Viscous Flow Behavior and Workability of Mg-Cu-(Ag)-Gd Bulk Metallic Glasses

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The thermomechanical properties and viscous flow behaviors of the $\text{Mg}_{65}\text{Cu}_{25-x}\text{Ag}_x\text{Gd}_{10}$ ($x = 0, 3, 10$ at%, namely, $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$, and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$) bulk metallic glasses in the supercooled viscous region under the loading condition were investigated using the thermomechanical analyzer. In this study, the supercooled viscous temperature windows, the minimum viscosity, the fragility parameter, and the deformability parameter would all be degraded with increasing Ag addition, leading to the negative factors for the micro-forming and nano-imprinting practices. The base $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ alloy appears to be more promising than the Ag containing alloys when the viscous forming is under consideration. [doi:10.2320/matertrans.MRA2008172]

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1. Introduction

Bulk metallic glasses (BMGs) will display great plasticity in the supercooled liquid region over $T_g < T < T_x$, where T_g is the glass transition temperature and T_x is the crystallization temperature, since the metallic glasses will become viscous melt at temperatures above T_g upon heating.¹⁾ In addition, BMGs also exhibit some unique physical properties such as high strength and elasticity as compared to their corresponding crystalline alloys. Hence, the capability of superplastic deformation over this supercooled temperature region^{2,3)} makes possible to form or emboss into complicated shapes or fine patterns.²⁾ For this purpose, the lower viscosity and higher thermal stability (against crystallization) in the supercooled liquid region of BMGs are the two primary factors necessary to consider for micro-forming or surface imprinting.

In early literatures,^{1,4-9)} the temperature dependence of viscosity of the Zr, Mg, La, and Pd based BMGs has been measured using various techniques to assess the glass fragility. Compared with the Zr, La and Pd based BMGs, Mg based BMGs exhibit sufficiently GFA,^{10,11)} a sufficiently wide supercooled liquid region before crystallization,^{12,13)} and high specific strength.^{14,15)} In addition, the Mg metallic glasses are provided with much lower T_g temperatures in the range of 413–433 K, enabling expediently low working temperatures for micro-forming,¹⁶⁾ thus the flow behaviors around and above T_g in metallic glasses are researched necessarily.

Park *et al.*^{17,18)} and Chang *et al.*¹⁹⁾ have reported that the replacement of Cu by 3–5 at% Ag atoms in the Mg-Cu-Gd(Y) BMG could increase the GFA (maximum diameter from 8 to 11 mm) because of the large difference in atomic sizes between Ag and other constituent elements, and the large negative heat of mixing for Ag-Mg and Ag-Y. The binary pair of Ag and Cu has positive mixing enthalpy, which might cause the change in the atomic bonding structure and provide atomic-scale local inhomogeneity. However, the effects of adding Ag in the Mg based BMGs on the thermomechanical properties and fragility, as well as formability behavior have

not been examined. This paper is focused on this issue using a thermomechanical analyzer.

2. Experimental Procedures

The compositions of the Mg-based metallic glasses examined in the present research are $\text{Mg}_{65}\text{Cu}_{25-x}\text{Ag}_x\text{Gd}_{10}$ ($x = 0, 3, 10$ at%), namely, $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$, and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$. The original ingot of Cu-(Ag)-Gd alloys were first prepared by arc melting high-purity Cu (99.999%), Gd (99.9%) and Ag (99.99%) under a Ti-gettered argon atmosphere. The Mg based BMG rods measuring 4 mm in diameter and 8 mm in length were prepared by injection melting of an appropriate mixture of Mg (99.99%) and Cu-Gd ingot plus silver addition in a boron nitride coated iron crucible under a purified argon atmosphere. The base alloy has a composition of $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ (in atomic percent), and the modified alloys are $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$ and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$, partially replacing Cu by 3 or 10 at% Ag.

