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Formation of ternary Mg–Cu–Dy bulk metallic glasses

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Abstract. The glass-forming ability (GFA) of ternary Mg–Cu–Dy alloys was systematically investigated by using differential scanning calorimetry (DSC) and X-ray diffractometry (XRD) techniques. The results showed that a series of ternary Mg–Cu–Dy bulk metallic glasses (BGMs) with a diameter of 4–8 mm were successfully fabricated in the system with conventional Cu-mold casting method. $Mg_{55}Cu_{32}Dy_{13}$, $Mg_{60}Cu_{27}Dy_{13}$, $Mg_{65}Cu_{25}Dy_{10}$ and $Mg_{70}Cu_{17}Dy_{13}$ BMGs exhibit a clear glass transition, a broad supercooled liquid region and different crystallization and melting behaviours. They have supercooled liquid region (ΔT_x) from 41 K to 65 K, reduced glass transition temperature (T_{rg}) from 0·5363 to 0·5974 and γ parameter from 0·4038 to 0·4136. The γ shows a relatively good agreement with the GFA of the BGMs. On the other hand, a high fracture compressive strength of 624 MPa was obtained for $Mg_{60}Cu_{27}Dy_{13}$ BMG.

Keywords. Mg–Cu–Dy; glass-forming ability; bulk metallic glass.

1. Introduction

Over the last two decades, bulk metallic glasses (BMGs) have attracted extensive interest due to their unique physical, chemical and mechanical properties attributed to their random atomic configurations. The fabrication technique, glass-forming ability (GFA), thermal stability of the BMGs and the factors that are controlling the properties have been systematically investigated. Recently, an attempt for a possible structural application of BMG has been made to develop an amorphous coating with Fe-based BMG on AISI 4140 substrate by laser surface processing (Basu *et al* 2008). Among the BMGs, much more attention was paid to Mg-based amorphous alloys because of their high specific strength and relatively low cost, which is attractive for the practical application as new light structural materials.

Rare earth elements play an important role in the Mg-based BMGs formation process. The first Mg-based bulk amorphous alloy with $Mg_{65}Cu_{25}Y_{10}$ composition, to exhibit a good GFA was synthetized by Inoue *et al* (1991). Later, based on the ternary $Mg_{65}Cu_{25}Y_{10}$ alloy, further improvement of GFA has been made by various complementary element additions so that metallic glass rods with the maximum diameter of 6–16 mm are fabricated by copper-mold casting method in quaternary, quinary and hexahydric systems such as Mg–Cu–Ag–Y (Park *et al* 2001; Ma *et al* 2005), Mg–Cu–Zn–Y (Men *et al* 2002), Mg–Cu–Y–Nd (Zheng *et al* 2006), Mg–Cu–Ni–Y–Nd (Li *et al* 2008) and Mg–Cu–Ni–Zn–Ag–Y (Ma *et al* 2003). On the other hand, the GFA of $Mg_{65}Cu_{25}RE_{10}$ alloys in which Y was replaced by other rare earth elements (RE) was also studied and some BMGs like $Mg_{65}Cu_{25}Gd_{10}$ (Men *et al* 2004) were obtained in the system. However, the formula composition for the Mg-based BMGs containing RE has not been optimized. More recently, we have successfully fabricated BMG with a diameter of 8 mm in a ternary Mg–Cu–Dy alloy system by conventional Cu-mold casting method. This paper intends to present the GFA, thermal stability and mechanical properties of Mg–Cu–Dy alloys.

2. Experimental

Ingots with nominal composition of $Mg_xCu_yDy_z$ ($50 \leq$ at.% $x \leq 70$, $15 \leq$ at.% $y \leq 35$ and $10 \leq$ at.% $z \leq 15$) were prepared by arc melting the mixture of pure metals (Mg, Cu and Dy) with a purity of more than 99·9% under a Ti-gettered Ar atmosphere. To ensure homogeneity of the samples, the ingots were re-melted several times. For the bulk samples, the 60 mm length cylindrical rods with different diameters were prepared by pouring liquid metal, which was melted using induction furnace, through a quartz nozzle into a copper mold under certain argon pressure as well as purified argon atmosphere. In addition, ribbon samples were prepared by melt spinning, are approximately 25 μm in thickness and 3 mm in width were obtained.

