Synthesis and Properties of Carbon Short Fiber Reinforced ZrCuNiAl Metallic Glass Matrix Composite

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Carbon short fiber reinforced Zr50.5Cu36.45Ni4.05Al9 metallic glass matrix composite was synthesized. The microstructure, thermal behavior, and compressive property of composite are investigated. The improvement of thermal stability and Young’s modulus are due to the addition of short carbon fiber. The limited reaction occurs between the matrix and short fiber by reducing the reactive time, and only a ZrC reaction zone with about 150 nm in width forms. Such interfacial reaction can improve the wettability and tighten the bonding at the interface, and consequently enhance the strength of composite. The effect of interfacial reactive production on the compressive property is also discussed. [doi:10.2320/matertrans.M2010028]

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1. Introduction

Monolithic bulk metallic glasses (BMGs) possess unusual mechanical properties compared with conventional crystalline alloys, such as large elastic limit, high yield strength, and hardness.1,2 And they are favorable matrix materials for composites because of their low melting points, low glass transition temperatures, and strong resistance against heterogeneous nucleation.3) Recently synthesizing the composites by introducing the structural heterogeneity in the metallic glass matrix is a hot topic. It is reported that malleable metal fibers,4) metal particles,5) and refractory ceramics6) have been successfully combined with the metallic glass matrix. Carbon fiber metallic glass matrix composites are also paid special attention in order to synthesize a promising high strength and lightweight material. Though the densities of carbon long and short fiber composites prepared by melt infiltration casting are much reduced, the lower compressive fracture strength of them are only under about 1200 MPa.7) The interfacial microstructure analyses revealed that a diffusion zone and a brittle crystalline reaction zone of (Zr+Ti)C form between the metallic glass matrix and fiber, and the max width of zones is up to 900 nm.8) It is speculated that such excessive interfacial reaction can weaken the interfacial cohesion, hardly transfer the loading efficiently during compression, and consequently worsen the mechanical property.

In this study, we synthesized carbon short fiber reinforced Zr50.5Cu36.45Ni4.05Al9 metallic glass matrix composite by similar powder metallurgy method. The improved compressive fracture strength and reduced density of carbon short fiber composite are attained compatibly by reducing the interfacial reaction. The microstructure of reactive crystalline phase at the interface and its effect on the compressive property are mainly discussed.

2. Experimental

Alloy ingots with a nominal composition of Zr50.5Cu36.45-Ni4.05Al9 were prepared by arc melting the mixtures of elemental pieces with a purity of 99.5% or better in a water-cooled hearth under Ti-gettered high purity argon atmosphere. Each ingot was re-melted at least four times to ensure the chemical homogeneity. Then the ingots were broken and ground mechanically into fine particle with a diameter of about 250 µm. The polyacrylonitrile (PAN) based amorphous carbon short fibers with a diameter of 7 µm and density of 2.2 g cm⁻³ were cleaned in acetone and ethanol, and preheated at 1273 K for 1 h under high vacuum before mixture. Carbon short fibers with different volume fractions were mixed uniformly with the ingot particles, and dried under vacuum for 2 h. Then the mixtures were coldly compressed into cylinders with a diameter of 5 mm. The cylinders were melted rapidly in a quartz tube by induction under high purity argon atmosphere, and injected into a copper mold to prepare rods of 3 mm in diameter and 60–70 mm in length. Densities of the composites and undoped BMG were measured by the Archimedes method. The as-cast rods were characterized by X-ray diffractometer (XRD, Cu-Kα radiation), transmission electron microscope (TEM) operated at 200 kV with energy-dispersive spectrometer (EDX), and differential scanning calorimeter (DSC). The TEM samples were obtained by ion thinning with liquid nitrogen cooling. DSC measurements were performed under a continuous argon flow at a heating rate of 0.33 K/s. Uniaxial quasistatic compression tests for cylindrical rods with a length/diameter ratio 2 : 1 were carried out on servo-hydraulic MTS 810 provided with a strain gauge under a constant strain rate of 2 × 10⁻⁴ s⁻¹ at room temperature. At least five compressive samples were tested for each alloy to get a statistical result. Fracture morphology of samples was observed by scanning electron microscope (SEM).
3. Results

