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Study on the formation of new Mg–Cu–Ti–Y quaternary bulk metallic glasses with high mechanical strength

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ABSTRACT

New Mg–Cu–Ti–Y quaternary bulk metallic glasses (BMGs) with diameter of 2 mm have been designed and successfully fabricated by conventional copper mold casting method. The X-ray diffractometer (XRD) and differential scanning calorimeter (DSC) examinations indicate that the as-cast Ti-containing $Mg_{60}Cu_{30-x}Ti_xY_{10}$ ($x=3$, 5, 8 at.%) alloys possess completely amorphous structures and large supercooled liquid region (59–64 K). The mechanical property testings demonstrate that this kind of new BMGs also have high compressive fracture strength (σ_f), big elastic strain (ε_e), high Vickers hardness (Hv) and low elastic modulus (E). Thereinto, the σ_f, ε_e, Hv and E values of the as-cast $Mg_{60}Cu_{27}Ti_3Y_{10}$ BMG sample reach up to 879 MPa, 3.04%, 347 and 34 GPa, respectively, which are much superior to the as-cast Ti-free $Mg_{60}Cu_{30}Y_{10}$ BMG. The as-cast alloys' fracture surface morphologies and dominant fracture behaviors have also been characterized and explained in detail.

1. Introduction

Bulk metallic glasses (BMGs) have many unique properties, like ultrahigh strength, super-elasticity, high resistance to corrosion, and good fatigue characteristics [1–3]. Due to the high glass forming ability (GFA) and excellent mechanical properties, especially the low density and high specific strength features, Mg-based BMGs are considered as new light weight structural materials with great application prospect that have captured public's growing attention and concern. Since Inoue et al. [4,5] first discovered the high GFA of Mg–Cu–Y ternary system, on the basis of $Mg_{65}Cu_{25}Y_{10}$ and $Mg_{60}Cu_{30}Y_{10}$ BMGs, many quaternary and quinary Mg-based BMGs have been produced and investigated by readjusting composition and partial substituting elements (such as Ag, Al, Li, Ni, Pd, Zn and RE = rare-earth elements etc.) [6–21]. Based on the above researches, some new Mg-based BMGs with improved mechanical properties are obtained, and their mechanical parameters including compressive fracture strength (σ_f), elastic strain (ε_e), Vickers hardness (Hv), elastic modulus (E) and samples size (D_c) are listed in Table 1. It is seen that the mechanical strength of Mg-based BMGs are much superior to that of normal Mg alloys. On the other hand, however, their high elastic modulus and low ductility become the most important issues that severely restrict their engineering application. Therefore, it is imperious to further improve such mechanical properties of Mg-based BMGs.

Minor addition as one of the simple and effective methods that has been widely used in the metallurgical fields, plays effective and important roles in formation, crystallization, thermal stability and property improvement of BMGs, which provides a powerful tool for the BMGs' development and design [26]. Recently, the transitional metal Ti has been selected as minor alloying element in BMG systems due to its effects on GFA and various properties. For instance, Inoue et al. find that the addition of Ti increased the GFA of Ni–Zr–Al BMGs, the obtained new Ni–Zr–Cu–Ti–Al BMGs finally exhibit high thermal stability and relatively large supercooled liquid region [27]. Chang et al. discover that the element Ti can improve the GFA of Y–Fe–B, making the critical diameter of bulk glassy rod from 2 mm to 3 mm [28]. Pauly et al. [29] and Lee et al. [30] report that Ti has a strong influence on the characteristics of the deformation behavior of Cu–Zr BMGs that can greatly enhance their plasticity as well as their fracture strength. All the above mentioned literatures strongly enlighten that the addition of alloying element Ti in the BMG systems will change the covalent interaction and microscaled structures that finally improve their GFA and mechanical properties. Based on the mentioned previous studies, in the present work one kind of new Mg-based BMGs containing minor alloying element Ti, namely $Mg_{60}Cu_{30-x}Ti_xY_{10}$ ($x=0$, 3, 5, 8, 10 at.%) have been realized. The phase structure, thermal stability, mechanical properties and fracture surface morphologies of the as-cast alloy samples are systematically investigated by X-ray diffractometry (XRD) and differential scanning calorimetry (DSC), mechanical testing machine and scanning electron microscopy (SEM), respectively.

