Thermodynamic determination of fragility in La-based glass-forming liquid

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Differences in the thermodynamic functions between the liquid and crystalline states of La-based bulk metallic glasses alloys were calculated with the specific heat capacity C_p and the fusion heat ΔH_f , which we measured. Fragility indexes having different thermodynamic definitions were calculated from the temperature dependence of excess entropy $\Delta S^{\text{liq-cry}}$. It is ambiguous for La-based glass-forming liquid to evaluate fragility from the intercepts of $\Delta S^{\text{liq-cry}}$ -temperature curves. We found that the thermodynamic fragility M_{AS} , denoted ΔS , decreases at the onset melting temperatures T_m rather than at glass transition temperatures T_g , and relates linearly with the kinetic fragility m . The correlations between thermodynamic fragility and kinetic fragility are discussed within the frameworks of the Adam-Gibbs relationship and potential energy landscape theory.

thermodynamics, fragility, La-based bulk metallic glasses, heat capacity

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The concept of liquid fragility has been widely used to classify the dynamic behavior of glass-forming liquids since first being introduced by Angell in 1985 [1]. According to the concept, glass-forming liquids are classified between two extremes: strong glass formers showing Arrhenius behavior and fragile glass formers that deviate from Arrhenius behavior. However, the fragility parameter m can only be calculated for systems with stable undercooled liquid. Recently, a new concept, the fragility of superheated melts M , defined as the rate of variation of the viscosity of superheated liquids towards the liquidus temperature, was proposed by Bian et al. [2]. A negative correlation between M and glass-forming ability (GFA) has been found in Al-based [2–4] and rare-earth-based alloy systems [5,6]. Moreover, the correlation between m and M has also been investigated [3,7].

The two fundamental aspects of phase transition are thermodynamics and dynamics. The Kauzmann paradox

suggests that the two are inherently related [8]. The Adam and Gibbs model [9], which is based on cooperatively relaxing regions in supercooled liquids, provided the first quantitative relation between the thermodynamic and kinetic properties of a liquid. Several attempts to correlate the fragility (the kinetic property) of supercooled liquids with thermodynamic behaviors have been made, and have mainly focused on changes in heat capacity [10] and entropy [11–14]. However, the thermodynamic fragility of metallic glasses has not been investigated systematically [11,14–17].

Heat capacity is the most fundamental thermodynamic nature of matter. In this paper, the specific heat capacity of six La-based bulk metallic glasses (BMGs) is measured for the crystalline solid, the supercooled liquid, and the superheated liquid. The differences in thermodynamic functions between the liquid and the crystalline states are calculated. With these data, the thermodynamic fragilities defined previously [12,14] are calculated and new thermodynamic fragility indexes are proposed to investigate the interconnection of thermodynamics and kinetic fragility.

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1 Experimental procedure

Ingots with nominal compositions of $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ (La-1), $\text{La}_{55}\text{Al}_{25}\text{Ni}_{15}\text{Cu}_5$ (La-2), $\text{La}_{55}\text{Al}_{25}\text{Ni}_5\text{Cu}_{15}$ (La-3), $\text{La}_{60}\text{Al}_{10}\text{Cu}_{20}\text{Ni}_{10}$ (La-4), $\text{La}_{55}\text{Al}_{25}\text{Cu}_{10}\text{Co}_5\text{Ni}_5$ (La-5), and $\text{La}_{62}\text{Al}_{14}\text{Cu}_{12}\text{Ni}_{12}$ (La-6) were prepared by arc-melting with 99.9 wt%–99.999 wt% pure Al, Co, Cu, Ni and industrially pure La in a Ti-gettered argon atmosphere. To ensure the homogeneity of the samples, the ingots were remelted at least three times in addition to being electromagnetically whisked. BMG rods with a diameter of 2 mm and a length of 50 mm were prepared by copper-mould suction casting in an arc furnace. The amorphous structure (except in the case of La-1) of the transverse cross sections of the rods was identified by X-ray diffraction using a D/Max-rB diffractometer and $\text{Cu K}\alpha$ radiation.

