Journal of Alloys and Compounds 504S (2010) S205–S207

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

# A correlation between superheated liquid fragility and supercooled liquid fragility in La- and Sm-based glass-forming alloys

Jing Guo[a], Xiufang Bian[b,*]

[a] School of Mechanical and Electronic Engineering, Shandong Agricultural University, Taian, Shandong 271018, China
[b] Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, Jinan 250061, China

ARTICLE INFO

*Article history:*
Received 3 July 2009
Received in revised form 30 March 2010
Accepted 2 April 2010
Available online 10 April 2010

*Keywords:*
Superheated liquid fragility
Supercooled liquid fragility
Glass-forming alloys

ABSTRACT

It is deduced that the parameter of supercooled liquid fragility, $m$, is proportional to the product of reduced glass transition temperature, $T_g/T_L$ ($T_g$ is the glass transition temperature, $T_L$ the liquidus temperature) and reciprocal of the parameter of superheated liquid fragility, $1/M$, based on the definitions of the two kinds of liquid fragility and the previously studied results. The experimental result in La- and Sm-based glass-forming alloys is consistent with the deduced result. The correlation relates superheated liquid fragility with supercooled liquid fragility.

## 1. Introduction

The concept of supercooled liquid fragility can date back to the mid of 1980s. Since then, it has attracted much attention from scientific and technological view points and thus has been studied both theoretically and experimentally [1–3]. Concerning the fragility, there are various quantitative definitions [4–7]. The most commonly used one was introduced by Angell, referring to deviations from Arrhenius temperature dependence of relaxation time or viscosity [4]. According to the definition of liquid fragility, Angell suggested that glass-forming liquids can be classified into three categories, i.e., strong glass formers, fragile glass formers, and intermediate glass formers. Strong liquids exhibit nearly Arrhenius temperature dependence of those dynamic properties. Fragile liquids generally display Vogel–Fulcher–Tamman behavior [8–10]. The slope of the temperature dependence of viscosity at $T_g$ (glass transition temperature) is defined as a fragility parameter, $m$, to evaluate the fragility of different liquids [11],

$$m = \left.\frac{d\log_{10}\tau(T)}{d(T_g/T)}\right|_{T=T_g} = \left.\frac{d\log_{10}\eta}{d(T_g/T)}\right|_{T=T_g} \tag{1}$$

The values of fragility parameter typically range between $m = 16$ for strong glass formers and $m = 200$ for fragile glass formers. Intriguingly, it has been found that $m$ has a negative correlation with the glass-forming ability for some glass formers [12] and recently researchers also found there is a close relationship between $m$ and the glass properties such as vibration, Poisson's ratio [13–15]. Novikov et al. presumed that the steepness of the temperature variations of the relaxation time or viscosity near $T_g$ is determined by the high-temperature behavior of the liquid [14].

It seems that supercooled liquid fragility is becoming one of the crucial subjects in the field of metallic materials. Nevertheless, it is usually difficult to determine $m$ for the glass formers with the low GFA since the glassy solids should be prepared beforehand and the sample size must be several millimeters at least. In view of the relatively easy measurement on viscosity of superheated liquid, Bian et al. proposed the concept of superheated liquid fragility [16]. They also found that the superheated liquid fragility can predict the GFA of the Al-based alloys. Based on the thermodynamic refinement, Meng et al. proposed the refined superheated fragility parameter ($M^* = M/\varepsilon$) for evaluating the GFA of BMGs [17]. It can be understood that not only the supercooled liquid fragility, the superheated liquid fragility are also closely related to the GFA of BMGs. Since they both closely correlate with GFA, there should be a relationship existing between the supercooled liquid fragility and the superheated liquid fragility. The correlation between them will be a further insight into the nature of the glass formation.

In this paper, we will deduce the correlation between $m$ with $M$ based on the definition of the two kinds of fragility and some previously studied results. Then the experimental results of Sm- and La- based glass-forming alloys will also be used to demonstrate the relationship between them.

