Glass-forming Mg–Cu–RE (RE = Gd, Pr, Nd, Tb, Y, and Dy) alloys with strong oxygen resistance in manufacturability

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Abstract

One of the unsolved problems for the manufacturability and the applications of bulk metallic glasses is that their glass-forming ability is very sensitive to the preparation vacuum and impurity of components because oxygen in the environments would markedly deteriorate the glass-forming ability. Here we report that the addition of rare earth elements can significantly improve the glass-forming ability and manufacturability of Mg-based alloys. The Mg-based glass-forming alloys can withstand very low vacuum in preparation process. The beneficial effects of the Gd addition on the glass-forming ability and oxygen resistance during the Mg-based glass formation are explored.
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1. Introduction

Metallic alloys with excellent glass-forming ability (GFA) allow the production of bulk metallic glasses (BMGs) by a conventional casting process at a low critical cooling rate [1]. However, the critical cooling rate for the formation of BMGs depends dramatically on oxygen level which can significantly deteriorate the GFA of an alloy [2,3]. Generally, high vacuum (better than 10^{-3} Pa) and high purity of constituent elements (better than 99.9 at.%, oxygen <250 ppm) are necessary for the fabrication of the BMG materials [3]. Therefore the preparation of the BMGs has to be performed in high vacuum or high purity argon atmosphere with strictly clean environment. The adverse effect of oxygen is a key factor to degrade the manufacturability of the BMGs and limits their applications. To improve the manufacturability, extensive work has been carried out

[3–6]. Our previous work shows that the Zr-based BMGs with a proper amount of yttrium addition can be obtained at low vacuum using low purity components (>1500 ppm of oxygen) [3]. The yttrium addition method afterward has been successfully applied to enhance the GFA and manufacturability of Fe-, Cu-based alloys [7,8].

The formation of the Mg-based BMGs was firstly reported in 1991 [9]. The BMGs have attracted more and more attention due to their high strength to weight ratio and relatively low cost. In addition, the low-density and friendly to environment of the BMGs are highly attractive for applications [9–12]. However, to make the Mg-based BMGs acceptable for industrial materials, it is vital to further improve their GFA and manufacturability, and enable the Mg-based alloys to withstand severe preparation and process environments such as low vacuum. In this paper, we report that with proper rare earth (RE) addition, a series of ternary Mg–Cu–RE alloys with exceptional GFA and high oxygen resistance during preparation are successfully prepared by the conventional Cu-mold casting. The MgCuGd alloy is selected

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as an example to explore and understand the beneficial role of the RE element in the glass formation and manufacturability of the alloys.

2. Experimental

The pure Cu and RE element (RE = Gd, Pr, Nd, Tb, Y, and Dy, the purity is ∼99.9 at.%) were arc-melted in a Ti-gettered argon atmosphere to produce the intermediate Cu–RE alloys. The master alloys were prepared by induction-melting the intermediate Cu–RE alloy together with Mg (purity 99.99 at.%) in a quartz tube under vacuum. When the master alloys were homogeneously melted, they were cast into a copper mold to get a 50-mm-long cylinder with diameter of 1–7 mm. The small mass Cu-mold without water cooling indicates that the cooling rate for the alloy melt is very low. To investigate the oxygen resistance of the MgCuRE alloys, the MgCuGd alloy is selected as an example to explore the beneficial role of the RE element in the glass formation and manufacturability. The intermediate Cu–Gd alloy and Mg (purity 99.99 at.%) were induction homogeneously melted in a quartz tube and then injected into a copper mold without water cooling under various degrees vacuums (including in air). The oxygen content of the as-cast cylinders was chemically analyzed by using a carrier gas hot extraction (O/N Analyzer TC-436/Leco). The amorphous nature of the samples was identified by X-ray diffraction (XRD) with CuK$_\alpha$ radiation, and confirmed by differential scanning calorimeter (DSC) performing at a heating rate of 20 K/min. Calorimeter was calibrated for temperature and energy at various heating rates with high purity indium and zinc. The values of the onset temperature for crystallization peak, glass transition and melting were determined from the DSC traces with the accuracy of ±1 K. The acoustic velocities were measured using a pulse echo overlap method with a measuring sensitivity of 0.5 ns [13,14]. Elastic constants (e.g., the Young's modulus E, the shear modulus G, and the bulk modulus, K) were derived from the acoustic velocities and the accuracy lies within 0.1% [13].

