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Effects of alloying elements with positive enthalpy of mixing in $Mg_{65}Cu_{25}Gd_{10}$ bulk-forming metallic glasses

J.S. Kyeong [a], D.H. Kim [a], J.I. Lee [b], E.S. Park [b], *

[a] Center for Non-crystalline Materials, Department of Metallurgical Engineering, Yonsei University, Seoul 120-749, Republic of Korea
[b] Research Institute of Advanced Materials, Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Republic of Korea

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ABSTRACT

The present study investigates the effects of a minor addition (MA) of alloying elements to $Mg_{65}Cu_{25}Gd_{10}$ bulk-forming metallic glass (BMG). First, we show that a MA of Y or Ca that has singular positive enthalpy of mixing relationship (PEMR) with a constituent element in $Mg_{65}Cu_{25}Gd_{10}$ BMG leads to an improvement in plasticity as well as glass-forming ability (GFA) in a limited composition range. Second, we show that a MA of Co with plural PEMRs and a large negative enthalpy of mixing relationship (NEMR) to $Mg_{65}Cu_{25}Gd_{10}$ BMG drastically deteriorates both GFA and plasticity due to large variation of matrix composition. Finally, the paper demonstrates that a MA of Be that has unfavorable mixing relationships with all constituent elements has no adverse effect on GFA and precipitates Be-rich secondary nanocrystals in the amorphous matrix, which leads to improved plasticity up to $\varepsilon_f = 3.41 \pm 0.10\%$ in $(Mg_{65}Cu_{25}Gd_{10})_{95}(Be)_5$ BMG. Consequently, our results suggest that a MA of a 4th alloying element with PEMR to $Mg_{65}Cu_{25}Gd_{10}$ BMG can result in different degrees of heterogeneity in the amorphous matrix depending on the overall combination of mixing enthalpies among atomic pairs, which significantly influences the plasticity as well as GFA of the BMGs.

1. Introduction

Recently there has been a strong demand for development of high strength and damage-tolerant materials with low specific weight in order to save energy and other natural resources. As a result, a considerable amount of research activities has been devoted to developing new types of lightweight aluminum- and magnesium-based alloys during the past few decades. In particular, Mg metals have advantages of the lowest specific weight, a large amount of deposits on the earth and their manageable reuse [1]. The recent development of Mg-based alloys with high glass-forming ability (GFA) has allowed the preparation of centimeter-scale Mg-based bulk-forming metallic glasses (BMGs) [2–5], which exhibit high hardness, high resistance against abrasive wear, and high strength up to 1 GPa, e.g. ~5 times higher for Mg-based BMGs than AZ91 (Mg-9Al-1Zn in wt.%, Mg-based crystalline alloy with a typical high specific strength). However, the Mg-based BMGs do not exhibit appreciable plastic deformation in a uniaxial mode at room temperature, preventing their engineering applications as structural materials. Thus, there is a strong need to improve ductility of Mg-based BMGs in order to fully exploit their engineering potential.

It is widely accepted that the selection of additional elements with large negative enthalpy of mixing relationship (NEMR) improves the local packing efficiency, restrains long-range diffusion of atoms, and thus provides a favorable condition for enhancing GFA [6]. On the other hand, it has recently been shown that a minor addition (MA) of an element that has positive enthalpy of mixing relationship (PEMR) with some of the constituent elements is an effective way to improve the plasticity of BMGs by providing chemical and/or structural heterogeneity in the amorphous matrix [7–15]. The heterogeneity of less than several nanometer scales originated by phase separation through the formation of miscibility gap could change the viscous flow of the BMGs and influence the formation and propagation of the shear bands during deformation. However, the heterogeneity mentioned here is different from the micrometer scale secondary crystalline phases in BMG matrix composites which generally decrease yield strength of BMGs due to different strength and Young's modulus with amorphous matrix [16]. $Mg_{65}Cu_{25}Gd_{10}$ ternary alloy has a significantly improved GFA compared to $Mg_{65}Cu_{25}Y_{10}$ alloy, enabling the fabrication of the BMG sample with the maximum diameter of 8 mm by the conventional Cu-mold casting method in air atmosphere [17]. Thereafter, it has been shown that an addition of alloying elements

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* Corresponding author. Tel.: +82 2 880 7221; fax: +82 2 883 8197.
E-mail address: espark@snu.ac.kr (E.S. Park).