## 2. Experimental procedure

The LaAlNi(Cu) and SmAlCo(Ni) alloy ingots with nominal compositions were made by alloying high-purity elements (99.9 wt% at least) in an arc furnace under

---

* Corresponding author. Tel.: +86 531 88392748; fax: +86 531 88395011.
*E-mail address:* xfbian@sdu.edu.cn (X. Bian).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.04.015

argon atmosphere. To ensure homogeneity of the samples, the ingots were remelted at least 5 times. Finally, cylindrical rods of 26 mm × 40 mm for viscosity measurement were prepared by suction casting method in an arc furnace under argon atmosphere. The temperature-dependent viscosities in superheated liquid state were measured using an oscillating vessel viscometer (RHEOTRONI C VIII) under a high vacuum atmosphere. The detailed measurement process for the superheated liquid can see the descriptions of Meng et al. [18]. In order to obtain supercooled liquid fragility, the glassy cylindrical rods with a diameter of 2 mm and a length of 60 mm were prepared by suck-casting into a Cu mold. The structure of the transverse cross sections of as-cast alloys was ascertained using X-ray diffraction (XRD, Cu Ka radiation). A differential scanning calorimeter (Netzsch DSC 404C) was used to study the thermodynamic properties at different heating rates.

## 3. Results and discussion

As we know, all viscosity or relaxation time curves should intersect at two points on the fragility plots: one is $T_g$, where the viscosity is $10^{13}$ Poise or the relaxation time is $10^2$ s; the other is the very high temperature, $T_g/T \to 0$, where all liquids have$\eta = \eta_0 = 10^{-4}$ Poise or the relaxation time, $\tau = \tau_0$, is $10^{-14}$ s. [14]. It indicates that, in fragility plot, a liquid with a steeper slope of $\log \eta$ near $T_g$ at the supercooled state should have a smaller slope of $\log \eta$ at high temperatures in the superheated liquid state. It suggests that the viscosity properties of supercooled liquids can be got by studying the viscosity properties of superheated liquids. Novikov et al. has found that a good linear correlation exists between fragility and $T_g/E$ based on the experimental data of some glass formers [14], as the following

$$m \propto \frac{T_g}{E}, \tag{2}$$

where $T_g$ is glass transition temperature, $E$ is active energy. The parameter of fragility, $m$, can be got by the thermodynamics method, by which the values of liquid fragility parameter are consistent with those obtained by kinetic method [6]. Previous studies demonstrated that the $Q$ (the heating rate) dependent $T_g$ describes the fragility equally well as the temperature dependence of viscosity [19]. Therefore, the dependence of $T_g$ on $Q$ can also be described by a VFT relation,

$$Q^{-1} = A \exp\left(\frac{DT_0}{T - T_0}\right) \tag{3}$$

$$m = \frac{DT_0 T_g}{(T_g - T_0)^2 \ln 10} \tag{4}$$

where $A$ is a constant, $T_0$ is the VFT temperature, and $D$ is the strength parameter.

The fragility parameter of superheated liquid was defined as [16],

$$M = \left| \frac{\partial \eta(T)/\eta(T_L)}{\partial T/T_L} \right| = \left| \frac{\partial \eta_r}{\partial T_r} \right| \tag{5}$$

which can be simplified as,

$$M = \frac{E}{RT_L} \tag{6}$$

where $T_L$ is the liquidus temperature, $E$ is active energy and $R$ the gas constant. Actually, $M$, is characterized by the temperature dependence of the viscosity scaled by the viscosity at the liquidus temperature. Since it reflects the bonding nature of atoms in liquids, viscosity exhibits a close correlation with the liquid phase stability. The low value of the $M$, means a stronger interaction among structural entities in the superheated liquids and slow structure rearrangement towards the liquidus temperature, whereas a liquid with high value of $M$ would change rapidly in structure upon solidification.

