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On the criteria of bulk metallic glass formation in MgCu-based alloys

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Abstract

$Mg_{65}Cu_{25}RE_{10}$ bulk metallic glass (BMG) forming system with 'continuous' range of atomic size and electronegativity are obtained which allow us to systematically explore the BMG-forming characteristics. Both atomic size and electronegativity differences among the main constituents are found to be crucial for BMG formation.
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Although some empirical rules give useful directions in general [1,2]. The development of new bulk metallic glass (BMG) is still a very time-consuming process of selection and screening of different element combinations. Therefore, finding a more specific criterion for bulk metallic glass formation is very important. The subject of alloy design of BMGs has been discussed from the topological theory [3–6]. Large atomic size ratio among main constituents seems to be a very important factor in the quantitative determination of the composition range [4]. Egami [6] suggest a correlation between atomic size and its concentration in certain metallic glasses. Also, Poon et al. [5] provides a succinct model that includes the short-range order as a backbone in the liquid or amorphous phase. Recently, Chen et al. [7] introduced both atomic size and e/a ratio–constant (the average valence electron number per atom) as two criteria to find the best BMG-forming composition. The electronegativity has also been introduced to explain the glass-forming ability (GFA) of the Al- and Mg-based alloys, which shows nearly a linear relationship with GFA [8,9].

In this study, a series of $Mg_{65}Cu_{25}RE_{10}$ BMGs (RE, rare-earth elements in lanthanide series) were produced. The effects of the atomic size and electronegativity of

rare-earth, RE, components on the GFA of the $Mg_{65}Cu_{25}RE_{10}$ (RE=La, Ce, Pr, Nd, Sm, Gd [10], Dy, Tb, Ho, Er and Yb) has been systematically investigated. It is found that the atomic size and electronegativity differences appear to be the crucial factors for the BMG formation. The results may be useful for eliminating discrepancies in understanding of BMG formation in earlier studies.

Cu–RE master-alloys were prepared by arc melting a mixture of Cu (99.99 wt%) and various RE elements (99.95 wt%) under a Ti-gettered argon atmosphere in a water-cooled copper crucible. The nominal composition of $Mg_{65}Cu_{20}RE_{10}$ alloys were obtained by induction melting each Cu–RE alloy with Mg (99.99 wt%) in a quartz tube under Ar atmosphere. The arc-melted alloys were then remelted and injected into a copper mold to get the rod-shaped samples with diameters from 0.5 to 8 mm. The amorphous nature of the samples was identified by X-ray diffraction (XRD) using a MAC M03 XHF diffractometer with Cu K_α radiation and confirmed by differential scanning calorimeter (DSC) measurements performed on a Perkin–Elmer DSC at a heating rate of 20 K/min by wrapping them in a tantalum foil. The compositions of the glasses have been checked using chemical analysis.

Fig. 1 shows XRD patterns of the as-cast cylindrical $Mg_{65}Cu_{25}RE_{10}$ (RE=La, Ce, Pr, Nd, Sm, Gd, Dy, Tb, Ho, Er and Yb) alloys with different diameters. As can be seen,

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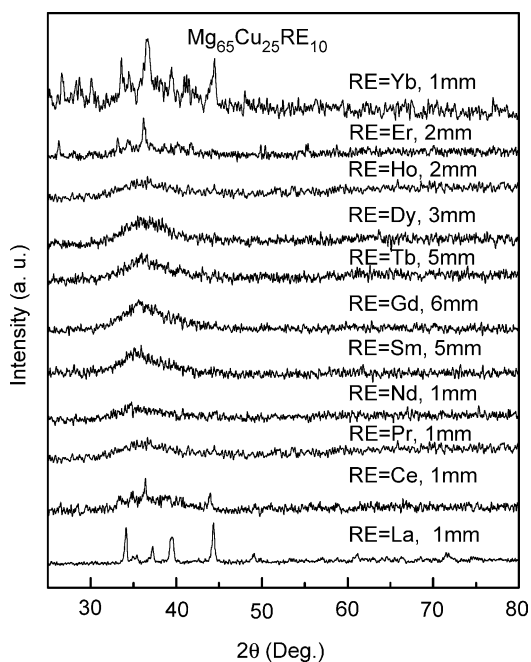 *E-mail address:* whw@aphy.iphy.ac.cn (W.H. Wang).

Fig. 1. XRD patterns of as-cast ternary $Mg_{65}Cu_{25}RE_{10}$ (RE=La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er or Yb) alloy systems.

