Crystallization and thermal stability of the Mg_{65}Cu_{25−x}Gd_{10}Ag_{x} (x = 0–10) amorphous alloys

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Abstract

Mg_{65}Cu_{25−x}Gd_{10}Ag_{x} (x = 0–10) amorphous alloy ribbons with 0.1 mm thickness were prepared by melt spinning. The thermal properties and microstructure development during the annealing of amorphous alloys have been investigated by the combination of differential scanning calorimetry (DSC), SEM with EDS capability, X-ray diffractometry (XRD) and TEM techniques. The XRD result reveals that all these as-quenched Mg_{65}Cu_{25−x}Gd_{10}Ag_{x} alloy ribbons exhibit broad diffraction patterns of amorphous phase. A clear T_g (glass transition temperature) and supercooled region (about 40 K) were revealed for all Mg_{65}Cu_{25−x}Gd_{10}Ag_{x} alloy ribbons. In addition, the single stage crystallization of the Mg_{65}Cu_{25}Gd_{10} alloy was found to change into three stage crystallization when the Ag element was added. In parallel, the glass transition temperature for the Mg_{65}Cu_{25−x}Gd_{10}Ag_{x} alloys exhibits an increasing trend with Ag content. However, the crystallization temperature T_x and supercooled region present a decreasing trend with Ag content.

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1. Introduction

Magnesium alloys have numerous advantages over steels, cast irons, copper, aluminium alloys and plastics, such as high specific strength/density ratio and high damping capacity [1–3]. However, due to inherent low stiffness and low workability of conventional magnesium alloys, application of magnesium alloys is limited. Therefore, great efforts have been devoted to the development of Mg-based amorphous alloys with high specific strength in bulk form with thickness of over several millimeters for applying as structural materials. The ternary Mg_{65}Cu_{25}Y_{10} alloy was the first to exhibit a good glass forming ability (GFA) so that metallic glass rods with diameters 4 and 7 mm could be fabricated using copper mold casting and high pressure die-casting methods, respectively [4,5]. The critical cooling rate to form the bulk metallic glass (BMG) was estimated about 10^2 K/s. Further improvement of GFA has been reported in the Mg–Cu–Y ternary alloy system where Cu is partially substituted with TM (TM: transition metal such as Ag, Pd, or Zn). For example, Mg_{65}Cu_{15}Ag_{10}Y_{10} [6], Mg_{65}Cu_{20}Zn_{10}Y_{10} [7], and Mg_{65}Cu_{15}Ag_{5}Pd_{5}Y_{10} [8,9] exhibit high GFA and can form metallic glass rods with diameters more than 6 mm by a Cu-mold injection method. More recently, significant improvement of GFA has been reported in Mg–Cu–Gd alloy system [10]. The ternary Mg_{65}Cu_{25}Gd_{10} BMG with diameter of at least 8 mm can be fabricated by conventional Cu-mold casting method in air. In addition, these Mg-based BMGs exhibit high compressive fracture strength up to 850 MPa [11–13], which is about twice as high as the highest strength for conventional Mg-based crystalline alloys.

In this study, the effect of substituting Ag for Cu in Mg_{65}Cu_{25}Gd_{10} alloy on GFA and crystallization behavior was investigated. Selection of Ag as the alloying element was due to following reasons: (1) a large difference in atomic size between Ag and the constituent elements; the atomic radius of Ag is 11% larger than that of Cu and is smaller than those of Mg and Gd by 10% and 19.5%, respectively [14]; (2) Ag and Cu belong to the same family in the periodic table and the number of valence electrons of Ag is the same as for Cu.

2. Experimental procedures

Chemical compositions of alloys for this study were based on Mg_{65}Cu_{25−x}Gd_{10}Ag_{x}, where x varies from 0 to 10. The CuY alloy ingots used in this investigation were pre-alloyed by arc melting in an argon atmosphere.
The CuY alloy was then melted together with Mg and Ag pieces by induction melting and single roller melt-spinning under argon atmosphere to obtain Mg$_{65}$Cu$_{25-10}$Gd$_{10}$Ag$_x$ ($x = 0$–$10$) alloy ribbons. The alloy ribbon samples with $0.1$ mm in thickness and $5$ mm in width. The liquidus temperatures of pre-alloyed samples were determined by Perkin-Elmer DTA 7 differential thermal analyzer (DTA). The thermal properties of the as-quenched samples were determined by TA Instruments DSC 2920 differential scanning calorimeter (DSC). The amorphous ribbons were isothermally annealed for various time at a temperature between glass transition temperature and crystallization temperature. The as-quenched structure and annealed samples were examined by X-ray diffraction (XRD) with monochromatic Cu K$_{\alpha}$ radiation, transmission electron microscopy (TEM), and nano-beam electron diffraction.

3. Results and discussion

Fig. 1 shows the XRD patterns of the Mg$_{65}$Cu$_{25-10}$Gd$_{10}$Ag$_x$ alloys. No detectable crystalline peak could be resolved and a broad maximum was observed for all as-quenched samples. This observation indicated that complete amorphization of these alloys had been achieved by the single roll melt spinning. In addition, the TEM observation also revealed a uniform amorphous morphology in the as-quenched ribbon for the Mg$_{65}$Cu$_{22.5}$Gd$_{10}$Ag$_{2.5}$ alloy, as shown in Fig. 2.