The structure of samples was checked by X-ray diffraction (XRD) with Cu-Kα radiation. Thermal stability

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associated with glass transition, supercooled liquid region and crystallization were examined by continuous heating in a differential thermal analysis (Perkin-Elmer Pyris Diamond TG/DTA) at a heating rate of 0·67 K/s under flowing high purity N_2 (200 ml/min). The DTA data were transformed into differential scanning calorimeter (DSC) data by using the Perkin–Elmer-edited computer program. Al_2O_3 pans were used and the mass of sample was between 20 and 30 mg. Compression experiments were carried out on a MTS-type axial-torsional load frame at room temperature. The compressive strain rate was $3{\cdot}0 \times 10^{-4}$ s^{-1}. Six rods with the same diameter and composition were compressed.

3. Results and discussion

The alloy compositions for forming BMGs studied in the Mg–Cu–Dy system are shown in figure 1. It is seen that BMGs with a diameter at least 4 mm was synthesized in the composition range shown in figure 1. Glass formation in a diameter as large as 8 mm was obtained in $Mg_{60}Cu_{27}Dy_{13}$ alloy.

Figure 2 shows XRD patterns obtained from the as-cast rods with different diameters prepared by the copper-mold casting for some compositions. The XRD patterns from $Mg_{55}Cu_{32}Dy_{13}$, $Mg_{60}Cu_{27}Dy_{13}$ and $Mg_{65}Cu_{22}Dy_{13}$ alloys consist a broad peak only indicating a fully amorphous structure, with no evidence of any crystalline Bragg peaks within the detectable limitation of the XRD when the diameters of their rod samples are 7, 8 and 6 mm, respectively, while a few sharp diffraction peaks corresponding to crystalline phases superimposed on the broad amorphous peaks are observed when the diameters of their rod samples increase to 8, 9 and 7 mm, respectively.

Figure 3 shows DSC traces of the as-cast $Mg_xCu_yDy_{13}$ BMGs with a heating rate of 0.67 K/s. All curves exhibit a clear endothermic heat event characteristic of the glass transition, followed by a broad supercooled liquid region and then exothermic reactions due to crystallization. The glass temperature, T_g, the onset temperature of the crystallization, T_x, the supercooled liquid region, $\Delta T_x = T_x - T_g$ for the alloys are listed in table 1. With increasing Mg content from 55 to 70 and decreasing Cu content from 32 to 17, T_g decreased from 445·67 K to 417·91 K, while T_x decreased from 487·13 K to 480·68 K with increasing Mg content from 55 to 65 and decreasing Cu content from 32 to 22 and then T_x increased to 483·44 K for the $Mg_{70}Cu_{17}Dy_{13}$ alloy. As a result, ΔT_x for $Mg_{55}Cu_{32}Dy_{13}$, $Mg_{60}Cu_{27}Dy_{13}$, $Mg_{65}Cu_{25}Dy_{10}$ and $Mg_{70}Cu_{17}Dy_{13}$ were 41·46, 63·68, 60·93 and 65·53 K, respectively and maximum ΔT_x was obtained in the $Mg_{70}Cu_{17}Dy_{13}$ alloy. The ΔT_x value was sometimes used as a measure for the GFA of alloys on the basis that a large ΔT_x value indicates a relatively stable glass (Inoue *et al* 1993). However, the current results demonstrate that although the ΔT_x value of $Mg_{60}Cu_{27}Dy_{13}$ BGM is not maximal in the four BGMs, its GFA is the strongest in all the four BGMs. Similar observations have also been made in many BGM systems (Inoue *et al* 2001; Men *et al* 2002; Ma *et al* 2003). Also, it is noticed that a large exothermic peak due to crystallization is observed for the $Mg_{55}Cu_{32}Dy_{13}$ and $Mg_{60}Cu_{27}Dy_{13}$ alloys during continuous heating. However, other two small exothermic reactions caused by crystallization appear in the DSC trace of the $Mg_{65}Cu_{25}Dy_{10}$ and $Mg_{70}Cu_{17}Dy_{13}$ alloys, indicating a change of crystallization behaviour with alloy compositions.