**Table 1**
The fragility parameters of supercooled liquid and superheated liquid, $m$ and $M$, respectively, the liquidus temperature, $T_L$, the glass transition temperature, $T_g$, the reduced glass transition temperature, $T_g/T_L$, and $(T_g/T_L) \times (1/M)$ of La- and Sm- based glass-forming alloys.

| | $m$ | $M$ | $T_L$ | $T_g$ | $T_g/T_L$ | $(T_g/T_L) \times (1/M)$ |
|---|---|---|---|---|---|---|
| $La_{55}Al_{25}Ni_{20}$ | 33 | 1.7747 | 941 | 491 | 0.521 | 0.2936 |
| $La_{55}Al_{25}Ni_{15}Cu_5$ | 36 | 1.6428 | 900 | 474 | 0.527 | 0.3208 |
| $La_{55}Al_{25}Ni_5Cu_{15}$ | 42 | 1.4509 | 878 | 459.1 | 0.523 | 0.3605 |
| $Sm_{50}Al_{30}Co_{20}$ | 33 | 1.9588 | 960 | 586 | 0.610 | 0.3114 |
| $Sm_{55}Al_{25}Ni_{10}Co_{10}$ | 36 | 1.8260 | 898 | 553 | 0.616 | 0.3373 |
| $Sm_{55}Al_{25}Cu_{10}Co_{10}$ | 28 | 2.1005 | 986 | 534 | 0.54 | 0.2861 |

Substituting Eq. (6) into Eq. (2), we can get the correlation between $m$ and $M$,

$$m \propto \left(\frac{T_g}{T_L}\right)\left(\frac{1}{M}\right) \tag{7}$$

Eq. (7) means that the parameter of supercooled liquid fragility is proportional to the product of reduced glass transition temperature, $T_g/T_L$, and reciprocal of the parameter of superheated liquid fragility, *1*/$M$, in bulk glass-forming alloys. Actually, the reduced glass transition temperature is one of the criterions for estimating GFA of glass-forming alloys proposed by Turnbull based on the assumption that the nucleation frequency of a melt scales as $1/\eta$ ($\eta$, viscosity of the liquid) [20]. Accordingly, the equation indicates the relationship between the supercooled liquid fragility and superheated liquid fragility and also suggests that both of them are indeed closely related to GFA of glass-forming alloys.

LaAlNi(Cu) and SmAlCo(Ni) alloys were well chosen to investigate the correlation between $m$ and $M$. The parameters of supercooled liquid for La-based alloys, determined by the thermodynamic method, were cited from the reference [21,22]. The values of m for Sm-based alloys were obtained by the Eqs. (3) and (4) based on DSC experiments at different heating rates, as shown in Table 1. Fig. 1 displays DSC curves of the $Sm_{55}Al_{25}Cu_{10}Co_{10}$ BMG with different heating rates. Figs. 2 and 3 are the superheated liquid fragility plots of La- and Sm-based glass formers, respectively. In the figures, $R^2$ is the square of correlation coefficient, reflecting the error of the fitting curve. The parameters of superheated liquid fragility determined by Eq. (6) are also list in Table 1.

Based on the data listed in Table 1, the plots of the correlation between $m$ and $(T_g/T_L) \times (1/M)$ are shown in Fig. 4. $R$ is the correlation coefficient, reflecting the error of the fitting line. It can be obviously observed that a good linear correlation exists

