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New criterion in predicting glass forming ability of various glass-forming systems*

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It has been confirmed that glass-forming ability (GFA) of supercooled liquids is related to not only liquid phase stability but also the crystallization resistance. In this paper, it is found that the liquid region interval ($T_\mathrm{l} - T_\mathrm{g}$) characterized by the normalized parameter of $T_\mathrm{g}/T_\mathrm{l}$ could reflect the stability of glass-forming liquids at the equilibrium state, whilst the normalization of supercooled liquid region ΔT_x=($T_\mathrm{x} - T_\mathrm{g}$), i.e. $\Delta T_\mathrm{x}/T_\mathrm{x}$ (wherein T_l is the liquidus temperature, T_g the glass transition temperature, and T_x the onset crystallization temperature) could indicate the crystallization resistance during glass formation. Thus, a new parameter, defined as $\xi = T_\mathrm{g}/T_\mathrm{l}+\Delta T_\mathrm{x}/T_\mathrm{x}$ is established to predict the GFA of supercooled liquids. In comparison with other commonly used criteria, this parameter demonstrates a better statistical correlation with the GFA for various glass-forming systems including metallic glasses, oxide glasses and cryoprotectants.

Keywords: glass-forming systems, glass forming ability, criterion
PACC: 6125, 6140

1. Introduction

Glass forming ability (GFA), as related to the ease of vitrification, is vital for understanding the origin of glass formation and is important for designing and developing new bulk metallic glasses (BMGs). Scientific efforts for searching proper GFA measure for metallic glasses have been initiated immediately after the first reported Au–Si metallic glass.[1] As a result, many GFA parameters or criteria have been proposed to reflect the relative GFA among BMGs on the basis of different calculation methods.[2−21] Among these GFA indicators, T_rg (=$T_\mathrm{g}/T_\mathrm{l}$) and $\gamma = T_\mathrm{x}/(T_\mathrm{g}+T_\mathrm{l})$ (wherein T_l is the liquidus temperature, T_g the glass transition temperature, and T_x the onset crystallization temperature) are the most widely used, since these two parameters are deduced from definite physical metallurgy points of view, and show a reasonable correlation with the GFA for various BMGs.[1−5] However, accumulated data show that both T_rg and γ still cannot, in some cases, properly reflect the GFA tendency of BMGs, as shown in Ref.[12]. As a GFA indicator, it follows that the more reliable of the parameter is, the better of the ability becomes to pinpoint the best composition for BMGs. Therefore, the interrelationship of characteristic parameters T_l, T_x, T_g with GFA for glass forming liquids still remain room for further examination.

As pointed out by Turnbull and Davies, any liquid can form a glass as long as the cooling rate is fast enough to suppress the crystallization event.[1,22] In this sense, glass formation can be well explained by time-temperature-transformation (TTT) diagram. Hence, the GFA of a liquid is directly associated with the location of the TTT curve in the time-temperature coordinate, that is, the position of the TTT curve along both the temperature axis and the time axis. Accordingly, in this paper, we aim at providing a more reliable indicator than the other current parameters to predict GFA for metallic glasses on the basis of viewpoint of physics and analysing the characteristic features of the TTT curves. Meanwhile, the ability of the new parameter to predict other glass-forming liquids such as glassy oxides, cryoprotectants are also evaluated.

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2. Theoretical analysis

Following the argument of Lu and Liu,[2−4] glass formation always involves a competing process between the liquid and the resulting crystalline solid phases. Thus, GFA has to include two key components: the liquid phase stability and the resistance to crystallization. It has long been recognized that the GFA of metallic glasses inversely related to the liquid phase stability which actually reveals, to what degree, the equilibrium liquid can exist against the solidification.[23−25] On this basis, let us start by discussing analysis of the liquid phase stability from the physical viewpoint.

