Journal of Alloys and Compounds 504S (2010) S38–S40

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Enhancement of the glass forming ability of La–Al–Cu glassy alloys by partial substitution of Al by Mg

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ARTICLE INFO

Article history:
Received 5 July 2009
Received in revised form 3 March 2010
Accepted 9 March 2010
Available online 15 March 2010

Keywords:
Bulk metallic glasses
Glass forming ability
Atomic size ratios

ABSTRACT

Partial substitution of Al by Mg was studied to reveal the influence of the neighboring element for glass forming ability (GFA) of $La_{62}Al_{14}Cu_{24}$ alloy. A series of quaternary $La_{62}Al_{14-x}Mg_xCu_{24}$ (x = 2.8, 3.2, 3.5, 4.2, 5.0) alloys were cast by copper mold casting. As a result, the La–Al–Mg–Cu alloys with full glassy rods of 10 mm in diameter were achieved, suggesting that partial substitution of Al by Mg dramatically enhances the GFA. The enhancement of GFA can be mainly attributed to the large atomic size ratios among these constituent elements.

1. Introduction

The bulk metallic glasses (BMGs) can be widely employed as magnetic applications, chemical applications and structural applications, owing to their extraordinary structural features and unique properties [1,2]. Especially, the rare earth (RE) based BMGs display many fascinating properties, such as heavy fermion behavior, thermoplastic properties near room temperature, excellent magnetocaloric effect, hard magnetism, and polyamorphism [3]. The development of BMGs, therefore, has attracted an increasing attention. However, one of the biggest stumbling blocks in practical application is the lack of glass forming ability. In this study, we tried to improve the GFA by elemental substitution.

Over several decades, since the first metallic glass was reported by Duwez and co-workers [4] in 1960, the work of investigation of GFA is never interregnum. It has been well known that the GFA are strongly composition-dependent [5], especially, the concentration of substituting elements can induce the remarkable influence on GFA and mechanical properties [6–8]. For the Ln–Al–TM (Ln = lanthanide metal; TM = Co, Ni, Cu) alloy system, a ternary La–Al–Ni BMG with a diameter of 2.5 mm were reported in 1990 [9], many new pseudo-ternary alloys Ln–Al–TM with high GFA were produced since, which can be generally classified into two groups: one is the substitution of Ln by another rare earth element. For example, $(La_{0.7}Ce_{0.3})_{65}Al_{10}Co_{25}$ alloy could be fabricated into a full glassy rod with a diameter of 25 mm [10]. The other is the substitution of TM by another TM element. For instance, $La_{65}Al_{13}Ni_{10}Cu_{12}$ [11], $La_{62.0}Al_{15.7}(Cu,Ni)_{22.3}$ [12], $La_{62}(Cu_{0.5}Ni_{0.5})_{24}Al_{14}$ [13] and $La_{62.5}Al_{12.5}Cu_{10}Ni_5Co_5Ag_5$ [14] alloys could be cast into a full glassy rod with a diameter of 10, 11, 12, and 12 mm, respectively. Recently, Jiang et al. [15] have prepared a $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ BMG with diameter up to 30 mm by the water quenching method, and Zhang [16] reported the $(La_{0.5}Ce_{0.5})_{65}Al_{10}(Co_{0.6}Cu_{0.4})_{25}$ BMG of 32 mm in diameter in 2009. These alloys have been testified that partial substitution can increase the GFA in the Ln–Al–Cu alloy system. However, the effect of substitution of the third element Al on the GFA in the Ln–Al–TM (TM = Co, Ni, Cu) alloys system was rarely reported in literature. Wang and co-workers revealed that Mg has a negative effect on the GFA of the Ce-based BMGs [5].

In the present work, the effect of partial substitution of Al by Mg on GFA in La–Al–Cu ternary BMGs was emphasized. Previous work reported that the critical diameter of ternary BMG $La_{62}Al_{14}Cu_{24}$ BMG was less than 5 mm [11,17]. In this work, the GFA can be dramatically improved by substitution of Al by Mg. As a result, the quaternary La–Cu-Al–Mg alloys can be easily cast into full glassy cylindrical rods with diameters of 10 mm.

