Thermal stability and crystallization kinetics of Mg–Cu–Y–B quaternary alloys


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Abstract

The thermal stability and crystallization kinetics of the Mg_{65}Cu_{25}Y_{10} and Mg_{65}Cu_{25-x}Y_{10}B_{x} (numbers indicate at.%, x = 1–10) amorphous alloys are examined and compared in terms of non-isothermal and isothermal differential scanning calorimetry measurements. It is demonstrated that, with the minor addition of 1–5 at.% B, the incubation time for crystallization is prolonged and the activation energy is increased, suggesting an improvement of the thermal stability. Nevertheless, the overall nucleation and growth characteristics of the parent and B-additive alloys are similar. The minor B element appears to impose resistance to the crystallization of the major Mg_{2}Cu phase, possibly by blocking the path of Mg and Cu diffusion. With further addition of B up to 10 at.%, secondary crystallization phases such as MgB_{4} or YB would be induced and thus lower the thermal stability.

1. Introduction

Among a large number of amorphous alloys, Mg-based alloys have attracted much attention especially due to its high strength to weight ratio and a low glass transition temperature. The new Mg-based amorphous alloys with high tensile strength and good ductility were first found in 1988 [1]. Until 1991, Inoue et al. [2–4] succeeded in finding new Mg-based amorphous alloys, such as Mg–Ln–TM (Ln, lanthanide metal; TM, transition metal) systems with high tensile strength. They also fabricated bulk metallic glass (BMG) with a diameter of 4–7 mm by injection casting the Mg_{65}Cu_{25}Y_{10} (numbers indicate at.%) alloy into a Cu mold. The follow-up investigations on the Mg-based BMG have been directed to the addition of the quaternary element to improve the glass forming ability (GFA). Recently, Park et al. [5] reported the effect of Ag as the substituting element for Cu to increase the atomic packing density of the liquid structure and GFA. Men et al. [6] also investigated the effect of substitution of Y in the Mg_{65}Cu_{25}Y_{10} alloy with Gd on the superior GFA and crystallization behavior. In addition, the Mg_{65}Cu_{20}Zn_{5}Y_{10} [7] and Mg_{65}Cu_{15}Ag_{5}Pd_{5}Y_{10} [8] alloys also exhibit high GFA.

From the above review, it seems that a proper addition of some quaternary elements might play an important role in improving the GFA. In our earlier paper [9], we found the improvement in GFA by the addition of the interstitial atom, B, into Mg_{65}Cu_{25}Y_{10}, due to the large atomic size difference to fill the free volume and also the strongly negative ΔH_{m} for Mg–B and Y–B (both around −50 kJ/mol). In this paper, the crystallization behavior of the B-additive Mg alloys during isothermal and non-isothermal annealing is presented.

2. Experimental methods

The master ingot of Cu–Y binary alloys were first prepared by arc melting high-purity Cu (99.999%) and Y (99.9%) under a Ti-gettered argon atmosphere. Then the master ingot was melted with pure Mg (99.99%) and B (99.5%) in an induction furnace under a purified argon atmosphere. After complete melting, the liquid alloy was poured onto the surface of Cu wheel. The wheel is rotated with high speed of 25 m/s (20 Hz) in order to reach the high cooling rate. The resulting specimen is thin ribbon type with...
~10 mm in width and ~100 μm in thickness. Thermal analysis was carried out using differential scanning calorimetry (DSC) under flowing argon atmosphere from 303 to 900 K. The specimens were placed in stainless steel crucibles and tightly sealed with a Ni ring, and heated with positive Ar atmosphere. Heating rates of 10–40 K/min were employed to reveal the crystallization and melting behavior.

3. Results and discussions

X-ray diffraction results as shown in Fig. 1 have confirmed that both the parent melt spun Mg65Cu25B10 alloy and the B-additive Mg65Cu25−xY10Bx (x = 1, 3, 5, 10) alloys are all amorphous. The thermal characteristics are compared in Table 1, including ΔT and γ parameters [10].