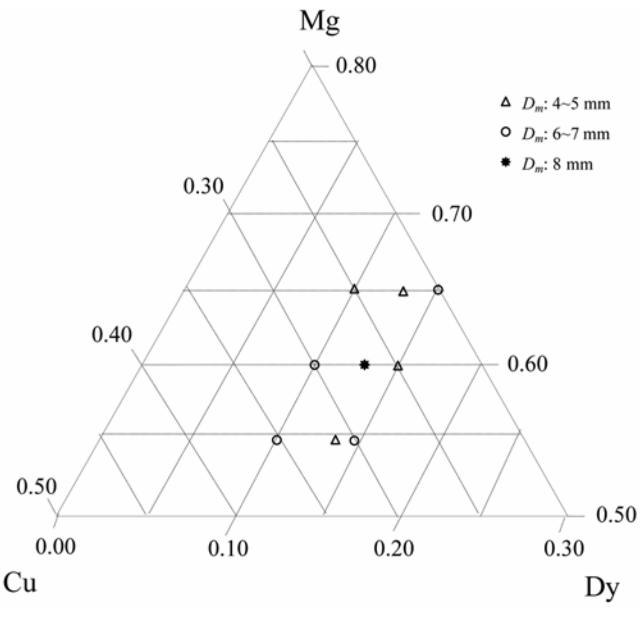

Figure 1. The alloy compositions for forming BMGs studied in the Mg–Cu–Dy system.

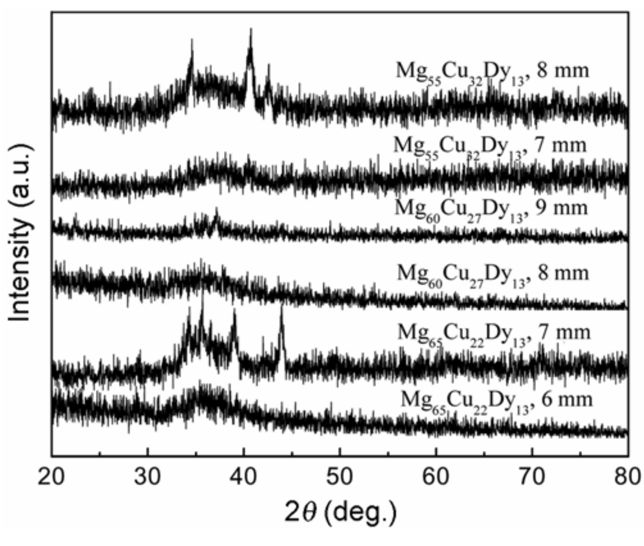

Figure 2. XRD patterns obtained from the as-cast rods with different diameters for $Mg_xCu_yDy_{13}$ alloys.

Table 1. The glass transition temperature T_g, the crystallization temperature T_x, the supercooled liquid region $\Delta T_x = T_x - T_g$, the melting temperature T_m, the liquids temperature T_l, the reduced glass transition temperature $T_{rg} = T_g/T_l$ and the parameter $\gamma T_x/T_g T_l$ for Mg–Cu–Dy alloys.

Alloys	T_g (K)	T_x (K)	ΔT_x (K)	T_m (K)	T_l (K)	ΔT_m (K)	T_{rg} (K)	γ
$Mg_{55}Cu_{32}Dy_{13}$	445·67	487·13	41·46	715·62	746·02	30·40	0·5974	0·4087
$Mg_{60}Cu_{27}Dy_{13}$	422·52	486·20	63·68	714·69	753·04	38·35	0·5611	0·4136
$Mg_{65}Cu_{22}Dy_{13}$	419·75	480·68	60·93	713·77	753·39	39·62	0·5571	0·4097
$Mg_{70}Cu_{17}Dy_{13}$	417·91	483·44	65·53	713·71	779·19	65·48	0·5363	0·4038