Fig. 2. DSC curves of the as-cast $Mg_{65}Cu_{25}RE_{10}$ alloy with a diameter of 1 mm.

the $Mg_{65}Cu_{25}La_{10}$ alloy has the poorest GFA, and obvious sharp crystalline diffraction peaks are visible in its XRD curve for the sample even with 1 mm diameter. With the increase of the atomic number of the RE element, the GFA increases gradually. For example, the as-cast $Mg_{65}Cu_{25}Ce_{10}$ alloy with 1 mm diameter is partially glassy state with weak diffraction peaks superimposed on the amorphous diffused peak. However, for the $Mg_{65}Cu_{25}Pr_{10}$ alloy, it consists of mainly glassy phase and no obvious crystalline diffraction peaks are seen. With the atomic number increasing further, the GFA of the corresponding alloys has been improved notably. The $Mg_{65}Cu_{25}Sm_{10}$, $Mg_{65}Cu_{25}Gd_{10}$, $Mg_{65}Cu_{25}Tb_{10}$ alloys can be cast into fully glassy state with a diameter of 5 mm. In particular, glassy $Mg_{65}Cu_{25}Gd_{10}$ alloy even can be produced up to 8 mm in diameter [10]. Nevertheless, when the atomic number is larger than that of Tb, the GFA of the alloys is decreased. For example, the XRD curve of the $Mg_{65}Cu_{25}Er_{10}$ alloy 2 mm in diameter shows crystalline diffraction peaks, and the $Mg_{65}Cu_{25}Yb_{10}$ rod with 1 mm diameter is almost crystalline state as shown in Fig. 1. The above results demonstrate that the substitution of different RE elements has the different effects on the GFA of the Mg–Cu based alloys, even though the RE elements have similar atomic fractions, chemical properties, valences and values of heat of mixing with Mg and Cu. The critical diameter size, D_c for glass formation in these alloys, which is a direct measure of the GFA is found initially increase with the increase of the atomic numbers reach a maximum for RE=Gd or Tb (D_c=5–6 mm), and then decrease with the further increase of the atomic number.
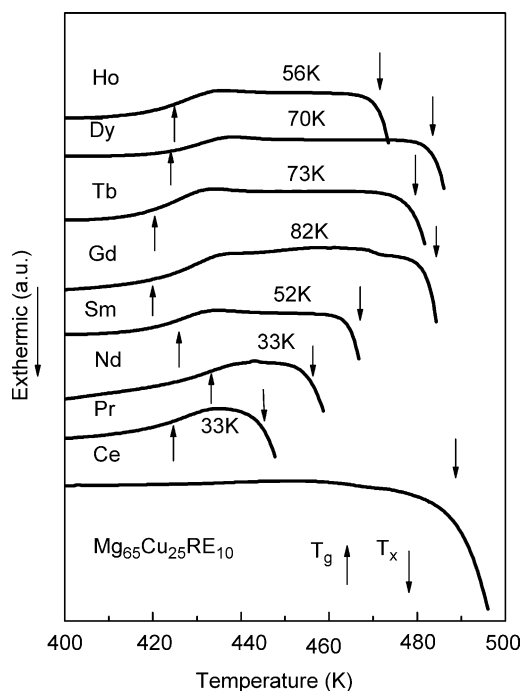
Fig. 2 shows DSC traces of some as-cast $Mg_{65}Cu_{25}RE_{10}$ alloys with a diameter of 1 mm. All the alloys show a distinct glass transition process starting at T_g and a crystallization event starting at T_x. The remarkable feature of these DSC traces is the large supercooled liquid region, $\Delta T (=T_x - T_g)$. The thermal parameters ΔT, T_g/T_m [11], and $T_x/(T_g+T_l)$ [12] of these BMGs are summarized in Table 1. As indicated by arrows in Fig. 2, one can clearly see that the ΔT of these alloys increases with the atomic number and reach a maximum value of 82 K for RE=Gd and 73 K for RE=Tb, and then decreases with the further increase of the atomic number. It is worth to mention that these BMGs also have similar final crystallization products which are identified to be Mg solid solutions (hcp structure), intermetallic REMg (CsCl structure) and intermediate phase Mg_2Cu (orthorhombic structure). Details about the crystallization studies of these alloys will be reported elsewhere.

Fig. 3a and b show the GFA (represented by both D_c, ΔT, T_{rg} and $\gamma = T_x/(T_g+T_l)$) for these alloys as a function of alloying RE elements. Fig. 3a and b clearly exhibit that ΔT and γ of the $Mg_{65}Cu_{25}RE_{10}$ alloys have similar trend with the atomic number of the RE alloying elements as D_c does, suggesting that γ have a strong correlation with D_c. These observations are consistent with previous results [2,12]. In the $Mg_{65}Cu_{25}RE_{10}$ alloys, however, T_{rg} does not correlate well with their GFA.