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doi:10.1016/j.jallcom.2010.03.102

2. Experimental procedure

A series of ingots with a nominal composition of $La_{62}Cu_{24}Al_{14-x}Mg_x$ (x = 2.8, 3.2, 3.5, 4.2 and 5.0) were prepared by arc-melting of pure La (99.5 at.%), Al (99.9 at.%), Cu (99.999 at.%) and Mg (99.99 at.%) under an argon atmosphere. Firstly, La–Cu–Al master alloys were re-melted at least four times to ensure compositional homogeneity; secondly, the master alloys were re-melted with Mg; and then, the melting alloys were sucked into a copper mold to be cast as cylindrical rods with a diameter of 10 mm under argon atmosphere.

Test sample were transversally cut from the 10 mm diameter cylindrical rod samples with a thickness of 1.5 mm at the position 6 mm from the bottom. The microstructures of these samples were characterized by X-ray diffraction (XRD) using Cu Kα radiation. The thermal stability of the glassy samples was evaluated using a differential scanning calorimeter (DSC) and differential thermal analyzer (DTA) under the protection of flowing argon at a heating rate of 0.33 K/s.

3. Results and discussion

XRD traces, shown in Fig. 1, were used to verified the formation of a glassy phase in the rapidly solidified rods for $La_{62}Cu_{24}Al_{14-x}Mg_x$ (x = 2.8, 3.2, 3.5, 4.2 and 5.0) alloys of 10 mm in diameter. As illustrated in Fig. 1, there are crystalline peaks superimposed on a wide diffused amorphous peak for the $La_{62}Cu_{24}Al_{11.2}Mg_{2.8}$ alloy, indicating that this sample is a mixture of amorphous and crystalline phases. In contrast, for the samples with x = 3.2, 3.5 and 4.2, the XRD traces consist only of broad diffraction peaks in the 2θ range from 25 to 38°, suggesting the formation of a single glassy phase in the rapidly solidified rods with the diameter of 10 mm. For the $La_{62}Cu_{24}Al_9Mg_{5.0}$ alloy, some small crystalline peaks appear on a diffused amorphous peak, demonstrating that the rod sample is mainly amorphous with a small amount of crystalline phases. This is identical to the case of $La_{62}Cu_{24}Al_9Mg_{2.4}$ alloy.

The XRD results indicate that the GFA of La–Cu–Al alloys system is quite sensitive to the Mg addition. Dramatic increase of d_c of full glassy cylindrical rods from less than 5 mm to at least 10 mm can be easily obtained with Mg partial substitution of less than 5 at.% into the $La_{62}Cu_{24}Al_{14}$ alloy. This result is not consistent with that reported by Zhang et al. [5]. They reported that the Mg free alloys $Ce_{70}Al_{10}Cu_{20}$ and $Ce_{70}Al_{15}Cu_{15}$ could be cast into a full glassy rod with a diameter of 2 mm, yet substitution of either Al or Cu by 5% Mg resulted in a reduction of d_c, e.g. in the $Ce_{70}Al_{10}Cu_{15}Mg_5$ alloy, d_c is less than 1 mm. This divergancy may be caused by different composition systems. In fact, the influence of Mg on GFA in Rare-earth-based BMGs should be carefully studied in the near future.

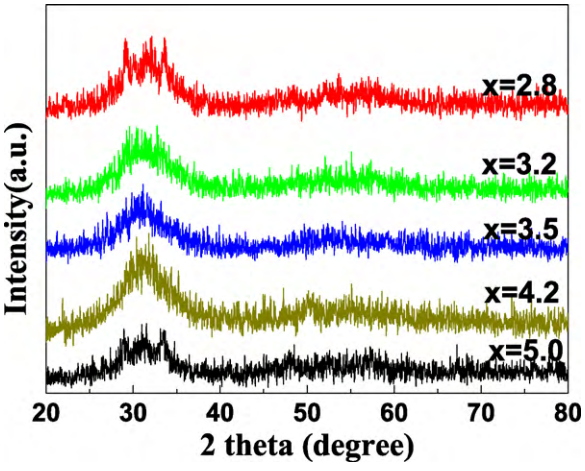

Fig. 1. XRD traces of the as-cast $La_{62}Cu_{24}Al_{14-x}Mg_x$ (x = 2.8, 3.2, 3.5, 4.2, 4.5 and 5.0) rods of 10 mm in diameter.

