Thermoplastic forming ability of a Mg-base bulk metallic glass composites reinforced with porous Mo particles

J.S.C. Janga,*, W.J. Li b, T.H. Li b, S.R. Jian b, J.C. Huang c, T.G. Niehd

*Department of Mechanical Engineering, Institute of Materials Science and Engineering, National Central University,300, Chung-Da Road, Chung-Li 32001, Taiwan, ROC
bDepartment of Materials Science and Engineering, I-Shou University, Kaohsiung 840, Taiwan 840, ROC
cDepartment of Materials and Optoelectronic Science, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung 804, Taiwan, ROC
dDepartment of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996, USA

A R T I C L E   I N F O
Article history:
Received 12 November 2009
Received in revised form
18 January 2010
Accepted 22 January 2010
Available online 18 February 2010

Keywords:
A. Composites
B. Glasses, metallic
B. Superplastic behavior
C. Plastic forming, hot
F. Electron microscopy, transmission

A B S T R A C T
The thermoplastic deformation behavior of the Mg58Cu28.5Gd11Ag2.5 metallic glass composites (BMGCs) reinforced with porous Mo particles was studied by means of thermal scanning calorimetry (DSC), thermal mechanical analysis (TMA) and high-temperature compression test in the supercooled liquid region. Based on the result obtained from DSC and TMA, the deformation behavior for Mg58Cu28.5Gd11Ag2.5 BMGC rod was investigated by compression test at different strain rates (1 × 10−2–1 × 10−1 s−1) and temperatures in the supercooled liquid region, namely 433 K, 438 K, and 443 K. The flow stresses obtained at a constant strain rate of 1 × 10−2 s−1 decrease with increasing temperature and reach a low stress about 10 MPa at 443 K. In addition, the X-ray diffraction results confirm that the Mg58Cu28.5Gd11Ag2.5 BMGC samples remain the amorphous nature after compression at 443 K. The current results indicate that the Mg58Cu28.5Gd11Ag2.5 BMGC possesses an excellent superplastic formability with the m-value (strain rate sensitivity) greater than 0.7 in the supercooled liquid region of 438–443 K at a strain rate around 1 × 10−2 s−1.

© 2010 Published by Elsevier Ltd.

1. Introduction
In the last decades, Mg-based bulk metallic glasses (BMGs) have attracted much attention as structural materials due to their high specific strength/density ratio as compared to other BMGs, such as the Zr-, Pd-, Cu-, Fe-, and Ni-based alloys [1–6]. Meanwhile, a series of Mg-based BMGs with high glass forming ability (GFA) have been developed by adding rare-earth element and substituting Cu with Ag [7–13]. However, the monolithic Mg-based BMG has been demonstrated to be the most brittle alloy system among all BMGs and they tend to break into pieces before yielding [7,14]. For solving the problem, extensive efforts have been devoted to develop Mg-based metallic glasses composites (BMGCs) recently. This includes the incorporation of in-situ precipitated nanocrystalline phases, ex-situ added ductile metals or refractory ceramic particles in the Mg-based BMGCs, which exhibit improved compressive strengths and remarkable plastic strains [15–24].

Following the toughening concept of composite materials, the current authors have successfully fabricated an extremely tough Mg-based BMGC rods which strengthened with porous Mo particles [20,24]. These porous Mo particles divide the amorphous matrix of BMG into the micron-scaled compartments. The small region can undergo great deformation without failure and limit the propensity of forming mature shear bands [25–30]. Besides, these porous Mo particles also behave as ductilizers (as in composites) and so as to significantly improve the plasticity. In addition, since the thermal properties of the Mg58Cu28.5Gd11Ag2.5 BMGC are nearly the same as its counterpart monolithic Mg58Cu28.5Gd11Ag2.5 BMG [24]. Therefore, this Mg58Cu28.5Gd11Ag2.5 BMGC was predicted to present viscous flow behavior in supercooled liquid region (SCL) with behavior similar to a Newtonian viscosity of conventional Mg-based BMGs, i.e., the strain rate sensitivity exponent (m) is near 1. Hence, combining high strength, high toughness, and the superplastic deformation ability in the SCL region, this Mg-based BMGC with Mo particles is anticipated can be manufacture into near-net-shape components, particularly for the complex-shaped micro-component for micro electro-mechanical systems (MEMS) [31–33]. The purpose of the present study is to figure out the process window for microforming the Mg58Cu28.5Gd11Ag2.5 BMGC with Mo particles (which possess high toughness and high glass forming ability) by means of a thermal mechanical analyzer (TMA) and a hot compression test at various temperature and strain rates.
2. Experimental procedures

The Mg-based BMGCs were prepared by selecting the composition of Mg$_{58}$Cu$_{28.5}$Gd$_{11}$Ag$_{2.5}$ as the raw alloy and adding with 25 vol% of porous Mo particles. High purity Cu and Gd (> 99.9%) were pre-alloyed into Cu–Gd master alloy ingot by arc melting in a Ti-getted argon atmosphere. Then the Cu–Gd master alloy was melted together with high purity Mg and Ag pieces to obtain the target composition by induction melting under the argon atmosphere. While melting, high purity porous Mo particles (99.9 wt% pure and fabricated by sintering method) with 40–70 μm diameter were added into the matrix alloy under the argon atmosphere. Mechanical stirring was exerted to enhance the homogeneous mixing of the particles within the melt. Furthermore, the composite alloy ingot was remelted by induction melting in a quartz tube and injected into a temperature-controlled Cu mold by argon pressure to obtain the BMGC rods with sizes of 4 mm in diameter.