The liquidus temperatures ($T_l$) for the Mg$_{65}$Cu$_{25-10}$Gd$_{10}$Ag$_x$ ($x = 0$–$10$) alloys exhibit a decreasing trend as the Ag content increases, as shown in Fig. 3. The lowest liquidus temperature (about 702 K) occurs at the Mg$_{65}$Cu$_{15}$Gd$_{10}$Ag$_{10}$ alloy. According to the analyses of Turnbull [15], the best metallic glass forming alloys are at or near deep eutectic compositions and result in obtaining highest reduced glass transition temperature $T_{rg}$. This implies that the alloy Mg$_{65}$Cu$_{15}$Gd$_{10}$Ag$_{10}$ may be the optimum composition for the best GFA in the Mg$_{65}$Cu$_{25-10}$Gd$_{10}$Ag$_x$ alloy system.

In Fig. 4, the results of DSC revealed a clear $T_g$ before crystallization for each amorphous alloy. According to the result of DSC analysis in Fig. 4, the $\Delta T_x = T_x - T_g$ exhibits an increasing trend with increasing Ag content, as shown in Fig. 5. The reduced glass transition temperature $T_{rg}$ (defined as $T_{rg} = T_g/T_l$) and $\gamma$ value (defined as $\gamma = T_{rg} + T_l$ [16]) as shown in Figs. 6 and 7 also revealed that the highest $\gamma$ value (0.407) and a relatively high $T_{rg}$ (0.58) occur for the Mg$_{65}$Cu$_{22.5}$Gd$_{10}$Ag$_{2.5}$ alloy. Compari-
Fig. 5. The $\Delta T_x$ of Mg$_{65}$Cu$_{25-x}$Gd$_{10}$Ag$_x$ amorphous alloys as a function of Ag content.

Fig. 6. The variation of $T_{rg}$ value with different Ag content for Mg$_{65}$Cu$_{25-x}$Gd$_{10}$Ag$_x$ amorphous alloy.

Fig. 7. The variation of $\gamma$ value with different Ag content for Mg$_{65}$Cu$_{25-x}$Gd$_{10}$Ag$_x$ alloy.

Fig. 8. Kissing plots of the DSC peaks for crystallization of Mg$_{65}$Cu$_{25-x}$Gd$_{10}$Ag$_x$ alloys.

Fig. 9. The activation energy estimated by Kissinger plots as a function of Ag content for Mg$_{65}$Cu$_{25-x}$Gd$_{10}$Ag$_x$ amorphous alloys.

The activation energy for crystallization of the Mg$_{65}$Cu$_{25-x}$Gd$_{10}$Ag$_x$ alloys were determined by the Kissinger plot [17]:

$$\ln \left( \frac{b}{T_p^2} \right) = -\frac{E_a}{RT} + \text{constant}$$

where $b$ is the heating rate, $T_p$ the crystallization peak temperature, $R$ the gas constant, and $E_a$ is the activation energy. The $\ln(b/T_p^2)$ as a function of $1/T_p$ is plotted in Fig. 8. Fig. 9 shows the activation energy of crystallization calculated by Kissinger plot as a function of silver content for Mg$_{65}$Cu$_{25-x}$Gd$_{10}$Ag$_x$ alloys. The activation energy of Mg$_{65}$Cu$_{25-x}$Gd$_{10}$Ag$_x$ alloys increases with Ag content and reaches the maximum (183 kJ/mol) for the Mg$_{65}$Cu$_{25}$Gd$_{10}$Ag$_7.5$ alloy. This indicates that the addition of Ag improves the thermal stability for the Mg$_{65}$Cu$_{25}$Gd$_{10}$ base alloy.

The kinetic study of crystallization was performed by using the Johnson–Mehl–Avrami (JMA) [18] isothermal analysis for volume fraction $\gamma$ transformed as a function of time $t$ based on
the following equation [2]:

\[ X(t) = 1 - \exp\left(-kt^n\right) \]  

(2)

Mg65Cu22.5Gd10Ag2.5 were annealed isothermally at several temperatures between \( T_g \) and \( T_x \), namely 433, 438, and 443 K. 

\( k \) is an effective rate constant and \( n \) is Avrami exponent. The Avrami plots of \( \ln[-\ln(1-X)] \) versus \( \ln(t) \), constructed for \( 0.1 \leq X \leq 0.9 \) at several different temperatures, are shown in Fig. 10. The result reveals that the average value of the Avrami exponent \( n \) was 2.3 ± 0.2 for Mg65Cu22.5Gd10Ag2.5 alloy. This indicates that Mg65Cu22.5Gd10Ag2.5 alloy presents diffusion controlled crystal growth with decreasing nucleation rate [18].

4. Conclusion

According to the results of DTA, DSC, X-ray diffraction, and TEM observation for the Mg65Cu25−xGd10Agx alloys with different Ag content, the effect of Ag on the glass forming abilities and thermal properties can be summarized as:

(1) The liquidus temperatures (\( T_l \)) for the Mg65Cu25−xGd10Agx alloys exhibit a decreasing trend with Ag content. The lowest liquidus temperature (about 702 K) occurs at the composition of Mg65Cu15Gd10Ag10. In addition, the highest \( \gamma \) value (0.407) and a relatively high \( T_{rg} \) (0.58) occur at the Mg65Cu22.5Gd10Ag2.5 composition. Comparison with the \( \gamma \) value and \( T_{rg} \) of Mg65Cu25Gd10 alloy (0.55 and 0.404) suggests that the Mg65Cu22.5Gd10Ag2.5 alloy would retain a high glass forming ability.

(2) The activation energy for crystallization of these Mg65Cu25−xGd10Agx alloys increases with Ag content and reaches the maximum (183 kJ/mol) at the Mg65Cu17.5Gd10Ag7.5. This indicates that addition of Ag improves the thermal stability for the Mg65Cu25Gd10 base alloy.

(3) The average value of the Avrami exponent \( n \) was 2.3 ± 0.2 for Mg65Cu22.5Gd10Ag2.5 alloy. This indicates that Mg65Cu22.5Gd10Ag2.5 alloy presents a crystallization process with decreasing nucleation rate.

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