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Consolidation behavior of Cu- and Ni-based bulk metallic glass composites

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Abstract

The Cu- and Ni-based bulk metallic glass matrix composites were fabricated by spark plasma sintering of a mixture of gas-atomized metallic glass powders and ductile brass powders. The brass powders added for the enhancement of plasticity are well distributed in the matrix after consolidation. The matrix of the composite materials remains as a fully amorphous phase after consolidation process. With increasing the brass content, the level of plasticity strain increased, although the level of strength decreased. The successful consolidation of metallic glass matrix composite with high density was attributed to viscous flow in the supercooled liquid state during spark plasma sintering.

Keywords: Metallic glasses; Powder metallurgy; Thermal analysis

1. Introduction

Bulk metallic glasses (BMGs) have shown superior properties such as high strength, low Young's modulus and large elastic limit [1]. However, the BMGs usually show little overall room temperature plasticity due to the formation of highly localized shear banding, resulting in a catastrophic failure. One way to overcome this problem is to produce the composite materials containing crystalline phase. Attempts have been made to enhance the ductility of BMGs by introducing crystalline phase into the metallic glass matrix: partial devitrification [2], adding particle or fibers during casting or consolidation process [3,4], and in situ formed ductile phase precipitates [5]. It was found that the plastic deformation of monolithic BMGs can be enhanced by adding some crystalline phase into the metallic glass matrix composites (MGMCs) [3–5]. This deformation behavior in MGMCs is achieved by the formation of multiple shear bands initiated at the interface between the reinforcing phase and the metallic glass matrix, and their confinement in metallic glass matrix composites [4,5]. The MGMCs with enhanced plasticity is expected to expand the application field of the BMGs. However, due to the requirement of high cooling rate for the formation of amorphous phase from a liquid state, the MGMCs have been restricted to alloy systems with high glass forming ability such as Zr- and Ti-based BMGs.

Large-scale BMGs have been produced by consolidation of metallic glass powders using the significant viscous flow in the supercooled liquid region [6–8]. However, consolidated monolithic BMGs have catastrophic failure characteristic without macroscopic plasticity.

In the present study, we report the consolidation of Ni- and Cu-based bulk metallic glass composites containing ductile brass phase by spark plasma sintering of metallic glass powders. The thermal and deformation behavior of the resulting MGMCs are also reported.

2. Experimental procedures

$Ni_{59}Zr_{15}Ti_{13}Si_3Sn_2Nb_7Al_1$ and $Cu_{54}Ni_6Zr_{22}Ti_{18}$ metallic glass powders used in this study were prepared by the high pressure gas-atomization process. The details of the processing procedures have been given elsewhere [7]. To produce the MGMCs containing a ductile phase, metallic glass powder (Cu- or Ni-based) and brass powders having a size smaller than 90 μm were uniformly blended. Besides the composite samples containing brass powders (10, 20 and 30 vol.%), and a monolithic BMG sample was prepared for comparison. The mixed powders were pre-compacted, and then consolidated to form disc-shape samples with 20 mm in diameter and 5 mm in thickness using a spark plasma sintering (SPS) method. The consolidation processes were performed in the

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supercooled liquid region of metallic glass powders with an external pressure 300 MPa. Structural characterization was performed by X-ray diffractometry (XRD) with Cu Kα radiation and optical microscopy (OM). The thermal properties of the samples were studied by differential scanning calorimetry (DSC). Mechanical properties of samples were measured at room temperature under compressive mode with a strain rate of $1 \times 10^{-4}\,\mathrm{s}^{-1}$. Test specimens with a dimension of 2 mm × 2 mm × 4 mm were prepared for compression tests. The viscosity experiments were performed by using a thermo-mechanical analyzer (TMA) with a quartz penetration probe (Ø 3.7 mm) under an argon atmosphere. Microstructure of the tested samples was observed using scanning electron microscopy (SEM).

