Viscous flow behavior and thermal properties of bulk amorphous Mg$_{58}$Cu$_{31}$Y$_{11}$ alloy

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Abstract

The viscous flow behavior of the Mg$_{58}$Cu$_{31}$Y$_{11}$ bulk amorphous rods in the supercooled viscous region is investigated using differential scanning calorimetry (DSC) and thermomechanical analyzer (TMA). Below the glass transition temperature, $T_g$, a linear thermal expansion coefficient of $3 \times 10^{-6}$ m/m K was obtained. In contrast, significant viscous deformation occurred as a result of a compressive load above $T_g$. The onset, steady state, and finish temperatures for viscous flow, determined by TMA, are slightly different from the glass transition and crystallization temperatures measured by DSC. The appropriate working temperature for microforming as determined by the steady state viscous flow temperature is about 460–474 K. The effective viscosity within this temperature range is estimated to be about $10^7$–$10^8$ Pa s, and it increases with increasing applied stress. The onset, steady state, and finish temperatures all decrease with increasing applied stress, suggesting accelerated crystallization in the present Mg$_{58}$Cu$_{31}$Y$_{11}$ under stress.

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1. Introduction

Metallic glassy alloys exhibit some unique physical properties such as excellent strength as compared to their corresponding crystalline counterparts. Significant plasticity can occur in the supercooled liquid region, $\Delta T_x (= T_x - T_g$, where $T_x$ is the crystallization temperature and $T_g$ the glass transition temperature), resulting from a drastic drop in viscosity [1]. It is well known that the Mg-based Mg$_{65}$Cu$_{25}$Y$_{10}$ system exhibits reasonably good glass forming ability (GFA) with a wide supercooled liquid region [2]. In 2005, Ma et al. [3] doubled the critical size of the alloys from 4 to 9 mm by modifying the composition of Mg$_{65}$Cu$_{25}$Y$_{10}$. The optimum composition with the highest GFA was determined to be Mg$_{58}$Cu$_{31}$Y$_{11}$.

Volkert and Spaepen in 1989 [4] reported the changes in the shear viscosity during relaxation in amorphous Pd-based bulk metallic glasses (BMGs). From 1995 to 1997, several studies [5,6] examined the flow behavior of different BMGs and established their temperature and strain rate dependence. The viscous flow phenomenon is associated with the high atomic diffusivity in the supercooled liquid region. A relationship between the non-isothermal viscous flow and the thermal expansion of a glassy alloy has been established using a free volume concept [6]. In 1999, Ye and Lu [7] applied external forces in an attempt to retard the crystallization, thus to raise $\Delta T_x$. However, the effect of pressure became unclear and, in fact, a pressure sometimes was found to enhance crystallization and reduce $\Delta T_x$, for example in the Al and Zr based [8] metallic glasses. In 2001, Myung et al. [9–11] also studied the non-isothermal viscous flow of the Co, Pd and Zr-based glassy alloys in the glass transition range in an attempt to identify the optimum temperature range for secondary processing. However, the majority of these studies were carried out by measuring...
the stress—strain curves at selected strain rates and temperatures using an Instron-type universal testing machine.

There have been only a few attempts to study the viscous flow behavior in BMGs, including Co, Pd, Zr and Mg-based systems, using the thermomechanical analyzer (TMA) under continuous heating conditions [9–13]. For example, Busch et al. [13] reported the thermodynamic analysis and viscous flow in the Mg_{58}Cu_{31}Y_{11} amorphous alloy. Very limited data are available on the effective viscosity and stress related viscous flow behavior in the Mg-based BMGs under TMA compressive pressure. The aim of this study is to explore the viscous flow properties of the Mg_{58}Cu_{31}Y_{11} glassy alloy, and to search the optimum superplastic forming condition.