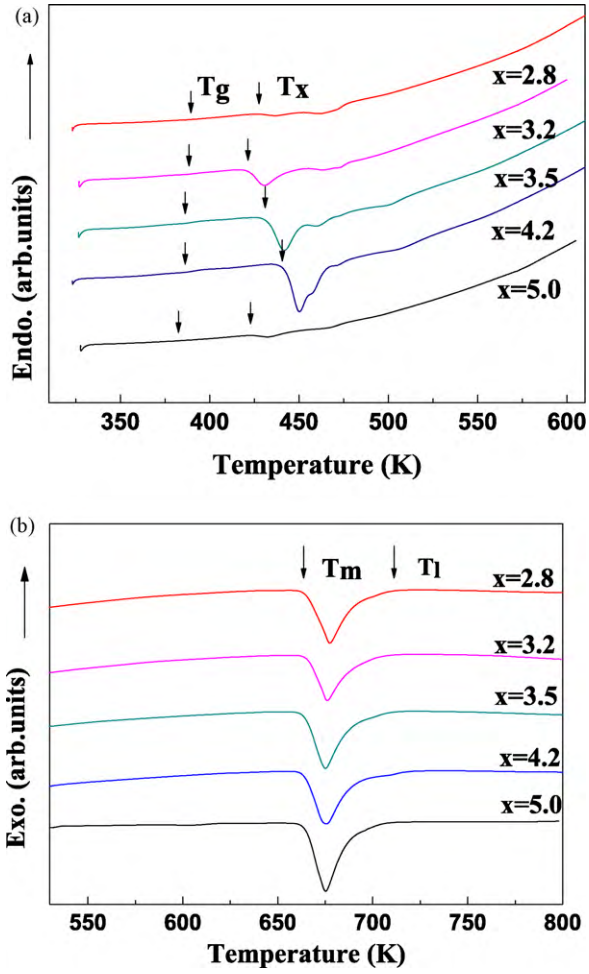

Fig. 2. (a) DSC and (b) DTA curves of as-cast $La_{62}Cu_{24}Al_{1-x}Mg_x$ (x = 0, 2.8, 3.2, 3.5, 4.2 and 5.0) alloys with 10 mm in diameter at a heating rate of 0.33 K s^{-1}.

DSC and DTA examination of the $La_{62}Cu_{24}Al_{14-x}Mg_x$ (x = 2.8, 3.2, 3.5, 4.2 and 5.0) BMGs were performed on samples with the corresponding diameters at a constant heating rate of 0.33 K/s. Figs. 2a and b shows the DSC and DTA curves, respectively. The structure and thermal parameters of these rapidly solidified rods, including the diameter of rapidly solidified rods (d_c), the glass transition temperature (T_g), the onset crystallization temperature (T_x), the melting temperature (T_m), the liquidus temperature (T_l), the supercooled liquid region, $\Delta T_x = T_x - T_g$, the reduced glass transition temperature $T_{rg} = T_g/T_l$ and the γ value ($\gamma = T_x/(T_g + T_l)$), are summarized in Table 1. Some results from other BMGs are also included for comparison.

Regarding the thermal parameters of Mg free alloys, all the values of thermal parameters (including T_g, T_x, T_m and T_l) decrease, which may be resulted from Mg addition. However, the alloy of $La_{62}Cu_{24}Al_{9.6}Mg_{4.2}$ shows the largest ΔT_x value of 56 K among these BMGs. The reduced glass transition temperature T_{rg} for the 10 mm full glassy rods (x = 3.2, 3.5 and 4.2) are 0.545, 0.542 and 0.536 respectively, which are lower than the other alloy (x = 2.8, T_{rg} = 0.548) and Mg free alloy $La_{62}Cu_{24}Al_{14}$ (T_{rg} = 0.546). The data above suggest that the experimental results do not agree well with the classical criteria that the values of T_{rg} are usually found to be near or larger than 0.6 [18]. This indicates that the parameter of T_{rg} cannot be extensively applied to predict the GFA in RE-based BMGs. This phenomenon was also reported by Lou and Wang [3].