3.1. Non-isothermal analyses

In order to estimate the activation energy for crystallization, the Kissinger relation is frequently used for non-isothermal DSC analysis, and can be expressed in the form as [11]

\[
\ln \left( \frac{\phi_m}{T_p^2} \right) = -\frac{Q}{RT_p} + \text{constant},
\]

where \( \phi_m \) is the heating rate, \( T_p \) corresponds to the peak temperature of transition in DSC curves, \( R \) the gas constant and \( Q \) is the transition activation energy. The other analysis can be done by the modified Kissinger equation [12]:

\[
\ln[-\ln(1 - X)] = n \ln \phi - 1.052m \frac{Q}{RT} + \text{constant},
\]

where \( n \) and \( m \) are the numerical factors relating to the nucleation and growth mechanisms, and \( m \) might equal \( n - 1 \) for early nucleation stage and would approach \( n \) at later stage with minimum nucleation. The \( n \) value could be obtained from the plot of \( \ln[-\ln(1 - X)] \) against \( \ln \phi \) at a specific temperature. And the value of \(-1.052mQ/R\) also could be obtained by plotting \( \ln[-\ln(1 - X)] \) versus reciprocal temperature for several heating rates.

Fig. 2 shows the typical Kissinger plots of \( \ln(\phi/T) \) against reciprocal \( T \) taken from the dependence of crystallization temperature on various heating rates (\( \phi = 10, 20 \) and 30 K/min) in the DSC curves for the onset and peak temperature of the exothermal peak, \( T_a \) and \( T_p \). The activation energy of the first crystallization for the Mg65Cu25Y10 amorphous alloy derived from the slope of Kissinger plot is 138 kJ/mol, as shown in Fig. 2a, compared with around 155 ± 3 kJ/mol for Mg65Cu25−xY10Bx (x = 3, 5, 10) in Fig. 2b. The B-additive alloys exhibit crystallization activation energy about 10% higher than the parent alloy, suggesting that the improvement of the thermal stability. It is interesting to note that the activation energy for the first phase transition (Mg2Cu) in Mg-based multicomponent alloys is the same as found by Sommer et al. [13] for the binary amorphous alloys Mg75Cu25 alloy which has the activation energy of 152 kJ/mol. It implies that the process of the primary crystallization is similar in the binary, ternary and quaternary Mg-based amorphous alloys.

Fig. 3 shows the plots based on the modified Kissenger equation, extracting the variation of \( n \) which is temperature dependence. In the early crystallization stage, because nuclei are in random distribution, the \( n \) values extracted from the plots for the initial transient stage will exceed 4 [14]. Since the \( n \) value is much larger than 1, bulk nucleation should be dominant in the early stage of phase transformation. With increasing temperature, the \( n \) value decreases to 1 and surface nucleation dominates the later stage of transformation until only growth process dominates.

On the other hand, Fig. 4 is the plots of \( \ln[-\ln(1 - X)] \) against the \( 1/T \) for several heating rates. From the slope, \(-1.052mQ/R\) can be obtained. Since no particular heat treatment was given to nucleate the samples before thermal analysis, the dimensionality of growth parameter \( m \) is taken to be equal to \( (n - 1) \) in the early crystallization stage and \( m \) is equal to \( n \) when a

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**Fig. 1.** X-ray diffraction patterns for the melt spun Mg65Cu25−xY10Bx alloy.

**Fig. 2.** The typical Kissinger plots of \( \ln(\phi/T) \) against reciprocal \( T \) taken from the dependence of crystallization temperature on various heating rates.

**Fig. 3.** The plots based on the modified Kissenger equation, extracting the variation of \( n \) which is temperature dependence.

