Glass forming ability and thermal properties of the Mg-based amorphous alloys with dual rare earth elements addition

J. S. C. Jang¹,*, C. C. Tseng¹, L. J. Chang¹, C. F. Chang¹, W. J. Lee¹, J. C. Huang², and C. T. Liu³

¹ Department of Materials Sci. & Eng., I-Shou University, Kaohsiung, Taiwan 840, ROC
² Institute of Materials Sci. & Eng., National Sun Yat-Sen University, Kaohsiung, Taiwan 804, ROC
³ Department of Materials Sci. & Eng., University of Tennessee, Knoxville, TN 37996-2200, USA

Abstract

The Mg₅₈Cu₃₁NdₓY₁₁₋ₓ (x=0 ~ 11) amorphous alloy rods with 3 ~ 10 mm in diameter were prepared by Cu-mold injection method. The glass forming ability, thermal properties, and microstructure development during isothermal annealing these amorphous alloys have been investigated by the combination of differential scanning calorimetry (DSC), SEM with EDS capability, X-ray Diffraction method (XRD) and TEM techniques. The XRD result reveals that these entire Mg₅₈Cu₃₁NdₓY₁₁₋ₓ alloy rods exhibit a broaden diffraction pattern of amorphous phase. A clear T_g (glass transition temperature) and supercooled region (about 70 K) were revealed for all of those Mg₅₈Cu₃₁NdₓY₁₁₋ₓ amorphous alloy rods. The single stage crystallization of the Mg₅₈Cu₃₁Y₁₁ alloy was found to change into two stages crystallization when large amount of Nd element was added into this alloy. In parallel, the crystallization temperature (T_x) and supercooled region (ΔT_x) present a decreasing trend with increasing Nd content. The highest γ value of 0.414 occurs at the alloy compositions of Mg₅₈Cu₃₁Nd₇Y₄ and Mg₅₈Cu₃₁Nd₅Y₆ in this alloy system. Therefore, suitable addition of Nd element can obviously increase the glass forming ability for the Mg₅₈Cu₃₁NdₓY₁₁₋ₓ alloy system. However, the addition of Nd plays a negative effect on the thermal stability of the Mg₅₈Cu₃₁NdₓY₁₁₋ₓ alloy system, such as activation energy of crystallization as well as incubation time of crystallization during isothermal annealing.

Key words: glass forming ability, thermal properties, Mg-based amorphous alloy, crystallization kinetics, differential scanning calorimetry (DSC)

Corresponding author: scjang@isu.edu.tw (J.S.C. Jang)
Introduction

Recently, Magnesium alloys are attracting great attention as structural materials because of it’s high specific strength/density ratio and high damping capacity [1-3]. However, up to now their application is limited because of the inherent low stiffness and low workability for conventional magnesium alloys. Therefore, great efforts have been devoted to the development of Mg-based amorphous alloys with high specific strength in a bulk form with a thickness of over several millimeters for applying as structural materials. The ternary Mg₆₅Cu₂₅Y₁₀ alloy was the first to exhibit a good glass forming ability (GFA) so that metallic glass rods with diameters 4 mm and 7 mm can be fabricated by using the copper mold casting and high pressure die-casting methods, respectively [4,5]. 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, Mg₆₅Cu₁₅Ag₁₀Y₁₀ [6], Mg₆₅Cu₂₀Zn₅Y₁₀ [7], and Mg₆₅Cu₁₅Ag₅Pd₅Y₁₀ [8,9] exhibit high GFA and enable to form metallic glass rods with diameters more than 6 mm by a Cu-mold injection method. More recently, the significantly improvement of GFA has been reported in Mg-Cu-Gd alloy system [10]. The ternary Mg₆₅Cu₂₅Gd₁₀ BMG with diameter of at least 8 mm can be fabricated by conventional Cu-mold casting method. In addition, these Mg-based BMGs exhibit high compressive fracture strength about 850 MPa [11-13], which is twice as high as the highest strength for conventional Mg-based crystalline alloys. In recent study, new optimum alloy designs are made based on the recent model of optimum composition extension from the binary eutectic pairs, originally proposed by Lu et al [14]. This model suggest that the optimum Mg based bulk metallic glasses might possess a composition with a lower amount of Mg and a higher amount of rare earth (RE) element, for example, the Mg₅₈Cu₃₁Y₁₁ and Mg₅₈Cu₃₁Gd₁₁. A series of Mg based BMGs with 50-60at% Mg and 10-15at% dual RE elements (Nd and Y) are prepared by atmosphere controlled induction melting and injection casting method. So, the improvement of glass-forming ability and crystallization behavior by using Nd to substitute Y in the Mg-Cu-Y alloy was investigated. The selection of Nd for partially replacing Y element is due to the difference between Nd and Y in covalent atomic radius (Nd: 0.164nm; Y: 0.162nm) electronegativity (Nd: 1.14, Y: 1.22), and electronic configuration (Nd: 4f⁴5d⁰6s², Y: 4d¹5s²), and Y–Nd binary system has a near-zero heat of mixing (these two elements form continuous solid solutions [15]). These differences may result in certain change of short range order in undercooled liquid of Mg₅₈Cu₃₁Y₁₁₋ₓNdₓ alloys, which favors the glass formation.
Experimental Procedures