3. Results

The Mg$_{65}$Cu$_{25}$RE$_{10}$ (RE = Gd, Nd, Pr, Y, Tb and Dy) BMGs are successfully prepared with a critical thickness at least 1 mm by the conventional Cu mold casting method without water cooling under vacuum. Fig. 1 presents the XRD patterns of these as-cast alloys prepared under vacuum (∼1.0 × 10^{-2} Pa). The critical diameter of the as-cast cylindrical Mg$_{65}$Cu$_{25}$RE$_{10}$ (RE = Pr, Nd, and Y) BMGs is about 1–3 mm. For the Mg$_{65}$Cu$_{25}$RE$_{10}$ (RE = Gd, Tb, and Dy) BMGs the
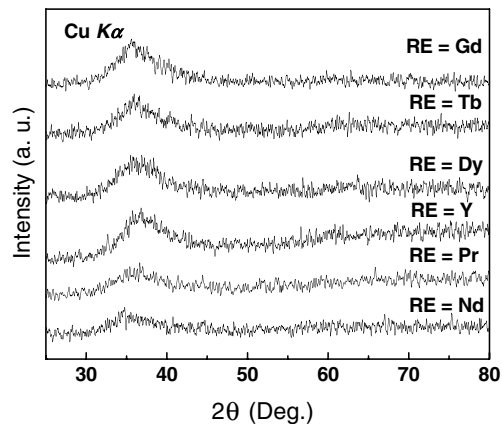

Fig. 1. XRD patterns of the as-cast rod of Mg$_{65}$Cu$_{25}$RE$_{10}$ (RE = Gd, Pr, Nd, Tb, Y, and Dy) alloy melt and injected under vacuum condition (1.0 × 10^{-2} Pa). The critical diameter of as-cast cylindrical Mg$_{65}$Cu$_{25}$RE$_{10}$ (RE = Pr, Nd, and Y) BMGs is about 1–3 mm. For the Mg$_{65}$Cu$_{25}$RE$_{10}$ (RE = Gd, Tb, and Dy) BMGs the critical diameter is at least about 5 mm.

critical diameter is at least about 5 mm. All the alloys exhibit broad diffraction maxima characteristic of glass without obvious crystalline Bragg peaks within the detectable limitation of the XRD. The XRD results demonstrate the amorphous structure in bulk and high GFA of these alloys. It is found that the GFA of the alloys are inert in the manufacturability environment and have high oxygen resistance (more details of the formation and properties of these BMGs will be published elsewhere), which is suggested to be an effective oxygen resistance role of the RE content. To understand the underlying mechanism of the RE addition on the GFA and oxygen resistance, the Gd is chosen as a representative RE to explore the effect on the glass formation and manufacturability of the Mg-based alloys. Fig. 2
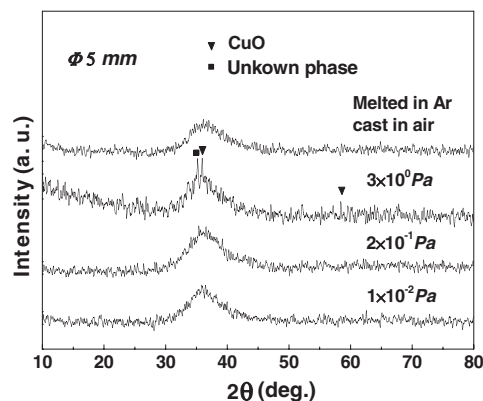

