Science Press

Trans. Nonferrous Met. Soc. China 17(2007) s1094−s1098

Transactions of Nonferrous Metals Society of China

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Effect of addition of Zn and Al elements on glass-forming ability and thermal stability of Mg-Cu-Y bulk metallic glasses

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Received 15 July 2007; accepted 10 September 2007

Abstract: After substituting partial Cu and Mg with Zn or Al elements for $Mg_{65}Cu_{25}Y_{10}$ alloy, respectively, the metallic glass plate samples with thickness of 2−3 mm were prepared by water-quenching, their respective glass-forming ability and thermal stability were studied by using differential thermal analysis (DTA) and X-ray diffraction (XRD). Using Kissinger equation, the activation energies of crystallization of these metallic glasses heated with a constant rate were calculated. The results show that Al element is greatly harmful to the glass-forming ability of Mg-Cu-Y alloys and cannot acquire bulk amorphous alloys; nevertheless, the effect of Zn element addition is indeterminate for various components. The magnitudes of thermal stability are also revealed.

Key words: Mg-based alloy; metallic glasses; glass-forming ability; thermal stability

1 Introduction

Mg-based alloys were paid more and more attention for their low density and high specific strength, specific stiffness in recent years. Mg-based metallic glasses are considered structure materials due to their high specific strength and other attractive mechanical and corrosion resistance properties. Since the glass-forming ability of Mg-based bulk metallic glass was developed greatly in the end of last century, the alloy systems and preparation methods were improved[1−5]. The proper addition of other elements affects the glass-forming ability and thermal stability of Mg-Cu-Y alloys[3−4]. As it is known to all, the nanocrystalline phase can be obtained from amorphous material by an appropriate heat treatment that leads to crystallization[6−7], so the control of this process is very important.

In this study, $Mg_{65}Cu_{20}Y_{10}Zn_5$, $Mg_{60}Cu_{25}Y_{10}Zn_5$ and $Mg_{65}Cu_{20}Y_{10}Al_5$ alloys were prepared for the substitution of partial Cu and Mg elements in $Mg_{65}Cu_{25}Y_{10}$ with Zn or Al. To be compared with $Mg_{65}Cu_{25}Y_{10}$ alloy, their glass-forming ability, thermal stability and effects of Zn and Al elements were investigated.

2 Experimental

Consulting the nominal compositions of Mg-Cu-Y metallic glasses, four types of pure metal of Mg, Cu, Y and Zn or Al were mixed and melted in the medium frequency-induced vacuum furnace to obtain the parent alloys with design composition. The parent alloys were smashed and milled into powders, and then the powders were put into a copper mould with a cavity of *d* 20 mm×5 mm and sealed. The copper mould was quickly heated to 700 ℃ in the above vacuum furnace, holding for 1 min, then quenched into the mixture of ice and water, and a plate sample with the thickness of 2−3mm was obtained.

The structure of the plate sample was determined by Miniflex XRD instrument, and its behavior of glass transition, crystallization and melting were detected by Diamond TG/DTA 6000 thermal analyzer, using α-Al_2O_3 as reference and protected by flow Ar gas with high purity. The chemical composition of parent alloys was measured by Magix(PW-2424) type of X fluorescence analyzer.

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3 Results and discussion

3.1 Glass-forming ability of the alloys

Table 1 shows the chemical compositions of the parent alloys.

Table 1 Chemical compositions of Mg-Cu-Y-Zn and Mg-Cu-Y-Al parent alloys (mass fraction, %)

Alloy	Mg	Cu	Y	Zn	Al	Si
A	38.754	31.577	20.655	8.47	0.303	0.129
B	32.502	37.973	20.196	7.756	0.272	0.069
C	40.042	34.179	21.722	−	3.747	0.153

Alloy	S	Ca	Mn	Fe	K	Ni
A	0.03	0.005	0.023	0.026	0.017	0.01
B	0.027	0.029	0.029	0.115	0.022	0.012
C	0.035	0.056	0.019	0.037	−	0.01

Changing mass fraction into mole fraction in Table 1, alloy A is $Mg_{65}Cu_{20}Y_{10}Zn_5$, alloy B is $Mg_{59}Cu_{26}Y_{10}Zn_5$ and alloy C is $Mg_{64.1}Cu_{20.9}Y_{9.5}Al_{5.4}$; apparently, the chemical compositions of parent alloys are consistent with the nominal compositions.

