VOLUME 91, NUMBER 11 PHYSICAL REVIEW LETTERS week ending 12 SEPTEMBER 2003

Glass Formation Criterion for Various Glass-Forming Systems

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(Received 17 March 2003; published 10 September 2003)

A conceptual approach to evaluate glass-forming ability for various glass-forming systems has been proposed from a physical metallurgy point of view. It was found that the glass-forming ability for noncrystalline materials was related mainly to two factors, i.e., $1/(T_g + T_l)$ and T_x (wherein T_x is the onset crystallization temperature, T_g the glass transition temperature, and T_l the liquidus temperature), and could be predicated by a unified parameter γ defined as $T_x/(T_g + T_l)$. This approach was confirmed and validated by experimental data in various glass-forming systems including oxide glasses, cryoprotectants, and metallic glasses.

DOI: 10.1103/PhysRevLett.91.115505 PACS numbers: 81.05.Kf, 61.43.Dq, 61.43.Er, 64.70.Pf

The emergence of synthetic bulk metallic glasses (BMGs) as a prominent class of functional and structural materials with a unique combination of properties has prompted new interest in gaining an understanding of noncrystalline matter in general. Until now, many types of noncrystalline materials, such as halide glasses, cryoprotective glasses, ceramic glasses, etc., have been successfully developed and commercialized for engineering applications utilizing their exceptional properties in areas including biology, communication technology, electronics, etc. [1–3]. However, one of the biggest stumbling blocks of making the best use of these noncrystalline materials is their low glass-forming ability (GFA), which is an outstanding problem far from being adequately solved. Understanding the nature of GFA is the key to develop new noncrystalline materials with improved properties and manufacturability for engineering applications.

In the past, a variety of schemes have been proposed to attain an understanding of why some systems can be vitrified and others not, and of what determines the composition ranges over which glasses can be made [4–11]. However, these approaches are concerned only with identifying the structural and thermodynamic factors which determine whether a material will form a glass when cooled from the liquid state; on the other hand, the kinetics of glass formation was not taken into account. In addition, these criteria are very difficult to be quantified in the realistic practices.

Several researchers have deduced some simple parameters to reflect the relative GFA for various systems from one or another of the kinetic processes, viz. the crystal growth rate, the nucleation rate, or transformation kinetics. Nevertheless, none of them performed satisfactorily [12]. Among them, the most famous is the reduced glass transition temperature T_{rg} ($= T_g/T_l$, where T_g and T_l are the glass transition temperature and the liquidus temperature, respectively), proposed by Turnbull based on the assumption that the nucleation frequency of a melt scales as $1/\eta$ (η, viscosity of the liquid) [13]. However, it was found that in many BMGs [12] and phosphate glass systems [14] T_{rg} cannot reflect the GFA effectively. Hence, it is essential to establish a simple approach being able to be quantified easily to assess the relative GFA for various glass-forming systems with overall considerations of all transformation kinetics.

In this paper, we aim at providing a new concept to understand the nature of GFA based on the analysis of the characteristic features of time-temperature-transformation (TTT) curves. A simplified parameter to predict GFA for various glass-forming systems will be established. The validity and liability of this approach will be vindicated by the experimental data for various kinds of glasses.

Glass formation is always a competing process between liquid phase and the resulting crystalline phases. If the liquid phase is stabilized upon cooling and the competing crystalline phases are difficult to precipitate out, then the glass formation of the melt would be facilitated. Thus, in this regard, the GFA of a liquid virtually includes two components, viz. liquid phase stability and the stability of the competing crystalline phases. Unlike previous approaches as mentioned earlier, which were based only on the stabilization of the liquid phase and ignored the composition effect on the stability of the crystalline phases [15,16], the TTT diagram in Fig. 1 contains all the information needed to predict the formability and stability of given glasses. As shown in Fig. 1, in order to create an amorphous solid material, the liquid must be cooled fast enough from above the liquidus temperature through the glass transition temperature without intersecting the TTT curve. The minimum cooling rate required to form a glass (i.e., critical cooling rate) is the cooling rate needed to bypass the knee of the TTT curve, as depicted by R_c in Fig. 1. Therefore, the GFA of a liquid is directly related to the location of the TTT curve in the time-temperature coordinates, i.e., the position of the TTT curve along the temperature axis and the time axis. In fact, the average position of the TTT curve along the temperature scale can be indicated by the line of $1/2(T_g + T_l)$ as shown in Fig. 1.