Fig. 2. XRD patterns of the as-cast 5 mm rods for a model alloy system Mg$_{65}$Cu$_{25}$GD$_{10}$ alloy melt and injected under different vacuum environments, illustrating the deoxidation effect of Gd on the glass formation.
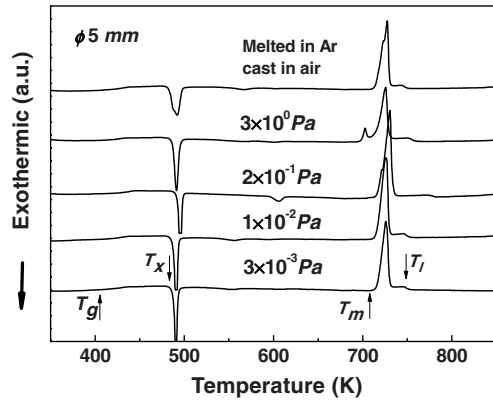
Fig. 3. DSC traces of as-cast 5 mm diameter rod of the $Mg_{65}Cu_{25}GD_{10}$ alloy melt and injected under different vacuum environments measured at a heating rate of 20 K/min. The T_g of $Mg_{65}Cu_{25}GD_{10}$ BMG is 406 K which is one of the lowest among known BMGs.

The Gd addition enables the Mg-based alloy to have enhanced the GFA and significantly improved manufacturability during preparation without obviously changing the mechanical and elastic properties of the BMGs.

Fig. 3 exhibits DSC traces of the as-cast $Mg_{65}Cu_{25}Gd_{10}$ alloy cast under different vacuum environments. All the alloys show a distinct glass transition onset at T_g, sharp crystallization onset at T_x and large supercooled liquid region, $\Delta T_x = T_x - T_g$ which further confirm the amorphous structure of the alloy. The values of T_g, T_x crystallization enthalpy, ΔH_x, melting temperature, T_m, the liquidus temperature, T_l, and ΔT of the alloys prepared under various conditions are listed in Table 1. The reduced glass transition temperature $T_{rg} = T_g/T_l$ [15], which is a critical parameter in determining the GFA of an alloy, is 0.54. The γ [$\gamma = T_x/(T_g + T_l)$], which is another GFA criterion proposed by Liu et al. [16], is about 0.42. The large values of T_{rg} and γ demonstrate the high GFA of the alloy. From the endothermal signal of the melting, one can deduce that the composition of the alloy is very close to the eutectic point. The oxygen content of the samples prepared under different oxygen environments is also listed in Table 1. One can see that the oxygen content increases when the preparation vacuum becomes poorer, while the values of T_{rg}, γ and ΔH_x are not dramatically changed with the different oxygen contents. These results further confirm that the GFA of the Mg–Cu–Gd alloy is not sensitive to oxygen environment.

To investigate the effect of Gd on the GFA of the MgCuGd alloy, the $Mg_{75-x}Cu_{25}Gd_x$ ($x = 5, 10, 15$, and 20 at.%) samples with different Gd contents were prepared in a 5 mm diameter cylinder under high vacuum ($x = 3.0 \times 10^{-3}$ Pa) and their XRD patterns are shown in Fig. 4. The patterns clearly illustrate that when Gd content is more or less than 10 at.%, there are some crystalline phase peaks appear indicating that crystals exist in the samples. Fig. 5 shows the DSC traces of the as-cast $Mg_{75-x}Cu_{25}Gd_x$ ($x = 10, 15, 20$) cylindrical alloys with 1 mm in diameter, all the alloys are of full glassy structure under this cooling rate. The DSC runs in Fig. 5 show that the alloys with more than 10% Gd content have off eutectic melting process, which is the main reason for the

shows the XRD patterns of the as-cast $Mg_{65}Cu_{25}Gd_{10}$ rod in a diameter of 5 mm which was melted and injected under different vacuum environments. No appreciable diffraction peaks due to the precipitation of crystalline phases are seen in the low vacuum conditions up to 2×10^{-1} Pa, which is indicative of no crystalline phase formed under the low vacuum. Even under very low vacuum (3.0 Pa), the as-cast alloy mainly consists of glassy phase with a little amount of precipitated crystalline phases (<10%) which are identified to be mainly Cu and Gd oxides. For the alloy induction melted in Ar atmosphere and cast in air, its XRD pattern in Fig. 2 demonstrates that the alloy is full glass with the detectable limit of the XRD. These results indicate that the GFA of the Mg–Cu–Gd alloy has a high oxygen resistance and is inert in the oxygen environment.