Fig.1 shows the XRD patterns and DTA curves of water-quenching samples of parent alloys, respectively. $Mg_{65}Cu_{20}Y_{10}Zn_5$ and $Mg_{59}Cu_{26}Y_{10}Zn_5$ quenched samples only exhibit a broad peak, indicating the formation of single amorphous phase. However, $Mg_{64.1}Cu_{20.9}Y_{9.5}Al_{5.4}$ quenched sample shows several sharp crystalline peaks, indicating the coexistence of Mg_2Cu, Al_2CuMg, YAl_3, and little unknown phase, as shown in Fig.1(a). The DTA curves of the above three type samples all exhibit clear exothermal peaks, as shown in Fig.1(b). From Fig.1, it can be deduced that the water-quenching samples of $Mg_{65}Cu_{20}Y_{10}Zn_5$ and $Mg_{59}Cu_{26}Y_{10}Zn_5$ form amorphous phase; as the heating temperature increases, they will be crystallized. The water-quenching sample of $Mg_{64.1}Cu_{20.9}Y_{9.5}Al_{5.4}$ almost cannot form amorphous phase, but it forms an unstable phase; as the heating temperature increases, the unstable phase will transform into a stable one. The above evidences demonstrate that the substitution of partial Cu for Al is harmful to $Mg_{65}Cu_{25}Y_{10}$ alloy, which decreases the glass-forming ability of $Mg_{65}Cu_{25}Y_{10}$ alloy greatly.

Table 2 lists the data of the glass transition temperature (T_g), onset temperature of crystallization (T_{x1}), supercooled liquid region (ΔT_x), reduced glass transition temperature (T_{rg}) and melting temperature(T_m) of $Mg_{65}Cu_{25}Y_{10}$, $Mg_{60}Cu_{30}Y_{10}$, $Mg_{65}Cu_{20}Y_{10}$ Zn_5 and $Mg_{59}Cu_{26}Y_{10}Zn_5$ metallic glasses with a heating rate of 20 ℃/min.

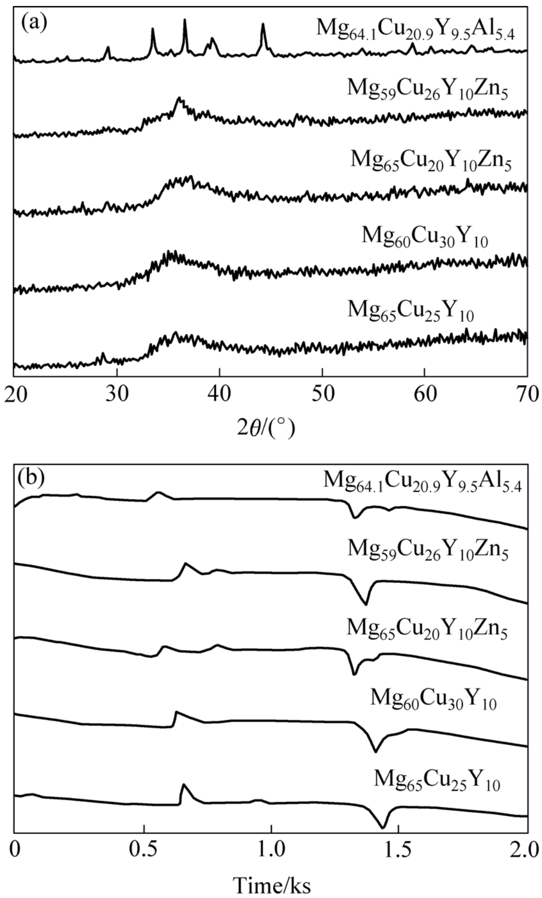

Fig.1 XRD patterns (a) and DTA curves (b) of water quenched alloys

Table 2 Data of T_g, T_{x1}, ΔT_x, T_{rg} and T_m obtained with DTA for metallic glasses with heating rate of 20 ℃/min

Metallic glass	T_g/K	T_{x1}/K	ΔT_x/K	T_m/K	T_{rg}
$Mg_{65}Cu_{25}Y_{10}$	415.3	471.2	55.9	743	0.559
$Mg_{60}Cu_{30}Y_{10}$	422.7	471	48.3	750.6	0.563
$Mg_{65}Cu_{20}Y_{10}$ Zn_5	414.6	467.8	53.2	738	0.562
$Mg_{59}Cu_{26}Y_{10}Zn_5$	410.9	446.9	36	728	0.564