3. Results

Fig. 1(a) and (b) shows typical optical micrographs of the polished cross-section of the $Cu_{54}Ni_6Zr_{22}Ti_{18}$ MGMC containing 10 vol.% brass and $Ni_{59}Zr_{15}Ti_{13}Si_3Sn_2Nb_7Al_1$ MGMC containing 10 vol.% brass, respectively. In both samples, the ductile brass powders were distributed relatively homogeneously in the metallic glasses matrix. No defect such as pores and cavities was observed at the interface between the brass powder and the metallic glass matrix, suggesting that the SPS process cause a severe viscous flow of the metallic glass phases in the supercooled liquid region, resulting in a full densification.

Fig. 2 shows typical XRD patterns obtained from the monolithic and BMGs and the MGMCs containing 20 vol.% brass. The monolithic BMGs showed a broad halo peak in the 2θ range of 35–47°, characteristic of an amorphous structure, while the MGMCs showed sharp peaks diffracted from the brass superimposed on a weak halo pattern, indicating that the matrix of the MGMCs consists of a fully amorphous phase.

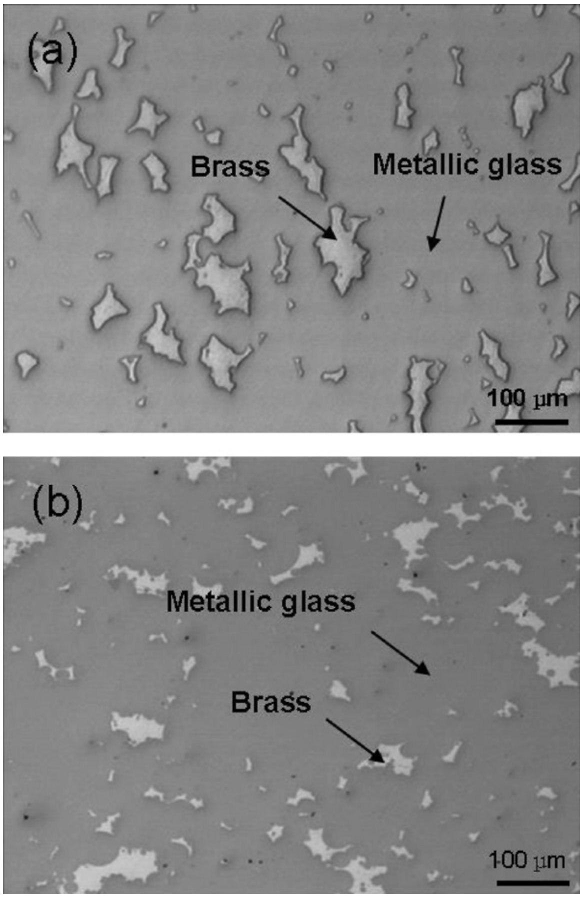

Fig. 1. Optical micrographs of the MGMC containing 10 vol.% brass: (a) $Cu_{54}Ni_6Zr_{22}Ti_{18}$ and (b) $Ni_{59}Zr_{15}Ti_{13}Si_3Sn_2Nb_7Al_1$.

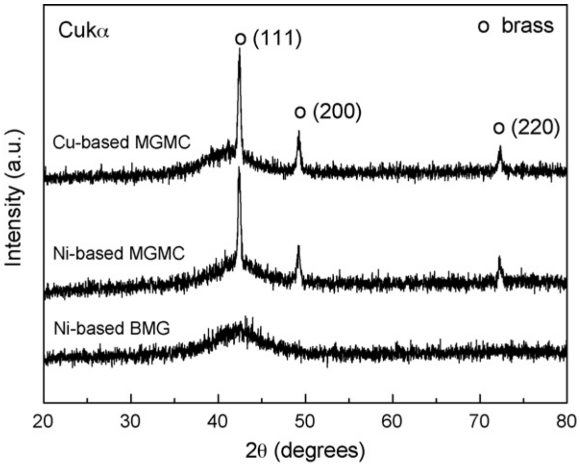

Fig. 2. XRD patterns of the monolithic BMG and MGMCs containing 20 vol.% brass.