**Fig. 4.** The plots of \( \ln[-\ln(1 - X)] \) against the \( 1/T \) for several heating rates.

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**Table 1.** Thermal properties of the Mg65Cu25−xY10Bx alloys

<table>
<thead>
<tr>
<th>Compositions</th>
<th>( T_a ) (K)</th>
<th>( T_p ) (K)</th>
<th>Δ( T ) (K)</th>
<th>( T_m^{\text{solid}} ) (K)</th>
<th>( T_m^{\text{liquid}} ) (K)</th>
<th>( T_g/T_m^{\text{liquid}} )</th>
<th>γ^m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg65Cu25Y10</td>
<td>410</td>
<td>468</td>
<td>58</td>
<td>728</td>
<td>770</td>
<td>0.532</td>
<td>0.397</td>
</tr>
<tr>
<td>Mg65Cu22Y10B1</td>
<td>410</td>
<td>471</td>
<td>61</td>
<td>720</td>
<td>758</td>
<td>0.541</td>
<td>0.403</td>
</tr>
<tr>
<td>Mg65Cu22Y10B3</td>
<td>410</td>
<td>476</td>
<td>66</td>
<td>715</td>
<td>738</td>
<td>0.556</td>
<td>0.415</td>
</tr>
<tr>
<td>Mg65Cu20Y10B5</td>
<td>420</td>
<td>470</td>
<td>50</td>
<td>712</td>
<td>736</td>
<td>0.571</td>
<td>0.407</td>
</tr>
<tr>
<td>Mg65Cu20Y10B10</td>
<td>420</td>
<td>465</td>
<td>45</td>
<td>720</td>
<td>740</td>
<td>0.568</td>
<td>0.400</td>
</tr>
</tbody>
</table>

^m γ is referred to \( T_g/(T_g + T_m) \) [10].
large number of nuclei exist in the final crystallization stage. The activation energy \( Q \) for the early stage with \( X = 0 \)–0.6 (or before the slope transition), extracted using the slope in Fig. 4 and the average value of \( m = nt \) to \( n - 1 \), is 172–217 kJ/mol for the parent Mg65Cu25Y10 alloy and 200–240 kJ/mol for the Mg65Cu22Y10B3 alloy. Again, the B-additive alloy possesses higher activation energy than the parent Mg65Cu25Y10.

From the view of the slope, it is apparent that the early crystallization stage has a nearly linear and steep slope (means higher activation energy for crystallization) and then suddenly decreases when pass through a break in the slope. This break in the slope above a specific volume fraction can be observed for each heating rate. Previous research\[15\] has inferred that the slope breaks on the \( \ln(-\ln(1-X)) \) versus \( 1/T \) plot is the saturation of nucleation sites. Below the break temperature, the activation energy includes the nucleation plus growth activation energy. On the contrary, due to the saturation of nucleation, only the growth activation energy remains above the break temperature. This inference is also consistent with the slope observed. Furthermore, it is noted that the slope breaks at nearly the same transformed volume fraction \( X \approx 0.6 \) for all the Mg-based amorphous alloys (Mg65Cu25\( \_x \)Y10B\( \_x \) with \( x = 0 \)–10). It means the basic crystallization behavior is similar in all Mg-based amorphous alloys.

### 3.2. Isothermal analyses and kinetics

The general form of Johnson–Mehl–Avrami (JMA) equation is given as

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

Then take the logarithm of Eq. (3) twice derives Eq. (4)

\[
\ln[- \ln(1 - X)] = n \ln k + n \ln t,
\]  

where \( n \) is the Avrami exponent and \( k \) is a kinetic coefficient which is a function of the absolute temperature. The samples of the Mg-based amorphous alloys are annealed isothermally at 433, 435, 438 and 440 K between \( T_g \) (410–420 K) and \( T_x \) (465–476 K). Since there are more than one phase nucleated, the multieutectic reaction is separated by using the PeakFit software. The following analysis is focused on the first and the primary Mg2Cu phase.
The degree of transformation as a function of time for all Mg-based amorphous alloys follows the classic S curves. With increasing annealing temperature, the incubation time and the time for a complete crystallization would both decrease. The incubation time at the annealing temperature of 433, 435, 438, and 440 K for the Mg$_{65}$Cu$_{25}$Y$_{10}$ amorphous alloy are 1420, 810, 580 and 373 s and for the Mg$_{65}$Cu$_{22}$Y$_{10}$B$_{3}$ amorphous alloys are 1568, 1031, 778 and 595 s, respectively. The B-additive alloys always exhibit longer incubation time as compared with the parent alloy.