2. Theory and calculation

It is widely accepted that the atomic size of the constituent elements, the mixing enthalpy among constituent elements and the numbers of

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Table 1
Mechanical properties (σ_f, ε_e, Hv, E and D_c) of normal Mg alloys and some typical Mg-based BMGs.

Alloys	σ_f (MPa)	ε_e (%)	E (GPa)	Hv	D_c (mm)	Reference
Normal Mg alloys	<300	–	35–50	<100	–	[22–25]
$Mg_{80}Cu_{10}Y_{10}$	820	0.2	–	220	1.5	[4]
$Mg_{65}Cu_{25}Y_{10}$	729	–	53	–	3	[6]
$Mg_{58}Cu_{25}Y_{10}Ag_7$	1330	–	75	–	2	[6]
$Mg_{65}Cu_{15}Y_{10}Ag_5Pd_5$	770	1.3	59	–	5	[9]
$Mg_{57}Cu_{31}Y_{6.6}Nd_{5.4}$	1188	2.4	54	–	1	[12]
$Mg_{58}Cu_{27}Zn_5Y_{10}$	870	1.4	55	–	3	[17]
$Mg_{58}Cu_{25}Zn_7Y_{10}$	1090	1.8	54	–	3	[17]
$Mg_{65}Cu_{20}Zn_5Y_{10}$	760–880	3.7	–	–	4	[16]
$Mg_{56}Li_9Cu_{25}Y_{10}$	615	–	46	213	2	[18]
$Mg_{65}Li_2Cu_{18}Ni_5Y_{10}$	729	2.28	36	253	2	[19]

component are the crucial factors for BMG formations [31]. For the sake of obtaining new Mg–Cu–Ti–Y BMGs with the ideal comprehensive properties theoretically, the Mg–Cu–Ti–Y alloys are designed and systemically investigated through theory and calculation according to the Modified Miedema Model [32–37]. First of all, the component elements' model parameters of Mg–Cu–Ti–Y alloys that formulated according to literatures [32–34] are listed in Table 2. Besides, the related parameters that used to calculate the component elements' standard forming enthalpies of Mg–Cu–Ti–Y alloy system are listed in Table 3. Thereinto, the standard forming enthalpies of binary alloys that calculated according to the Modified Miedema Model [35–37] are defined by the following details:

$$\Delta H_f^0 = f(c)\cdot S(c)\cdot V_B^{2/3}\cdot\left[-P(\Delta\Phi_*)^2 + Q\left(\Delta n_{WS}^{1/3}\right)^2\right]/\left(n_{WS}^{-1/3}\right)_{av} \quad (1)$$

$f(c)$ is a function of alloy composition for including the effect of the chemical short-range-order (CSRO) of an ordered intermetallic compound on the standard formation enthalpy, and is expressed by a simple analytical formula:

$$f(c) = c_A^S c_B^S\left[1+\gamma\left(c_A^S c_B^S\right)^2\right] \quad (2)$$

γ is the CSRO parameter for the intermetallic compound and taken as a constant, i.e., $\gamma=8$. P and Q are empirical constants. $Q/P=9.4$. When binary alloy formed by nontransition elements, $p=10.70$. When binary alloy formed by a transition element and a nontransition element, $p=12.35$. The prefactor $S(c)$ is defined to describe the effect of the atom size difference on the contact interface and the bonding energy, and is expressed as follows:

$$S(c) = 1-c_B^S\left|V_A^{2/3}-V_B^{2/3}\right|/\left(c_A^S V_A^{2/3}+c_B^S V_B^{2/3}\right) \quad (3)$$

$V_B^{2/3}$ and $V_A^{2/3}$ are the surface areas of solute and solvent atoms, respectively; C_B^S and C_A^S are the concentrations of the solute surface area and the solvent surface area, respectively, which can be calculated by the following formula:

$$c_A^S = c_A\cdot V_A^{2/3}/\left(c_A V_A^{2/3}+c_B V_B^{2/3}\right) \quad (4)$$

Table 2
The component elements' model parameters of Mg–Cu–Ti–Y alloys.

Metal	Electron density (n_{WS})	$n_{WS}^{1/3}$	Atomic radius (R)pm	Mole volume (V_m)	$Vm^{2/3}$	Electronegativity (Φ^*)
Mg	1.60	1.17	160	14.00	5.81	3.45
Cu	3.18	1.47	128	7.12	3.70	4.45
Ti	3.51	1.52	145	10.58	4.82	3.80
Y	1.77	1.21	178	19.90	7.34	3.20

Table 3
Related parameters used for calculating the forming enthalpy of binary alloys.