The chemical compositions of the Mg-based alloys were analyzed using scanning electron microscopy (SEM, JEOL 6400) linked with energy dispersive spectrometry (EDS). For the structural and thermal analyses, thin specimens with 4 mm in diameter were cut from the as-cast rods. The amorphous nature of the as-quenched BMG rod samples were confirmed using X-ray diffractometry (XRD, Siemens D5000) with a monochromatic Cu-K α radiation. The basic thermal analysis of these amorphous alloys was measured by differential scanning calorimetry (DSC, PYRIS Diamond DSC) to determine the glass transition temperature T_g , crystallization temperature T_x , and the temperature range of the melting endotherm during continuous heating with a heating rate of 10 K/min. The temperature and heat flow of the DSC were calibrated by using pure In and Zn standard samples. The hardness of the samples was measured using a Vicker's Micro-hardness tester (SHIMADZU HMV-2000). The thin specimens with 4 mm in diameter applied a load of 200 g and duration of 15 seconds.

The effective viscosity, effective linear expansion coefficient, and relative displacement as a function of temper-

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ature were measured and calculated by using a thermomechanical analyzer (TMA, Perkin Elmer Diamond TMA 7) under the non-isothermal condition at a heating rate of 10 K/min from 300 to 500 K and an applied compressive load of 50 mN. The TMA was also calibrated by using pure In and Zn samples as standards. Under several compressive loads and temperatures, the displacement data were assembled synchronously upon heating. Using TMA under a constant load of 100, 300, and 500 mN and a constant temperature of $T_g + 0.5\Delta T_x$, the thermal stability under loading or forming of these Mg-based glassy alloys in the supercooled liquid state was evaluated. To prevent from the oxygen pick-up and surface oxidation effect of the tested specimens during the TMA scan as discussed by Yamasaki *et al.*,²⁰ N₂ protective atmosphere is maintained. Since the examined temperature window for the current Mg based BMGs is rather low (within 400 to 500 K), the oxygen contamination effect is considered to be minor.

3. Results and Discussion

3.1 Thermal characteristics

Figure 1(a) indicates XRD patterns taken from the cross-sectional surfaces of the as-cast Mg₆₅Cu_{25-x}Ag_xGd₁₀ ($x = 0, 3, 10$ at%) amorphous alloy rods. DSC traces of the metallic glasses are shown in Fig. 1(b). The samples exhibit a clear glass transition, followed by a broad supercooled liquid region, and the exothermic reactions due to crystallization. Each DSC trace shows two or three exothermic peaks, corresponding to the multiple crystallizations of the initial amorphous structure. The glass transition temperatures T_g are marked by downward arrows on each of the DSC traces. With the addition of silver, T_g slightly increases at $x = 3$ and then decreases at $x = 10$. The crystallization temperatures T_x of the alloys are assigned to be the onset temperature of the first exothermic peak (upward arrows). In this study, the supercooled liquid range $\Delta T_x (= T_x - T_g)$ is seen to decrease from 60 K of the base alloy to around 40–45 K in the Ag-additive alloys (Table 1). The melting solidus temperature of Mg₆₅Cu₂₅Gd₁₀, T_m , and the liquid temperature, T_l , are 679 and 726 K, respectively. With Ag addition, both T_m and T_l are seen to decrease (Table 1). The liquidus temperature range, $\Delta T_l (= T_l - T_m)$, becomes narrower in the Ag-additive alloys, implying that the Ag-additive alloy melt could be quenched into glass more easily, or corresponding to a higher GFA. This trend is the same if we use the reduced glass temperature, $T_{rg} (= T_g/T_l)$, as the GFA parameter, which are 0.565, 0.586, and 0.580 for Mg₆₅Cu₂₅Gd₁₀, Mg₆₅Cu₂₂Ag₃Gd₁₀, and Mg₆₅Cu₁₅Ag₁₀Gd₁₀, respectively (Table 1). This is probably why the addition of Ag was claimed to impose positive effect on GFA of the Mg based BMGs.^{10,11,18,19} However, in terms of the widely accepted γ

Fig. 1 (a) X-ray diffraction patterns of the as-quenched Mg₆₅Cu₂₅Gd₁₀, Mg₆₅Cu₁₅Ag₁₀Gd₁₀, and Mg₆₅Cu₂₂Ag₃Gd₁₀ rod samples. (b) DSC thermograms of the Mg₆₅Cu₂₅Gd₁₀, Mg₆₅Cu₁₅Ag₁₀Gd₁₀, and Mg₆₅Cu₂₂Ag₃Gd₁₀ bulk metallic glasses obtained at a heating rate of 10 K/min.

