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ORIGINAL REPORT



Unusual relation between glass-forming ability and thermal stability of high-entropy bulk metallic glasses

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ABSTRACT

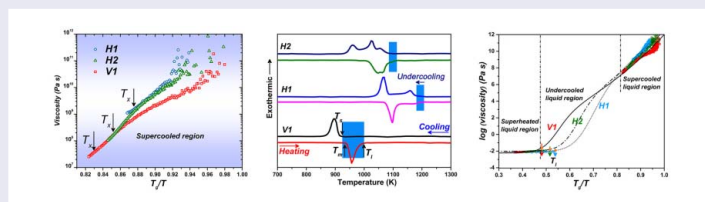
It is generally accepted that good glass formers have a high thermal stability against crystallization upon heating. In this paper, we report an unusual relationship between thermal stability and glass-forming ability (GFA) for high-entropy bulk metallic glasses (HE-BMGs). As compared with their conventional counterparts in the same alloy system, the HE-BMGs have a lower energy barrier for atomic diffusion during undercooling, which facilitates crystallization and then reduces the GFA. Our results clearly demonstrate that the GFA of BMGs is governed by the kinetics of the undercooled liquid, whilst their thermal stability is controlled by atomic diffusion in the glass-transition regime.

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KEYWORDS

High-entropy bulk metallic glasses; thermal stability; glass-forming ability; viscosity; fragility



IMPACT STATEMENT

The undercooled liquid behavior of HE-BMGs plays a key role in determining glass formation, but the thermal stability is controlled by the atomic rearrangement in glassy solid state.

1. Introduction

High-entropy alloys (HEAs) are defined as the alloys containing four or more elements in equimolar or near-equimolar ratios [1]. Recently, high-entropy bulk metallic glasses (HE-BMGs) have been developed, which exhibit a unique combination of promising properties, such as high strength and excellent corrosion resistance, due to their equimolar or near-equimolar ratios of constituents combined with amorphous structures. In comparison with conventional BMGs, HE-BMGs in the same alloy system usually exhibit higher stability against crystallization upon heating [2]. For example, the $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMG shows higher activation energy for crystallization (i.e. 281 kJ/mol) and much more sluggish growth of the crystallized phases when compared with its conventional BMG counterpart Vitreloy1 (i.e. 165 kJ/mol) [2]. It is known that glass

formation is a competitive process between an amorphous phase and the competing crystalline phases [3]. Therefore, the glass with large thermal stability against crystallization is generally believed to have good glass-forming ability (GFA) [4]. In light of this wisdom, HE-BMG alloys are expected to possess better GFA than their conventional BMGs consisting of the same constituents. However, this is not the case as reported in our previous work; the $\text{Be}_{20}\text{Cu}_{20}\text{Ni}_{20}\text{Ti}_{20}\text{Zr}_{20}$ HE-BMG was found to have the worse GFA [5,6] (the maximum attainable diameter for glass formation, d_{max} , is less than 3 mm) with respect to its BMG counterpart Vitreloy1 ($d_{\text{max}} > 20$ mm) [7]. This unusual relationship between thermal stability and GFA is indeed a common phenomenon observed in HE-BMGs. In other words, the GFA decreases, while the thermal stability increases substantially, when the conventional BMG alloys are

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extended to the HE-BMG alloys with equimolar constituents.

Based on our previous work [2], in this letter, we made an in-depth analysis on the relation between thermal stability and GFA of HE-BMGs and tried to understand the GFA of HE-BMGs from a new perspective. This correlation can provide a good guideline for designing BMGs with appropriate thermal stability and GFA for practical applications, especially at elevated temperatures.