A liquid that manages to get below T_l without crystallizing is called a supercooled liquid. As a supercooled liquid is cooled to a lower temperature, the viscosity increases and the atom clusters move more and more slowly. At a certain temperature the atom clusters will move so slowly that they do not have a chance to rearrange significantly before the temperature is lowered further. At temperatures not much lower than this, the time scales for atom cluster rearrangements become hopelessly long in comparison with the time scale of the experimental observations. The structure of this material is "frozen" for practical purposes, and we call it a glass. The temperature at which the "frozen" occurs is called glass transition temperature, i.e T_g. It is important to emphasize that the glass transition is not a first-order phase transition. It is a kinetic event which depends upon the crossing of an experimental time scale and the time scales for atom cluster rearrangements. Furthermore, glasses are not crystals or liquid crystals. They are liquids which are "frozen" on the time scale of experimental observation. Therefore, a supercooled liquid which has not solidified to glass may be regarded as being in equilibrium.[26] Therefore, the liquid region interval $(T_l - T_g)$ can be used to indicate the relative stability of stable glass-forming liquids; the lower of the interval value the larger stability of the liquid.

For conventional binary alloy systems, the T_g is typically assumed to be less dependent on composition, while T_l often decreases more strongly. In this case, the changing trend of liquid region interval $(T_l - T_g)$ is consistent with the normalized parameter of T_g/T_l. The interval between T_l and T_g thus generally decreases and T_g/T_l increases with increasing alloying concentration so that the probability of being able to cool through 'dangerous' range without crystallization is enhanced, i.e. GFA is increased.[24,27] Figure 1 shows a hypothetical case where T_x and T_g remain unchanged but T_l decreases. The figure demonstrates that, in comparison with liquid "a", liquid "b" ($^aT_l < {}^bT_l$) exhibits a higher critical cooling rate ($^aR_c < {}^bR_c$). This means that a decrease in T_l, i.e. the increase of T_g/T_l, will lead to a decrease in R_c and hence an increase in the GFA. Therefore, the GFA is positively associated with the parameter of T_g/T_l for an alloy when T_g remains constant. As such, the correlation between the GFA of metallic glasses and liquid region interval $(T_l - T_g)$ can be expressed as follows:

$$\text{GFA} \propto \frac{T_g}{T_l}. \tag{1}$$

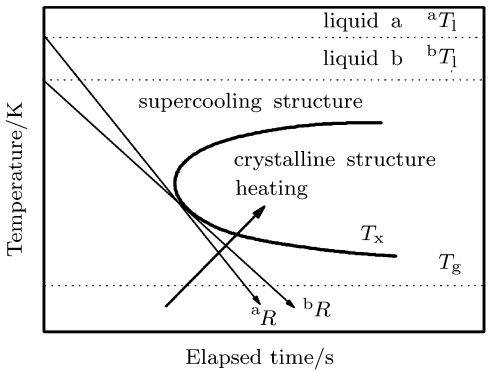


Fig.1. Schematic TTT diagram showing the correlation between T_l and R_c when T_x and T_g is fixed.

Hence, we have a crucial physical parameter to characterize the liquid phase stability which is positive to the GFA of BMGs. This is also the reduced glass forming temperature suggested by Turnbull, which based on the assumption that the nucleation frequency of a melt scale as $1/\eta$ (viscosity of the liquid).[1] The implication of this theory is that the great GFA is always associated with low-melting eutectics (i.e. deep eutectics), as has been demonstrated in many binary systems (e.g. Ti–Be).[24] This is probably reliable for conventional binary alloy system whose T_g is typically assumed to be less dependent on composition.[28,29] However, the values of T_l and T_g can differ significantly for multicomponent systems if the compositions are changed, as shown by Lu and Liu.[2−4] Obviously, in this case, the values of T_g/T_l could not be able to judge accurately the liquid temperature interval $(T_l - T_g)$ and the function of T_g on GFA under the conditions of different T_l needs to be considered.

This will involve the consideration of the function of crystallization resistance of glass-forming liquids on

the GFA. The crystallization resistance is determined by the mechanism of crystallization involving crystal nucleation and growth. In general, complex crystal structure and crystallization reactions requiring long-range diffusion would lead to a high crystallization resistance. It is well known that the supercooled liquid region ΔT_x=($T_x - T_g$) determined upon devitrification is a quantitative measure of the stability of the supercooled liquid, i.e. crystallization resistance. A large ΔT_x value may indicate that the undercooled liquid can remain stable in a wide temperature range without crystallization, thus leads to a larger GFA of the alloy. This speculation has been well confirmed in several glass-forming alloy systems in which the supercooled liquid region correlates reasonably well with the GFA of alloys.[30−34] This can be demonstrated clearly from TTT curves.

