Materials Science and Engineering A 509 (2009) 23–30

Contents lists available at ScienceDirect

Materials Science and Engineering A

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

On the new criterion to assess the glass-forming ability of metallic alloys

Zhilin Long[a,b,*], Guoqiang Xie[c], Hongqing Wei[a], Xuping Su[b], Jian Peng[a], Ping Zhang[a], Akihisa Inoue[c]

[a] *Institute of Fundamental Mechanics and Material Engineering, Xiangtan University, Xiangtan, Hunan 411105, China*
[b] *Key Laboratory of Materials Design and Preparation Technology of Hunan Province, Xiangtan University, Xiangtan, Hunan 411105, China*
[c] *Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan*

ARTICLE INFO

Article history:
Received 11 August 2008
Received in revised form 19 December 2008
Accepted 7 January 2009

Keywords:
Criterion
Glass-forming ability
Metallic glasses
Thermal analysis

ABSTRACT

Based on the analysis of time–temperature-transformation (TTT) diagrams of glass-forming liquids using the fragility concept, a dimensionless criterion ω, expressed by $T_g/T_x - 2T_g/(T_g + T_l)$ (T_g the glass transition temperature, T_x the onset crystallization temperature and T_l the liquidus temperature), is proposed for quickly evaluating the glass-forming ability (GFA) of metallic glasses. From the available experimental data reported in the literature, the criterion ω exhibits the strongest correlation with the critical cooling rate R_c for glass formation among all currently available GFA indicators, including $T_{rg}(=T_g/T_l)$, $\Delta T_x(=T_x - T_g)$, $\Delta T_{rg}(=(T_x - T_g)/(T_l - T_g))$, $\delta(=T_x/(T_l - T_g))$, $\gamma(=T_x/(T_g + T_l))$, $\gamma_m(=(2T_x - T_g)/T_l)$, $\varphi(=T_{rg}(\Delta T_x/T_g)^{0.143})$, $\alpha(=T_x/T_l)$, $\beta(=T_x/T_g + T_g/T_l)$, $\beta(=T_x \times T_g/(T_l - T_x)^2)$ and $\zeta(=T_g/T_l + \Delta T_x/T_x)$. An empirical equation is induced to elucidate the R_c in different metallic alloys based on the measured ω value of the corresponding alloy. It is also demonstrated that this ω criterion has a strong ability to measure or/and predict the GFA of cryoprotectants and oxide glasses, especially in the case of cryoprotectants.

1. Introduction

Glass-forming ability (GFA), as related to the ease of devitrification, is very crucial for understanding the underlying mechanism of amorphization and also important for exploring the criterion for glass formation and developing new bulk metallic glasses (BMGs). Since the first synthesis of metallic glass by Klement et al., Glass formation has been extensively studied [1,2]. Nevertheless, studies on factors governing GFA still remain at the empirical level such as the three rules proposed by Inoue et al. [3]. It is well known that the GFA of a melt can be quantitatively evaluated by means of the critical cooling rate R_c for glass formation, above which no crystallization occurs during solidification, and lower R_c always corresponds to higher GFA [4]. However, R_c measurement is complex and even difficult due to some uncertain factors (e.g., temperature variations, heterogeneous nucleation, etc.) [5]. Therefore, many researchers have tried to establish relations between GFA and some simple parameters/criteria associating with the glass transition temperature T_g, the onset of crystallization temperature T_x and liquidus temperature T_l, etc., to quantify easily the GFA for metallic glasses. In the past years, various GFA parameters or criteria have been put forward, such as $T_{rg}(=T_g/T_l)$, $\Delta T_x(=T_x - T_g)$, $\Delta T_{rg}(=(T_x - T_g)/(T_l - T_g))$, $\delta(=T_x/(T_l - T_g))$, $\gamma(=T_x/(T_g + T_l))$, $\gamma_m(=(2T_x - T_g)/T_l)$, $\varphi(=T_{rg}(\Delta T_x/T_g)^{0.143})$, $\alpha(=T_x/T_l)$, $\beta(=T_x/T_g + T_g/T_l)$, $\beta(=T_x \times T_g/(T_l - T_x)^2)$, hereafter referred to as β_l), and $\zeta(=T_g/T_l + \Delta T_x/T_x)$ [6–15]. Although these parameters show reasonable correlations with the GFA for many metallic glass alloys, they still cannot reflect the real GFA of alloys in some cases [8,16,17]. So, the GFA parameters consisting of T_g, T_x and T_l still remain room for further investigations. It is also of interest to determine the effectiveness of these established parameters serving as GFA gauge. In this paper, we aim at suggesting a more reliable indicator than the other current parameters to reflect the relative GFA among metallic glasses on the basis of analyzing the characteristic features of the time–temperature-transformation (TTT) diagrams using the fragility concept. An estimation of R_c will also be formulated in terms of this new parameter. Additionally, the ability of this new parameter to predict other glass-forming liquids, such as cryoprotectants and glassy oxides, will be evaluated.