2. Experimental methods

Two typical HE-BMGs, i.e. ZrTiCuNiBe (H1) and ZrTiHfCuNiBe (H2) [6] were selected to compare with their benchmark BMG Vit1 (i.e. $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$, denoted as V1 hereafter). These BMG rods with a diameter of 3 mm and a length of about 30 mm were prepared by copper-mold suction casting. The onset temperature of glass transition and crystallization was measured by using the Netzsch DSC 404 F1 differential scanning calorimeter (DSC) at various heating rates. The melting and solidification behaviors of the BMGs were characterized by DSC at a heating/cooling rate of 10 K/min. The tensile creep tests were conducted by a dynamic mechanical analyzer (TA, DMA Q8000) under nitrogen atmosphere and a constant stress of 5 MPa to obtain viscosity information. The samples used for the DMA measurements are thin wires with a diameter of 0.1 mm and a length of 25 mm. High-temperature melt viscosity measurements were accomplished with an oscillating viscometer. The samples were placed in a vessel hung by a torsional suspension, and the vessel was set in oscillation around a vertical axis, the resulting motion was gradually damped on account of frictional energy absorption and dissipation within the melt [8]. The samples sealed in a vacuum of 10^{-1} Pa were overheated to 250 K above their liquidus temperatures and held at the temperature for 30 min. Then the samples were cooled to the studied temperature and held for 20 min before the viscosity measurement. At each temperature, the viscosity was measured three times.

3. Results and discussion

3.1. Viscosity in supercooled liquid region

It is known that the viscosity and fragility in supercooled liquid regions of BMGs are two important parameters to associate with GFA. Therefore, these two parameters were measured to understand kinetic behavior of the supercooled liquid of HE-BMGs and then to understand the unusual relation between GFA and thermal stability of HE-BMGs. Figure 1 exhibits the viscosity as a function

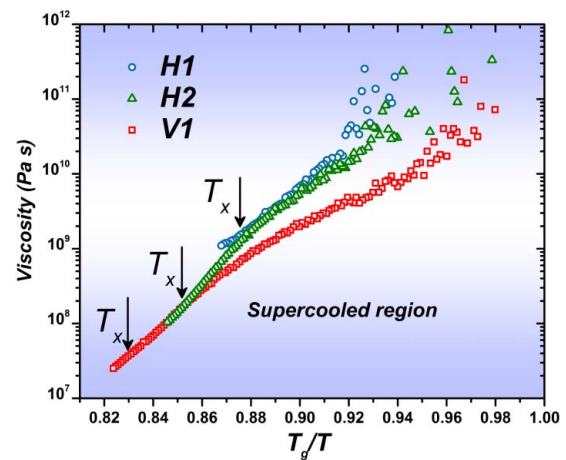


Figure 1. Viscosity measured by the tensile creep technique performed at a heating rate of 5 K/min and under a constant stress of 5 MPa. The temperature was normalized to the T_g value measured at the same heating rate.

of temperature for H1 and H2, in comparison with that of the traditional BMG V1. By loading the sample in a constant tension stress and measuring the strain change with time, the viscosity can be calculated from [9]:

$$\eta = \sigma / 3\dot{\epsilon}, \quad (1)$$

where σ and $\dot{\epsilon}$ are the tensile stress and the strain rate [10], respectively. As the temperature increases above T_g , the viscosity decreases by several orders of magnitude, reflecting the softening of the BMGs in their supercooled liquid regions. The large viscosity of supercooled liquid corresponds to the high thermal stability since it implies sluggish kinetics in this temperature region [11]. As shown in Figure 1, the HE-BMGs show the larger viscosity in its supercooled liquid region, indicating that the HE-BMGs possess more sluggish kinetics upon heating, which is consistent with our previous study [2].

3.2. Fragility parameter in the supercooled liquid region

It is well known that the temperature span of glass transition is a function of heating rate, and the heating rate dependence of the kinetic glass transition is a measure for the fragility of a glass [12,13]. A glass with a small heating rate dependence of glass transition is termed as a “fragile” glass, while a large heating rate dependence is characteristic of a “strong” glass [12]. Figure 2 shows the relation between the inverse heating rate and the onset temperature of glass transition (T_g). The data are fitted with the Vogel-Fulcher-Tammann (VFT)-type equation