Fig. 3 shows DSC traces measured from the monolithic BMG samples and MGMC samples with a continuous heating rate of 0.67 K/s. Both the $Ni_{59}Zr_{15}Ti_{13}Si_3Sn_2Nb_7Al_1$ monolithic BMG and MGMC samples showed an endothermic event, which is characteristic of glass transition to supercooled liquid and an exothermic reaction is corresponding to crystallization process. The monolithic $Ni_{59}Zr_{15}Ti_{13}Si_3Sn_2Nb_7Al_1$ BMG showed glass transition temperature (T_g) of 839 K, onset temperature of crystallization (T_x) of 891 K and integrated heat of crystallization of 44.7 J/g. These values are almost similar to those from the metallic glass powders, indicating that no devitrification occurred during SPS process. Note that, the ΔH of the MGMC sample containing 20 vol.% brass was around 80% of that of monolithic BMG, again confirming that no devitrification occurred in the MGMC samples during consolidation. The XRD and DSC results indicate that the matrix of the monolithic BMGs and MGMCs remains as a fully amorphous phase after consolidation process.

Fig. 4 shows the stress–strain curves of the monolithic BMG and MGMC samples tested under the uniaxial compressive condition at room temperature. The monolithic $Cu_{54}Ni_6Zr_{22}Ti_{18}$ BMG samples exhibited the fracture strength of about 1.9 GPa similar to that of as-cast samples (∼2.0 GPa), which can be attributed to good bonding characteristics between the metallic glass powders. However, no plastic deformation region was observed, possibly due to the occurrence of structural relaxation in the amorphous structure during SPS process. This type stress–strain behavior has been commonly observed in the monolithic BMGs consolidated from metallic glass powders [7,8]. In contrast, the MGMC samples show some macroscopic plasticity after yielding, although the levels of strength decreased. For example, the fracture strength and total strain of the $Ni_{59}Zr_{15}Ti_{13}Si_3Sn_2Nb_7Al_1$ MGMC containing 10 and 30% were 2100 MPa and 2.2%, and 1480 MPa and 2.9%, respectively.

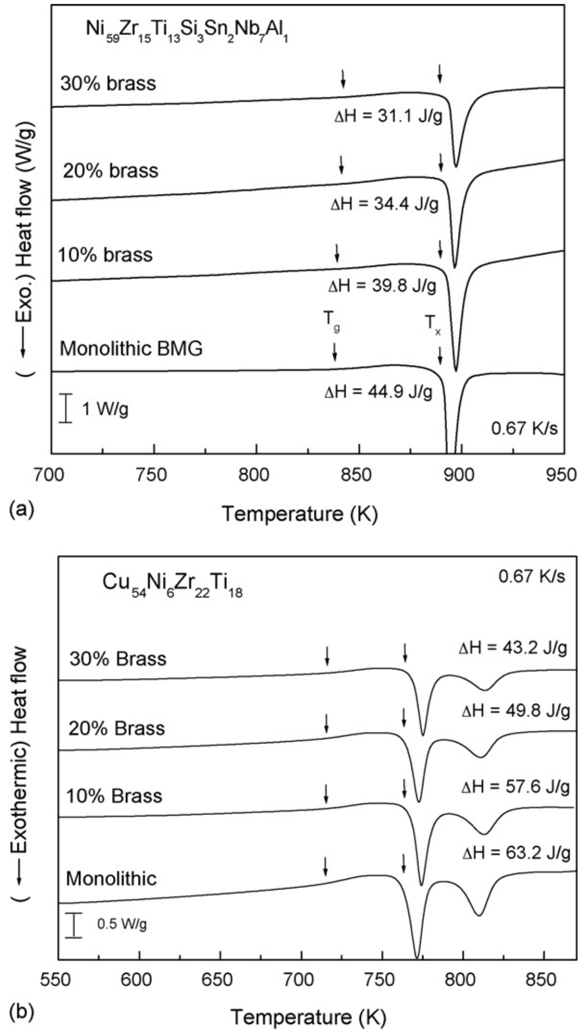

Fig. 3. DSC traces obtained from the monolithic BMGs and MGMCs: (a) Ni$_{59}$Zr$_{15}$Ti$_{13}$Si$_3$Sn$_2$Nb$_7$Al$_1$ and (b) Cu$_{54}$Ni$_6$Zr$_{22}$Ti$_{18}$.