A Netzsch DSC404 differential scanning calorimeter (DSC) was used to determine the characteristic temperature and the specific heat capacity of the alloys. For heat-flux differential scanning calorimetry, the resultant signal is expressed as

$$Q = K \cdot \text{DSC} = C_p \cdot m \cdot HR, \quad (1)$$

where K is the sensitivity coefficient, DSC is the measurement result, C_p is the specific heat capacity of unit mass, m is the sample mass and HR is the heating rate. With the same heating rate HR , the measured absolute heat flow minus the baseline (the heat flow of the pan itself) is directly proportional to the heat capacity ($C_p \cdot m$), and it can be expressed at a certain temperature as

$$\frac{Q_{\text{sam}} - Q_{\text{pan}}}{Q_{\text{std}} - Q_{\text{pan}}} = \frac{C_p(T)_{\text{sam}} \cdot m_{\text{sam}}}{C_p(T)_{\text{std}} \cdot m_{\text{std}}}, \quad (2)$$

where m is the mass in the unit of grams and C_p is the specific heat capacity in the unit of Joules per gram per degree Kelvin. The subscripts sam, std and pan indicate the metal sample, the sapphire standard and the sample pan respectively.

At a heating rate of 20 K/min, by successively performing calorimetric measurements on a sample pan by itself, on a sapphire standard in the sample pan and on the metal sample in the sample pan, the absolute specific heat capacity of the metal sample is determined according to

$$C_p(T)_{\text{sam}} = \frac{(Q_{\text{sam}} - Q_{\text{pan}}) \cdot C_p(T)_{\text{std}} \cdot m_{\text{std}}}{(Q_{\text{std}} - Q_{\text{pan}}) \cdot m_{\text{sam}}}. \quad (3)$$

The mass of each sample is approximately 30 mg. The amorphous rods were heated nearly to their melting temperatures T_m , determined beforehand using the DSC, for C_p measurements and then cooled to room temperature freely to form the crystallized samples. The crystallized samples were heated to ~200 K above starting melting temperatures to obtain the specific heat capacity of both the crystallized

solid and liquid metals. During heating, all samples were first heated to 373 K and held isothermally for 10 min and then heated at a constant rate of 20 K/min for C_p measurements. Each experiment was carried out under a high-purity argon atmosphere.

2 Results

2.1 Thermodynamics

Upon heating the amorphous alloys at a constant rate, the alloys go through glass transition, crystallization, and fusion. Such behavior of $\text{La}_{55}\text{Al}_{25}\text{Ni}_5\text{Cu}_{15}$ (La-3) is shown in Figure 1 as an example. By integrating the area of the melting event (from solidus temperature T_m to liquidus temperature T_l), the total heat of fusion ΔH_f is calculated. The entropy of fusion can then be estimated as $\Delta S_f = \Delta H_f / T_f$. T_f is the temperature at which the Gibbs free energy of the crystal is equal to that of the liquid. T_f between T_m and T_l is likely to be very close to the melting start temperature T_m . Thus, T_m is adopted as T_f in calculating ΔS_f . The characteristic temperatures and the heats and entropies of fusion of these La-based alloys are summarized in Table 1. T_g of La-1, for which we did not obtain a fully amorphous rod, is cited from [18]. There are slight differences in characteristic temperatures between our work and [18–21], as is usually the case for different raw materials and laboratory facilities.

The measured specific heat capacity is shown in Figure 2. The heat capacity of glass is similar to that of crystal at low temperatures. However, when heated above the glass transition temperature T_g , the glass phase relaxes into the supercooled liquid state and its C_p value assumes the higher heat capacity of a liquid [22]. Inoue et al. [21] and Lu et al. [20] reported that the specific heat capacity of $\text{La}_{55}\text{Al}_{25}\text{Ni}_{10}\text{Cu}_{10}$ alloy is 42.0 and 39–41 $\text{J mol}^{-1} \text{K}^{-1}$ respectively throughout the undercooled liquid region; our measurement results are similar. C_p values for several La-based BMGs have so far been reported [21]; however, this is the first time that C_p for

Figure 1 DSC heat flow curve of La-3 at a heating rate of 20 K/min.