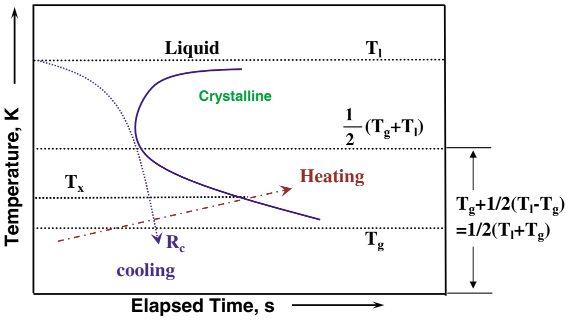

FIG. 1 (color online). Schematic time-temperature-transformation (TTT) diagram. Crystallization occurs between T_l and T_g, and can be avoided by sufficiently cooling of the liquid (R_c); when the amorphous solids are isochronally heated at a constant heating rate, the sample starts to crystallize at an onset temperature denoted as T_x.

From a physical point of view, liquid phase stability should be specified as a nature of the molten state (without referring to all kinetic factors). Liquid phase stability for glass-forming liquids should include two aspects: (i) the stability of the liquid at the equilibrium state (i.e., stable state), and (ii) the stability of the liquid during undercooling (i.e., metastable state). When two glass-forming liquids have the same T_g but different T_l, their relative liquid phase stability is then dominated by the stability of their stable states (i.e., the values of T_l). The lower the value of T_l, the higher the liquid phase stability. In the case that two liquids have the same T_l but different T_g, their relative liquid phase stability is then dominated by the stability of their metastable states (i.e., the T_g values). The lower the T_g, the higher will be the liquid phase stability. If two liquids have different T_l and T_g, then their liquid phase stability has to be measured by $1/2(T_g + T_l)$, which is the average of the stability of the liquids at equilibrium and metastable states. In general, a glass-forming liquid having a smaller value of $1/2(T_g + T_l)$ should have a relatively higher liquid phase stability. As shown in Fig. 1, this quantity also represents the average position of TTT curve along the temperature axis.

On the other hand, as Thornburg [17] and Clavaguera *et al.* [18] have pointed out, it is possible to determine experimentally a portion of the lower part of the TTT curve from rate-dependent thermograms upon reheating. This was recently confirmed by the results in Zr- and Pd-based BMGs; at temperatures below the nose, the times to the onset of crystallization (hereafter we refer to this time as onset time) measured on the reheated amorphous samples coincide with the onset times measured on samples cooled from above T_l. The TTT curves at below nose temperatures are indeed the same in both cases [19,20]. When the amorphous solid is isochronally heated from the temperature below T_g at a low heating rate, the sample will start to crystallize at an onset temperature T_x, as illustrated in Fig. 1.

If all liquids have the same liquid phase stability, then the glass-forming ability of a liquid can be reflected by the quantity of T_x alone, as shown in Fig. 2, which schematically illustrates the T_x effect on GFA. The materials with a higher T_x likely have longer onset times and a higher resistance to crystallization. Compared with liquid "a," liquid "b" has a larger onset crystallization temperature ${}^bT_x$ (${}^aT_x < {}^bT_x$) and longer onset times, thus consequently a lower critical cooling rate ${}^bR_c$ (${}^bR_c < {}^aR_c$). Therefore, the onset crystallization temperature T_x measured upon continuous reheating alone can assess the GFA under the special condition that the liquids have the same liquid phase stability.

However, in realistic cases, glass-forming systems always have different liquid phase stabilities. To manifest the relative GFA among those liquids, T_x should be normalized to the average position of the TTT curve along the temperature axis [e.g., $1/2(T_g + T_l)$] such that all liquids have the same stabilities. Hence, the normalized T_x, denoted as γ, can be used as a universe gauge for GFA, which can be expressed as

$$\gamma \propto T_x\left[\frac{1}{2(T_g + T_l)}\right] \propto \frac{T_x}{T_g + T_l}. \qquad (1)$$