In order to see the effect of introducing brass phase in the metallic glass matrix on the fracture, fracture surface of the failed MGMC sample was observed by using scanning electron microscopy. The compressive fracture takes place along the maximum shear plane, which is declined by about 43° to the direction of compressive load. As shown in Fig. 5, the fracture surface of failed Cu$_{54}$Ni$_6$Zr$_{22}$Ti$_{18}$ MGMC sample containing 20 vol.% brass shows the classic vein-like fracture pattern occurred at the monolithic metallic glass powders mixed with regions of ductile dimple-type fracture at the brass powders.

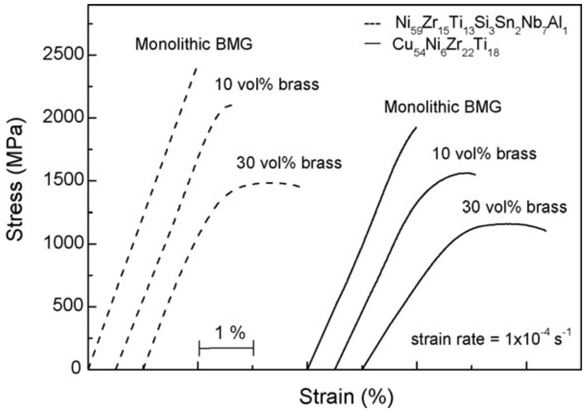

Fig. 4. Stress–strain curves of the monolithic BMG and MGMCs.

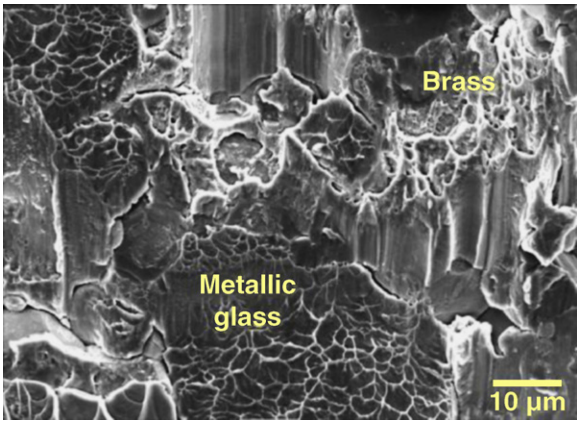

Fig. 5. Scanning electron micrograph of compressive fracture surface of failed Cu$_{54}$Ni$_6$Zr$_{22}$Ti$_{18}$ MGMC containing 20 vol.% brass.

4. Discussion

As shown in Fig. 4, the catastrophic failure can be avoided by introducing a ductile brass phase in the metallic glass matrix. It has been reported that the enhanced plasticity of the extruded MGMC results from the formation of multiple shear bands initiated from the interface between the second ductile phase and metallic glass matrix [4,5]. During deformation, the plastic deformation initially occurs in the ductile second phase, and then load is transferred to the surrounding metallic glass matrix, causing the initiation of shear bands [4,5]. It is also reported that the shear bands are confined within the matrix region between brass phases without propagation though the neighboring brass powders, indicating that the ductile brass phases are effectively played a role to inhibit of propagation of shear bands [4].

The strength of the consolidated metallic glass samples depends on both the density and the bonding characteristics between the powder particles. The densities of injection-cast and consolidated Cu$_{54}$Ni$_6$Zr$_{22}$Ti$_{18}$ BMG are 7.43 and 7.37 g/cm^3, respectively. Almost full densification can be achieved in the consolidated product. The results of density measurement indicate that the monolithic BMGs can be successfully fabricated by SPS process of the metallic glass powders using viscous flow in the supercooled liquid state. It also has been reported that the spark plasma cleans surface by spattering the oxide films and stains on surface of powders [9]. Therefore, the high strength of the consolidated BMGs is considered to be due to the good interparticle bonding between the metallic glass powders, which are achieved by flow deformation of powders in the supercooled liquid region, and the nearly full densification.