The thermal properties of the BMG sample were characterized by DSC (differential scanning calorimeter, TA Instruments DSC 2920) and TMA (thermal mechanical analyzer, Perkin-Elmer Diamond TMA) under flowing purified argon with a heating rate of 20 K/min. According to our previous report [24], there is 10 K difference of SCL ($\Delta T_c = T_c - T_g$; $T_c$: crystallization temperature, $T_g$: glass transition temperature) between the base BMG (69 K) and the 25 vol% Mo BMGC (59 K) due to the heterogeneous

![Fig. 1](image1.png)

Fig. 1. TMA curves for the Mg-based BMGC with 25 vol% Mo particle rods test with different compressive stress (namely 7.96, 23.88, and 39.8 kPa) at the heating rate of 0.33 K/s: (a) Curves of strain as a function of temperature, (b) converted curves of viscosity as a function of temperature.

![Fig. 2](image2.png)

Fig. 2. True stress–strain curve of compression test for Mg-based BMGC with 25 vol% Mo particle at different temperature and different strain rate.

![Fig. 3](image3.png)

Fig. 3. X-ray diffraction patterns of the Mg-based BMGC rods after compression testing at 445 K and $1 \times 10^{-1}$–$1 \times 10^{-2}$ s$^{-1}$. 
nucleation surface of Mo particles. However, 59 K of SCL is large enough for the thermoplastic deformation study. Therefore, several temperatures between $T_g$ and $T_x$ (namely 433, 438, and 443 K) were selected for high-temperature compression tests by a MTS-810 mechanical test system with different strain rates ranges, namely $1 \times 10^{-2}$, $2 \times 10^{-2}$, $5 \times 10^{-2}$, and $1 \times 10^{-1}$ s$^{-1}$, to study the deformation behavior within the SCL region. The compression samples with the height ($h$) to diameter ($d$) ratio of 2:1 ($h = 8$ mm versus $d = 4$ mm) were cut in parallel and carefully polished to insure the end flatness. Multiple compression tests were conducted for confirming the reproducible trend and the scattering of the stress and strain was less than ±5%. The structure of the specimen was characterized by Scintag X-400 X-ray diffractometer with monochromatic Cu-$K_\alpha$ radiation. The microstructure of the interface between porous Mo particles and matrix was examined by transmission electron microscopy (Philip Tecnai G$^2$-TEM) operated at 200 kV.

3. Results and discussions

The TMA curves of the Mg-based BMGC with 25 vol% Mo particles tested at a heating rate of 0.33 K/s with different applied stress is illustrated as Fig. 1(a). When the temperature is lower than $T_g$, the linear coefficient of thermal expansion (CTE) for amorphous solid ($\alpha_{am}$) is $2.27 \times 10^{-5}$ m/m K. As the temperature exceeds $T_g$, the CTE for crystalline solid ($\alpha_{crystal}$) changes to $2.09 \times 10^{-5}$ m/m K, suggesting that this CTE is similar to the conventional engineering Mg alloys, such as the AZ91 Mg alloy ($2.6 \times 10^{-5}$ m/m K). With increasing temperature, the relative displacement is enhanced appreciably with increasing the magnitude of loading, especially approaching the $T_{onset}$. Additionally, to convert the result of Fig. 1(a) into the plot of viscosity versus temperature by the equation of $\eta = \sigma_{flow}/\dot{\varepsilon}$ (in which $\sigma_{flow}$ is flow stress and $\dot{\varepsilon}$ is strain rate), as shown in Fig. 1(b). There is a clear viscosity transition at $T_g$, the glassy solid exhibits the rigid matter at the temperature below $T_g$. 

