiscattered in all directions because of the random distribution of multiple scatterers. This leads to the strong ultrasonic attenuation and wave absorption ability. Acoustic attenuation caused by the anharmonicity in amorphous solids increases proportional to the square of incident frequency,[9–11] namely, $\alpha_a \sim f^2$. However, for a solid containing the scatterers, acoustic attenuation keeps varied law of frequency depending on the diameters, the volume fractions, the mass of scatterers, and other complex factors. On the other hand, the significant increase of ultrasonic attenuation with increasing volume fraction of CNTs indicates that the CNTs dispersing in the glass matrix also have a significant effect on ultrasonic attenuation. Challis *et al.* calculated the Rayleigh wave scattering caused by mass defects and concluded that the scattering efficiency P ($P = E^{(s)}/E^{(0)}$, where $E^{(0)}$ and $E^{(s)}$ are the energy per unit time of the incident wave and the scattered wave, respectively) caused by mass defects is proportional to $(\Delta m)^2 f^5$; namely, $P \propto (\Delta m)^2 f^5$ (Δm indicates the variation in the mass due to the introduction of the defects; f is the frequency of the incident wave).[13] For a fixed frequency of 10 MHz, $P \propto (\Delta\rho)^2$ ($\Delta\rho = \rho - \rho_0$, where ρ and ρ_0 are the density of the BMG and the composites, respectively). Figure 2 shows the dependence of $(\Delta\rho)^2$ on the volume fraction of CNT addition. It is seen that $(\Delta\rho)^2$ (or P) increases significantly with increasing CNT addition, implying that the scattering efficiency P increases significantly with increasing CNT content. When the addition of CNTs increases, the total volumes of the scattering phases per unit volume also increase, and raise the probability that an impinging wave will be scattered, resulting in an increase of P. Furthermore, in the process of the interfacial reaction between the additional CNTs and the glassy matrix, the dissolution of carbon atoms into the glassy matrix induces denser random packed microstructure of the glassy matrix, and results in stronger interatomic interaction and larger anharmonicity. This also causes the increase in ultrasonic absorption.[4]

In conclusion, the CNT reinforced composites have strong ultrasonic attenuation characteristics and excellent wave absorption ability. Ultrasonic attenuation coefficients are very sensitive to the addition of CNTs and increase dramatically with increasing volume fractions of CNT addition. The excellent ultrasonic absorption ability of the composites originates from the strong multiscattering induced by the mixed structure of residual CNTs and crystalline ZrC phase dispersing randomly in the glass matrix, and the interfaces between the glassy phase and CNTs.

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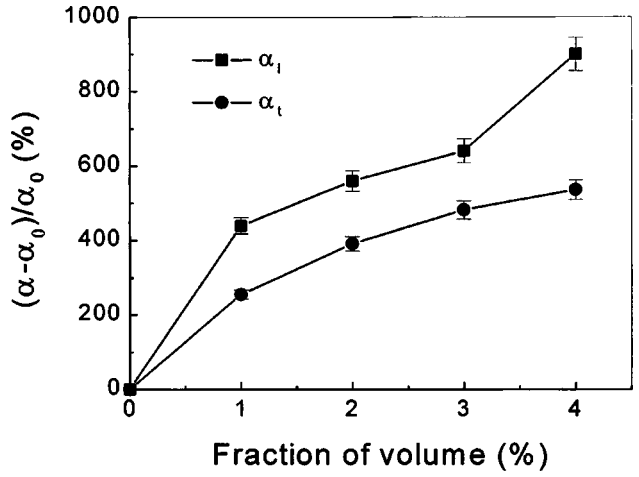

FIG. 1. Relative changes $\Delta\alpha/\alpha_0 = (\alpha - \alpha_0)/\alpha_0$ of the longitudinal and transverse ultrasonic attenuation (α_l and α_t) of $Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_5$ BMGCs with increasing volume fractions of CNT addition. (α_0 is attenuation coefficient of the undoped BMG; α are attenuation coefficients of the composites).

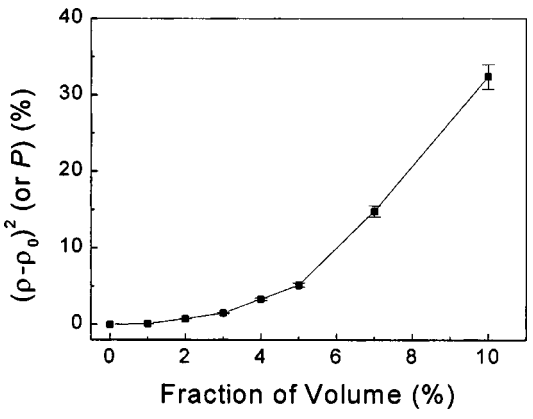

FIG. 2. Dependence of $(\Delta\rho)^2$ (or the scattering efficiency P) on volume fraction of CNT addition.

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