It is noted that the atomic size ratio between the solute and solvent atoms dramatically influences the ability of forming bulk

Table 1
Composition dependence of d_c, T_g, T_x, T_m, T_l, ΔT_x, T_{rg} and γ for the La–Al–Cu–Mg alloys.

Compositions	d_c (mm)	T_g (K)	T_x (K)	T_m (K)	T_l (K)	ΔT (K)	T_{rg}	γ	Reference
$Ce_{70}Al_{10}Cu_{20}$	2	341	408	647	722	67	0.471	0.386	[5]
$Ce_{70}Al_{15}Cu_{15}$	2	364	406	660	686	42	0.470	0.356	[5]
$Ce_{70}Al_{10}Cu_{15}Mg_5$	<1			643	744				[5]
$La_{62}Al_{14}Cu_{24}$	<5	401	449	673	734	48	0.546	0.396	[17]
$La_{62}Al_{14-x}Mg_xCu_{24}$									This work
$La_{62}Cu_{24}Al_{11.2}Mg_{2.8}$	<10	390	426	661	711	36	0.548	0.387	
$La_{62}Cu_{24}Al_{10.8}Mg_{3.2}$	10	387	421	663	710	34	0.545	0.384	
$La_{62}Cu_{24}Al_{10.5}Mg_{3.5}$	10	386	431	599	712	45	0.542	0.392	
$La_{62}Cu_{24}Al_{9.8}Mg_{4.2}$	10	386	440	660	719	56	0.536	0.398	
$La_{62}Cu_{24}Al_{9.0}Mg_{5.0}$	<10	382	423	662	706	41	0.541	0.388	

metallic glasses [19]. Amand and Giessen [20] reported that the difference between atomic sizes influenced liquid viscosity and hence amorphous alloy formation.

In the present alloy system, the atomic radii of La, Mg, Al and Cu are 0.188 nm, 0.160 nm, 0.143 nm and 0.128 nm, respectively [21]. The atomic radius of Mg is 0.028 nm smaller than that of La, yet 0.017 nm larger than that of Al. This means that Mg has the more suitable atomic size to locate in the atomic size gap between La and Al. This atomic radius configuration will improve the packing efficiency. The atomic radius ratio ($R_{i/j} = (r_i - r_j)/r_j$, r_i represents atomic radius size of the i atom) among the three elements in the La–Al–Cu ternary alloys system are calculated as $R_{La/Al}$ = 31.5%, $R_{La/Cu}$ = 46.9% and $R_{Al/Cu}$ = 11.7%, respectively. When the Al element is partially substituted by Mg, the atomic radius ratio between Mg and the other 3 elements are $R_{La/Mg}$ = 17.5%, $R_{Mg/Al}$ = 11.9%, and $R_{Mg/Cu}$ = 25.0%, respectively. The empirical rules proposed by Inoue that the main constituent elements should differ significantly in atomic size (by more than 12%). In the present work, the atomic radius ratios are quite large among the four constituent elements, even though the small one between the Al and Cu is near to 12%. The addition of neighboring element Mg will benefit the sequential change of the atomic size distribution. Chen [22] reported that the effect of the mismatch in atomic size will result in an increase in the mismatch energy, leading to a decrease in T_g. As shown in Table 1, the substitution of Mg for Al gives rise to a lower T_g, implying that the mismatch energy influences the GFA in the La–Cu–Al–Mg system. The addition of Mg element adds the atomic confusion to the La–Al–Cu–Mg quarternary alloy. The increased confusion in the atomic configuration makes it possible to produce denser atomic packing, and therefore a higher viscosity of liquid. Moreover, the change in atomic interaction may also contribute to the stronger liquid behavior. The more viscous melt would lead to higher nucleation energies and slower growth rates for crystalline phase formation during the solidification, leading to higher GFA [23]. The contribution of the atomic size ratio of the constituent elements for the formation of amorphous phase has also been recognized in $Mg_{65}Cu_{25}RE_{10}$ alloys [23]. Therefore, the enhancement of GFA of quaternary La–Al–Cu–Mg alloys can be mainly attributed to the large atomic size ratios among these four constituent elements.