2. Criterion analysis

As pointed out by Turnbull and Davies, any liquid can form a glass as long as the cooling rate is enough to suppress the crystallization event [18,19]. In this sense, the time–temperature-transformation (TTT) diagram in Fig. 1 contains all the information needed to predict the formability and stability of any given glass. Liquid can be undercooled and form the glass state only if crystallization is kinetically constrained due to a rapid increase in the viscosity and relaxation time during quenching. Crystallization may occur in the temperature interval between T_l and T_g and an incubation time is required to start the crystallization. The temperature dependence

---

* Corresponding author. Tel.: +86 732 8298287; fax: +86 732 8293240.
E-mail address: longzhilin@tom.com (Z. Long).

doi:10.1016/j.msea.2009.01.063

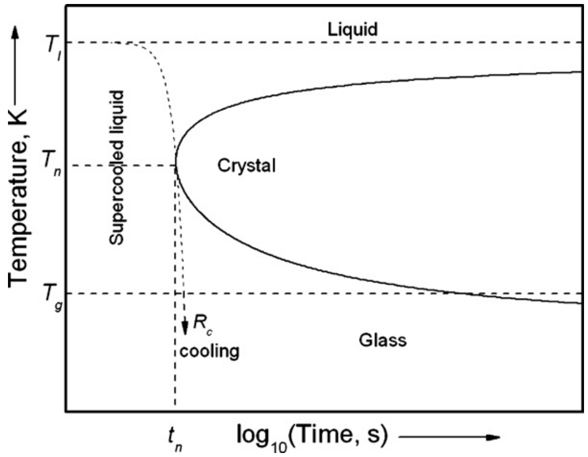

Fig. 1. Schematic time–temperature-transformation (TTT) diagram for the onset of crystallization of a glass-forming liquid. Crystallization occurs between T_l and T_g, and it can be avoided when the liquid is chilled with the cooling rate $R \geq R_c$.

of the incubation time exhibits a typical "C" shape, and the minimum time t_n, which is required to start crystallization, occurs at a temperature T_n located between T_l and T_g. This temperature can be expressed in the light of T_l and T_g as $T_n = a(T_g + T_l)$, where parameter a is between 0.45 and 0.55, and it is generally close to 0.5, i.e., $T_n = 0.5(T_g + T_l)$ [20]. To avoid crystallization, the cooling curve should not intersect the TTT curve, and the minimum (critical) cooling rate R_c required to form a glass is the cooling rate needed to bypass the nose of the TTT curve (see Fig. 1). Therefore, R_c is inversely proportional to t_n and can be virtually defined as $R_c \approx (T_l - T_n)/t_n$. It is reasonably to assume that t_n is proportional to the relaxation time τ_n of the supercooled liquid at $T = T_n$. During supercooling of liquid, the relaxation time (τ) for atom rearrangements can increase in a non-Arrhenius fashion by many orders of magnitude in a narrow temperature range. The magnitude of departure from Arrhenius behavior is called liquid fragility and the non-Arrhenius behavior of $\tau(T)$ can be described well by the Vogel-Fulcher-Tammann (VFT) equation [21]:

$$\tau = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right) \tag{1}$$

where τ_0, D and T_0 are parameters and T is the temperature in Kelvin. At $D \geq 100$, the behavior is very much like Arrhenius and with D decreasing to below 10, the behavior becomes more fragile. The parameter D is therefore called the strength parameter. The parameter T_0 depends on D in such a way that when D approaches infinity, T_0 moves toward zero and when D approaches to zero, T_0 becomes equal to T_g. Based on analysis of the relaxation time of the glass-forming liquids at near liquidus temperatures using the VFT relation, Eq. (2) was proposed to evaluate the relation between $\log_{10} R_c$ and $\log_{10}(1/\tau_n)$ by Senkov [22]:

$$\log_{10}(R_c) \propto \log_{10}\left(\frac{1}{\tau_n}\right) = -\frac{m_{\min}(T_g - T_0)}{0.5(T_g + T_l) - T_0} \tag{2}$$

where $m_{\min} \approx 16$. Thus, the above relation can be rewritten as follows:

$$\log_{10}(R_c) \propto \log_{10}\left(\frac{1}{\tau_n}\right) \propto -\frac{T_g - T_0}{0.5(T_g + T_l) - T_0} = -\frac{T_g - T_0}{T_n - T_0} \tag{3}$$