2. Experimental procedure

The Mg_{58}Cu_{31}Y_{11} (in at%) alloy rod with a diameter of 4 mm was prepared by a copper mold injection casting technique in an argon atmosphere with pure Mg and pre-alloyed Cu–Y ingots as the starting materials. The composition of the samples was verified by using energy dispersive spectroscopy (EDS). The amorphous nature of the as-quenched BMG rod sample was confirmed using X-ray diffractometry (XRD, Siemens D5000) with a monochromatic Cu Kα radiation.

The basic thermal properties were measured in a continuous heating mode with a heating rate of 10 K/min by differential scanning calorimetry (DSC, TA Instruments DSC 2920). The temperature and heat flow of the DSC were calibrated by using pure In and Zn standard samples. Cu pans were used for both the samples and the reference. A thermomechanical analyzer (TMA, Perkin Elmer Diamond) was employed to measure the temperature dependence of the effective viscosity, relative displacement (where the displacement is the absolute value of contraction plus the penetration depth), and steady state viscous flow temperature as a function of applied compression stress and heating rate. Due to the brittle nature of the current Mg_{58}Cu_{31}Y_{11} BMG, compressive mode was used throughout. Stresses of 0.8, 2.4, 7.1, 117.8, and 318.5 kPa were applied by the TMA ceramic flat-end probe which was 3.0 mm in diameter. The test specimens used for TMA measurements were cylindrical rods 4 mm in diameter and 4 mm in length, which correspond to a probe to sample area ratio of 0.56. The heating rate was fixed at 10 K/min, the same as that used for DSC. The effective linear expansion coefficient (α), or the specimen displacement response under the flat-end probe compression was measured in a temperature range of 300–600 K, from which the effective viscosity of the alloy was extracted.

3. Results and discussion

The X-ray diffraction pattern from the as-cast rod Mg_{58}Cu_{31}Y_{11} sample is displayed in Fig. 1, which indicates that the alloy is amorphous. The DSC thermogram of the alloy measured at a heating rate of 10 K/min is shown in Fig. 2. From the DSC curve, it is evident that there is a distinct glass transition with one exothermic crystallization peak and another one for melting peak. The supercooled temperature range is about 66 K. Comparison of the thermal properties is made in Table 1 between the current Mg_{58}Cu_{31}Y_{11} BMG and the classic Mg_{65}Cu_{25}Y_{10} alloy. It can be seen in Table 1 that Mg_{65}Cu_{25}Y_{10} seems to be closer to the ternary eutectic composition with a smaller ΔT_l (=T_1 - T_m, where T_1 and T_m are the liquidus and solidus temperatures, respectively). However, Ma et al. [3] pointed out that a large change of T_l as a result of a minor change in composition, is a result of a steep liquidus slope for a typical deep eutectic. The composition of the best glass former is about 5 at% away from the eutectic point, on the Cu-rich side. In this study, we found that the T_g value (=T_x/(T_g + T_l)) of the Mg_{58}Cu_{31}Y_{11} alloy is not much different from, and actually is slightly smaller than, that of the Mg_{65}Cu_{25}Y_{10} alloy, consistent with another report [3]. However, the γ value (=T_x/(T_g + T_l)) of Mg_{58}Cu_{31}Y_{11} is higher. In fact, the maximum diameter of the Mg_{58}Cu_{31}Y_{11} BMG can reach 12 mm, which is greater than the 7 mm for the Mg_{65}Cu_{25}Y_{10} rod.
Temperature dependence of the relative displacement of the as-cast bulk amorphous Mg$_{58}$Cu$_{31}$Y$_{11}$ alloys measured by TMA operated in a compression mode at various stress levels and a fixed heating rate of 10 K/min is shown in Fig. 3. All curves exhibit a similar trend, except the maximum displacement lengths ($\Delta L_{\text{max}}$) appear to increase with increasing applied stresses. At temperatures below $T_g$, the curves in Fig. 3 show a small positive linear thermal expansion coefficient ($\alpha_\ell$) with an average value of $3 \pm 1 \times 10^{-5}$ m/m K. This can be compared with the $\alpha_\ell = 26 \times 10^{-6}$ m/m K for the pure Mg and $6 \times 10^{-6}$ m/m K for the crystalline Mg$_2$Cu intermetallic phase.