$Mg_{65}Cu_{20}Y_{10}$ Zn_5 metallic glass possesses lower T_g by little, T_{x1} by about 3.4 K and T_m by about 5 K than $Mg_{65}Cu_{25}Y_{10}$, and its DTA trace has a trend of moving forward, compared with $Mg_{65}Cu_{25}Y_{10}$. $Mg_{60}Cu_{25}Y_{10}$ Zn_5 metallic glass has lower T_g by 11.8 K, T_{x1} by 24.1 K and T_m by 22.6 K than $Mg_{60}Cu_{30}Y_{10}$. Compared with the thermal parameters of $Mg_{65}Cu_{20}Y_{10}Zn_5$, the thermal parameters of $Mg_{59}Cu_{26}Y_{10}Zn_5$ have larger changes and its DTA trace moves forward more prominently. From the view of glass-forming, the supercooled liquid region ΔT_x of $Mg_{65}Cu_{25}Y_{10}$ decreases about 2.7 K after replacing Cu with Zn, whereas the reduced glass transition temperature T_{rg} increases slightly, from 0.559 to 0.562; ΔT_x of $Mg_{60}Cu_{30}Y_{10}$ decreases about 12.3 K after replacing Cu with Zn, and T_{rg} keeps at 0.563, these similar phenomena also appear in Zr-Ti-Cu-Ni-Be and Cu-Zr-Ti alloys[8−11]. From the preparation process of the sample, it can be seen that the decrease of ΔT_x does not exhibit the descendant of the glass forming ability. It demonstrates that the glass forming ability is not only determined by ΔT_x, T_{rg} is also an important reference index. Comparing $Mg_{65}Cu_{20}Y_{10}Zn_5$ with $Mg_{60}Cu_{25}Y_{10}Zn_5$, the former has a larger ΔT_x about 17.2 K than the latter, both almost have the same value of T_{rg}, which shows that the former has a strong glass forming ability than the latter, as the same as the situation of metallic glasses without Zn.

3.2 Thermal stability

In order to study the crystallization processes of $Mg_{65}Cu_{20}Y_{10}Zn_5$ and $Mg_{59}Cu_{26}Y_{10}Zn_5$ metallic glasses, the DTA traces were measured at various heating temperature rates of 10, 20, 30, 40 and 50 K/min, respectively. Both of the DTA traces with a constant heating rate of 20 K/min of $Mg_{65}Cu_{20}Y_{10}Zn_5$ and $Mg_{59}Cu_{26}Y_{10}Zn_5$ metallic glasses show two exothermal peaks, i.e. the crystallization process divides two stages. The first peak of $Mg_{65}Cu_{20}Y_{10}Zn_5$ is big, and the second is small; whereas the DTA trace of $Mg_{59}Cu_{26}Y_{10}Zn_5$ shows two big exothermal peaks, as shown in Fig.1(b). Fig.1(b) only shows the DTA curves with a constant heating rate of 20 K/min, similar DTA curves are also obtained for other heating rates. This illustrates that the crystallization of amorphous $Mg_{65}Cu_{20}Y_{10}Zn_5$ mainly focuses on the first stage; the crystallization amount of the second one is less relatively. Contrarily, the crystallization amounts of the two stages are big for $Mg_{59}Cu_{26}Y_{10}Zn_5$. As heating rate increases, both T_{x1} and T_p of all metallic glasses increase, and the difference ΔT_{px} ($\Delta T_{px}=T_p-T_{x1}$) between T_p and T_{x1} also increases, as listed in Tables 3−6.

Table 3 Initial and peak temperatures of crystallization for $Mg_{65}Cu_{25}Y_{10}$ metallic glass with various heating rates

Heating rate/(K·min^{-1})	T_{x1}/K	T_p/K	ΔT_{px}/K
10	463	473	10
20	471	481	11
30	472	488	16
40	487	505	18
50	493	515	22

Table 4 Initial and peak temperatures of crystallization for $Mg_{60}Cu_{30}Y_{10}$ metallic glass with various heating rates

Heating rate/(K·min^{-1})	T_{x1}/K	T_p/K	ΔT_{px}/K
10	467.1	471.2	4.1
20	471	478.3	7.7
30	472.8	483.6	10.8
40	479.3	490.6	11.3
50	487.5	502	14.5

Table 5 Initial and peak temperatures of crystallization for $Mg_{65}Cu_{20}Y_{10}Zn_5$ metallic glass with various heating rates