The Mg$_{58}$Cu$_{31}$Y$_{11-x}$Nd$_x$ (x = 0 ~ 11) was selected in this investigation. The Cu-(Y, Nd) master alloy ingots were pre-alloyed by arc melting in an argon atmosphere. Then the Cu-(Y, Nd) alloys were melted together with Mg pieces by induction melting under argon atmosphere to obtain Mg$_{58}$Cu$_{31}$Y$_{11-x}$Nd$_x$ alloy ingots. The alloy rods with 3 to 10 mm in diameter and 60 mm long were prepared by Cu-mold injection method in an argon atmosphere from these pre-alloyed Mg$_{58}$Cu$_{31}$Y$_{11-x}$Nd$_x$ alloy ingots. Thermal analysis of the as-cast rods was carried out using the TA Instruments DSC 2920 differential scanning calorimeter (DSC) under flowing argon atmosphere. Heating rates of 10 to 60 K/min were selected for the non-isothermal DSC analysis to reveal the crystallization behavior. Several temperatures between glass transition temperature, T$_g$, and T$_x$ (namely 443, 448, 453 and 458 K) were selected for the isothermal DSC analysis to study the crystallization kinetics. The as-quenched and annealed structure was examined by X-ray diffraction (Scintag X-400 X-ray diffractometer) with monochromatic Cu-K$_\alpha$ radiation, transmission electron microscopy (Philip Tenai G2 TEM with 200 kV), and nano-beam electron diffraction pattern, respectively.

Results and Discussion

Figure 1(a) shows the X-ray diffraction patterns obtained from the as-cast Mg$_{58}$Cu$_{31}$Nd$_x$Y$_{11-x}$ alloy rods with dimension of 4 mm in diameter. There is no resolvable crystalline peak in the 2$\theta$ range of 20$^\circ$ - 80$^\circ$, but only a broad diffuse peak is observed in the range of 30$^\circ$ - 50$^\circ$ for all of the alloys in this study. This indicates that amorphous state for all of these alloys had been achieved by Cu-mold injection method process. In parallel, amorphous rods with diameter of 5 ~ 10 mm can be formed for Mg$_{58}$Cu$_{31}$Y$_6$Nd$_5$ alloy and the evident amorphous state of X-ray diffraction patterns are shown in Figure 1(b). A typical outlook of the amorphous rods from 3 to 10 mm with minimum porosity for the Mg$_{58}$Cu$_{31}$Y$_6$Nd$_5$ alloy (as shown in Fig. 2) shows the characteristic shining surface. These amorphous rods exhibit reasonable toughness and can be dropped to the ground without damage or breakage. In addition, the TEM observation also revealed that a uniform amorphous morphology in the as-cast rods for the Mg$_{58}$Cu$_{31}$Y$_6$Nd$_5$ alloy, as shown in Figure 3.