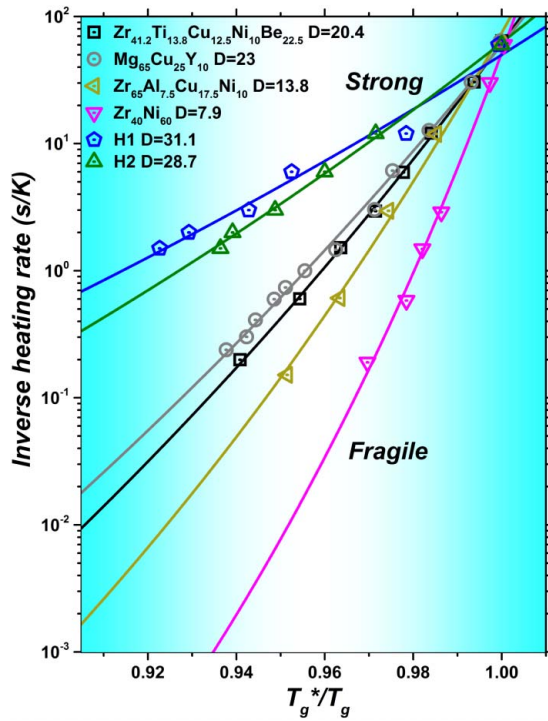


Figure 2. Relation between inverse heating rate and T_g^*/T_g . T_g^* is the T_g value measured at the rate of 0.1667 K/s. The data for other MGs from Ref. [11] were selected for comparison.

[14], as follows:

$$\tau = \tau_0 \times \exp\left(\frac{D^* \times T_0}{T_g - T_0}\right), \quad (2)$$

where τ is the inverse heating rate, D^* is the fragility parameter, and T_0 is the VFT temperature where the flow barrier would go to infinity. Figure 2 shows the results for H1 and H2 HE-BMGs, in comparison with those of other typical metallic glasses (MGs) [11]. The best fit of the experimental data yields $D^* = 31.1$ and $T_0 = 313$ K for H1 and $D^* = 28.7$ and $T_0 = 346$ K for H2. In comparison with V1 ($D^* = 20.4$) and other BMGs [11], the current HE-BMGs show a similar behavior to the strong glasses in terms of their larger fragility parameter D^* .

As shown in Figure 1, the viscosity of the HE-BMG supercooled liquids is much higher than that of V1. For example, the viscosity at $T_g/T = 0.92$ is 2.8×10^{10} Pa s for H1 and 1.4×10^{10} Pa s for H2, one order of magnitude higher than that of V1 ($\sim 4.6 \times 10^9$ Pa s). Moreover, the

crystallization activation energies E_x of the HE-BMGs are higher than that of V1 [2]. These data indicate that the HE-BMGs have higher thermal stability against crystallization upon reheating, which is consistent with thermal stability parameters including the larger fragility D^* , higher T_g and crystallization temperature T_x , as listed in Table 1. Nevertheless, the width of supercooled liquid region $\Delta T_x = (T_x - T_g)$ shows a contradictory trend with the higher thermal stability for HE-BMGs, i.e. ΔT_x of H1 and H2 is smaller than that of V1. The smaller ΔT_x for the HE-BMGs is mainly attributed to the remarkable increase in T_g (~ 50 K), as compared with the V1 BMG. In general, MGs possessed high thermal stability upon reheating usually exhibit superior GFA. However, this is not the case for the HE-BMG, as evidenced by their small $d_{\max}$ values (Table 1).

Glass formation always occurs during undercooling of glass-forming liquids, i.e. within the temperature range between T_g and the liquid temperature T_l . Figure 3 shows the melting and solidification curves of the HE-BMGs and V1. As can be seen, both of the HE-BMGs show multiple endothermic melting peaks upon heating while V1 exhibits only a single peak, indicating that these two HE-BMG alloys are far away from their eutectic compositions. In addition, the onset melting temperature T_m of V1 is around 941 K, much lower than that of H1 and H2 (i.e. 1079 and 1015 K, respectively), as demonstrated in Table 1. From these melting curves, it is clear