To evaluate the superplastic behavior of MGMC in the supercooled liqud region, the viscosities of the injection-cast BMGs and consolidated MGMCs were measured using a TMA within the temperature range of $T_g < T < T_x$. Fig. 6 shows the

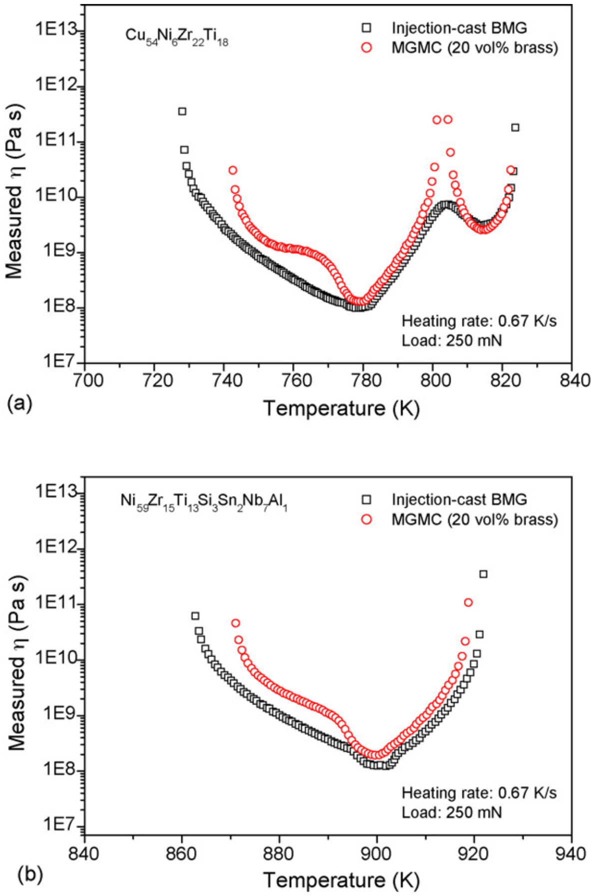

Fig. 6. Viscosity of the injection-cast BMGs and MGMCs containing 20 vol.% brass: (a) $Cu_{54}Ni_6Zr_{22}Ti_{18}$ and (b) $Ni_{59}Zr_{15}Ti_{13}Si_3Sn_2Nb_7Al_1$.

measured viscosity in the supercooled liquid for the injection-cast BMGs and consolidated MGMCs, which was performed at a heating rate of 0.67 K/s and a force of 250 mN. The apparent viscosity η can be obtained by $\eta = \sigma/3\dot{\varepsilon}$, where σ and $\dot{\varepsilon}$ are compressive stress and strain rate, respectively. The viscosity first decreased smoothly with increasing temperature upon heating from the amorphous solid through the glass transition into the supercooled liquid state. And then, the crystallization at higher temperature led to an increase of the apparent viscosity. The calculated minimum values of viscosity are 1.0×10^8 Pa s for the injection-cast $Cu_{54}Ni_6Zr_{22}Ti_{18}$ BMG and 1.3×10^8 Pa s for the consolidated $Cu_{54}Ni_6Zr_{22}Ti_{18}$ MGMC, respectively. In the injection-cast $Ni_{59}Zr_{15}Ti_{13}Si_3Sn_2Nb_7Al_1$ BMG and consolidated $Ni_{59}Zr_{15}Ti_{13}Si_3Sn_2Nb_7Al_1$ MGMC, the minimum values of viscosity were estimated to be 1.2×10^8 and 2.0×10^8 Pa s, respectively. The minimum viscosity of MGMC was slightly higher than that of injection-cast BMG. This result shows that the MGMC shows similar superplastic behavior to the injection-cast BMG, indicating that possibility of fabrication in the supercooled liquid region.

5. Conclusion

The $Cu_{54}Ni_6Zr_{22}Ti_{18}$ and $Ni_{59}Zr_{15}Ti_{13}Si_3Sn_2Nb_7Al_1$ MGMCs reinforced by brass powders have been successfully synthesized by spark plasma sintering of gas-atomized metallic glass powders at the supercooled liquid state. Full densification of MGMCs was achieved by the viscous flow of the metallic glass powders and lower flow stress of ductile brass powders in the supercooled liquid region during consolidation process. The MGMCs samples show some macroscopic plasticity after yielding, which is related to the formation of multiple shear bands and confinement of propagation of shear bands, although the levels of strength decrease.

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