The DSC scans of the selected Mg$_{58}$Cu$_{31}$Y$_{11-x}$Nd$_x$ alloys with dimension of 4 mm in diameter are shown in Figure 4. All of the samples exhibit a clear glass transition followed by a supercooled liquid region and then exothermic reaction due to crystallization. The
crystallization exothermic reactions for these alloys in their DSC curves, one single peak of the Mg58Cu31Y11 alloy was found to change into two peaks when the Nd element was added up to 9 at% in this alloy. This indicates that the single stage crystallization of the Mg58Cu31Y11 alloy would change into more complicated two stage crystallization of the Mg58Cu31Y11-xNd_x (x  9). In addition, the lowest liquidus temperature (about 758 K) occurs at the Mg58Cu31Y2Nd9 alloy, as show in Table 1. According to the analyses of Turnbull [16], the best metallic glass forming alloys are at or near deep eutectic composition and also result in obtaining highest reduced glass transition temperature T_γ. This implies that the alloy Mg58Cu31Y2Nd9 may perform a better GFA (glass forming ability) among these Mg58Cu31Y11-xNd_x alloys.

According to the result of DSC analysis in Table 1, the relatively high value of ΔT_x (above 65 K) occurs at the alloy with Nd content less than 7 at%. As increasing the addition of Nd in the Mg58Cu31Y11-xNd_x alloy, the ΔT_x decreases obviously down to 59 K and 48 K for the Mg58Cu31Y2Nd9 and Mg58Cu31Nd11 alloy, respectively. In addition, the highest γ value (0.414, defined as γ = T_x/T_g+T_l [17]) and a relatively high T_γ (0.55, defined as T_γ = T_g/T_l) occurs at the alloy composition of Mg58Cu31Y6Nd5 and Mg58Cu31Y4Nd7, respectively. In comparison the T_γ and γ value with the Mg58Cu31Y11 base alloy, it is suggested that the Mg58Cu31Y6Nd5 and Mg58Cu31Y4Nd7 alloys would posses a high GFA.

The activation energy for crystallization of the Mg58Cu31Nd_xY11-x alloys were determined by means of the Kissinger plot [18],

\[
\ln\left(\frac{b}{T_p^2}\right) = -\frac{E_a}{RT} + \text{constant} \quad (1)
\]

Where b is the heating rate (namely 0.167K/s, 0.33 K/s, 0.5 K/s, and 0.67 K/s), T is the specific temperature, R is the gas constant, and E_a is the activation energy. By substituting T with T_p (peak temperature of crystallization) in equation (1), the activation energy of crystallization can be determined from the slope of a plot of the ln(b/T_p^2) against 1/T_p. The ln(b/T_p^2) as a function of 1/T_p is plotted in Figure 5(a). Fig. 5(b) shows the activation energy of crystallization calculated by Kissinger plot as a function of Nd content for Mg58Cu31Y11-xNd_x alloys. The activation energy of these Mg58Cu31Nd_xY11-x alloys exhibits irregular trend with the addition of Nd content and the highest value of 150 kJ/mole occurs at the Mg58Cu31Y8Nd3 alloy.

The kinetic study of crystallization was performed by using the Johnson-Mehl-Avrami (JMA) [19] isothermal analysis for volume fraction x transformed as a function of time t based on the following equation (2):
\[ x(t) = 1 - \exp\left[-(kt)^n\right] \]  

(2)

selected \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11-x}\text{Nd}_x \) (\( x = 3, 5, 7 \)) alloys which performed higher GFA were annealed isothermally at several temperatures between \( T_g \) and \( T_x \), namely 443, 448, 453 and 458 K, as shown in Figure. DSC traces of isothermally annealing at different temperature for these \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11-x}\text{Nd}_x \) (\( x = 3, 5, 7 \)) alloys are shown in Figure 6(a)-6(c). To construct the JMA plots, the volume fraction of crystallization at time \( t \) was assumed to be the same as that of heat released. Therefore, the fraction of crystallization \( x \) was obtained by measuring the partial area under peak up to time \( t \). The volume fraction transformed versus the annealing time plot is shown in Figure 6(d)-6(f). In parallel, the incubation time as a function of isothermal temperature, as shown in Figure 7, exhibits a decreasing trend with Nd addition and implies that the addition of Nd presents a negative effect on thermal stability of the \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11-x}\text{Nd}_x \) alloy system. However, for those \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11-x}\text{Nd}_x \) (\( x = 3, 5, 7 \)) alloys isothermal annealed at 443 K, their incubation time before crystallization still keep more than 15 min and shows enough time for hot forming these amorphous alloys within their supercooled liquid temperature region. Additionally, Equation (2) can be written as:

\[
\ln[\ln(1/(1-x))] = n \ln(k) + n \ln(t)
\]