$[= T_x/(T_g + T_l)]^{21}$ or the new γ_m parameters $[= (2T_x - T_g)/T_l]$,^{22,23} the γ values are 0.414, 0.406, and 0.408, and the γ_m values are 0.730, 0.702 and 0.708 for Mg₆₅Cu₂₅Gd₁₀, Mg₆₅Cu₂₂Ag₃Gd₁₀, and Mg₆₅Cu₁₅Ag₁₀Gd₁₀, respectively, also compiled in Table 1. These two parameters both indicate that the Ag-additive alloys possess inferior GFA, opposite to previous findings. But the DSC results are only for the thermal properties of these alloys, the behavior under loading or forming needs to be explored by TMA. Coupled with the TMA results presented below, it is demonstrated in this study that the Ag addition in Mg-Cu-Gd might not have the promising character as we have expected.

3.2 Thermomechanical analysis and viscous flow behavior

The temperature dependence of the compressive strain curves of the Mg₆₅Cu₂₅Gd₁₀, Mg₆₅Cu₂₂Ag₃Gd₁₀ and

Table 1 Summary of the thermal and thermomechanical properties of the three Mg-Cu-Ag-Gd BMGs, measured by DSC and TMA.

Alloy	T_g (K)	T_x (K)	ΔT_x (K)	T_m (K)	T_l (K)	ΔT_l (K)	T_{rg} (K)	γ	γ_m	T_{onset} (K)	T_{vs} (K)	T_{finish} (K)
Mg ₆₅ Cu ₂₅ Gd ₁₀	410	470	60	679	726	47	0.565	0.414	0.730	428	463	469
Mg ₆₅ Cu ₂₂ Ag ₃ Gd ₁₀	413	454	41	663	705	42	0.586	0.406	0.702	419	449	452
Mg ₆₅ Cu ₁₅ Ag ₁₀ Gd ₁₀	407	452	45	664	702	38	0.580	0.408	0.708	425	457	452

Fig. 2 The compressive strain curves of the $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$, and $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$ bulk metallic glasses with a constant applied load of 50 mN under isochronal heating scan at 10 K/min.

$\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$ BMGs under TMA isochronal heating scan are shown in Fig. 2. The onset temperature T_{onset} is defined as the initial temperature with distinct viscous flow, T_{vs} is defined as the temperature for viscosity at the quasi-steady state or the temperature with the lowest viscosity, and T_{finish} is defined as the finish temperature with viscous flow or the starting temperature for the fully crystallized alloy. These typical TMA temperatures for these three alloys are also listed in Table 1. Note that the viscous flow temperature region under the loading in TMA, $\Delta T_m^* (= T_{\text{finish}} - T_{\text{onset}})$, is 41, 33 and 27 K for $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$ and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$, suggesting that the working window becomes gradually narrower with increasing Ag content. The true compressive strain (ϵ) is calculated by $\epsilon = \ln(l/l_0)$, where l and l_0 are the specimen final and initial length (~ 8 mm), respectively. Usually, there is not evident deformability in the rigid glassy state of BMGs specimens until the temperature is above T_g . During the supercooled region, samples continuously deform with increasing temperature until the primary crystallization occurs. It is demonstrated that the base alloy $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ has a largest deformability with a 6.5% plastic strain, as compared to $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$ and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$, which exhibit lower strains of 2.5 and 0.9%, after the entire temperature scan.