Figure 1 shows typical XRD patterns of $\text{Zr}_{50.5}\text{Cu}_{36.45}\text{Ni}_{4.05}\text{Al}_9$ monolithic BMG and composites with 5%, 7% of carbon short fiber. XRD patterns of these composites show a superposition of a broad diffuse diffraction peak characteristic for the amorphous matrix and several small peaks representative for a crystalline phase. The intensities and amounts of crystalline peaks increase with volume fraction of fiber increasing. The crystalline peaks are identified as ZrC phase. In addition, no other crystalline phases are detected within the sensitivity limit of XRD.

Figure 2 shows the SEM image of cross-section surface for the composite with 7% of carbon short fiber. The fibers are distributed uniformly in the featureless amorphous matrix. The distribution is mainly due to the processing of mixing the fibers with the particles of master alloy prior to the casting. The density of $\text{Zr}_{50.5}\text{Cu}_{36.45}\text{Ni}_{4.05}\text{Al}_9$ BMG and composites with 3%, 7% of fiber is about 6.7, 6.5, and 6.3 g cm$^{-3}$ respectively. The results show that the prepared composites are fully dense according to the rule-of-mixture.

Thermal behaviors of $\text{Zr}_{50.5}\text{Cu}_{36.45}\text{Ni}_{4.05}\text{Al}_9$ BMG and the composite with 7% of carbon short fiber are shown in Fig. 3. They all exhibit an endothermic event, characteristic for glass transition, followed by a clear exothermic events corresponding to the crystallization reaction. The glass transition temperature ($T_g$), the melting temperature ($T_m$), and the liquid temperature ($T_l$) of both alloys show no obvious difference. But the crystallization temperature ($T_x$) of composite clearly shifts to the high temperature compared with that of BMG. So the corresponding super-cooled liquid region ($T_x - T_g$) increases, indicating the improvement of thermal stability. The possible reason is attributed that some carbon atomic with smaller size relative to other constituent element can dissolve into the matrix of composite, enhance the amorphous structure and make the rearrangement of the atoms more difficult.

Figure 4 shows TEM micrographs of the interface between the metallic glass matrix and carbon short fiber. The matrix and fiber are all no obvious contrast as shown in Fig. 4(a). The darker region is the matrix. Its corresponding selected area diffraction (SAD) pattern illustrates two diffuse rings characteristic for the amorphous structure as shown in the lower-right inset of Fig. 4(a). The lighter region is a carbon short fiber. The SAD pattern shows a superposition of turbine shape and amorphous ring, as shown in the upper-left inset of Fig. 4(a). The patterns of matrix and fiber show that the primary states of them are retained after processing. It is clear that a reactive zone forms at the interface between the matrix and carbon short fiber as shown in Fig. 4(a). The zone in width is about 150 nm. It mainly consists of crystalline particles with a size of about 100 nm and some small particles. The particles were further characterized as f.c.c. ZrC phase by SAD pattern. The corresponding pattern is shown in Fig. 4(b). The result is also supported by EDX analyses of particles. And no other crystalline phase is detected between the zone of ZrC and BMG by tilting the sample within a wide degree,
indicating that the interfacial production cannot induce the structural heterogeneity of BMG.

Figure 5 shows the compressive stress-strain curves of Zr\textsubscript{50.5}Cu\textsubscript{36.45}Ni\textsubscript{4.05}Al\textsubscript{9} BMG and composites with 3%, 7% of carbon short fiber. They all fail after elastic deformation and almost no plastic deformation occurs. It is clear that the fracture strength of fiber composite is higher than that of BMG. The fracture strength of monolithic BMG, composites with 3% and 7% of carbon short fiber is about 1923 ± 10 MPa, 2020 ± 10 MPa, and 2182 ± 10 MPa respectively. In addition, the Young’s modulus of composites with 3% and 7% of carbon short fiber is about 96 ± 5 GPa, 104 ± 5 GPa respectively, and they are higher than that of BMG, 81 ± 5 GPa.