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that have PEMR with some of constituent elements such as Ag (Cu–Ag: +5 kJ/mol) [3,18], Ni (Cu–Ni: +26 kJ/mol) [19] and Fe (Mg–Fe: +62 kJ/mol, Cu–Fe: +35 kJ/mol) [20,21] improved GFA and/or plasticity in monolithic BMGs or BMG composites. However, there is little systematic documentation on the effects of adding 4th alloying elements with PEMR to Mg–Cu–Gd BMG. In the present study, we further explore the role of a MA of 4th alloying elements to $Mg_{65}Cu_{25}Gd_{10}$ BMG by tailoring the combination of mixing enthalpy among the atomic pairs. In our experiments, first, we show that a MA of Y or Ca with a singular PEMR and two NEMRs with constituent elements in $Mg_{65}Cu_{25}Gd_{10}$ BMG (Y–Gd: 0 kJ/mol; Ca–Gd: +41 kJ/mol [21]) leads to an improvement in plasticity as well as GFA. Second, we show that a MA of Co with two PEMRs and one relatively large NEMR with constituent elements in $Mg_{65}Cu_{25}Gd_{10}$ BMG (Co–Mg: +10 kJ/mol, Co–Cu: +35 kJ/mol, Co–Gd: −67 kJ/mol [21]) drastically deteriorates both GFA and plasticity. However, a MA of Be which has plural PEMRs and one relatively small NEMR with constituent elements in $Mg_{65}Cu_{25}Gd_{10}$ BMG (Be–Mg: +92 kJ/mol, Be–Gd: +12 kJ/mol, Be–Cu: −4 kJ/mol [21]), which is similar to an addition of a 4th element with three PEMRs, has no adverse effect on the GFA and precipitates 4th element-rich secondary nanocrystals in amorphous matrix, which leads to improved plasticity up to $\varepsilon_f = 3.41 \pm 0.10\%$, high GFA up to 9 mm in diameter and high compressive strength of ~1.2 GPa in $(Mg_{65}Cu_{25}Gd_{10})_{95}(Be)_5$ BMG.

2. Experimental

A Cu–Gd–X (X = Y, Ca, Co, Be) master alloy was prepared by arc melting Cu, Gd and X metals (except Cu–Be 4 wt.%) (purity > 99.9%) under a Ti-gettered argon atmosphere in a water-cooled copper crucible. The master alloy was then alloyed with Mg (99.9%) in a boron nitride– (BN–) coated graphite crucible under a dynamic Ar atmosphere using an induction furnace. The alloy ingots were melted several times to help improve compositional homogeneity. After complete melting, the liquid alloy was poured into a Cu mold in air. The copper mold was cone-shaped, 45 mm in height, 15 mm in diameter at the top, and 6 mm in diameter at the bottom. Rapidly solidified and injection-cast specimens were prepared by remelting the alloys in quartz tubes and ejecting them with an over-pressure of 50 kPa through a nozzle onto a Cu wheel rotating with a surface velocity of 40 m/s and into the Cu mold with cylindrical cavities of 1–5 mm in diameter.

The structure of the samples was examined preliminarily by X-ray diffraction (XRD, Rigaku CN2301, Tokyo, Japan) using monochromatic Cu K_α radiation for a 2θ range of 10–90°. Thermal analysis of the samples was carried out to determine the glass transition temperature, T_g, and the crystallization onset temperature, T_x, by differential scanning calorimetry (DSC, Perkin Elmer DSC7, Boston, MA) using a constant heating rate of $0.667\ K\ s^{-1}$. The microstructures of the bulk samples were examined using the high resolution transmission electron microscope (HRTEM, JEOL 2100F, 200 kV, Tokyo, Japan) linked with an energy dispersive spectrometer (EDS, Oxford 6498, Oxford, UK). Thin foil specimens for HRTEM were prepared by Ar ion milling using Gatan (Model 600, Vienna, OH) at 2.6 keV and ~5 mA with liquid nitrogen cooling. Extreme care was taken with the HRTEM analysis since Mg-based BMG thin foils oxidize readily upon exposure to air. The density of the BMG samples was measured using a gas pycnometer (Micromeritics AccuPycTM 1330, Norcross, GA). Compressive test (Housefield; H25 K-T, Redhill, UK) was performed at a strain rate of $1 \times 10^{-4}\ s^{-1}$. To exclude kinetic effects as much as possible, we measured the compressive mechanical properties using injection-cast samples of 1 mm in diameter. The loading surfaces were polished to be parallel with accuracy of less than 10 μm and the samples were fixed in a jig designed to ensure parallel ends. At least five samples of each alloy were tested to ensure the reliability of the data. The strain was determined from the platen displacement after correction for the machine compliance.

