Processing of carbon-fiber-reinforced $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ bulk metallic glass composites

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Carbon-fiber-reinforced bulk metallic glass composites are produced by infiltrating liquid $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ into carbon fiber bundles with diameter of the individual fiber of 5 μm. Reactive wetting occurs by the formation of a ZrC layer around the fibers. This results in a composite with a homogeneous fiber distribution. The volume fraction of the fibers is about 50% and the density of the composite amounts to 4.0 g/cm^3. [DOI: 10.1063/1.1390317]

Recently developed bulk metallic glass (BMG) forming alloys[1,2] have interesting engineering properties such as high yield strength and good corrosion resistance. They are also interesting matrix materials for composites because of their low melting points of around 1000 K and due to their high resistance against heterogeneous nucleation of crystals. It has been shown that BMG reinforced with metal or ceramics particulates[3–5] as well as metal fibers[6] can be successfully processed and the glassy state of the matrix can be retained after processing.

Another interesting approach is to introduce carbon fibers into a metallic glass matrix to produce a stiff, lightweight, and high strength material. In this letter we report on the processing of carbon fiber reinforced BMG matrix composites. As a matrix material the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (Vit 1) alloy is used, which is one of the best BMGs discovered. It will be shown that under proper processing conditions the BMG forming liquid easily wets the carbon fibers and that this results in uniform fiber distribution.

Carbon fiber of PAN(polyacrylonitrile) type with a diameter of 5 μm and density of 1.8 g/cm^3 are cleaned in acetone and ethanol and preheated at 1273 K under vacuum in a quartz tube. Subsequently prealloyed $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ (Vit 1) melt is infiltrated into the bundle of carbon fibers in a vertical quartz tube by applying an argon pressure of 5×10^4 Pa for 120 s at a temperature of 1173 K. The composites are investigated by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), x-ray diffraction, and transmission electron microscopy (TEM).

Figure 1 shows the backscattered SEM image of the carbon fiber reinforced composite. The carbon fibers are uniformly distributed in the Vit 1 matrix, and the matrix appears to be uniform and free of heterogeneity. The volume fraction of carbon fibers was estimated to be 50% by image analysis of the polished cross section of the sample. The carbon fibers are equally spaced with an average distance of 9 μm. The density of the composite is 4 g/cm^3.

The glass transition and the crystallization behavior of the amorphous matrix of the composites were investigated in DSC scans. Figure 2 shows DSC scans of pure amorphous Vit 1 and carbon fiber reinforced Vit 1 composite using a heating rate of 0.33 K/s. The DSC scans show that the composite sample exhibits an endothermic heat event characteristic of the glass transition followed by two characteristic exothermic heat release events indicating the successive stepwise transformations from supercooled liquid state to crystalline phases. Both crystallization patterns are not identical, because the matrix composition in the composite is

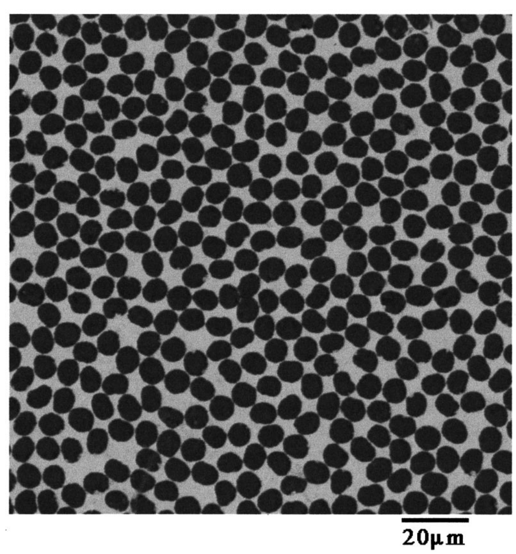

FIG. 1. Backscattered SEM image of carbon fiber reinforced bulk metallic glass composite.

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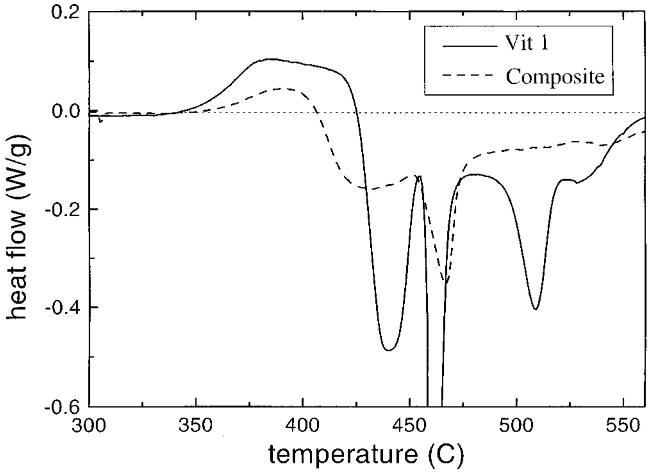

FIG. 2. DSC thermogram (heating rate of 0.33 K/s) of carbon fiber reinforce bulk metallic glass composite and Vit 1.

altered due to the formation of (ZrTi)–C at the interfaces between matrix and fibers, which leads to a depletion of the matrix of Zr and Ti.

Figure 3 shows the x-ray diffraction patterns with Cu $K\alpha$ radiation of pure amorphous Vit 1, pure carbon fiber, and the composite sample. The magnitude of the signal of the pure carbon fiber can be neglected on the intensity scale of the pure Vit 1 and the carbon fiber reinforced Vit 1. The x-ray diffraction pattern of the composite shows a superposition of a broad maxima typical for the amorphous matrix material and a number of sharp peaks characteristic for a crystalline phase, suggesting the presence of a mixture of amorphous and crystalline phase in this composite. The diffraction peaks were identified as a ZrC lattice pattern. The formation of a ZrC layer has been reported in the past where it formed between $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ and SiC and WC.[7] From the peak shift with respect to pure ZrC, the Ti concentration of the carbide was estimated to be 7%. No considerable amounts of other phases were detected within the sensitivity limit of x-ray diffraction.