Figure 6 shows the fracture surface of composite with 7% of carbon short fiber. A carbon short fiber is broken along radial direction, and a portion of carbon short fiber is held on the fracture surface. One side of the fiber shows vein-like pattern characteristic for typical fracture feature of BMG, and another side shows smooth region. They suggest that the fiber can hinder the matrix flow to some extent during the final deformation event. In addition, the thin amorphous layer with vein-like pattern sticks on the fiber, and the fresh surface of fiber exists on the fracture surface. It is deduced that the crack may occur at the interface.

4. Discussion

It is important to synthesize the composite with desirable property by designing and controlling the interfacial reaction.\textsuperscript{10} Some brittle crystalline phases are easily produced by interfacial reaction because of relative high reactive temperature and long time for \textit{ex-situ} fiber or particle composites during the processing. For example, WZr intermetallic form at the interface for tungsten wire reinforced Zr-based BMG composites.\textsuperscript{4,11} They can decrease the interfacial bonding, and accordingly hamper the properties. So more efforts are preformed to minimize the reactions in order to strength the bonding as possibly, such as, optimizing the process parameters, infiltration temperature and time,\textsuperscript{12} or tailoring the matrix composition by microalloy method.\textsuperscript{13} Another hand, it is reported that \textit{in-situ} ZrC particle reinforced Zr\textsubscript{55}Al\textsubscript{10}Ni\textsubscript{5}Cu\textsubscript{30} metallic glass matrix composite shows higher fracture strength and larger plastic strain compared with \textit{ex-situ} composite with the same matrix and reinforcement. The reason is mainly attributed to the improvement of interfacial bonding by use of \textit{in-situ} reaction.\textsuperscript{14,15} These operative methods give the clue to prepare carbon short fiber composite that performing the reasonable processing to reduce the interfacial reaction to attain the better interfacial
bonding. Earlier studies show that carbon long or short fiber composite was prepared by melt infiltration casting with infiltration temperature, about 1173 K, and infiltration time, about 2–15 min. It is expected that shortening the reaction time can reduce the interfacial production. In contrast, the time is much decreased to about 4–8 second, so only a reactive zone of ZrC particle form at the interface, and no diffuse zone exists for carbon short fiber composite prepared by similar powder metallurgy method in our work. Such limited interfacial reaction can contribute to the improvement of strength.\textsuperscript{16,17} They can improve the wettability and bonding between the matrix and short fiber, ensure the good loading transfer to the fiber with higher strength and Young’s modulus, and hence enhance the fracture strength and Young’s modulus of short fiber composite. In addition, carbon short fiber is a stiff reinforcement. So the fibers cannot effectively hamper the local rapid spread of shear bands (SBs) and induce the seeding of multiple SBs. When the interfacial cohesion cannot accommodate the loading, the composite is ruptured subsequently. Actually the bonding between the matrix and reactive crystalline ZrC particle is rather stronger than the bonding between ZrC particle and carbon short fiber. So the mismatch of interfacial bonding may lead to the fracture earlier occur prior along the interface between ZrC particle and carbon short fiber.

5. Conclusions

In summary, carbon short fiber reinforced Zr\textsubscript{50.5}Cu\textsubscript{36.45}Ni\textsubscript{4.05}Al\textsubscript{9} BMG matrix composite was successfully synthesized by similar powder metallurgy method. Carbon short fibers are well distributed in the matrix. Only a ZrC particle reaction zone with about 150 nm in width forms between the matrix and fiber by reducing the reaction time. The limited reaction can strengthen the interfacial bonding. The good distribution of short fiber and the increase of bonding both contribute to improve the compressive fracture strength of composite. The thermal stability and Young’s modulus of composite are increased due to the introduction of carbon short fiber. These results show that carbon short fiber reinforced Zr-based metallic glass matrix composite is a promising high strength and lightweight materials.

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