Figure 2 demonstrates that under the same T_x, compared with liquid "a", liquid "b" (^bT_g <^aT_g) exhibits a longer onset time ($t_a < t_b$) (Fig.2(a)) or needs a higher heating rate (Fig.2(b)) for the occurrence of crystallization process. This means that a decrease in T_g, i.e. the increase of ΔT_x will lead to an increase of resistance of crystallization and hence an increase in the GFA.

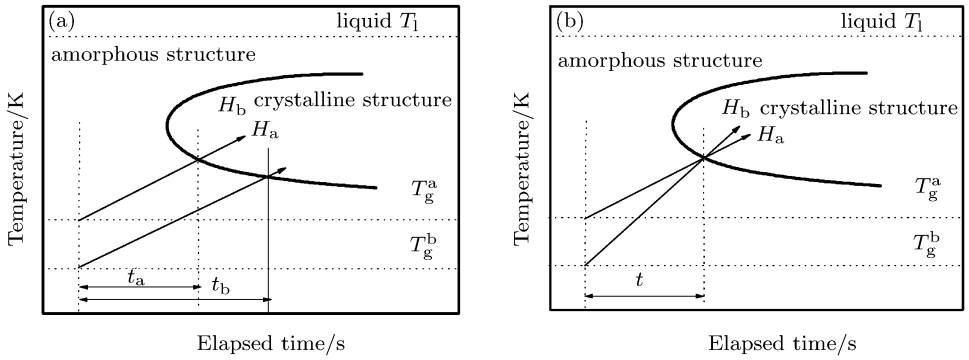


Fig.2. Schematic TTT diagram showing the relationship between ($T_x - T_g$) and the resistance to recrystallization.

Compared with T_g, the crystallization transition temperature T_x is a more important characteristic temperature that relates to the crystallization process for glass-forming alloys. A parameter without unit is obtained if ΔT_x is normalized by T_x, which can be used to measure the GFA of multicomponent systems. Their correlation can be expressed as follows:

$$\text{GFA} \propto \frac{T_x - T_g}{T_x} = \frac{\Delta T_x}{T_x}. \tag{2}$$

As discussed above, GFA of metallic glasses associated with two factors, T_g/T_l and $\Delta T_x/T_x$, from the perspective of crystallization resistance and liquid stability during the cooling of the supercooled liquid. By combining the effects in Eqs.(1) and (2) in the way to get a parameter without units, we can simply write down an expression as

$$\text{GFA} \propto \left(\frac{T_x - T_g}{T_x}, \frac{T_g}{T_l}\right). \tag{3}$$

For simplicity, we introduce a single parameter ξ, which is a summation of the two factors $\Delta T_x/T_l$ and T_x/T_l. Then we have:

$$\xi = \frac{\Delta T_x}{T_x} + \frac{T_g}{T_l}. \tag{4}$$

Understanding of the deduction for the new parameter ξ is schemed in Fig.3.

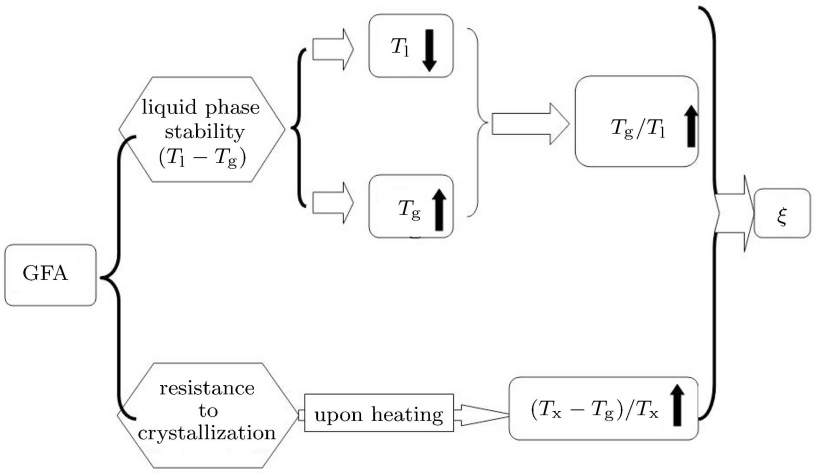


Fig.3. The approach for deduction of the new parameter.