The elastic constants of Young's modulus, E, shear modulus, G, and bulk modulus, K calculated from the acoustic data for the BMG prepared at high vacuum condition are 50.6, 19.3, and 45.0 GPa respectively. For the BMG prepared at 3.0 Pa, The E, G, and K are 52.7, 20.0, and 48.1 GPa respectively. The obtained elastic data show that there is no significantly difference between the two BMGs obtained at different conditions.

Table 1
Thermal parameters (heating rate: 20 K/min) of T_g, T_x, ΔT_x, T_m, T_l, T_{rg}, and γ, and oxygen content for the $Mg_{65}Cu_{25}Gd_{10}$ rod with a diameter of 5 mm prepared under different conditions

Sample cast at various conditions	T_g (K)	T_x (K)	ΔT_x (K)	T_m (K)	T_l (K)	T_{rg}	γ	Oxygen content (at.%)	ΔH_x (J/g)
3.0×10^{-3} Pa	406	488	82	716	751	0.541	0.422	0.1	80.7
1.0×10^{-2} Pa	406	488	82	716	753	0.539	0.421	0.2	76.8
2.0×10^{-1} Pa	413	483	70	715	751	0.550	0.415	0.4	73.1
3.0×10^{0} Pa	420	494	74	716	781	0.538	0.411	0.9	72.1
Melted in Ar and cast in air	413	487	74	699	759	0.544	0.416	0.5	

For the thermal parameters of T_g, T_x, ΔT_x, T_m, and T_l, the accuracy is about of ±1 K, For the crystallization enthalpy, ΔH_x, and oxygen content, the accuracies are about of ±2 J/g and ±0.05 at.%, respectively.
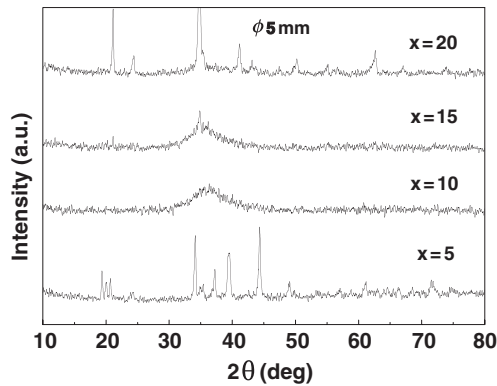
Fig. 4. XRD patterns of the as-cast 5mm diameter rods for the $Mg_{75-x}Cu_{25}Gd_x$ alloys illustrating the Gd effect on GFA of the alloy.
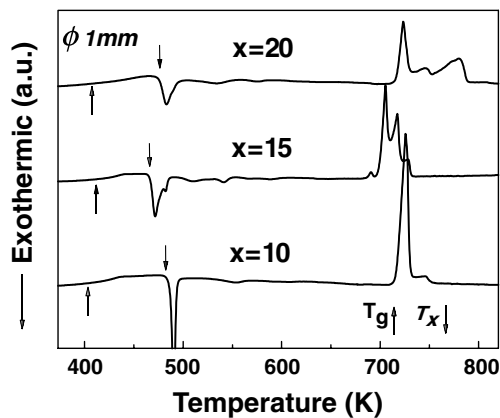

Fig. 5. DSC runs of as-cast 1mm diameter rods of the $Mg_{75-x}Cu_{25}Gd_x$ alloys. All these alloys are of full glassy structure when cast in 1mm diameter rod.

content. The obtained elastic data show that the Gd content has significant effect on the elastic properties of the alloys, because the acoustic property is particularly sensitive to the microstructure and composition of an alloy [13]. The markedly differences in elastic properties of the alloys are mainly induced by primary crystallization of the alloys as shown in Fig. 2. Similar phenomenon was also observed in oxide glass and other BMGs [14].

4. Discussion

The role of the RE element on the GFA of the Mg-alloy can be understood according to the empirical BMG formation criterions [17]. The RE elements have larger radii (ranges from 0.178 to 0.182nm) comparing with that of other metals (the radii of Cu and Mg are 0.128, 0.160nm, respectively) [18]. The proper adding of RE causes the more sequential change in the atomic sizes and fairly optimizing atomic size distributions and, at the same time increase the complexity of the alloys which limit the solid-state solubility of these elements and, therefore, the alloys require large composition fluctuation to form crystalline phase critical nuclei. The RE also has larger negative heat of mixing with Mg and Cu components in the alloy which can form more atomic pairs. Consequently, the packing density and viscous of the undercooled liquid are increased and the liquidus temperature is decreased with adequate amount of RE addition. Thus, the stability of supercooled liquid state of the alloys with low atomic diffusivity is enhanced, and then the GFA is improved.