(3)

where \( k \) is the effective rate constant and \( n \) is the Avrami exponent. The Avrami plot of \( \ln[-\ln(1-x)] \) versus \( \ln(t) \), yields a strait line with slope \( n \) and intercept \( n\ln(k) \). The Avrami plots at four different temperatures exhibit a reasonably linear relationship as shown in Figure 6(g)-6(i). The value of Avrami exponent \( n \) remains insensitive with the annealing temperature being above 2.50 at temperature of 443, 448, 453 and 458 K. Based on these results obtained from Figure 6(d)-6(i), indicate that an increasing nucleation rate of crystallization is revealed for these \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11-x}\text{Nd}_x \) (\( x = 3, 5, 7 \)) alloys at the supercooled temperature region [20].

**Conclusion**

According to the results of DSC, X-ray diffraction, and TEM observation for the \( \text{Mg}_{58}\text{Cu}_{31}\text{Nd}_x\text{Y}_{11-x} \) amorphous alloys, the effect of Nd on the glass forming ability and thermal properties can be summarized as:

(1) Amorphous state for all of the \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11-x}\text{Nd}_x \) alloy rods with diameter of 4 mm can be achieved by Cu-mold injection method process. In addition, amorphous rod of 10 mm in diameter can be formed for \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{6}\text{Nd}_5 \) alloy which performed high GFA.

(2) The single stage crystallization of the \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11} \) alloy changes into more complicated two stage crystallization of the \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11-x}\text{Nd}_x \) (\( x \geq 9 \)). The highest \( \gamma \) value (0.414)
and a relatively high $T_{rg}$ (0.55) occur at the Mg$_{58}$Cu$_{31}$Y$_6$Nd$_5$ and Mg$_{58}$Cu$_{31}$Y$_4$Nd$_7$ alloy. In comparison the $T_{rg}$ and $\gamma$ value with the base alloy, it is suggested that the Mg$_{58}$Cu$_{31}$Y$_6$Nd$_5$ and Mg$_{58}$Cu$_{31}$Y$_4$Nd$_7$ alloys would possess a high GFA. Therefore, suitable addition of Nd element can obviously increase the glass forming ability for the Mg$_{58}$Cu$_{31}$Nd$_x$Y$_{11-x}$ alloy system.

3) The activation energy of these Mg$_{58}$Cu$_{31}$Nd$_x$Y$_{11-x}$ alloys exhibits irregular trend with the addition of Nd content and the highest value of 150 kJ/mole occurs at the Mg$_{58}$Cu$_{31}$Y$_8$Nd$_3$ alloy. In addition, the incubation time before crystallization exhibits a decreasing trend with Nd addition and implies that the addition of Nd presents a negative effect on thermal stability of the Mg$_{58}$Cu$_{31}$Y$_{11-x}$Nd$_x$ alloy system.

4) The value of Avrami exponent $n$ remains insensitive with the annealing temperature being above 2.50 at temperature of 443, 448, 453 and 458 K. This indicates that an increasing nucleation rate of crystallization occurs at these Mg$_{58}$Cu$_{31}$Y$_{11-x}$Nd$_x$ ($x = 3, 5, 7$) alloys within the supercooled temperature region.

Acknowledgement

The authors would like to gratefully acknowledge the sponsorship from the National Science Council of ROC under the project NSC93-2216-E-214-002, NSC93-2216-E-214-008, and NSC94-2218-E-110-009. In addition, The authors are also very grateful for the assistance of TEM by the Micro and Nano Laboratory, Department of Materials Science and Engineering, I-Shou University.

References

Table Caption:
Table 1 Thermal properties of Mg$_{58}$Cu$_{31}$Nd$_x$Y$_{11-x}$ amorphous alloy rods with diameter of 4 mm at the heating rate of 0.67 K/s.