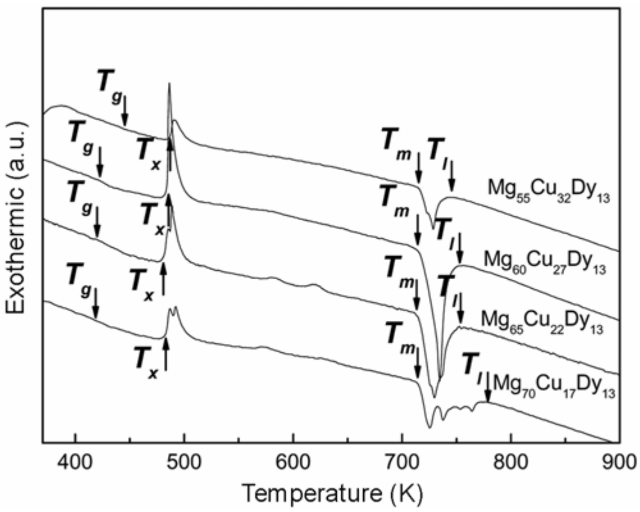

Figure 3. DSC traces of the as-cast $Mg_xCu_yDy_{13}$ BMGs with a heating rate of 0·67 K/s.

Figure 3 also shows the melting behaviours of the as-cast $Mg_xCu_yDy_{13}$ BMGs. It can be seen that Mg or Cu content significantly affects the melting behaviours of these alloys. The solidus temperature T_m and liquidus temperature T_l are assumed to be the onset and end temperatures of the endothermic melting, respectively. With increasing Mg content from 55 at.% to 70 at.% and decreasing Cu content from 32 at.% to 17 at.%, T_l increased from 746·02 K to 779·19 K. The $Mg_{70}Cu_{17}Dy_{13}$ alloy showed a rather high T_l (~ 779 K) and a melting process consists of one major endothermic event, followed by some minor secondary event, resulting in a large melting point of about 65 K, which indicates that this alloy is at off-eutectic composition. In the DSC scan of the $Mg_{55}Cu_{32}Dy_{13}$, $Mg_{60}Cu_{27}Dy_{13}$ and $Mg_{65}Cu_{25}Dy_{10}$ alloys, the T_l were 746·02, 753·04 and 753·39 K, respectively. Their melting processes showed single endothermic peak and narrow melting temperature points of about 30, 38 and 39 K, respectively, suggesting that the three alloys are quite close to a ternary eutectic composition. A critical parameter to determine the glass-forming ability (GFA) of an alloy is the reduced glass transition temperature, T_{rg}, defined as the glass transition temperature T_g divided by the liquidus temperature T_l ($T_{rg} = T_g/T_l$). Another GFA criterion proposed recently by Liu *et al* is the parameter γ (Lu and Liu 2002), where $\gamma = T_x/(T_g + T_l)$. By taking the data of the T_l for the $Mg_xCu_yDy_{13}$ BMGs, T_{rg} and γ of the alloys were obtained, which are also given in table 1. With increasing Mg content from 55 at.% to 70 at.% and decreasing Cu content from 32 at.% to 17 at.%, T_{rg} value decreased from 0·5974 K to 0·5363 K, which is not consistent with the GFA of the alloys. The γ values of $Mg_{55}Cu_{32}Dy_{13}$, $Mg_{60}Cu_{27}Dy_{13}$, $Mg_{65}Cu_{25}Dy_{10}$ and $Mg_{70}Cu_{17}Dy_{13}$ alloys are 0·4087 0·4136, 0·4097 and 0·4038, respectively, which is consistent with the GFA of the alloys. Therefore, γ should be a good criterion for the GFA in the present Mg-Cu–Dy alloy system.

Figure 4 shows the quasistatic compressive stress–strain curve at room temperature for the as-cast $Mg_{60}Cu_{27}Dy_{13}$ BMG rod with a diameter of 8 mm and a length of 16 mm. It can be seen that the curve displays an initial elastic deformation behaviour with almost no plasticity and a high fracture compressive strength of 624 MPa at room temperature, which is the typical characteristic of BMGs.