Table 1 Characteristic temperatures and the heats and entropies of fusion of La-based alloys

Alloys	T_g (K)	T_m (K)	T_l (K)	ΔH_f (kJ mol ⁻¹)	ΔS_f (J mol ⁻¹ K ⁻¹)	T_k (K)
La-1	491 ^{a)}	700	950	7.612	10.9	339
La-2	447	661	873	6.220	9.41	343
La-3	433	656	828	7.043	10.7	320
La-4	412	680	773	7.948	11.7	329
La-5	492	665	887	7.744	11.6	356
La-6	410	671	758	8.084	12	292

a) From Ref. [18].

Figure 2 DSC heat capacity measurements obtained from initially liquid ($\star$), crystalline ($\square$) and glassy ($\triangle$) samples, and the fitting lines of eq. (4) (solid lines) and eq. (5) (dashed lines). For La-1, the glassy data were not measured, but a value of 40 J mol⁻¹ K⁻¹ at 500 K, 10 K higher than T_g , was assigned to allow the determination of the fitting constant for the liquid specific heat capacity ($\blacktriangle$).

the both supercooled liquid and the melts has been measured to ensure fitting of the following eq. (5).

The heat capacity of a crystal well above the Debye

temperature can be described by [23]

$$C_p^{\text{cry}}(T) = 3R + aT + bT^2, \quad (4)$$

and the heat capacity of a liquid can be described by

$$C_p^{\text{liq}}(T) = 3R + cT + dT^{-2}, \quad (5)$$

where the gas constant $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$, and a , b , c and d are fitting constants. The fitting curves and T_m and T_l are shown in Figure 2. If an equilibrium liquid continuously cools to a supercooled liquid without solidification, which is required in glass formation, C_p does not abruptly change and the C_p curve throughout the equilibrium and supercooled range coincides with eq. (5) [21,24–27]. Table 2 summarizes the fitting constants for both eqs. (4) and (5).

The specific heat capacity of La-1 ($\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$) in the undercooled liquid that initially forms upon heating BMGs could not be measured since a fully amorphous rod was not obtained. Of the other five alloys in this work, the heat capacity is highest at a temperature about 10 K higher than T_g , and it has an average value of about 40 J mol⁻¹ K⁻¹. The glass transition temperature T_g of $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ is reported to be 490 K [18]. Thus, we assume a data point of 40 J mol⁻¹ K⁻¹ at 500 K for the data fitting of the liquid specific heat capacity.

Since the heat capacity of liquid and crystalline states and the enthalpy of fusion ΔH_f have been experimentally determined, the enthalpy and entropy differences between the liquid and crystalline states of the alloy can be calculated as functions of temperature:

$$\Delta H^{\text{liq-cry}}(T) = \Delta H_f - \int_T^{T_f} \Delta C_p^{\text{liq-cry}}(T') dT', \quad (6)$$

$$\Delta S^{\text{liq-cry}}(T) = \Delta S_f - \int_T^{T_f} \frac{\Delta C_p^{\text{liq-cry}}(T')}{T'} dT', \quad (7)$$

where $\Delta C_p^{\text{liq-cry}} = C_p^{\text{liq}} - C_p^{\text{cry}}$. As mentioned above, T_f is substituted with T_m for the calculation. Figure 3 shows the calculated differences in the enthalpy and entropy between the liquid and crystalline states of La-1 as an example. On the plot, we mark T_g , T_m and the calculated Kauzmann temperature T_k . At T_k , the entropy of the liquid is equal to the entropy of the crystal. The values of T_k are also listed in Table 1.

Table 2 Fitting constants for the heat capacity data, according to eq. (4) for crystalline states and eq. (5) for liquid

Alloys	a (10^{-3} J mol $^{-1}$ K $^{-2}$)	b (10^{-5} J mol $^{-1}$ K $^{-2}$)	c (10^{-3} J mol $^{-1}$ K $^{-2}$)	d (10^6 J K mol $^{-1}$)
La-1	-3.30	1.23	9.34	2.60
La-2	-4.74	1.46	9.61	2.31
La-3	-1.36	0.697	5.00	2.61
La-4	-5.79	0.156	3.78	2.44
La-5	-2.68	1.19	6.87	3.72
La-6	-0.443	0.836	4.24	2.00

Figure 3 Calculated differences in enthalpy (solid lines) and entropy (dash lines) between the liquid and crystalline states of La-1.