Figure Captions:
Fig. 1. (a) XRD patterns of Mg$_{58}$Cu$_{31}$Y$_{11-x}$Nd$_x$ amorphous alloy rods with diameter of 4mm; (b) XRD patterns of Mg$_{58}$Cu$_{31}$Y$_6$Nd$_5$ amorphous alloy rods with diameter of 6mm, 8mm and 10mm
Fig. 2. Outer shape and surface appearance of Mg$_{58}$Cu$_{31}$Y$_6$Nd$_5$ amorphous alloy rods with diameter of 3mm ~ 10mm
Fig. 3. TEM images of the as-cast Mg$_{58}$Cu$_{31}$Y$_6$Nd$_5$ BMGs alloy amorphous alloy rods with diameter of 4mm
Fig. 4. DSC plots of as-cast Mg$_{58}$Cu$_{31}$Y$_{11-x}$Nd$_x$ amorphous alloy rods with diameter of 4 mm with a heating rate of 0.67 K/s
Fig. 5. (a) Kissinger plots of DSC peaks for crystallization of Mg$_{58}$Cu$_{31}$Y$_{11-x}$Nd$_x$ (x = 0 ~ 11) amorphous alloy rod with diameter of 4 mm; (b) The activation energy estimated by Kissinger plots as a function of Nd content for Mg$_{58}$Cu$_{31}$Y$_{11-x}$Nd$_x$ amorphous alloys.
Fig. 6. (a)-(c) Isothermal DSC curves at different temperature, (d)-(f) the fraction transformed versus the annealing time, and (g)-(i) the Avrami plot for the Mg$_{58}$Cu$_{31}$Nd$_x$Y$_{11-x}$ (x = 3,5,7) amorphous alloys
Fig. 7. Incubation time as a function of isothermal annealing temperature for Mg$_{58}$Cu$_{31}$Nd$_x$Y$_{11-x}$ (x = 0 ~ 9)
Table 1  Thermal properties of Mg$_{58}$Cu$_{31}$Nd$_x$Y$_{11-x}$ amorphous alloy rods with diameter of 4 mm at the heating rate of 0.67 K/s.

<table>
<thead>
<tr>
<th>composition</th>
<th>$T_x$(K)</th>
<th>$T_g$(K)</th>
<th>$T_m$(K)</th>
<th>$T_f$(K)</th>
<th>$\Delta T_x$(K)</th>
<th>$\Delta T_m$(K)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$<em>{58}$Cu$</em>{31}$Nd$_{11}$</td>
<td>429</td>
<td>501</td>
<td>736</td>
<td>787</td>
<td>72</td>
<td>51</td>
<td>0.54</td>
</tr>
<tr>
<td>Mg$<em>{58}$Cu$</em>{31}$Nd$<em>{11}$Y$</em>{10}$</td>
<td>427</td>
<td>500</td>
<td>722</td>
<td>787</td>
<td>73</td>
<td>65</td>
<td>0.54</td>
</tr>
<tr>
<td>Mg$<em>{58}$Cu$</em>{31}$Nd$<em>{11}$Y$</em>{8}$</td>
<td>426</td>
<td>500</td>
<td>712</td>
<td>789</td>
<td>74</td>
<td>77</td>
<td>0.54</td>
</tr>
<tr>
<td>Mg$<em>{58}$Cu$</em>{31}$Nd$<em>{11}$Y$</em>{6}$</td>
<td>430</td>
<td>503</td>
<td>715</td>
<td>783</td>
<td>73</td>
<td>68</td>
<td>0.55</td>
</tr>
<tr>
<td>Mg$<em>{58}$Cu$</em>{31}$Nd$<em>{11}$Y$</em>{4}$</td>
<td>426</td>
<td>492</td>
<td>713</td>
<td>764</td>
<td>66</td>
<td>51</td>
<td>0.56</td>
</tr>
<tr>
<td>Mg$<em>{58}$Cu$</em>{31}$Nd$<em>{11}$Y$</em>{2}$</td>
<td>424</td>
<td>483</td>
<td>716</td>
<td>758</td>
<td>59</td>
<td>42</td>
<td>0.56</td>
</tr>
<tr>
<td>Mg$<em>{58}$Cu$</em>{31}$Nd$_{11}$</td>
<td>424</td>
<td>472</td>
<td>715</td>
<td>786</td>
<td>48</td>
<td>71</td>
<td>0.54</td>
</tr>
</tbody>
</table>

$\Delta T_x = T_x - T_g$,  $\Delta T_f = T_f - T_m$
Fig. 1
Fig. 4
(a) \( \ln(T_p^{1/2}/b) \) vs. \( T^{-1} (K^{-1}) \)

(b) Activation energy (KJ/mole) vs. Nd content (at%)
Fig. 6
Fig. 6
(g) Fig. 6

(h) Fig. 6

(i) Fig. 6
Fig. 7