3. The efficiency of the new parameter

In order to compare the efficiency of the currently proposed GFA criteria γ_m with previous parameters such as γ ($=T_g/T_x+T_l$), α ($=T_x/T_l$), ΔT_x, T_{rg}, $T_x/(T_l - T_g)$ and $(T_x - T_g)/(T_l - T_g)$, we can all plot them against the R_c for a number of metallic glasses. The characteristic temperatures T_g, T_x and T_l together with the critical cooling rates R_c for various BMGs including Mg-, Zr-, La-, Pd-, Fe-, Cu-, Au- and rare earth-based alloys can be found in Refs.[2–4, 35–45]. The relationship between the ξ, T_{rg} and the critical cooling rate $\log_{10}R_c$ for glass formation in these representative metallic glasses is shown in Fig.4(a). An overall linear relation between $\log_{10}R_c$ and ξ is clearly observed. A linear regression analysis shows that the relation between R_c with ξ can be expressed as $\log R_c = 6.23–8.23\xi$. For comparison, the critical cooling rate of metallic glasses as a function of the Turnbull's parameter T_{rg} is plotted in Fig.4(b). In comparison with Fig.4(a), we find that the data in this plot are much scattered. From the regression analysis of the plots between the various GFA criteria and R_c, the statistical correlation factor, R^2, has been evaluated. The R^2 value can give an idea of the effectiveness and consistency of different GFA parameters. The higher the R^2 value, the better is the correlation between the proposed GFA parameter and R_c. Table 1 compares the R^2 values for $\log_{10}R_c$ with various GFA parameters. It is evident from Table 1 that the newly proposed ξ gives an R^2 value of 0.90 with $\log_{10}R_c$, which is the highest among all the tabulated GFA criteria, indicating that ξ has the strongest correlation with GFA for metallic glasses among these criteria.

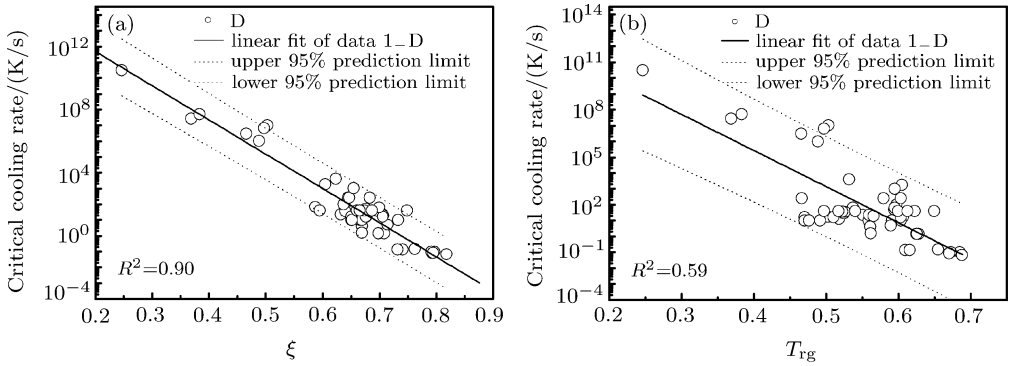


Fig.4. The correlation between the critical cooling rate and the parameter ξ (a) and T_{rg} (b) for different metallic glasses.

Table 1. Comparison between different GFA parameters using the data of different glass-forming systems.

parameter		ξ	$T_x/(T_g+T_l)$	T_x/T_l	ΔT_x	T_{rg}	$T_x/(T_l-T_g)$	$(T_x-T_g)/(T_l-T_g)$
R^2	metallic glasses	0.90	0.87	0.82	0.60	0.59	0.62	0.67
	glassy oxides	0.85	0.79	0.83	0.03	0.76	0.54	0.44
	cryoprotective agents	0.90	0.87	0.85	0.78	0.54	0.66	0.79

To testify the ability of the currently proposed GFA criterion ξ to predict various glass-forming liquids, the relationship between ξ and the critical cooling rate for some other kinds glass-forming materials, such as oxide glasses (Fig.5(a)) and cryo-protective solutions (Fig.6(a)), is also explored. For comparison, the critical cooling rate of oxide glasses and cryoprotective solutions as a function of the Turnbull's parameter T_{rg} is also plotted in Figs.5(b) and 6(c), respectively. The characteristic temperatures, the critical cooling rates for some typical oxide glasses and cryoprotectants are from Refs.[2–4]. Similarly, a linear interrelationship is observed for both glassy oxides and cryoprotectants (Fig.5(a), Fig.6(a)). However, the data in Figs.5(b) and 6(b) are much scattered, indicating that T_{rg} has a weaker correlation with GFA for oxide glasses and cryoprotectants than the current suggested ξ. From Table 1, R^2 values for these two regressions are also very high, suggesting that the newly proposed ξ is also applicable to these noncrystalline materials.