According to the empirical BMG formation criteria [1,2], the bulk glass-forming alloys should satisfy: (1) the multicomponent alloy systems consist of more than three

Table 1
Thermal parameters (heating rate: 20 K/min) of T_g, T_x, ΔT_x, T_m, the liquidus temperature (T_l), $T_{rg} = T_g/T_m$ and $\gamma = T_x/(T_g + T_l)$ for the glassy $Mg_{65}Cu_{25}RE_{10}$ alloys with a diameter of 1 mm, together with the attainable maximum size (D_c)

Glass formers ($Mg_{65}Cu_{25}RE_{10}$)	T_g (K)	T_x (K)	ΔT_x (K)	T_m (K)	T_l (K)	T_{rg}	γ	D_c (mm)
Tb	414	487	73	713	733	0.581	0.425	5
Sm	418	470	52	711	723	0.588	0.410	5
Gd	406	488	82	716	751	0.567	0.422	6
Dy	422	492	70	735	750	0.574	0.420	3
Pr	413	446[a]	33	724	784	0.570	0.373	1
Nd	423	456[a]	33	727	744	0.582	0.391	1
Ho	417	473	56	736	751	0.567	0.405	1
Ce	*	489		–	–	–	–	0.5
La	–	–	–	–	–	–	–	<0.5

*Cannot be measured due to the small size of the glassy sample available, but do not affect the trend of the data and the conclusion in the context.
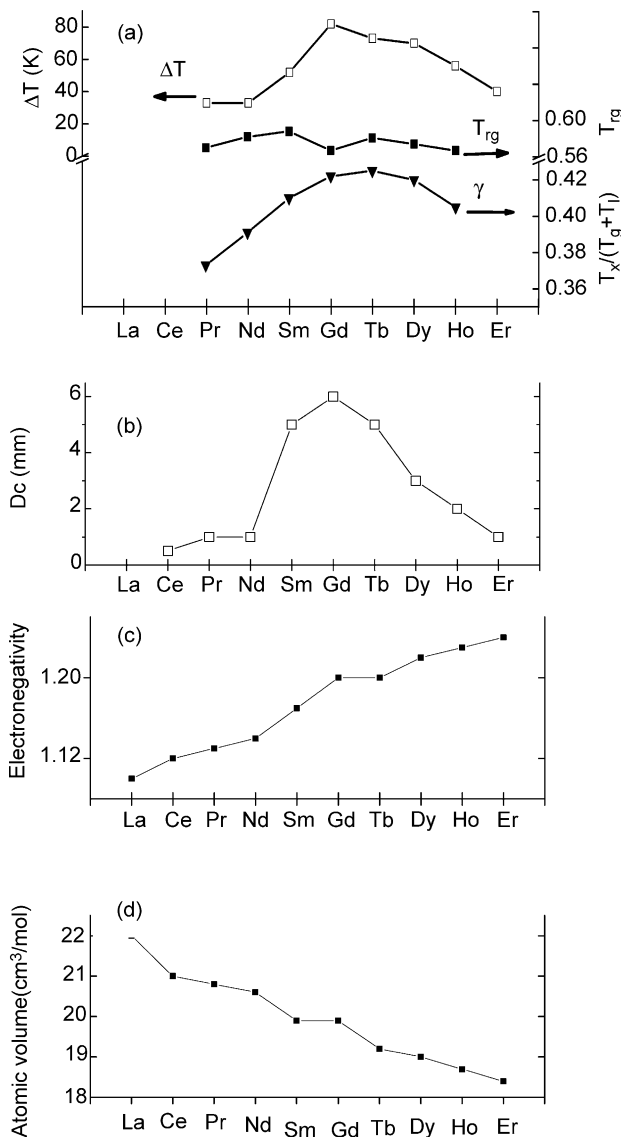

Fig. 3. The GFA parameters of the MgCuRE alloys: (a) super cooled liquid region, $T_x - T_g$ (upper curve, □), T_{rg} [T_g/T_m] (middle curve, ■), and $T_x/(T_g + T_l)$ (lower curve, ▼) as a function of Lns, (b) D_c of the as-cast alloys, (c) electronegativity of RE elements, and (d) atomic size of RE elements. The lines are used to guide the eye.

elements, (2) there is a significant difference, of $>12\%$, in the atomic size ratios of the major constituent elements, (3) negative heats of mixing occur among the major elements, and (4) alloy compositions are close to the deep eutectic point. For the lanthanide elements, they have the following characteristics: (1) all are near eutectic composition [13], and (2) have similar chemical properties and valences (they are often considered as one element). The enthalpies of mixing between the RE element and Mg at the equiatomic composition, which is an important factor influencing on GFA and stability of the supercooled liquid region, have been calculated with Miedema's semiempirical method [14]. The calculated values are very close to Mg–Gd system and in good agreement with available experimental enthalpy data [15]. The main differences among these lanthanide elements are the atomic size (atomic radii range from 0.178 to 0.225 nm) and electronegativity. However, the BMGs have markedly different GFA (i.e. different attainable maximum diameters). Therefore, $Mg_{65}Cu_{25}RE_{10}$ alloys can be used as a model system to explore dominant factors on the GFA in BMG-forming-alloys.