To completely understand the high oxygen resistance role of the RE in the alloys, more work is needed. Nevertheless, from a thermodynamic point of view, RE elements have a stronger affinity with the oxygen compared with that of Mg and Cu in the alloy. The enthalpy of formation of the RE oxide is about 1800–2000 kJ/mol, and much higher than that of the oxides of other constituent elements (e.g. MgO, 601.6 kJ/mol; CuO, 157.3 kJ/mol) [19]. The reaction between RE and oxygen is thermodynamically favored compared to other oxidation reactions in the alloy. Therefore, in the molten liquid, the RE element can prohibit the reaction between

degraded GFA of the alloys with more Gd addition. Therefore, a proper RE content (10–15at.% Gd) is necessary for improving the GFA in the Mg–Cu alloy.

The measured acoustic velocities, density and elastic constants of E, σ, G, and K calculated from the acoustic data for the $Mg_{75-x}Cu_{25}Gd_x$ ($x = 5, 10, 15, 20$) alloys prepared at high vacuum condition are listed in Table 2. From Table 2, one can see that the V_1, V_s, ρ and elastic constants show large relative change with increasing Gd

Table 2
The measured density and velocities at ambient conditions, and the elastic constants of E, G, σ, and K calculated from the acoustic data for the $Mg_{75-x}Cu_{25}Gd_x$ ($x = 5, 10, 15,$ and 20) alloys rods with 3mm in diameter prepared at high vacuum condition

Sample[a]	ρ (g/cm^3)	V_s (km/s)	V (km/s)	G (GPa)	K (GPa)	E (GPa)	σ
$Mg_{70}Cu_{25}Gd_5$ (C)[a]	3.44	4.818	2.669	24.5	47.2	62.7	0.279
$Mg_{65}Cu_{25}Gd_{10}$ (A)	3.79	4.319	2.254	19.3	45.1	50.6	0.313
$Mg_{60}Cu_{25}Gd_{15}$ (A+C)	4.22	4.164	2.171	16.2	38.0	42.6	0.313
$Mg_{55}CU_{25}Gd_{20}$ (A+C)	4.65	4.131	2.157	21.6	50.5	56.8	0.313

[a] A: amorphous; A + C: amorphous + crystalline; C: crystalline.

Mg and oxygen during melting and casting processes. The Mg oxide and Laves phase are similar in crystalline structure [20], the formation of the Laves phase triggered by Mg oxide, can act as a heterogeneous nucleus sites and induce significant nucleation in the supercooled liquid, finally make the alloy lose its excellent GFA [1]. This is the main reason why the glass-forming alloy is so sensitive to the oxygen content [3,4]. The RE oxide nucleus with markedly different structure compared with that of Laves phase cannot induce the formation of the Laves phases. The small RE oxide particles centralizing the most oxygen in the alloy were observed by electron transmission microscopy to uniformly distribute in the glassy matrix [7]. Thus, the excellent GFA of remaining liquid was maintained because of the alleviation of the harmful effect of oxygen, and thereby the alloy behaves both highly GFA and high oxygen resistance. In addition, RE also plays a purification role in the alloying process [21]. RE elements have high affinity with other impurities such as H, S, and C which also have harmful effect on the GFA [3], and can improve the manufacturability by scavenging other impurities from the melting alloys via the formation of innocuous RE compounds [21].

5. Conclusions

A series of new ternary Mg–Cu–RE (RE = Gd, Pr, Nd, Tb, Y, and Dy) BMGs with highly GFA are successfully fabricated under high oxygen environment. Although further work is necessary to clarify the mechanism of the RE element in the high oxidation resistance effect, it is clearer that the Mg-based BMG forming alloys with RE content are inert in the oxygen environment and have very high oxidation resistance and good manufacturability. The present results suggest that the high oxidation resistance of the RE elements in the formation of BMGs could be used to develop new BMGs and has potentials in application of BMG materials.

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