This parameter is coincidently the same as what we obtained previously based on the experimental data for metallic glasses alone [12]. Figure 3 shows the correlation between the critical cooling rate R_c and this simple indicator for 49 metallic glasses (data were taken from Refs. [12,21]). Most of the data were measured at a heating rate of 20 K/min by a differential scanning calorimeter (DSC). A linear interrelationship is observed between γ values and $\log_{10} R_c$, as demonstrated by the solid line, that is,

$$R_c = C_1 \exp[(-\ln C_1/\gamma_0)\gamma]. \qquad (2)$$

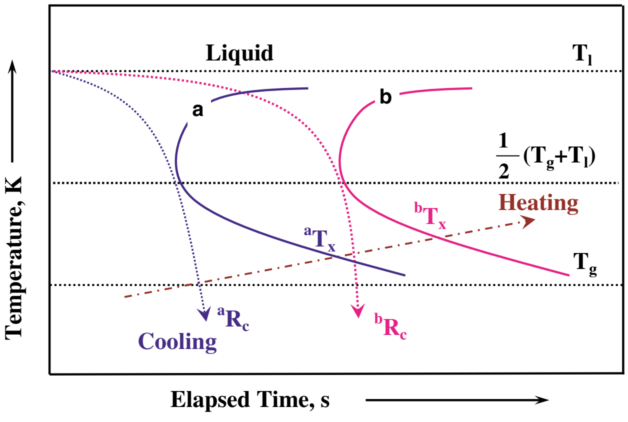

FIG. 2 (color online). Schematic TTT curves showing the effect of T_x measured upon continuous heating for different liquids with similar T_l and T_g; liquid b with higher onset crystallization temperature ${}^bT_x$ (${}^aT_x < {}^bT_x$) shows a lower critical cooling rate ${}^bR_c$ (${}^bR_c < {}^aR_c$).

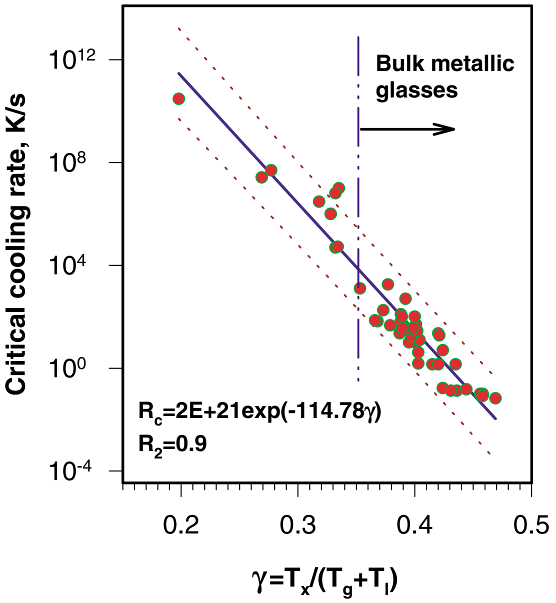

FIG. 3 (color online). The correlation between the critical cooling rate and the parameter γ for 49 metallic glasses. Data were taken from Refs. [12,21].

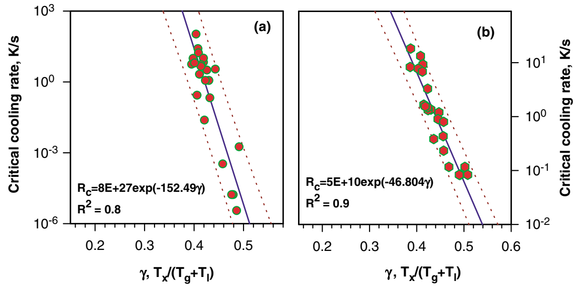

FIG. 4 (color online). The correlation between the critical cooling rate and the parameter γ for 23 glassy oxides (a) [data were taken from Refs. [22–29]] and 25 cryoprotective aqueous solutions (b) [data were taken from Refs. [30–37]].

wherein C_1 and γ_0 are constants, C_1 represents the critical cooling rate for a material with a γ value of zero, and γ_0 is the corresponding γ value for a material having a R_c value of 1 K/s. For metallic glasses, C_1 and γ_0 are 5.1×10^{21} K/s and 0.427, respectively. Also, the statistical correlation parameter R^2, which indicates how closely the estimated values for the regression line correspond to the actual experimental data, was computed to be 0.92 for this fit, indicating a solid correlation between R_c and γ defined by Eq. (1).

Furthermore, we have collated the characteristic temperatures and R_c values for 23 oxide glasses (Refs. [22–29]) and 31 cryoprotective solutions (Refs. [30–37]). Most of the temperatures were obtained by DSC at a heating rate of 5 K/ min. Figure 4 shows the correlation between GFA (critical cooling rate) and the calculated γ values for oxide glasses [4(a)] and cryoprotective solutions [4(b)], respectively. Similarly, a linear interrelationship was observed for both glassy oxides and cryoprotectants. R^2 values for these two regressions are also high, suggesting that the γ parameter is also applicable to these noncrystalline materials. However, the regression formulas for these three types of noncrystalline materials are variant; this could be due to the diverse definitions of characteristic temperatures in different kinds of glasses. For comparison, the critical cooling rate of cryoprotectants as a function of the Turnbull's parameter T_{rg} is plotted in Fig. 5. Compared with Fig. 4(b), the data in this plot are much scattered, and widespread data results in a much lower R^2 value of 0.4, indicating that γ has a stronger correlation with GFA for these cryoprotective agents than Turnbull's criterion T_{rg}. The solid relationship between γ and R_c validates our current physical metallurgy approach for predicting the GFA among various types of noncrystalline systems.