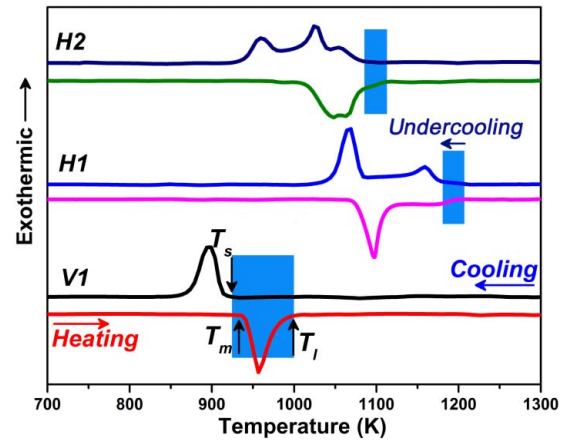


Figure 3. Melting and solidification curves of HE-BMGs and V1 alloys at the rate of 10 K/min.

Table 1. The fragility parameter, D^* ; the width of supercooled liquid region, ΔT_x ; glass-transition temperature, T_g ; crystallization temperature, T_x ; reduced glass-transition parameter, T_{rg} ; critical diameter, $d_{\max}$; melting temperature, T_m ; liquid temperature, T_l , the solidus temperature, T_s ; and the degree of undercooling, $\Delta T_L (= T_l - T_s)$.

Alloys	D^*	ΔT_x	T_g	T_x	T_{rg}	T_m (K)	T_l (K)	T_s (K)	ΔT_L	$d_{\max}$ (mm)
V1	20.4	73	628 [2]	701 [2]	0.627	941	986	919	67	> 20 [7]
H1	31.1	41	691 [2]	732 [2]	0.578	1079	1193	1166	27	3 [5]
H2	28.7	62	681 [2]	743 [2]	0.583	1015	1112	1076	36	15 [6]

that the composition of alloy V1 is close to a much “deeper” eutectic in the Zr–Ti–Cu–Ni–Be system, whilst the HE-BMGs are associated with high-temperature non-eutectic. It is well accepted that the “deep” eutectic alloys often have better GFA based on the framework of phase competition [15]. In addition, the solidus temperature T_s , i.e. the starting temperature for forming primary crystalline phase during cooling, of V1 is 919 K, much lower than that of H1 and H2 (see Table 1). It is clear that V1 has a larger degree of undercooling ΔT_L value than H1 and H2, its liquid is more thermally stable during cooling and is therefore has higher GFA.

Moreover, the T_{rg} parameter is often used to evaluate the GFA of MGs and reflects the stability of undercooled liquids [16,17]. The larger $T_{rg}(=T_g/T_l)$ value corresponds to the higher stability of liquids, which is beneficial to the glass formation, i.e. the better GFA [18]. In our case, the V1 BMG has the highest T_{rg} value of 0.627, indicating that it possesses the highest stability to inhibit crystallization during cooling. The relatively lower T_{rg} for H1 and H2 implies that the HE-BMGs are featured with lower thermal stability upon cooling, leading to a poorer GFA. These results demonstrate that the HE-BMGs indeed possess high thermal stability during reheating, but apparently are not favorable for glass formation in terms of their liquid stability and phase competition scenario.

3.3. Viscosity in the superheated liquid region

According to our above results, the unusual phenomenon between high thermal stability and poor GFA for the HE-BMGs is probably originated from different mechanisms controlling glass formation during cooling and thermal stability upon heating. To verify this speculation, the viscosity of superheated liquids as a function of temperature was measured by an oscillating viscometer from the temperature of 250 K above T_l to T_l (i.e. the superheated state) and the results are shown in Figure 4(a). As shown, the viscosity of H1 and H2 is $9.4 (\pm 0.5)$ mPa s and $12.3 (\pm 0.5)$ mPa s at their liquidus temperatures of 1196 and 1112 K, respectively, much lower than that of V1 ($14.7 (\pm 0.3)$ mPa s). The Arrhenius equation is often adopted to describe the metallic viscosity at superheated temperatures [19],

$$\eta = \eta_0 \exp\left(\frac{E}{RT}\right), \quad (3)$$

where η_0 is the pre-exponential viscosity, T is the temperature, R is the gas constant ($8.314 \text{ J}/(\text{mol}\cdot\text{K})$), and E is the activation energy which is the required energy to move flow unit from one balanced position to another one in the melt [20]. The measured