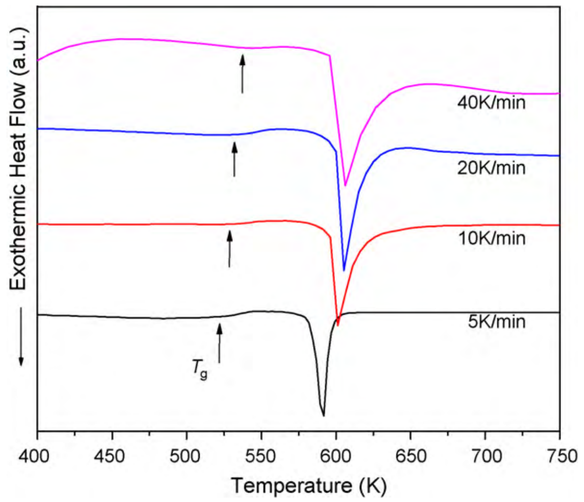

**Fig. 1.** DSC curves of the $Sm_{55}Al_{25}Cu_{10}Co_{10}$ BMG with different heating rates.

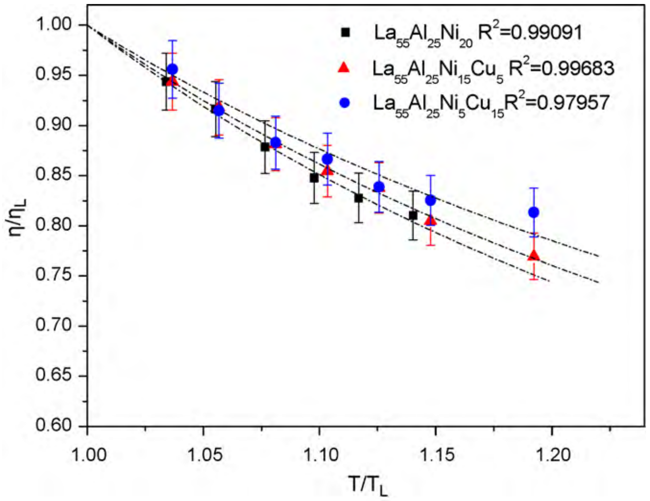

**Fig. 2.** The scaled experimental viscosity data (as single points) and fitting curves (as continuous curves) for La-based system alloys.

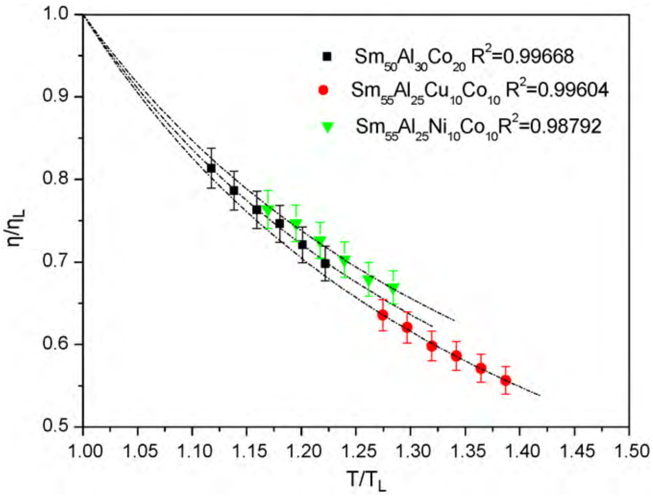

**Fig. 3.** The scaled experimental viscosity data (as single points) and fitting curves (as continuous curves) for Sm-based system alloys.

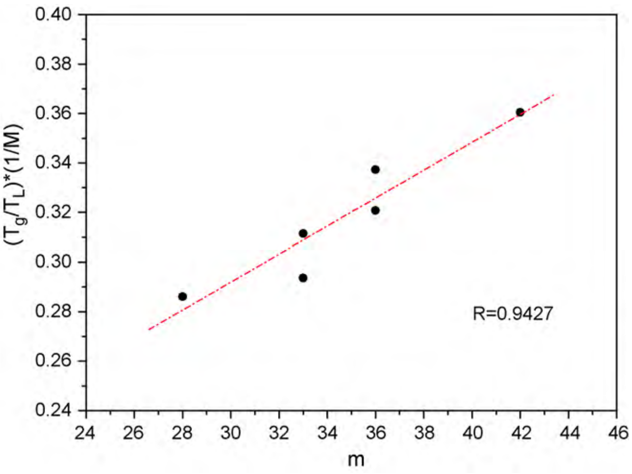

**Fig. 4.** Correlation between the parameter of supercooled liquid fragility, $m$, and $(T_g/T_L) \times (1/M)$ of the La- and Sm-based glass-forming alloys.

between them for La- and Sm-based glass-forming alloys. The experimental result in La- and Sm-based alloys is consistent with the result deduced from the definitions of the two kinds of liquid fragility.