Moreover, it was reported that oxygen impurity could drastically deteriorate the GFA of Zr-based BMGs [38–40]. By experimentally constructing TTT curves from isothermal annealing experiments, Lin *et al.* [38] found that increasing oxygen contents shifts the TTT curves to higher temperatures and to shorter times in these alloys, and concluded that the GFA of these alloys was dramatically dependent on the oxygen impurity level. A further investigation by Gebert *et al.* [39] and Liu *et al.* [40] in a similar Zr alloy revealed that the oxygen-triggered formation of more stable $NiZr_2$ crystalline phases rather than the equilibrium phases $CuZr_2$ and $NiAl_2Zr_6$ was responsible for the deterioration of the GFA. In other words, the oxygen impurity stabilized the competing crystalline phases (a lower T_x value and, consequently, a shorter nose time) and destabilized the liquid phases (a small increase in T_g and a higher position of TTT curve), thus reducing the value of γ and degrading the GFA of these alloys. This is exactly consistent with our analyses.

It is important to point out that the term $1/2(T_g + T_l)$ can be rewritten as $T_g + 1/2(T_l - T_g)$. The former item T_g gives a benchmark of the TTT curve location along temperature axis, and the latter item $1/2(T_l - T_g)$ is actually the width of the TTT curve which indicates the undercooled liquid region during cooling. Both of them should be taken into account as far as the liquid phase stability for glass-forming liquids is concerned. Equation (1) also suggests that the best glass formers in a system be around the eutectic composition with low lying T_l (which can give the small sum of T_g and T_l), but not necessarily be at the eutectic point because the T_x effect should be taken into account as well. In other words, the glass formation will also depend on the stability of the competing crystalline phases, although the eutectic usually has the highest liquid phase stability. This was confirmed recently in some BMG systems [41].

Additionally, Eq. (1) can be easily quantified by just a single DSC scan. Thus, this equation can be used as a

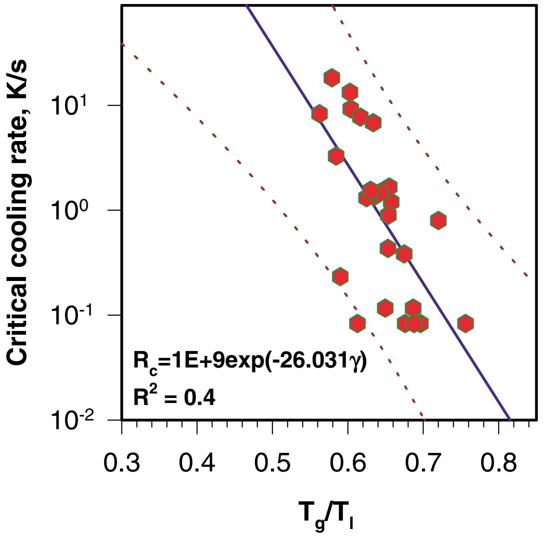

FIG. 5 (color online). The critical cooling rates as a function of the reduced glass transition temperature T_{rg} for cryoprotective agents. Data were taken from Refs. [30–37].

powerful guideline to identify new good glass formers. Note that T_g, T_x, and T_l are, to a certain extent, all heating rate dependent, and, consequently, so are the resultant γ values. Therefore, a constant heating rate is required when comparing the gamma values across the board. Meantime, it is worthwhile to notice that γ is dependent but not too sensitive to heating rates. This is because all the temperature parameters are commensurate with the heating rates and, to some degree, γ can be self-adjusted. Based on our previous work on some BMGs, the change in γ values is within 5% as the heating rate is altered from 10 to 40 K/ min.

This research was sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC05-00OR-22725 with UT-Battelle, LLC.