Heating rate/(K·min^{-1})	T_{x1}/K	T_p/K	ΔT_{px}/K
10	460.3	468.8	8.5
20	467.8	478.5	10.7
30	478.1	492.2	14.1
40	483.8	499.2	15.4
50	498.3	504.3	17

Table 6 Initial and peak temperatures of crystallization for $Mg_{59}Cu_{26}Y_{10}Zn_5$ metallic glass with various heating rates

Heating rate/(K·min^{-1})	T_{x1}/K	T_p/K	ΔT_{px}/K
10	430.3	438.4	8.1
20	446.9	457.6	10.7
30	450.2	463.3	13.1
40	455.5	469.6	14.1
50	460.7	477.6	16.9

Using Kissinger equation, $\ln(r/T^2)=-E/RT+\text{constant}$, and the data of Tables 3−6, the lines can be obtained from the diagrams of $\ln(T^2/r)$ vs $1/T$, as shown in Fig.2. The slope of line is E/R, and the activity energy of crystallization, E, under different conditions can be calculated, whose values are as follows.

Put T_{x1} into Kissinger equation, the activity energies of crystallization of $Mg_{65}Cu_{25}Y_{10}$, $Mg_{60}Cu_{30}Y_{10}$, $Mg_{65}Cu_{20}Y_{10}Zn_5$ and $Mg_{59}Cu_{26}Y_{10}Zn_5$ metallic glasses are 78.66, 127.97, 96.47 and 81.78 kJ/mol, respectively. Put T_p into Kissinger equation, E values of them are 56.92, 92.32, 78.92 and 66.27 kJ/mol, respectively.

From the above results, it can be seen that E values of amorphous $Mg_{65}Cu_{20}Y_{10}Zn_5$ and $Mg_{59}Cu_{26}Y_{10}Zn_5$ are similar to those of $Mg_{65}Cu_{25}Y_{10}$ and $Mg_{60}Cu_{30}Y_{10}$, as putting T_{x1} and T_p into Kissinger equation, E values of the former are larger than those of the latter. The reason is that while $T_p>T_{x1}$, atoms diffuse faster for possessing