The interfaces between carbon fibers and the matrix were investigated by transmission electron microscopy. Figure 4 shows the dark field TEM image of an interfacial region between a carbon fiber and the Vit 1 matrix. The composite was prepared for TEM investigations and EDX analysis by the standard polishing, dimpling, and ion milling technique. A carbide reaction zone is observed surrounding the carbon fibers. The following general observations were made relative to the interface between the glass matrix and the carbon fibers. Starting from the carbon fibers a diffusion zone within the fibers was observed in which traces of Ni and Cu were found indicating that Cu and Ni diffuses into the carbon. This zone has a thickness between 0.1 and 0.3 μm. However, since NiC and CuC are thermodynamically not very stable, especially compared to (Zr+Ti)C, no individual NiC or CuC layers form. A crystalline reaction layer of 0.3–0.6 μm is observed at the former surface of carbon fibers. The reaction zone consists of two different layers. There is a 0.1–0.2 μm "granular" layer and a layer of large crystals at the matrix interface. Both layers have a (Zr+Ti)C structure as the TEM diffraction patterns reveal. The large crystals are high in Zr; the glass matrix adjacent to these crystals appeared lower in Zr. The "granular" layer close to the fibers showed a gradient in the Ti content with more Ti towards the fiber interface. Reaction zones between bulk metallic glass matrix and reinforcement in which a ZrC or (Zr+Ti)C layer formed have been previously reported between SiC and $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ as well as between WC and $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$.[4] The formation of (Zr+Ti)C has been observed at the interface between SiC and $Cu_{47}Ti_{34}Zr_{11}Ni_8$.[7]

In conclusion, carbon-fiber-reinforced bulk metallic glass matrix composites were successfully processed. (Zr+Ti)C was formed at the interface between carbon fiber and the matrix. During solidification, no heterogeneous nucleation in the BMG is observed at the interface between (Zr+Ti)C and matrix. The metallic matrix retained the amorphous state even though Zr is depleted near the (Zr+Ti)C interface to some extent. These results suggest that carbon-fiber-reinforced bulk metallic glass composites are promising candidates for lightweight, stiff materials with improved mechanical properties compared to metallic glass itself.

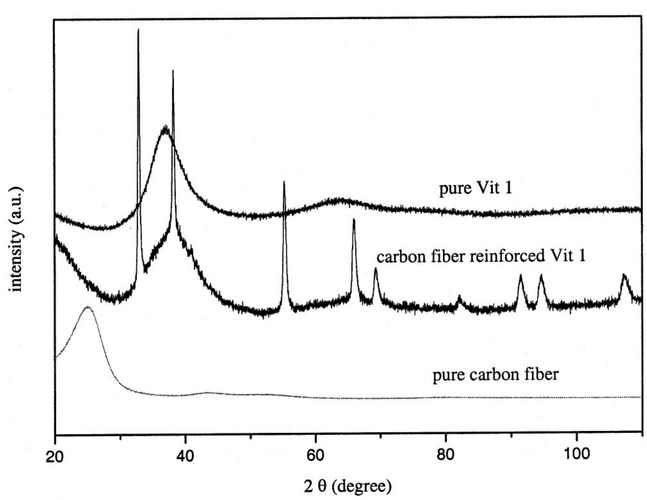

FIG. 3. X-ray diffraction patterns of the pure amorphous Vit 1, pure carbon fiber, and a composite sample.

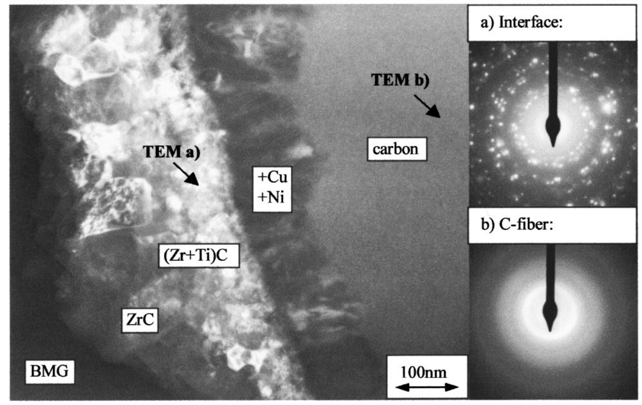

FIG. 4. Dark field TEM of the interfacial region between a carbon fiber and the Vit 1 matrix. The diffraction pattern of the imaged region is also shown.

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[1] A. Peker and W. L. Johnson, Appl. Phys. Lett. **63**, 2342 (1993).
[2] X. Lin and W. L. Johnson, Mater. Trans., JIM **38**, 475 (1997).
[3] H. Choi-Yim and W. L. Johnson, Appl. Phys. Lett. **71**, 3808 (1997).
[4] H. Choi-Yim, R. Busch, U. Köster, and W. L. Johnson, Acta Mater. **47**, 2455 (1999).
[5] J. Eckert, A. Kübler, and L. Schultz, J. Appl. Phys. **85**, 7112 (1999).
[6] R. B. Dandliker, R. D. Conner, and W. L. Johnson, J. Mater. Res. **13**, 2896 (1998).
[7] H. Choi-Yim, R. Busch, and W. L. Johnson, J. Appl. Phys. **83**, 7993 (1998).