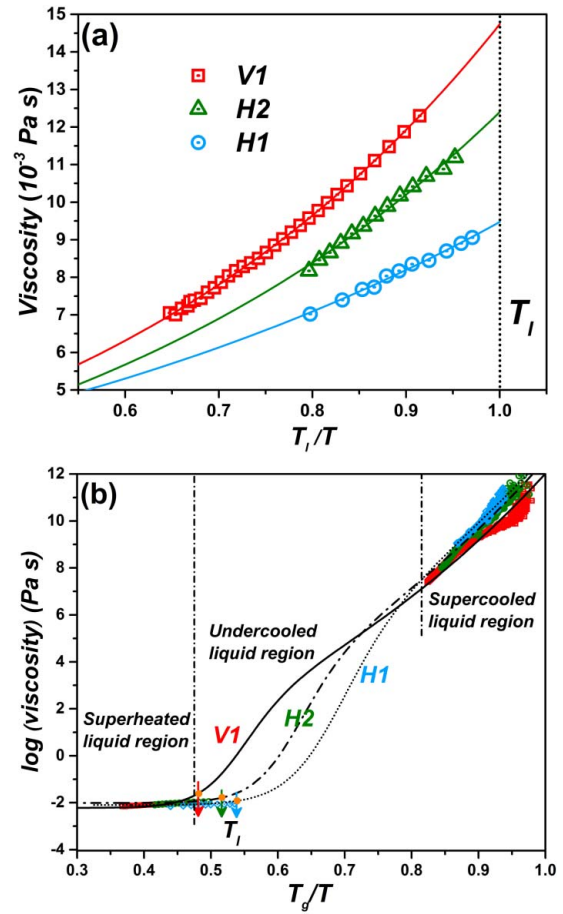


Figure 4. (a) The viscosity of superheated liquid as a function of T_l/T . (b) Viscosity of V1, H1 and H2 BMGs as a function of the T_g/T . The solid and dash lines show a sketch of the undercooled liquid region for the three types of BMGs.

data for these alloy melts well obey the Arrhenius equation. The solid curves represent the fitting of the experimental data according to Equation (3). The values of the fitting parameters η_0 and E for the alloys are also listed in Table 2. The HE-BMGs exhibit a lower viscosity η_L ($9.4 \times 10^{-3} \text{ Pa s}$) at T_l and lower activation energy E ($13.9 \pm 0.4 \text{ kJ/mol}$) for viscous flow, as compared with V1 with $\eta_L = 14.7 \times 10^{-3} \text{ Pa s}$ and $E = 17.3 \pm 0.1 \text{ kJ/mol}$. According to the Stokes–Einstein equation [21,22], $D_{\text{eff}} = kT/3\pi\eta a$, where D_{eff} is the diffusion coefficient, a is atomic distance, k is the Boltzmann constant, and η is the viscosity of the liquid. The reduction of liquid viscosity would promote atomic diffusion and rearrangement, thus enhancing the possibility of nucleation and growth of crystalline phases and reducing the GFA. Although HE-BMGs have higher thermal stability and sluggish atomic diffusion in supercooled liquid region, it seems that the high-entropy effects cannot stabilize the high temperature melt but decrease GFA.

In fact, glass formation is closely related to the temperature range between T_g and T_l during the cooling of

Table 2. Viscosity at the liquid temperature, η_L ; pre-exponential viscosity, η_0 ; activation energy for viscosity flow, E ; and the optimized viscosity parameters, W_1 , W_2 , C_1 , and C_2 obtained by fitting Equation (4).