[1] G. M. Fahy, D. R. MacFarlane, C. A. Angell, and H. T. Meryman, Cryobiology **21**, 407 (1984).
[2] J. E. Lovelock and M.W. Bishop, Nature (London) **183**, 1394 (1959).
[3] D. C. Tran, G. H. Siegel, Jr., and B. Bendow, J. Lightwave Technol. **2**, 566 (1984).
[4] M. H. Cohen and D. Turnbull, Nature (London) **189**, 131 (1961).
[5] D. E. Polk, Acta Metall. **20**, 485 (1972).
[6] S. R. Nagel and J. Tauc, Phys. Rev. Lett. **35**, 380 (1975).
[7] H. S. Chen and B. K. Park, Acta Metall. **21**, 395 (1973).
[8] K. S. Dubey and P. Ramachandrarao, Int. J. Rapid Solidification **5**, 127 (1990).
[9] P. Ramachandrarao, Z. Metallkd. **71**, 172 (1980).
[10] T. Egami and Y. Waseda, J. Non-Cryst. Solids **64**, 114 (1984).
[11] S. H. Whang, Mater. Sci. Eng. **57**, 87 (1983).
[12] Z. P. Lu and C. T. Liu, Acta Mater. **50**, 3501 (2002).
[13] D. Turnbull, Contemp. Phys. **10**, 473 (1969).
[14] M. Ouchetto, B. Elouadi, and S. Parke, Phys. Chem. Glasses **32**, 22 (1991).
[15] H. S. Chen, Acta Metall. **22**, 1505 (1974).
[16] H. S. Chen, Rep. Prog. Phys. **43**, 353 (1980).
[17] D. D. Thornburg, Mater. Res. Bull. **9**, 1481 (1974).
[18] N. Clavaguera, M. T. Clavaguera-mora, and J. Casas-vazquez, J. Non-Cryst. Solids **22**, 23 (1976).
[19] J. Schroers, J. F. Loffler, E. Pekarskaya, R. Busch, and W L. Johnson, Mater. Sci. Forum **360–362**, 79 (2001).
[20] J. Schroers, R. Busch, S. Bossuyt, and W. L. Johnson, Mater. Sci. Eng. A **304–306**, 287 (2001).
[21] N. Nishiyama and A. Inoue, Mater. Trans. JIM **43**, 1913 (2002).
[22] T. Wakasugi, R. Ota, and J. Fukunaga, J. Am. Ceram. Soc. **75**, 3129 (1992).
[23] R.-G. Duan, K.-M. Liang, and S.-R. Gu, J. Eur. Ceram. Soc. **18**, 1131 (1998).
[24] C.-Y. Fang, H. Yinnon, and D. R. Uhlmann, J. Non-Cryst. Solids **57**, 465 (1983).
[25] K. Matusita and M. Tashiro, J. Non-Cryst. Solids **11**, 471 (1973).
[26] R. Ota, T. Wakasugi, W. Kawamura, and B. Tuchiya, J. Non-Cryst. Solids **188**, 136 (1995).
[27] T. Wakasugi, T. Kobayshi, R. Ota, and J. Fukunaga, J. Ceram. Soc. Jpn. **103**, 63 (1995).
[28] E. Asayama, H. Takebe, and K. Morinaga, ISIJ International **33**, 233 (1993).
[29] A. A. Cabral, Jr., C. Fredericci, and E. D. Zanotto, J. Non-Cryst. Solids **219**, 182 (1997).
[30] B. Wowk, M. Darwin, S. B. Harris, S. R. Russell, and C. M. Rasch, Cryobiology **39**, 215 (1999).
[31] A. Baudot and P. Boutron, Cryobiology **37**, 187 (1998).
[32] A. Baudot, C. Cacela, M. L. Duarte, and R. Fausto, Cryobiology **44**, 150 (2002).
[33] P. Boutron, D. Delage, and B. Roustit, J. Chim. Phys. **77**, 567 (1980).
[34] A. Baudot, L. Alger, and P. Boutron, Cryobiology **40**, 151 (2000).
[35] J. M. Hey and D. R. Macfarlane, Cryobiology **33**, 205 (1996).
[36] P. Boutron, Cryobiology **27**, 55 (1990).
[37] P. Boutron, P. Mehl, A. Kaufmann, and P. Angibaud, Cryobiology **23**, 453 (1986).
[38] X. H. Lin, W. L. Johnson, and W. K. Rhim, Mater. Trans. JIM **38**, 473 (1997).
[39] A. Gebert, J. Eckert, and L. Schultz, Acta Mater. **46**, 5475 (1998).
[40] C. T. Liu, M. F. Chisholm, and M. L. Miller, Intermetallics **10**, 1105 (2002).
[41] Y. Li (personal communication).