**Fig. 4.** TEM images of the Mg-based BMGC with 25 vol% Mo particles after hot compression testing at 443 K and $5 \times 10^{-2}$ s$^{-1}$: (a) bright field image, (b) high resolution transmission electron microscope image of the circle area in (a), and (c) nano diffraction pattern of Mo-particle with $\mathbf{B} = [011]$. 

```
and becomes viscous matter in the supercooled liquid region. A relatively low viscosity between $10^7$ and $10^8$ Pa s occurs at the temperature interval of supercooled liquid region (between $T_{\text{onset}}$ and $T_x$). As the temperature increases to $T_x$ (about 475 K), the viscosity of the BMGC sample increases rapidly to $10^{10}$ Pa s as a result of crystallization and becomes a rigid matter again.

According to the real glass transition and crystallization temperature (419 K and 478 K respectively) in our previous study [20,24] and the current TMA results, the viscous flow behavior of Mg-based BMGC rods with 25 vol% Mo particles were investigated by compression tests at various temperatures near and below the $T_{\text{onset}}$ with different strain rates ($1 \times 10^{-2}$–$1 \times 10^{-1}$ s$^{-1}$) in the SCL region. The true stress–strain curves of the BMGC samples deformed at 433, 438, and 443 K with different strain rate between $1 \times 10^{-2}$ and $1 \times 10^{-1}$ s$^{-1}$ are summarized in Fig. 2. The entire Mg-based BMGC specimen exhibits an initial stress overshoot followed by an extended regime of homogeneous steady state flow. At higher temperature and lower strain rates, the elastic regime of the Mg-based BMGC samples transforms directly into a steady state flow curve (without overshoot). In addition, the flow stress also decreases clearly with lower compressive strain rate and higher compression temperature. The lowest flow stress, 11 MPa, was obtained at 443 K and $1 \times 10^{-2}$ s$^{-1}$. In addition, the X-ray diffraction results reveal that no crystalline phase is detected from these Mg-based BMGC specimens after compression at 443 K, as shown in Fig. 3. Moreover, a clean and good bonded interface between the Mo-particle and glassy matrix was observed by TEM examination for the Mg-based BMGC specimen after compression at 443 K with strain rates of $1 \times 10^{-2}$–$1 \times 10^{-1}$ s$^{-1}$, as shown in Fig. 4. However, some tiny nanocrystalline phase with dimension about 3 nm was found in small area of the BMGC sample after hot compression test at 443 K with a strain rate of $1 \times 10^{-2}$ s$^{-1}$, by the TEM observation, as illustrated in Fig. 5. These nanocrystals were identified to be the orthorhombic Mg$_2$Cu phase.

To further discuss the flow behavior of the Mg-based BMG, the Backofen function, $\sigma_{\text{flow}} = K \varepsilon^m$, is introduced [34], where $\sigma_{\text{flow}}$ is the flow stress, $K$ is a constant, $\dot{\varepsilon}$ is strain rate and $m$ is the strain sensitivity exponent. The plots of the flow stress (ln$\dot{\varepsilon}$) as a function of strain rate (ln$\dot{\varepsilon}$) at different temperature are shown in Fig. 6. The strain rate sensitivity exponent ($m$) can be obtained from the slope of the curve for the Mg-based BMGC with 25 vol% Mo particles deformed at 433, 438, and 443, respectively. The $m$-value increases with increasing the temperature of hot compression test. However, the datum fitting presents relatively a greater degree of scattering at the higher compression temperatures, suggesting that the small amount of tiny nanocrystals (3 nm in size) formed at the higher compression temperatures (e.g., 443 K at a slow strain rate) may raise the viscosity and disturb the flow of BMGC within the supercooled region. On the other hand, the viscosity would decrease significantly with increasing compression temperature and compensate the negative effect of nanocrystals. Overall, all $m$-values of the Mg-based BMGC with 25 vol% Mo particles at each compression temperature are in a level greater than 0.7. Considering that the $m$-value is usually between 0.3 and 0.8 for most superplastic crystalline alloys and an $m$-value of 0.5 is commonly associated with excellent plasticity [35,36]. In comparison with the $m$-values of the Cu-based (0.4–0.6) [37] and Zr-based (0.4–0.56) [38] BMGs, the current Mg-based BMGCs with 25 vol% Mo particles
posses higher m-values and the current BMGCs are demonstrated to have an excellent superplasticity capability and promising potential for fabricating miniature industrial parts.

4. Conclusion

According to the results of DSC, TMA, and hot compression test, the deformation behavior of the Mg-based BMGC with 25 vol% Mo particles within the SCL region reveals a relatively low viscosity between $10^7$ and $10^8$ Pa·s. In addition, the X-ray results show that the Mg-based BMGC samples remain basically the amorphous nature after compression at 443 K and $2 \times 10^{-2}$ s$^{-1}$ (except the specimen tested at 443 K and the lower strain rate of $1 \times 10^{-2}$ s$^{-1}$). Some minor tiny nanocrystalline Mg$_2$Cu phase crystallized during the hot compression test. Meanwhile, strain rate sensitivity exponent ($m$) greater than 0.7 are obtained for the Mg-based BMGC samples, as deformed at 433, 438, and 443 K, indicating that the current Mg-based BMGCs possess an excellent superplasticity capability, favorable for shaping into bulk or MEMS devices.

Acknowledgement

The authors would like to gratefully acknowledge the sponsorship from the National Science Council of ROC under the project NSC95-2211-E-214-015-MY3, NSC98-2221-E-008-116-MY3, and NSC96-2218-E-110-001. In addition, the authors are also very grateful for the assistance of TEM by the Micro and Nano Laboratory, Department of Materials Science and Engineering, I-Shou University.

References