Furthermore, for the evaluation of the Avrami exponent $n$, $\ln[-\ln(1-X)]$ is plotted versus $\ln(t)$ for different annealing temperatures. The extracted values of the Avrami exponent $n$ for the Mg$_{65}$Cu$_{25}$Y$_{10}$ and Mg$_{65}$Cu$_{22}$Y$_{10}$B$_{3}$ amorphous alloys are temperature dependent during the isothermal crystallization process. Form the slopes of the straight lines, the average values of $n$ for Mg$_{65}$Cu$_{25}$Y$_{10}$ and Mg$_{65}$Cu$_{22}$Y$_{10}$B$_{3}$ are both about 3.4 $\pm$ 0.2. It means that the crystallization is mainly controlled by three-dimensional nuclei with constant growth rate until the whole amorphous phase is completely crystallized.

In isothermal analyses, the activation energy can also be evaluated by the isothermal curves of crystallized volume fraction versus annealing time at different temperatures. This is carried out by using the Arrhenius equation, $t = t_0 \exp(Q/RT)$. For each annealing temperature, the time to reach the integer multiple of 10% crystallization is selected and the plots of $\ln t$ versus $1/T$ for Mg-based amorphous alloys are made, as shown in Fig. 5. From the slopes, the average activation energies determined for the Mg$_{65}$Cu$_{25}$Y$_{10}$ and Mg$_{65}$Cu$_{22}$Y$_{10}$B$_{3}$ amorphous alloys are 156 and 200 kJ/mol, respectively. This indicates that the boron can increase the activation energy of crystallization for the Mg$_{65}$Cu$_{25}$Y$_{10}$-based alloy and results in the improvement of the thermal stability against crystallization, consistent with the finding from the non-isothermal analyses. The B element appears to impose resistance to the crystallization of the major Mg$_2$Cu phase, possibly by blocking the path of Mg and Cu diffusion.

Based on the non-isothermal analysis using Kissinger or modified Kissinger equation or the isothermal analysis using the JMA or Arrhenius equation, the modified alloys containing an optimum amount of B to 3% consistently exhibit higher
crystallization activation energy values by 20–50kJ/mol, indicating higher thermal stability. However, with further addition of B to 10 at.%, secondary crystallization phases such as MgB₄ or YB have been found to be induced and thus lower ΔT and γ (Table 1) as well as the thermal stability.

4. Conclusions

The thermal stability and crystallization behavior of the B-additive Mg₆₅Cu₂₅₋ₓY₁₀Bₓ alloys are examined under the non-isothermal and isothermal DSC scans. It is demonstrated that, with the minor addition of 1–5 at.% B, the crystallization incubation time is prolonged by about 200s and the activation energy is increased by about 20–50kJ/mol, suggesting that the B-additive amorphous alloys are more thermally stable. Nevertheless, the overall nucleation and growth characteristics of the parent Mg₆₅Cu₂₅Y₁₀ and Mg₆₅Cu₂₅₋ₓY₁₀Bₓ alloys are similar, judging from the similar Avrami exponent n (~3.4) and site saturation volume fraction X (~60%). The B element appears to impose resistance to the crystallization of the major Mg₂Cu phase, possibly by blocking the path of Mg and Cu diffusion. With further addition of B to 10 at.%, secondary crystallization phases such as MgB₄ or YB would be induced and thus lower the thermal stability.

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References