Fig. 3d presents the atomic size of the lanthanide elements. Comparing with Fig. 3a and b, it is clearly seen that GFA increases significantly with atomic size decreasing, shows a maximum for Gd and then decreases with further atomic size decreasing. The changing tendency of the GFA with the atomic size of the RE element indicates that the importance of the atomic size difference for the bulk glass formation. The significant contribution of the atomic size ratio of the constituent elements for the formation of amorphous phase has also been recognized for BMG formation in Cu–(Zr, Hf)–(Ti, Nb, Ta) and Ni–Nb–(Ta,Ti) system, and non-metallic glass formation in SiC system under high pressure [16]. As plotted in Fig. 3a and c, ΔT or the GFA of the $Mg_{65}Cu_{25}RE_{10}$ alloys indeed strongly depends upon electronegativity because the electronegativity of neighboring atoms and the number of neighboring atoms are also changed with the increasing RE atom size. Similar phenomenon was also observed in Al-based conventional metallic glasses where the ΔT increases almost linearly with the electronegativity of the RE [8].

This discrepancy could be explained by the Pauling's theory [17], i.e. electronegativity range in the RE elements of lanthanide series extends to the optimum value for the best MgCu-based glass-forming alloy. From above results, one can therefore rationalize the maximum GFA at gadolinium if the atomic size mismatch (Gd/Mg) and electronegativity difference (Mg–Gd) between Gd and Mg are nearly optimum. Therefore, increasing this mismatch or difference by lanthanons of lower atomic number and decreasing this mismatch or difference by lanthanons of higher atomic number would in both instances lower GFA. Combining these two factors, Sm, Gd and Tb bearing MgCu-based glasses have the highest GFA among other lanthanons.

The dominant effect of the atomic size differences on the GFA indicates a predominant role of kinetic factor in BMG formation. This is because the appropriate large atomic size difference may induce highly dense packed microstructure and stabilizes the supercooled liquid state of the alloy [1], resulting a dramatic increase of the viscosity of the melt state. The more viscous melt would lead to higher nucleation activation energies and slower growth rates for crystalline phase formation during the solidification, and thus resulting in higher GFA. The conjecture that kinetic factors such as atomic mobility and viscosity of the melt are the key factors in the formation of BMGs has also been confirmed by high pressure solidification of the BMG-forming-alloys [18]. High pressure can enhance the GFA of the BMG-forming-alloys by suppressing the growth rate and long-range atomic diffusion in the melt [16].

In conclusion, a series of novel $Mg_{65}Cu_{25}RE_{10}$ BMGs (RE=Pr, Nd, Sm, Dy, Tb, Ho) with different critical diameters and near eutectic composition are obtained. It is found that the GFA in the MgCuRE alloys strongly depends upon atomic size and electronegativity of the alloying RE metals. An optimum value of the atomic size mismatch and electronegativity difference among the main alloying elements in the MgCuRE alloys leads to stabilization of the supercooled liquid and high GFA.

References

[1] Johnson WL. MRS Bull 1999;24:42.
[2] Inoue A. Acta Mater 2000;48:279.
[3] Senkov ON, Miracle DB. MRS Bull 2001;36:2183.
[4] Liou SH, Chien CL. Phys Rev B 1987;35:2443.
[5] Poon SJ, Shiflet GJ, Guo FQ, Ponnambalam V. J Non-Cryst Solids 2003;317:1.
[6] Egami T. Mater Sci Eng A 1997;226:261.
[7] Chen W, Wang Y, Qiang J, Dong C. Acta Mater 2004;51:1899.
[8] Louzguine DV, Inoue A. Appl Phys Lett 2001;79:3410.
[9] Fang SS, Xiao XS, Xia L, Li WH, Dong YD. J Non-Cryst Solids 2003; 321:120.
[10] Men H, Kim DH. J Mater Res 2003;18:1502.
[11] Turnbull D. Contemp Phys 1969;10:473.
[12] Lu ZP, Liu CT. Phys Rev Lett 2003;91:115505.
[13] Xi XK, Zhao DQ, Pan MX, Wang WH. J Non-Cryst Solids 2004;344:189.
[14] James AM, Lord MP. In: Macmillan's chemical and physical data. London: Macmillan; 1972 p. 1020.
[15] Ouyang YF, Zhang BW, Liao SZ, Jin ZP. Rare Metal Mater Eng 1995; 24:32.
[16] Tang MJ, Yip S. Phys Rev Lett 1995;75:2738.
[17] Pauling L. In: The nature of the chemical bond. New York: Cornell University Press; 1960 p. 30.
[18] Wang WH, Okada T, Wen P, Wang XL, Pan MX, Zhao DQ, Utsumi W. Phys Rev B 2003;68:184105.