4. Conclusions

By partially substitution of Al by Mg in the La–Al–Cu system, a series $La_{62}Cu_{24}Al_{14-x}Mg_x$ (x = 3.2, 3.5 and 4.5) BMGs of 10 mm in diameter were prepared, indicating that minor Mg addition effectively improve the GFA of La–Al–Cu alloys. Thermal and atomic structure analyses reveal that the remarkable GFA improvement is due to the large atomic size ratios among these four constituent elements.

Acknowledgements

This work was financially supported by Program for New Century Excellent Talents in University (NCET-08-0631), National Nature Science Foundation of China (10504010 and 50501008), Key Project of Fujian Provincial Department of Science & Technology (2009H0019 and 2006H0018), and 2008100217.

References

[1] A. Inoue, N. Nishiyama, MRS Bull. 32 (2007) 651.
[2] W.H. Wang, C. Dong, C.H. Shek, Mater. Sci. Eng. R 44 (2004) 45.
[3] Q. Lou, W.H. Wang, J. Non-Cryst. Solids 355 (2009) 759.
[4] W. Clement, R.H. Willens, P. Duwez, Nature 187 (1960) 869.
[5] B. Zhang, D.Q. Zhao, M.X. Pan, R.J. Wang, W.H. Wang, Acta Mater. 54 (2006) 3025.
[6] R. Li, F. Liu, S. Pang, Mater. Trans. JIM 48 (2007) 1680.
[7] B.L. Shen, A. Inoue, Appl. Phys. Lett. 85 (2004) 4911.
[8] J. Yin, G.Y. Yuan, Z.H. Chu, J. Zhang, W.J. Ding, J. Mater. Res. 24 (2009) 2130.
[9] A. Inoue, T. Zhang, T. Masumoto, Mater. Trans. JIM 31 (1990) 425.
[10] R. Li, S.J. Pang, C.L. Ma, T. Zhang, Acta Mater. 55 (2007) 3719.
[11] E.R. Arata, F.H.D. Torre, J.F. Löffler, Acta Mater. 56 (2008) 651.
[12] H. Tan, Y. Zhang, D. Ma, Y.P. Feng, Y. Li, Acta Mater. 51 (2003) 4551.
[13] Y. Zhang, H. Tan, Y. Li, Mater. Sci. Eng. A 375 (2004) 436.
[14] W. Zhang, F. Jia, A. Inouue, Mater. Trans. JIM 48 (2007) 68.
[15] Q.K. Jiang, G.D. Zhang, L. Yang, X.D. Zhang, K. Saksl, H. Franz, R. Wunderlich, H. Fecht, J.Z. Jiang, Acta Mater. 55 (2007) 4409.
[16] T. Zhang, J. Alloys Compd. 483 (2009) 60.
[17] Q.K. Jiang, G.Q. Zhang, L.Y. Chen, J.Z. Wu, H.G. Zhang, J.Z. Jiang, J. Alloys Compd. 424 (2006) 183.
[18] D. Turnbull, Contemp. Phys. 10 (1969) 473.
[19] D.B. Miracle, W.S. Sanders, O.N. Senkov, Philo. Mag. 38 (2003) 2409.
[20] R. Amand, B. Giessen, Scr. Mater. 12 (1978) 1021.
[21] A. Takeuchi, A. Inoue, Mater. Trans. JIM 46 (2005) 2817.
[22] H. Chen, Rep. Prog. Phys. 43 (1980) 353.
[23] X.F. Xi, W.H. Wang, Intermetallics 13 (2005) 638.