The present results show that Mg–Cu–Dy alloy system has very high GFA, a series of BGMs could be successfully fabricated in the system with conventional Cu-mold casting method and maximal critical diameter reaches 8 mm. The Mg–Cu–Dy alloy system with high GFA has been recognized to satisfy three empirical rules (Inoue *et al* 1997), i.e. (i) multi-component systems consisting of more than three elements, (ii) significant atomic mismatches above 12% among the main three constituent elements and (iii) mixing of negative heats among the main elements. Dy has larger radii (0·186 nm) when compared with that of Mg and Cu (the radii of Cu and Mg are 0·128 and 0·160 nm, respectively). The accurate addition of Dy causes the more sequential change in the atomic sizes and fairly optimizing the atomic size distributions. At the same time, increases the complexity of the alloys which limit the solid-state solubility of these elements. Therefore, the alloys require large composition fluctuation to form crystalline phase critical nuclei (Xi *et al* 2005). The Dy also has larger mixing of negative heat with Mg and Cu components in the alloy which can form more atomic pairs. Thus, the local atomic structure of the liquid, tending to form local clusters consisting of the atomic pairs in ternary Mg–Cu–Dy alloys can lead to an increase in the degree of dense random packed atomic configurations, the liquidus temperature is decreased with difficulty. This favours the stabilization of the liquid phase, adequate amount of Dy addition and make the rearrange-

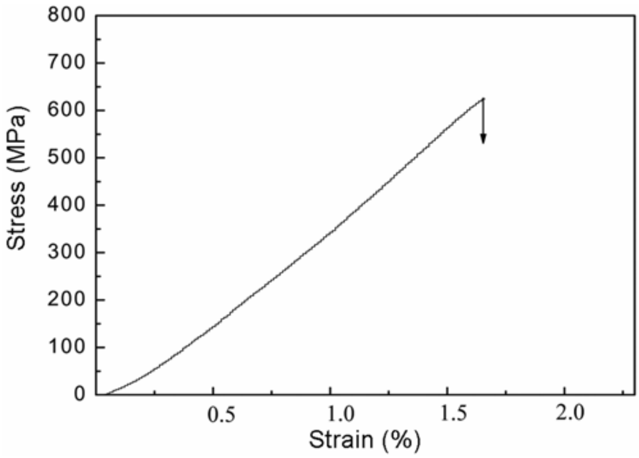

Figure 4. The Stress–strain curve of $Mg_{60}Cu_{27}Dy_{13}$ BMG.

ment of the constituent elements on a long-range scale with respect to competing crystalline phases during solidification and then improves the GFA of the alloys.

It is well known that lowering the liquidus temperature and altering the alloy composition up to the eutectic or near the eutectic are key steps in fabricating BMGs. The Mg–Cu, Mg–Dy and Cu–Dy binary systems have a deep binary eutectic point at composition $Mg_{86}Cu_{14}$, $Mg_{89}Dy_{11}$ and $Cu_{90}Dy_{10}$ with a binary eutectic temperature T_E of 758, 834 and 1128 K, respectively. The ternary alloy system reported in this paper were developed based on this binary eutectic composition. The $Mg_{55}Cu_{32}Dy_{13}$, $Mg_{60}Cu_{27}Dy_{13}$, and $Mg_{65}Cu_{25}Dy_{10}$ alloys have a low liquidus temperature T_l and composition close to ternary eutectic point (figure 3), which can avoid the precipitation of the primary crystalline phase in the $Mg_xCu_yDy_{13}$ alloys with the larger or smaller amount of Mg (the smaller or larger amount of Cu). Thus, their liquid structures are more stable than those of other $Mg_xCu_yDy_{13}$ alloys such as $Mg_{70}Cu_{17}Dy_{13}$ alloy which exhibits a high T_l and off-eutectic composition attributed to the precipitation of the primary crystalline phase during solidification, resulting in the improvement of GFA and the forming of BMGs with large critical diameters.

4. Conclusions

A series of ternary Mg–Cu–Dy bulk metallic glasses (BGMs) with a diameter of 4–8 mm were successfully fabricated in the system with conventional Cu-mold casting method. $Mg_{60}Cu_{27}Dy_{13}$ alloy can form BGM with maximal critical diameter of 8 mm. $Mg_{55}Cu_{32}Dy_{13}$, $Mg_{60}Cu_{27}Dy_{13}$, $Mg_{65}Cu_{25}Dy_{10}$ and $Mg_{70}Cu_{17}Dy_{13}$ BMGs exhibit a clear glass transition, a broad supercooled liquid region and different crystallization and melting behaviours. Parameter γ shows a relatively good agreement with the maximum diameter of the BGMs, while supercooled liquid region ΔT_x and reduced glass transition temperature T_{rg} have poor relationship with their GFA. In addition, the $Mg_{60}Cu_{27}Dy_{13}$ BMG exhibits a high compressive fracture strength of 624 MPa.

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