The viscosity, η , is calculated by the Stefan equation²⁴⁾ with the geometrical correction of viscous flow,

$$\eta = (\sigma/3\dot{\epsilon}) \cdot [1 + d_0^2/8l_0^2(1 + \epsilon_n)^2]^{-1}, \quad (1)$$

where σ , $\dot{\epsilon}$, d_0 and ϵ_n are the true stress, strain rate, initial sample diameter, and nominal strain, respectively. In the equation, the true compressive stress σ is calculated using $\sigma = (F/A_0)(l/l_0)$, where F and A_0 are the applied load and initial cross-sectional area (12.56 mm^2), respectively. Note that eq. (1) already assumes the Newtonian flow behavior, with the stress being linearly proportional to the strain rate or with the strain rate sensitivity of 1. In order to confirm the validity of the current data, the applied stress is plotted against the measured strain rate of the isothermally tested specimens under three applied loads of 100, 300 and 500 mN, as shown in Fig. 3. Even with some scattering, the three

Fig. 3 The variation of the applied stress as a function of the measured strain rate for the three alloys tested under the isothermal condition at three load levels of 100, 300 and 500 mN.

Fig. 4 Measured viscosities of the three alloys in the supercooled liquid region at a heating rate of 10 K/min.

alloys all show nearly Newtonian relationship. Thus the use of eq. (1) is logical.

Figure 4 shows the viscosities for the three metallic glasses above the T_g . The viscosity values of these alloys are between from 10^6 to 10^{10} Pa·s, and decreasing initially with increasing temperature and then reaching a minimum. Crystallization is anticipated to take place with continuous heating (particularly under loading for the stress-induced crystallization effect) and viscosity increases. The minima for the three alloys occur at a slightly different temperature, approximately at their corresponding crystallization temperatures. Figure 5(a) shows the viscosities as a function of temperature ($\eta \cdot T^{-1}$) for the three metallic glasses above the T_g . The temperature at the viscosity of 10^{12} Pa·s, T_g^* , is noted to decrease with the Ag addition, as seen in Table 2.

The viscosity trend as a function of temperature of the current Mg-Cu-(Ag)-Gd BMGs is consistent with those for other Mg, Zr and Au BMGs²⁴⁻²⁷⁾ and the η_{min} values are indeed $\leq 10^8$ Pa·s within the supercooled liquid region. In the case of Mg-Cu-(Ag)-Gd BMGs, the η_{min} values,

Fig. 5 (a) Temperature dependence of the viscosity of the $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$, and $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$ bulk metallic glasses, (b) the Angell plots the current three alloys, as compared with $\text{Zr}_{46.5}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ ²⁵⁾ and $\text{Au}_{77}\text{Ge}_{13.8}\text{Si}_{9.4}$ ²⁷⁾ alloys. All experimental results are fitted by the VFT equation.

Table 2 Summary of the fragility and viscous deformation related parameters of the three Mg-Cu-Ag-Gd BMGs.

Alloy	T_g^* (K)	$\eta_{\min}$ (Pa·s)	D^*	T_0 (K)	T_0/T_g	d^*	ΔT_x^*	v_0 (nm ³)	ΔG^m (eV)
$\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$	393	1.5×10^6	~ 15	260	0.662	5.83	0.193	6.90	1.17
$\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$	380	2.6×10^6	~ 16	241	0.634	5.59	0.189	6.78	0.83
$\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$	384	1.4×10^7	~ 20	232	0.604	4.85	0.177	6.49	1.61

obtained at the same isochronal heating rate of 10 K/min, are 1.5×10^6 , 2.6×10^6 , and 1.4×10^7 Pa·s for $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$, and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$ alloys, respectively (Table 2). Judging from the increase of $\eta_{\min}$ from 1.5×10^6 to 1.4×10^7 Pa·s with the addition of Ag content, it is for sure that the Ag addition would cause a negative effect for viscous flow to form over this supercooled temperature region.

All viscosity data calculated in the supercooled liquid can be described well with the Vogel-Fulcher-Tammann (VFT) equation,²⁸⁾

$$\eta = \eta_0 \exp[D^*T_0/(T - T_0)]. \quad (2)$$

Equation (2) represents a formulation of the VFT relation that includes η_0 ($\sim 10^{-5}$ Pa·s), the fragility parameter, D^* , and the VFT temperature, T_0 (at which the viscosity diverges). In general, the strong glass formers, such as SiO_2 , are one extreme, exhibiting a high fragility parameter D^* (~ 100) and very low VFT temperature T_0 , but the fragile glass formers like o-terphenyl, show a low fragility parameter D^* (~ 5) and VFT temperature close to T_g^* . Figure 5(b) is the Angell plot⁴⁾ of Mg-Cu-(Ag)-Gd BMGs and their VFT equation fitting results. The data of $\text{Au}_{77}\text{Ge}_{13.6}\text{Si}_{9.4}$ and