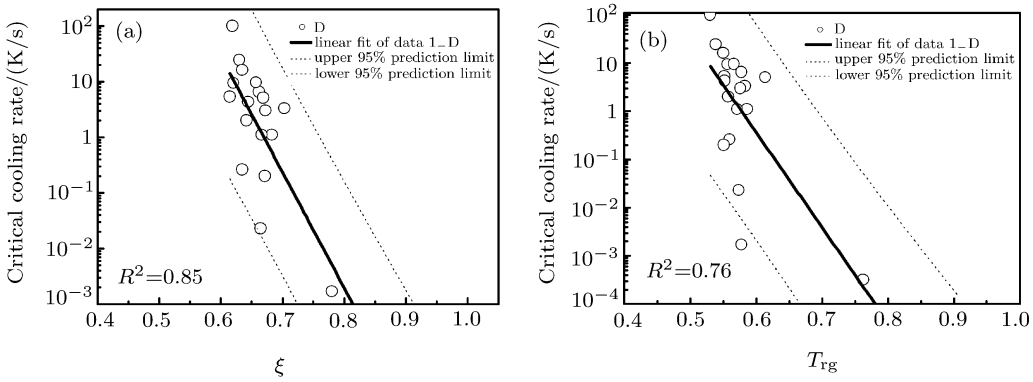


Fig.5. The correlation between the critical cooling rate and the parameter ξ (a) and T_{rg} (b) for different glassy oxides.

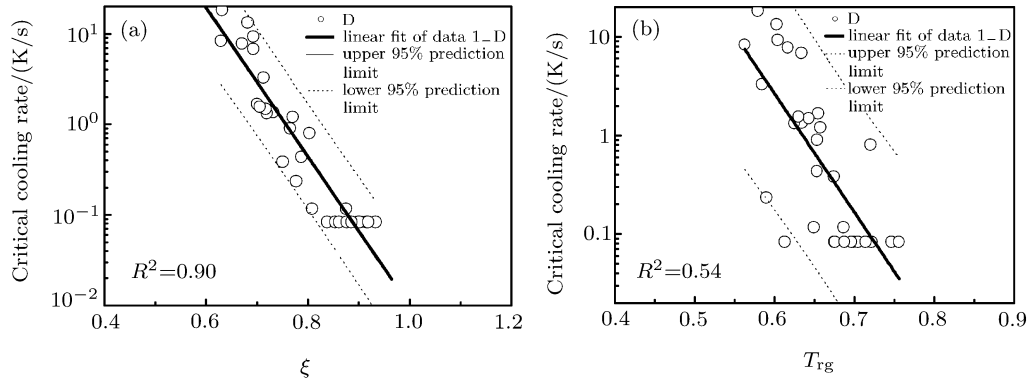


Fig.6. The correlation between the critical cooling rate and the parameter ξ (a) and T_{rg} (b) for different cryoprotective agents.

4. Conclusion

In summary, this paper proposes a GFA parameter ξ, defined as $\Delta T_{\rm x}/T_{\rm x}+T_{\rm g}/T_{\rm l}$. This parameter also reflects the effects of $T_{\rm g}$, $T_{\rm x}$ and $T_{\rm l}$ which are basically measured upon devitrification of glassy samples, the same as the previous commonly used criteria. However, the present result shows that the ξ parameter exhibits the best correlation with GFA among some parameters suggested so far for various glass-forming systems. This is because the current indicator correctly considers all related factors for the liquid phase stability and the crystallization resistance during glass formation. Since the ξ parameter can be calculated simply by data on $T_{\rm g}$, $T_{\rm x}$ and $T_{\rm l}$, the current parameter is a simple and user-friendly indicator.

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