The relative displacements become significant at temperatures greater than $T_g$ indicating the high deformability of the glassy alloy in the supercooled liquid region. The maximum displacements ($\Delta L_{\text{max}}$) occurred in the supercooled liquid region are 60.9, 162.6, 265.3, 748.8, and 923.3 µm (where $\ell_a$ is the original specimen height) of 1.52%, 4.07%, 6.63%, 18.72%, and 23.08% ($\gamma$), respectively, as also listed in Table 2. These displacements correspond to engineering strains ($\varepsilon$), because the alloy readily deformed by the compressive load from the probe at temperatures above $T_g$. At a temperature above $T_g$, the thermal expansion of the soft viscous glass (probably in the order of $\sim 10^{-4}$ m/m K [9]) is expected to be overshadowed by the large viscous compressive strain ranging from 1% to 25%.

The curves of the TMA and the differential thermomechanical analysis (DTMA) measured at a stress of 7.1 kPa are shown in Fig. 4. The DTMA curve is obtained from the derivative of the displacement with respect to time. For the viscous flow, the onset temperature, $T_{\text{onset}}$, the quasi-steady-state or the temperature with the lowest viscosity, $T_{\text{vs}}$, and the finish temperature, $T_{\text{finish}}$, are marked on the TMA and DTMA curves. Note that the so-called “quasi-steady-state” has often been observed in organic glasses in which a nearly constant viscosity is maintained over a wide temperature range. Since the metallic glasses tend to crystallize again at a higher temperature, the quasi-steady-state is difficult to maintain. Instead, a narrow temperature regime with a lowest viscosity is observed; $T_{\text{vs}}$ is defined as the temperature for the peak of the DTMA curve, and is close to the temperature for the minimum viscosity. These characteristic temperatures are listed in Table 2. They are noted to be different from the $T_g$ and $T_x$ obtained from the DSC curve, although both experiments were performed at the same heating rate of 10 K/min. Comparing Tables 1 and 2, it is evident that $T_{\text{onset}}$ (430–450 K) is higher than $T_g$ (413 K) but $T_{\text{finish}}$ (467–475 K) is lower than $T_x$ (479 K). When the BMGs are subjected to superplastic microforming or micro-imprinting, in order to achieve the maximum die filling, the appropriate working temperature is expected to be close to $T_{\text{vs}}$. For the current alloy it is around 460–474 K, depending on the applied stress level.

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**Table 1**

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_g$ (K)</th>
<th>$T_x$ (K)</th>
<th>$\Delta T_x$ (K)</th>
<th>$T_m$ (K)</th>
<th>$T_f$ (K)</th>
<th>$\Delta T_m$ (K)</th>
<th>$\gamma$</th>
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<tr>
<td>Mg$_{58}$</td>
<td>413</td>
<td>479</td>
<td>66</td>
<td>711</td>
<td>754</td>
<td>43</td>
<td>0.547</td>
</tr>
<tr>
<td>Cu$<em>{31}$Y$</em>{11}$</td>
<td>307</td>
<td>462</td>
<td>55</td>
<td>708</td>
<td>738</td>
<td>30</td>
<td>0.551</td>
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</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Applied stress (kPa)</th>
<th>$\Delta L_{\text{max}}$ (µm)</th>
<th>$\Delta L_{\text{max}}/L_0$</th>
<th>$T_{\text{onset}}$ (K)</th>
<th>$T_{\text{vs}}$ (K)</th>
<th>$T_{\text{finish}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>60.9</td>
<td>1.52</td>
<td>450</td>
<td>474</td>
<td>475</td>
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<tr>
<td>2.4</td>
<td>162.6</td>
<td>4.07</td>
<td>447</td>
<td>471</td>
<td>473</td>
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<tr>
<td>7.1</td>
<td>265.3</td>
<td>6.63</td>
<td>431</td>
<td>469</td>
<td>472</td>
</tr>
<tr>
<td>11.7</td>
<td>748.6</td>
<td>18.72</td>
<td>435</td>
<td>466</td>
<td>470</td>
</tr>
<tr>
<td>318.5</td>
<td>923.3</td>
<td>23.08</td>
<td>430</td>
<td>460</td>
<td>467</td>
</tr>
</tbody>
</table>

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![Fig. 3](image-url) Temperature dependence of relative displacement of the bulk amorphous Mg$_{58}$Cu$_{31}$Y$_{11}$ alloys obtained by TMA operated in the compression mode at various stress levels and a fixed heating rate of 10 K/min. Inset is the extraction of the thermal expansion at temperatures below $T_g$.