2.2 Fragility

Besides consideration of the viscosity, thermal scanning is thought to be a reliable way to obtain the fragility of the supercooled liquid [28]. Previous studies have demonstrated that the kinetic heating rate ϕ dependence of the glass transition temperature T_g describes the fragility as well as the temperature dependence of viscosity [29]. Values of m for La-1, La-2 and La-3, determined using the method employed in [6], are cited from [18], while values for the other three alloys were obtained employing the same method used in the DSC experiments at different heating rates; values are presented in Table 3.

Ito et al. [12] used a Kauzmann plot to define the thermodynamic fragility of glass-forming liquids, and found that thermodynamic fragility and kinetic fragility have the same order for the different liquids. By this definition, a liquid for which there is a more rapid drop in $\Delta S/\Delta S_f$ with decreasing T/T_f is more thermodynamically fragile. Two

thermodynamic fragility parameters were assumed [12]. One is $F_{1/2,cal}=T_{1/2}/T_m$, with $T_{1/2}$ being the temperature at which $\Delta S/\Delta S_f=1/2$. The other is $F_{0.8}$, which is the fraction of fusion entropy lost $(1-\Delta S/\Delta S_f)$ by $T/T_m=0.8$ when cooling. Figure 4(a) shows the excess entropy ΔS normalized by ΔS_f versus T normalized by T_m . It is seen that $F_{1/2,cal}$ and $F_{0.8}$ coincide; thus, we only calculate $F_{0.8}$, as listed in Table 3.

In Figure 4(a), however, we find that $F_{0.8}$ does not show the rapidity of the ΔS decrease thoroughly owing to the appearance of crossing points. ΔS for La-4, with $F_{0.8}$ (0.227) close to that for La-2 (0.237) and that for La-5 (0.232), has a rate of decrease in the scaled excess entropy similar to that of La-1 (0.199) and that of La-3 (0.182). In Ref. [12], there is no crossing point between any two scaled excess entropy curves, and the larger $F_{0.8}$ results from a more rapid drop of $\Delta S/\Delta S_f$ with diminishing T/T_m and thus larger T_g/T_m . Generally, this is an ambiguous definition. Breakdowns of the coherence between this kind of thermodynamic fragility and kinetic fragility have been observed for molecular glass-forming liquids [13].

Similar to Ref. [12], Martinez and Angell [14] plotted excess entropy ΔS scaled by ΔS_g (excess entropy at T_g) versus T_g/T , which is similar to the Angell plot for kinetic fragility [1]. Following the idea of the mode of kinetic fragility $F_{1/2}=2T_g/T_{1/2}-1$ [30], a thermodynamic fragility parameter $F_{3/4}=2T_g/T_{3/4}-1$ is proposed, with $T_{3/4}$ the temperature at which $\Delta S_g/\Delta S=3/4$ [14]. In Figure 4(b), we plot $\Delta S_g/\Delta S$ versus T_g/T and mark the $\Delta S_g/\Delta S=3/4$ line. To distinguish from $F_{0.8}$ defined in Ref. [12], we write the thermodynamic fragility parameter defined by ΔS_g scaled entropy in Ref. [14] as $G_{3/4}$, and the values are listed in Table 3.

Thermodynamic fragilities $F_{0.8}$ and $G_{3/4}$ and kinetic fragility m are compared in Figure 5(a). Both $F_{0.8}$ and $G_{3/4}$ are positively correlated with the kinetic fragility for the most

Table 3 Thermodynamic and kinetic fragility indexes of La-based alloys

Alloys	m	$F_{0.8}$	$G_{3/4}$	$m_{\Delta S}$	$M_{\Delta S}$
La-1	33	0.199	0.647	2	0.742
La-2	36	0.237	0.776	3.09	0.886
La-3	42	0.182	0.715	2.58	0.675
La-4	41	0.227	0.8	3.75	0.945
La-5	38	0.232	0.68	2.25	0.822
La-6	29	0.122	0.626	2.11	0.402

Figure 4 (a) Kauzmann plot of $\Delta S/\Delta S_f$ against scaled temperature T/T_m , with extrapolation below T_g to T_k (dashed lines) and above T_m , in which the intercept lines at $T/T_m=0.6, 0.8$ and 1.2 are marked. (b) S_g -scaled excess entropy versus T_g -scaled temperature, with extrapolation above T_m (dashed lines) and below T_g , in which the intercept lines at $\Delta S/\Delta S_f=0.6, 0.75$ and 1.2 are marked.

part, although the correlation with $G_{3/4}$ appears better. Since both lie central to the fragility range from T_g to T_m [14,30], the difference between the trends of $F_{0.8}$ and $G_{3/4}$ stems from the different values of the scaled excess entropy ΔS , at T_g and T_m . Both T_g and T_m vary for different metallic glasses, and variation in one characteristic temperature is thus ignored in the two definitions.