$\text{Zr}_{46.5}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ from the literature^{25,27)} are also included in Fig. 5(b) for comparison. The fragility parameter D^* is found to increase from ~ 15 for the base alloy $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ to 16–20 for the Ag containing alloys, as listed in Table 2. Meanwhile, the VFT temperature, T_0 , is found to decrease from 260 K for the base alloy $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ to 232–241 K for the Ag containing alloys, also listed in Table 2. Both the trends of D^* and T_0 indicate that the $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$ and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$ are relatively closer to the strong glass state. This is consistent with the higher $\eta_{\min}$ values in the Ag-additive alloys.

3.3 Mechanical formability

BMGs are the easier and better forming materials for the special shapes with finer surface-printability or compression die.^{29,30)} Hence, it is important to explore in details the formability and forming temperature range of the metallic glasses under the loading condition. The formability of metallic glasses in the supercooled liquid state can be expressed by a simple deformability parameter, d^* ,²⁴⁾ which has been defined as

$$d^*(\alpha) = \log[\eta(T_g^*)/\eta(T_{\text{finish}}(\alpha))], \quad (3)$$

Fig. 6 Determination of the STZ sizes of the Mg-Cu-(Ag)-Gd alloys based on the TMA data after the correction for coefficient of thermal expansion.

where α is the heating rate, and $\eta(T_{\text{finish}}(\alpha)) = \eta_{\text{min}}(\alpha)$. And another facile parameter $\Delta T_x^* = (T_{\text{finish}} - T_g^*)/T_g^*$,²⁴⁾ represents the supercooled temperature range (forming temperature range) of the BMGs under forming loads. In this study, with $\alpha = 0.167$ K/s, $d^*(\alpha)$ can be obtained based on the information in Fig. 4. And the d^* values are calculated to be 5.83, 5.59 and 4.85, for $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$ and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$, respectively. The forming temperature range ΔT_x^* is calculated to decrease with the Ag addition from 0.193 down to 0.177. The decreasing trends of the deformability parameter d^* and forming temperature range ΔT_x^* in the Ag-containing Mg based BMGs again indicate the degraded properties in terms of superplastic micro-forming or nano-imprinting within the supercooled region.

3.4 Deformation model

The reason for the degraded deformability of the Ag-additive Mg-Cu-Gd metallic glasses during the supercooled state is explored further here. Spaepen³¹⁾ and Argon³²⁾ developed a free-volume model, and the homogeneous deformation for BMGs can be described. The stress-strain-temperature relationship follows:

$$\dot{\gamma} = 2 \exp(-\beta v^*/v_f)(\gamma_0 v_0/\Omega)J \times \exp(-\Delta G^m/kT) \sinh(\gamma_0 v_0 \tau/2kT), \quad (4)$$

where $\dot{\gamma}$ is a shear strain rate, β is the geometrical factor, v_f is the average free volume of an atom, v^* is the effective hard-sphere size of the atom, γ_0 is the shear strain of a shear transition zone (STZ), Ω is the atomic volume, J is the atomic vibration frequency, k is the Boltzmann constant, T is the absolute temperature, τ is the applied shear stress, v_0 is the volume of a flow unit, and ΔG^m is the thermal activation energy. At low stresses and a fixed temperature, eq. (4) can be simplified³³⁾ to

$$\ln(\dot{\gamma}) = (\gamma_0 v_0/2kT)\tau + A, \quad (5)$$

where $A = \ln((\gamma_0 v_0/\Omega)J) - (\beta v^*/v_f) - (\Delta G_m/kT)$ is a constant as function of temperature. The current TMA was conducted under the compressive mode with the corrected strain rate and the measured stress.²⁵⁾ The material constant

Fig. 7 Extraction of the activation energy of the Mg-Cu-(Ag)-Gd alloys during shear deformation within the supercooled temperature region.