At $T = T_g$, the logarithmic form of Eq. (1) is expressed as

$$\log_{10}\left(\frac{\tau_g}{\tau_0}\right) = \frac{DT_0}{(T_g - T_0)\ln 10} \tag{4}$$

where τ_g is the relaxation time at T_g. Considering the fact that τ_g is a constant of 100 s, and τ_0 is approximately 10^{-14} s for many liquids [23], the following relation between D and T_0 is given by

$$D = \frac{m_{\min}(T_g - T_0)}{T_0} \ln 10 \tag{5}$$

Eq. (5) indicates that T_g depends on the values of D and T_0. Moreover, T_0 is often smaller than T_g. By systematically changing the values of D and T_0, liquids with hypothetical T_{rg} ranging from 0.46 to 0.78 were investigated. T_g was calculated using Eq. (5) and then T_l was obtained based on the corresponding T_{rg}. The values of calculated T_g and T_l were used to study the interrelationship between $(T_g - T_0)/(T_n - T_0)$ and T_g/T_n. It is found that there is a trend for $(T_g - T_0)/(T_n - T_0)$ to increase with an increase in T_g/T_n. In order to confirm this relation, some available experimental data were collected and analyzed. Fig. 2 shows the plot of $(T_g - T_0)/(T_n - T_0)$ and T_g/T_n for 9 metallic glasses from Table 1 [22,24–37]. For these metallic glasses, data points were fitted to an exponential function, and the fitted result is as follows:

$$\frac{T_g - T_0}{T_n - T_0} = -1.13 \times 10^8 \exp\left[\frac{-(T_g/T_n)}{0.032}\right] + 0.525 \tag{6}$$

The correlation coefficient R^2 of Eq. (6) is 0.94, implying that there is a solid correlation between $(T_g - T_0)/(T_n - T_0)$ and T_g/T_n. Based on the above discussions, Eq. (3) could be modified as

$$\log_{10}(R_c) \propto \log_{10}\left(\frac{1}{\tau_n}\right) \propto -\frac{T_g}{T_n} = -\frac{T_g}{0.5(T_g + T_l)} = -\frac{2T_g}{T_g + T_l} \tag{7}$$

or

$$\log_{10}\left(\frac{1}{R_c}\right) \propto \frac{T_g}{T_n} = \frac{2T_g}{T_g + T_l} = 2\left(1 + \frac{1}{T_{rg}}\right)^{-1} \tag{8}$$

It is seen in Eq. (8) that a larger T_g/T_n value always corresponds to a larger T_{rg} value and hence a lower R_c, i.e., higher GFA, which is in consistent with T_{rg} criterion suggested by Turnbull, which based on the assumption that the nucleation frequency of a melt scales as $1/\eta$ (η, viscosity of the liquid) [6]. Therefore, it is concluded that Eqs. (7) and (8) can qualitatively reflects the relation between $\log_{10}(R_c)$ and $-2T_g(T_g + T_l)^{-1}$, although the above deduction from Eqs. (3)–(8) is not rigorous. On the other hand, the same conclusion as Eq. (7) or (8) also can be derived from the physical metallurgy viewpoints suggested by Lu and Liu [20]. The GFA of glass-forming liquids is closely related to the liquid stability, which can be measured by the magnitude of $T_n = (T_g + T_l)/2$. In general, without considering the effect of the competing crystalline phases, a glass-forming liquid having a lower value of T_n should have a relatively higher liquid phase stability and thus a larger GFA. In realistic cases, glass-forming liquids

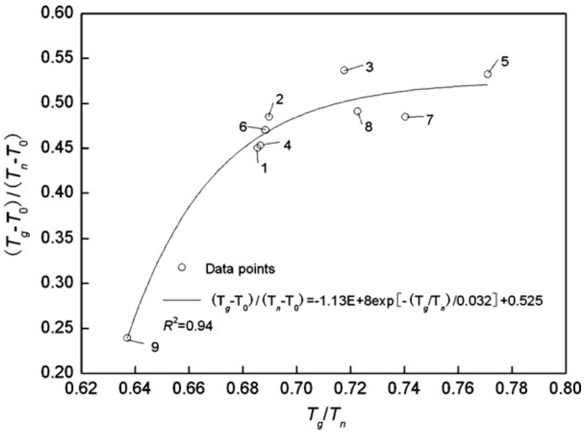

Fig. 2. The dependence $(T_g - T_0)/(T_n - T_0)$ as a function of T_g/T_n for 9 metallic glasses listed in Table 1 (open circles). The data are fitted to an exponential function (solid line).