3. Results and discussions

3.1. MA of alloying elements with singular PEMR with a constituent element

Fig. 1 shows enthalpy of mixing among the additional element and constituent elements in Mg–Cu–Gd–(Sub) (Sub: Ag, Ni, Y, and Ca) alloy system. All additional elements in the Fig. 1(a)–(d) exhibit PEMR with only one constituent element and NEMRs with others in $Mg_{65}Cu_{25}Gd_{10}$ BMG, which may result in phase separation of quaternary alloys to two ternary-rich compositions such as Mg–Cu–Gd-rich region and Mg–Gd–Ag-rich region in Mg–Cu–Gd–Ag alloy system. In these cases, the GFA of quaternary Mg–Cu–Gd–(Sub) alloy is mainly dependent on that of matrix alloy. As previously reported, a MA of Ag which has a relatively small PEMR with Cu (Ag–Cu: +5 kJ/mol) and NEMRs with others exhibits an improvement in plasticity as well as GFA, e.g. $Mg_{65}Cu_{20}Ag_5Gd_{10}$ exhibits maximum diameter of 11 mm and plastic strain of 0.5% [3]. On the other hand, a MA of Ni which has a relatively large PEMR with Cu (Ni–Cu: +26 kJ/mol) and NEMRs with others deteriorates GFA, but slightly improves plasticity, e.g. $Mg_{65}Cu_{20}Ni_5Gd_{10}$ exhibits plastic strain of 0.15% [19]. To further investigate the correlation, we explore the effects of adding Y and Ca which have PEMR with Gd and NEMRs with others in $Mg_{65}Cu_{25}Gd_{10}$ BMG (Y–Gd: +0 kJ/mol; Ca–Gd: +41 kJ/mol [21]).

Fig. 2 shows a map for GFA (D_{max}) as a function of alloy composition, determined by XRD and DSC experiments in $(Mg_{65}Cu_{25}Gd_{10})_{100-x}(Sub)_x$ (x = 0–5, Sub = Y and Ca) BMGs. A MA of Y leads to slightly improved GFA up to 9 mm at $x = 1$, followed by a gradual decease with a further increase in x. On the other hand, a MA of Ca leads to a relatively large improvement in GFA up to 11 mm at $x = 1$, followed by a large decrease with a further increase in x. These results show that a MA of an alloying element with singular PEMR to $Mg_{65}Cu_{25}Gd_{10}$ BMG can improve the stability of the liquid state in a limited composition range by disturbing the formation of the competing crystalline phases. In particular, the large atomic mismatch between Ca and constituent elements (Mg–Ca: +23%, Cu–Ca: +54%, Gd–Ca: +9.4%) and similar atomic radius ratio among constituent elements ($R_{Mg}/R_{Cu} \approx R_{Ca}/R_{Mg} \approx R_{Gd}/R_{Ca} \approx 1.1$) [22], which are better conditions for high GFA than those of Y addition, result in the formation of denser liquid with lower fragility and higher viscosity, indicating higher GFA [6].

To evaluate the effect of a MA with singular PEMR with Gd on the mechanical properties of Mg–Cu–Gd–(Sub) BMGs, compression tests were performed for the alloys with the composition of $(Mg_{65}Cu_{25}Gd_{10})_{100-x}(Sub)_x$ (x = 0, 1, 3, 5, 7 at.%, Sub = Y and Ca). To exclude both the relaxation effect and cooling rate effect during solidification as much as possible, we measured the mechanical properties by using samples with 1 mm in diameter. Fig. 3 shows the compressive stress–strain curves obtained from the $(Mg_{65}Cu_{25}Gd_{10})_{100-x}(Sub)_x$ (x = 0, 1, 3, 5, 7 at.%, Sub = Y and Ca) samples. The σ_f and ε_f of the alloy $x = 0$ were 830 ± 20 MPa and 2.00 ± 0.10%, respectively. The alloy $x = 0$ failed, showing no evidence of macroscopic yielding and plasticity, as reported for most of the Mg-based BMGs. However, a MA (1 at.%) of Ca (relatively large PEMR with Gd) increased plasticity up to $\varepsilon_f \sim 2.99\% \pm 0.10\%$, although with a further increase in Ca, the sample showed nearly no plasticity. This result has some analogy with earlier studies on $Mg_{65}Cu_{20}Ag_5Gd_{10}$ [3], $Cu_{43}Zr_{43}Al_7Ag_7$ [10], and $Cu_{46}Zr_{42}Al_7Y_5$ BMGs [12], showing that a MA of alloying elements with singular PMER