![Fig. 4](image-url) Typical TMA and DTMA curves measured at a stress level of 7.1 kPa for as-cast bulk amorphous Mg$_{58}$Cu$_{31}$Y$_{11}$ alloys.
By plotting the applied stress and the induced $\Delta L/L_0$ (or the engineering strain), the stress-strain curve can be deduced, as shown in Fig. 5. The curves for $\Delta L/L_0$ extracted from data at $T = T_{\text{onset}}$, $T_{\text{vs}}$, and $T_{\text{finish}}$ have similar appearance, which is typical for viscous flow for supercooled glasses or viscous polymers. The slopes extracted from the intermediate stage are, however, different, being $\sim 29$, 2.7, and 1.3 MPa for $T = T_{\text{onset}}$, $T_{\text{vs}}$, and $T_{\text{finish}}$, respectively. These slopes are often referred to as the moduli of as-cast alloys under the supercooled viscous condition. These values are significantly smaller than the elastic modulus of $\sim 50$ GPa for the rigid Mg–Cu–Y BMGs at room temperature. Specifically, the modulus of the viscous glass at temperatures between $T_x$ and $T_g$ is less than 1/1000 of the modulus of the rigid glass at temperature below $T_g$ (less than 400 K). Accompanied with the drastic decrease in modulus, the stress levels used for the current TMA experiment were noted to be small, all less than 350 kPa, which is 1/1000 smaller than the compression strength of 700–800 MPa for the same amorphous alloy at room temperature. The soft and viscous behavior of the BMG within the supercooled region is obviously favorable for microforming applications. Note that the current induced maximum strain in Fig. 3 approaches $\sim 25\%$ at the applied stress of 318.5 kPa. If a strain of 200% is needed for superplastic microforming of a complicated pattern and shape, the predicted applied stress is about 2–5 MPa at the optimum viscous temperature, $T_{\text{vs}}$.

The effective viscosity value at any temperature during a non-isothermal heating process can be computed from the equation $\eta = \sigma \varepsilon$ where $\sigma$ and $\varepsilon$ are the compressive stress and strain rate, respectively [14]. The temperature dependence of the effective viscosity for the given applied stresses at a heating rate of 10 K/min is shown in Fig. 6. This figure includes data at temperatures higher than $T_g$; the corresponding $T_{\text{vs}}$ and $T_x$ temperatures are also labeled. Below $T_{\text{vs}}$, the effective viscosity of all samples decreases with increasing temperature, with the highest value of effective viscosity ($\sim 10^9$ Pa s) occurring at the largest applied compressive stress (318.5 kPa). Overall, the extracted effective viscosity ranges from $10^7$ to $10^9$ Pa s and increases with increasing applied stress. It is noted that a lower applied stress would produce a lower rate of decrease in viscosity with increasing temperature, namely, it would take longer time to reach the steady state under a lower applied load. Between $T_{\text{vs}}$ and $T_x$, the effective viscosity approached a constant value at each stress level.