The correlation between the fragilities of supercooled liquid and superheated liquid is of significance to estimate the fragility of supercooled liquid and even the GFA of an alloy by the investigation on high-temperature behavior of the normal liquidis. It has been noticed that although great progress has been made in the work concerning the fragility of supercooled liquid, some problems restricting the investigation on the fragility of supercooled liquid still remain. Especially for the liquid with an unstable supercooled liquid state, the glassy solids should be prepared beforehand. Hence, for the alloys with low glass-forming ability, it is nearly impossible to obtain the fragility of supercooled liquid. In this case, the fragility can be estimated via the behaviors of a high-temperature liquid and its liquidus temperature without any reference to the glass transition or supercooled regime of the liquid state.

## 4. Conclusion

The correlation between the fragilities of supercooled liquid and superheated liquid was investigated based on the definitions of the two kinds of liquid fragility and the previously studied results. The parameter of supercooled liquid fragility, $m$, was found to be proportional to the product of the reduced glass transition temperature, $T_g/T_L$ and reciprocal of the parameter of superheated liquid fragility, $1/M$, in glass-forming alloys. The experimental result in La- and Sm-based glass-forming alloys was consistent with the deduced result. The relationship between the fragilities of supercooled liquid and superheated liquid is a further insight into the nature of the glass formation.

## Acknowledgments

We would like to acknowledge financial support from the National Natural Science Foundation of China (Grant Nos. 50831003 and 50871062), National Basic Research Program of China (2007CB613901), Youth Science and Technology Innovation Fund of Shandong Agricultural University P.R. China and Foundation of Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, P.R. China.

## References

[1] C.A. Angell, Science 267 (1995) 1924–1935.
[2] F. Sciortino, P. Tartaglia, E. Zaccarelli, Phys. Rev. Lett. 95 (2005), 15802-1–3.
[3] T. Scopigno, G. Ruocco, F. Sette, G. Monaco, Science 302 (2003) 849–852.
[4] C.A. Angell, J. Non-Cryst. Solids 73 (1985) 1–17.
[5] L.M. Martinez, C.A. Angell, Nature 410 (2001) 663–667.
[6] K. Ito, C.T. Moynihan, C.A. Angell, Nature 398 (1999) 492–495.
[7] D.H. Huang, B. Gregory, Mckenna, J. Chem. Phys. 114 (2001) 5621–5630.
[8] H. Vogel, Phys. Z 22 (1921) 645–646.
[9] G.S. Fulcher, J. Am. Ceram. Soc. 8 (1923) 339–355.
[10] G. Tamman, W. Hesse, Z. Anorg, Allg. Chem. 156 (1926) 245–257.
[11] D.J. Plazek, K.L. Ngai, Macromolecules 24 (1991) 1222–1224.
[12] R. Busch, A. Masuhr, E. Bakke, Mater. Res. Soc. Symp. Proc. 455 (1997) 369–374.
[13] V.N. Novikov, A.P. Sokolov, Nature London 431 (2004) 961–963.
[14] V.N. Novikov, Y. Ding, A.P. Sokolov, Phys. Rev. E 71 (2005), 061501-1–12.
[15] W.H. Wang, J. Appl. Phys. 99 (2006), 093506-1–9.
[16] X.F. Bian, B.A. Sun, L.N. Hu, Y.B. Jia, Phys. Lett. A 335 (2005) 61–67.
[17] Q.G. Meng, S.G. Zhang, M.X. Xia, J.G. Li, J.K. Zhou, Appl. Phys. Lett. 90 (2007), 031910-1–3.
[18] Q.G. Meng, J.K. Zhou, H.X. Zheng, Scr. Mater. 54 (2006) 777–781.
[19] R. Busch, E. Bakke, W.L. Johnson, Acta Mater. 46 (1998) 4725–4732.
[20] D. Turnbull, Contemp. Phys. 10 (1969) 473–488.
[21] Z.P. Lu, X. Hua, Y. Lia, S.C. Ng, Mater. Sci. Eng. A 304–306 (2001) 679–684.
[22] Z.P. Lu, C.T. Liu, Acta Mater. 50 (2002) 3501–3512.