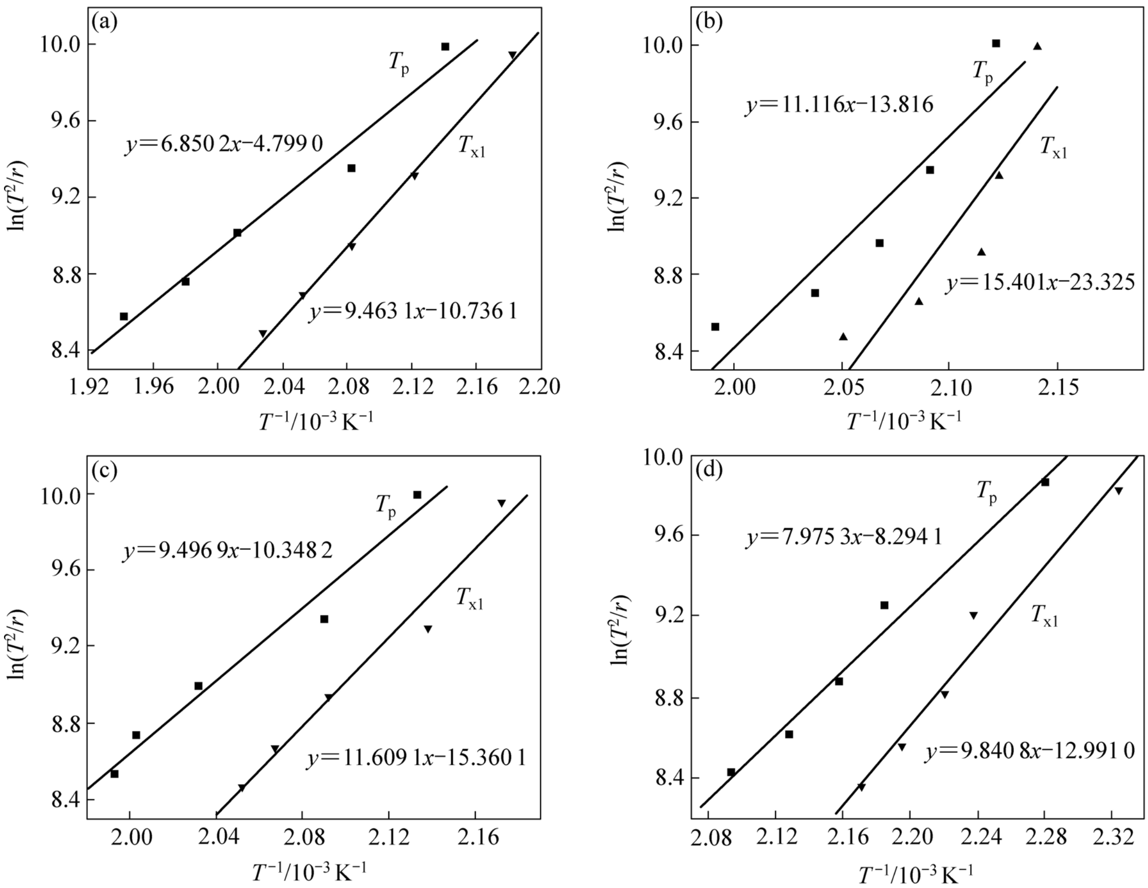

Fig.2 Kissinger plots of DTA of water-quenching metallic glasses: (a) $Mg_{65}Cu_{25}Y_{10}$; (b) $Mg_{60}Cu_{30}Y_{10}$; (c) $Mg_{65}Cu_{20}Y_{10}Zn_5$; (d) $Mg_{59}Cu_{26}Y_{10}Zn_5$

higher energy and bigger momentum at high temperature; there exists partial crystallization in the front of crystallization process, the potential energy that atoms need to get across is lower. So the E values calculated from T_{x1} is higher. Putting either T_{x1} or T_p into Kissinger equation, the E value of amorphous $Mg_{65}Cu_{20}Y_{10}Zn_5$ is larger than that of $Mg_{65}Cu_{25}Y_{10}$, demonstrating that the thermal stability of $Mg_{65}Cu_{25}Y_{10}$ substituting Cu with Zn gets stronger from the results of crystallization with a constant heating rate, according with that of isothermal annealing. E value of amorphous $Mg_{59}Cu_{26}Y_{10}Zn_5$ is lower than that of amorphous $Mg_{60}Cu_{30}Y_{10}$, demonstrating that the thermal stability of $Mg_{60}Cu_{30}Y_{10}$ substituting Cu with Zn gets weaker. E value of amorphous $Mg_{65}Cu_{20}Y_{10}Zn_5$ is bigger than that of amorphous $Mg_{59}Cu_{26}Y_{10}Zn_5$, demonstrating that the former possesses the thermal stability higher than the latter does.

4 Conclusions

1) $Mg_{65}Cu_{25}Y_{10}$ alloy substituting partial Cu with Al can't obtain amorphous structure by water-quenching; the addition of Al element is very harmful to the glass-forming ability of $Mg_{65}Cu_{25}Y_{10}$ alloy.

2) After substituting Cu with Zn to form $Mg_{65}Cu_{20}Y_{10}Zn_5$, ΔT_x of $Mg_{65}Cu_{25}Y_{10}$ metallic glass lowers slightly, whereas T_{rg} lifts a little, glass-forming ability doesn't weaken distinctly, and thermal stability improves remarkably, the thermal stability temperature rises from 423 K to 473 K.

3) The glass-forming ability of $Mg_{60}Cu_{30}Y_{10}$ doesn't decrease obviously, but whose thermal stability decreases from 533 K to 423 K while substituting Cu with Zn to form $Mg_{59}Cu_{26}Y_{10}Zn_5$. The thermal stability of $Mg_{65}Cu_{20}Y_{10}Zn_5$ is 50 K higher than that of $Mg_{59}Cu_{26}Y_{10}Zn_5$ during the process of isothermal crystallization.

4) With the comparison of glass-forming abilities of $Mg_{65}Cu_{20}Y_{10}Zn_5$ and $Mg_{59}Cu_{26}Y_{10}Zn_5$, the former has larger ΔT_x and T_{rg} than the latter does, which shows that $Mg_{65}Cu_{20}Y_{10}Zn_5$ alloy has stronger glass-forming ability than $Mg_{59}Cu_{26}Y_{10}Zn_5$, as the same as those without Zn.

Acknowledgements

The authors gratefully acknowledge the financial supports from the Science and Technology Foundation of Education Department and Industrial Plan of Science and

Technology Bureau of Jiangxi Province, P.R.China under the contract of No.18, 2004 and No.188, 2006, respectively.

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(Edited by HE Xue-feng)