The variation of $T_{\text{onset}}$, $T_{\text{vs}}$, and $T_{\text{finish}}$ as a function of the applied stress is shown in Fig. 7. These characteristic temperatures all decrease with increasing applied stress. Myung et al. [11] reported a similar result in a Pd-based amorphous alloy. This result apparently indicates a stress-enhanced crystallization, as demonstrated previously in homogeneous deformation of other BMGs [15]. The accelerated crystallization behavior is expected to affect the microforming operation. For example, if a higher stress is used for forming complicated shapes, the operation must be performed at a lower temperature with a shorter working time.
Temperature dependence of \( \eta \) of alloy liquid including its supercooled liquid region is usually fitted by the Vogel–Fulcher–Tammann (VFT) equation [16],

\[
\eta = \eta_0 \exp\left[D^* (T - T_o)\right]
\]

where \( \eta_0, D^* \) and \( T_o \) are constants. In general, \( \eta_0 \) is a constant corresponding to the minimum viscosity achievable in the system under consideration (or \( \sim 10^{-3} \) Pa s in the current case), \( D^* \) is fragility index, and \( T_o \) is the VFT temperature. The viscosity data on \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11} \), as a function of \( 1/T \), along with the fitted curve in accordance with the VFT equation is shown in Fig. 8. The best fit in Fig. 8 using the iteration method yields \( D^* \approx 25 \) and \( T_o \approx 265 \) K. Also included in Fig. 8 are the viscosity dependence of two non-metallic materials, namely, the oxide glass SiO$_2$ and the organic glass \( \alpha \)-terphenyl. A strong glass former such as SiO$_2$, has a high \( D^* \) value of \( \sim 100 \), a very low VFT temperature, and high melt viscosity. On the other hand, a fragile glass former such as \( \alpha \)-terphenyl exhibits a low \( D^* \) value \( \sim 2 \), a VFT temperature near the glass transition temperature, and low melt viscosity. The current \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11} \) BMG behaves between the strong and fragile glasses.

In fact, the alloy is comparable to the Zr–Ti–Cu–Ni–Be BMG with \( D^* = 7.9–13.8 \) [17]. The lowest viscosity within the viscous flow regime for both the Mg and Zr based BMGs is typically about \( 10^6–10^7 \) Pa s. Both BMGs are much more viscous than pure metals or some binary alloys, in which the viscosity value is about \( 5 \times 10^3 \) Pa s. Busch et al. [13] reported the strong liquid behavior of BMGs, as reflected by the temperature dependence of their viscosity. They pointed out that a high viscosity is indicative of lower atomic mobility and, thus, a sluggish nucleation and growth kinetics for crystalline phases in the supercooled liquid region. In the case of the current \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11} \) amorphous alloy, judging from the measured viscosity ranging from \( 10^7 \) to \( 10^{12} \) Pa s throughout the supercooled liquid region, and the fact that the alloy has a medium \( D^* \) and \( T_o \), it is reasonable to conclude that the present Mg-based BMG behaves like a strong liquid, similar to the Zr–Ti–Cu–Ni–Be alloys.

### 4. Conclusions

In this paper, the viscous flow behavior of an \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11} \) BMG rod, 4 mm in diameter, was characterized using DSC and TMA. The following conclusions are reached.

The glass transition and crystallization temperatures were determined by DSC at a heating rate of 10 K/min to be 413 and 479 K, respectively.

Below \( T_g \), a linear thermal expansion coefficient (\( \alpha_L \)) of about \( 3 \pm 1 \times 10^{-8} \) m/m K was measured. Above \( T_g \), significant viscous deformation occurred as a result of applied compressive load, and the deformation strain increases with increasing applied load.

The onset (430–450 K), quasi-steady-state (460–474 K) and finish temperatures (467–475 K) for viscous flow determined by TMA are dependent upon the applied stress. They all decrease with increasing applied stress.

The onset and finish temperatures for viscous flow determined by TMA are lower than the glass transition and crystallization temperatures determined by DSC, respectively. This difference was caused by the stress-enhanced crystallization during the TMA tests.

The working temperature and time for the microforming of BMG must be properly controlled because of the accelerated crystallization under stresses.

According to the extracted fragility index \( D^* \) and the VFT temperature \( T_o \), the current \( \text{Mg}_{58}\text{Cu}_{31}\text{Y}_{11} \) amorphous alloy is considered to be a sufficiently strong viscous liquid in the supercooled region, similar to the Zr–Ti–Cu–Ni–Be alloys.

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