$\gamma_0 v_0$ can be determined from the slope in eq. (5), as shown in Fig. 6. The base metallic glass $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ has a slope of about $7.53 \times 10^{-8} \text{ Pa}^{-1}$, and the silver-additive amorphous alloys $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$ and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$ have a slightly lower value of $7.40 \times 10^{-8} \text{ Pa}^{-1}$ and $7.08 \times 10^{-8} \text{ Pa}^{-1}$, respectively. With the value of γ_0 is 0.125,³⁴⁾ the volume of a basic flow unit during shear, v_0 , is calculated to be 6.90, 6.78 and 6.49 nm^3 for $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$ and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$, respectively. Therefore, adding the silver atoms appears to decrease slightly the size of flow unit.

At a low stresses and a fixed strain rate, eq. (4) can also be simplified to

$$\tau = BT + (2\Delta G^m/\gamma_0 v_0), \quad (6)$$

where $B = (2k/\gamma_0 v_0)[\ln \dot{\gamma} - \ln((\gamma_0 v_0/\Omega)J) + (\beta v^*/v_f)]$ is a strain rate dependent constant. The thermal activation energy of a single STZ, ΔG^m , can be determined from the intercept of eq. (6), as shown in Fig. 7 for a representative strain rate of $4 \times 10^{-4} \text{ s}^{-1}$. The extracted thermal activation energy, ΔG^m for $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$ and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$ are 1.17, 0.83 and 1.61 eV, respectively. It should be noted that the extraction of the activation energy needs to use the extrapolation method to cover a wider temperature range, which might lead to higher uncertainty. The wider scattering of the extracted activation energy data makes it difficult to reach conclusive judgment. But it is likely that, with abundant Ag addition to 10 at%, the thermal activation energy of a single STZ during the viscous flow of $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ would increase.

Based on the above analyses, the Mg based amorphous alloys, such as $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$, are attractive along this line owing to their low price (compared with Pd, Pt, or Zr-based BMGs), the lower forming temperature (~ 423 K), lower viscosity ($\sim 10^6 \text{ Pa}\cdot\text{s}$), and promising workability. With the addition of Ag, the supercooled viscous temperature window for micro-forming would become narrower, the minimum viscosity level would be higher, and the deformability parameter becomes lower. In other words, with the consideration of micro-forming or nano-imprinting, the Ag additive Mg based BMGs are not as promising as the Ag-free alloys.

4. Conclusions

The thermal and thermomechanical properties of the $\text{Mg}_{65}\text{Cu}_{25-x}\text{Ag}_x\text{Gd}_{10}$ ($x = 0, 3, 10$ at%, namely, $\text{Mg}_{65}\text{Cu}_{25}\text{-Gd}_{10}$, $\text{Mg}_{65}\text{Cu}_{22}\text{Ag}_3\text{Gd}_{10}$, and $\text{Mg}_{65}\text{Cu}_{15}\text{Ag}_{10}\text{Gd}_{10}$) bulk metallic glasses are examined in the supercooled liquid region using DSC and TMA. The following conclusions are reached based on the current experimental and analytical results:

- (1) In this study, the addition of Ag into Mg-Cu-Gd would degrade slightly the glass forming ability in terms of the γ and γ_m parameters.
- (2) The supercooled viscous temperature windows, irrespective of the $\Delta T_x (= T_x - T_g)$ measured from DSC, the $\Delta T_m^* (= T_{\text{finish}} - T_{\text{onset}})$ measured from TMA, or the $\Delta T_x^* = (T_{\text{finish}} - T_g^*)/T_g^*$ extracted from the analysis, all show to be narrower with the addition of Ag, leading to the negative factor for forming practices.
- (3) The minimum viscosity η_{min} and the fragility parameter D^* would both increase with increasing Ag addition, suggesting the stronger glass nature. As a consequence, the deformability parameter d^* would also decrease accordingly, leading to another negative factor for the forming purpose.
- (4) The current results suggest that the Mg based BMGs are promising candidates for micro-forming or nano-imprinting over the supercooled viscous regime. But under the loading condition during forming, the Ag-containing Mg BMGs are less promising as compared with the base $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ alloy.

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