Composition	η_L (10^{-3} Pa s)	η_0 (10^{-3} Pa s)	E (kJ/mol)	$\log \eta_\infty$ (Pa s)	W_1	C_1	W_2	C_2
V1	14.7 ± 0.3	1.77	17.3 ± 0.1	-2.13	2552	16559	0.00038	613
H1	9.4 ± 0.5	2.22	13.9 ± 0.4	-2.15	5542	18076	0.00044	951
H2	12.3 ± 0.5	1.95	15.7 ± 0.2	-1.95	3887	15401	0.00036	724

liquids (i.e. the undercooled state), but it is difficult to directly characterize any properties of these undercooled liquids due to the occurrence of crystallization. Nevertheless, the viscosity of the undercooled liquids can be estimated by a model based on the extension of MYEGA expression [24,25]:

$$\log \eta = \log \eta_\infty + \frac{1}{T \left[W_1 \exp \left(-\frac{C_1}{T} \right) + W_2 \exp \left(-\frac{C_2}{T} \right) \right]}, \quad (4)$$

where C_1 and C_2 are two constraint onset conditions of two different structural mechanisms caused by the floppy-to-rigid transitions, W_1 and W_2 are normalized weighting factors, and η_∞ is a pre-exponential factor, which is the viscosity at infinite high temperature. When $C_1 = C_2$, the standard three-parameter MYEGA expression is recovered [24]. The fitting parameters are listed in Table 2. Figure 4(b) shows the estimated viscosity data of the HE-BMGs and V1. It can be seen that Equation (4) is capable for describing the viscosity behavior for both supercooled and superheated liquids. As is evident in Figure 4(b), when the liquid is cooled, a fragile to strong transition occurs, and the viscosity increases with decreasing temperature. For example, the viscosity of V1 increases much quicker and becomes much higher than that of HE-BMGs, which is consistent with the previous report that an order-disorder transition exists from the supercooled liquid region to the liquid state above T_l in V1 [23]. The higher viscosity at the undercooled state could stabilize the melt and favors glass formation. Therefore, the lower viscosity of the undercooled HE-BMGs suggests that the HE-BMGs are kinetically less stable and have faster atomic diffusion during cooling, leading to easier crystallization and smaller GFA.

Based on the above results, the high-mixing entropy can retard atomic diffusion upon reheating of glassy solids, leading to a sluggish crystallization kinetics and thus high thermal stability. However, high-mixing entropy cannot effectively stabilize the undercooled liquids. According to the Adam-Gibbs model [26], $\eta = \eta_0 \exp(A/TS)$ (where A is a constant and η_0 is a reference dynamic viscosity coefficient at one atmosphere pressure), a larger mixing entropy would result in a smaller liquid viscosity, which is consistent with the measured viscosity of superheated melts, i.e. the HE-BMGs have

the lower viscosity above T_l with respect to the conventional V1 BMG. Clearly, high-mixing entropy has great impact on both thermal stability and GFA of MGs. The implication of this finding is that one can balance the GFA and thermal stability through regulating the entropy effect during alloy design.

Therefore, the decisive mechanisms of GFA and thermal stability in BMGs are different. The high-mixing entropy can retard atomic diffusion upon reheating of glassy solids, leading to a sluggish crystallization kinetics and thus high thermal stability. However, GFA is dictated by the stability of undercooled liquids, which is strongly dependent on alloy composition. It seems that the high-mixing entropy cannot effectively stabilize the undercooled liquids of HE-BMGs. The low viscosity of the high-entropy undercooled liquids facilitates crystallization and hinders the glass formation.

4. Conclusions

In summary, the unusual relation between thermal stability and GFA in the HE-BMGs was revealed by measuring the fragility and viscosity data upon heating. The fragility and viscosity of the supercooled liquid suggest that the HE-BMGs are strong liquid, and the high-mixing entropy can effectively enhance thermal stability of glassy solids. Nevertheless, the melting solidification behavior and the viscosity data of the undercooled HE-BMG liquids uncover that the fast atomic diffusion and low activation energy for viscous flow facilitate crystallization and reduce the GFA. Our findings confirm that GFA is mainly governed by the liquid properties at the undercooled state, but the thermal stability is controlled by the atomic rearrangement in glassy solid state. Therefore, the undercooled liquid behavior during cooling plays the key role in determining glass formation, and careful attention should be paid when using the fragility and viscosity derived from the heating process to assess GFA of BMGs.

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