$\Delta S_f/(T_m-T_k)$ [11], the average entropy-temperature dependence from T_m to T_k , has been found to positively correlate with kinetic fragility in metallic glass-forming liquids. For the index of $\Delta S_f/(T_m-T_k)$, if the variation in entropy for different glasses is eliminated by scaling the index with ΔS_f , as in the method employed to deduce thermodynamic fragilities in Refs. [12] and [14], then $1/(T_m-T_k)$ or the reduced isentropic temperature T_k/T_m seems to coincide with the original intention of thermodynamic fragility definition of the entropy slope [11,12,14].

As in the definition of kinetic fragility m , we suppose that thermodynamic fragility $m_{\Delta S}$ can be represented by the drop in excess entropy approaching T_g , which can be written as

$$m_{\Delta S} = \frac{d(\Delta S_g/\Delta S)}{d(T_g/T)} \bigg|_{T=T_g} \quad (8)$$

Another concept of fragility, the fragility of superheated melts M [2], is defined as the rate of change in viscosity at

the liquidus temperature. M is an index of the kinetic structure sensitivity to the temperature change approaching the phase transition of solidification [2], while m corresponds to the glass phase transition. Fusion and solidification are opposing phase transitions. Thus, thermodynamic fragility $M_{\Delta S}$, reflecting the change rate of excess entropy approaching solidification/fusion, can be assumed according to Figure 4(a) as

$$M_{\Delta S} = \frac{\partial \Delta S/\Delta S_f}{\partial T/T_m} \bigg|_{T=T_m} \quad (9)$$

Values of $m_{\Delta S}$ and $M_{\Delta S}$ are listed in Table 3. We plot the relations between the two indexes and m in Figure 5(b).

It is interesting that we find nearly linear proportional correlations between $M_{\Delta S}$ and m . The correlation between $M_{\Delta S}$ (i.e., the excess entropy slope at T_m instead of the excess entropy slope below T_m) and m may provide more detailed information about the correlation between the thermodynamics and kinetics of a liquid, which is discussed in the next section.

3 Discussion

Fragility was originally so named to infer that fragile liquids experience rapid breakdown of structure with decreasing

Figure 5 Correlation of the thermodynamic and kinetic fragilities: (a) $F_{0.8}$ and $G_{3/4}$ versus m , (b) $M_{\Delta S}$ and $m_{\Delta S}$ versus m .

crucial role in determining the structural stability of glass-forming liquid in the fragility range.

4 Conclusion

Absolute values of the specific heat capacity C_p of six La-based BMGs were measured with respect to sapphire standards for the crystal, supercooled liquid, and melts. The differences in entropy ($\Delta S^{\text{liq-cry}}$) and enthalpy ($\Delta H^{\text{liq-cry}}$) between liquid and crystal as functions of temperature were calculated with C_p and the fusion heat ΔH_f . Thermodynamic fragility having different definitions was calculated and discussed for La-based glass-forming liquid on the basis of the $\Delta S^{\text{liq-cry}}$ -temperature dependence. In La-based glass-forming liquid, using the interception of scaled excess entropy ΔS curves as fragility indexes may result in randomness and ambiguity. We put forward thermodynamic fragilities $m_{\Delta S}$ and $M_{\Delta S}$ by evaluating the slope of the temperature dependence of the excess entropy at T_g and T_m respectively. The correlation between thermodynamic and kinetic fragilities was discussed on the basis of Adam-Gibbs and potential energy landscape theories. The thermodynamic fragility of the melt $M_{\Delta S}$, rather than that of the supercooled liquid $m_{\Delta S}$, relates linearly with kinetic fragility m and the height of energy barriers separating the minima $\Delta\mu$.

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