Metal	R^* (%)	$\Delta n_{WS}^{1/3}$	$\Delta Vm^{2/3}$	$\Delta\Phi^*$	P	Q	C_A/C_B	ΔH (kJ/mol)
Mg–Cu	25.00	0.30	2.11	1.00	12.35	116.09	1:1	−7.29
Mg–Ti	10.34	0.35	0.99	0.35	12.35	116.09	1:1	20.14
Mg–Y	11.25	0.04	1.53	0.25	12.35	116.09	1:1	−11.69
Cu–Ti	13.28	0.05	1.12	0.65	14.1	132.54	1:1	−11.56
Cu–Y	39.06	0.26	3.64	1.25	14.1	132.54	1:1	−21.07
Y–Ti	22.76	0.31	2.52	0.6	14.1	132.54	1:1	17.51

$$c_B^S = c_B\cdot V_B^{2/3}/\left(c_A V_A^{2/3}+c_B V_B^{2/3}\right) \quad (5)$$

$\Delta\Phi^*$ is the electronegativity difference between the two constituent metals. $\Delta n_{WS}^{1/3}$ is the discontinuity of the electron density at the boundaries between the dissimilar atoms.

For all the calculating Eqs. (1)–(5), the parameters$\Delta\Phi^*$, $\Delta Vm^{2/3}$, $\Delta n_{WS}^{1/3}$, P and Q (derived from electronegativity Φ^*), atomic size ratios R^*, including the calculated standard forming enthalpies ΔH are tabulated in Table 3. According to Inoue's statement, the alloys with the stabilized supercooled liquid state have three features in their alloy components, i.e., multicomponent systems, significant atomic size ratios above 12%, and negative heats of mixing [1]. In this view, the alloys with the three empirical rules can have a high GFA that are in favor of forming BMGs. Comparing with the Ti-free Mg–Cu–Y ternary alloy system, the Mg–Cu–Ti–Y quaternary alloy system possesses increased component elements, large atomic size ratios R^* and significant negative forming enthalpies ΔH (as seen Table 3), which is in accord with the three empirical rules of Inoue and tend to form BMGs. Moreover, it is also notable that the element Ti has positive forming enthalpies with Mg and Y (Mg–Ti: 20.14 kJ/mol; Y–Ti: 17.51 kJ/mol), which may cause the change in the atomic bonding structure influencing local chemical inhomogeneity or local free volume inhomogeneity, thereby affecting the formation and propagation of shear bands that can lead to an improvement mechanical properties of BMGs [38,39].

Based on the above theoretical calculation and analysis, it is reasonable to predict that the introduction of the element Ti to Mg–Cu–Y system can obtain new Mg-based BMGs with better comprehensive performances. Moreover, our following calculation and experimental results indicate that the new Mg–Cu–Ti–Y BMGs are indeed of good GFA and excellent mechanical properties. Thereinto, the as-cast $Mg_{60}Cu_{27}Ti_3Y_{10}$ BMG sample has a supercooled liquid region (SLR) of 64 K, and its compressive fracture strength (σ_f), elastic strain (ε_e), Vickers hardness (Hv) and elastic modulus (E) are determined to be 879 MPa, 3.04%, 347 and 34 GPa.

3. Experimental procedures

Nominal compositions (at.%) of Mg-based alloys investigated in the present study were $Mg_{60}Cu_{30-x}Ti_xY_{10}$ ($x=0$, 3, 5, 8, 10 at.%). The Cu–Ti–Y intermediate alloys were firstly prepared by arc melting high-purity Cu (99.98 wt.%), Ti (99.9 wt.%) and Y (99.96 wt.%) in a copper crucible under Ti-gettered argon atmosphere. The alloy ingots were melted 3–5 times to ensure compositional homogeneity. Then, the Cu–Ti–Y intermediate alloys were melted together with high-purity Mg (99.98 wt.%) by induction melting under argon atmosphere to obtain the required alloys. At last, the rod samples with a diameter of 2 mm were obtained by remelting the required alloys in a quartz tube and subsequently injecting into a copper mold in a purified inert atmosphere.

The amorphous nature and crystalline phases of the as-cast samples were identified by X-ray diffractometry (XRD, Rigaku D/max IIIA, Cu Kα) with a scan size of 0.02°. Thermal stability associated with glass