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A new glass-forming ability criterion for bulk metallic glasses

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Abstract

A new indicator of glass-forming ability (GFA) for bulk metallic glasses (BMGs) is proposed based on crystallization processes during cooling and reheating of the supercooled liquid. The interrelationship between this new parameter and the critical cooling rate or critical section thickness is elaborated and discussed in comparison with two other representatives, i.e. reduced glass transition temperature T_{rg} ($= T_g/T_1$, where T_g and T_1 are the glass transition temperature and liquidus temperature, respectively) and supercooled liquid range ΔT_{xg} ($= T_x - T_g$, where T_x is the onset crystallization temperature and T_g the glass transition temperature). Our results have shown that ΔT_{xg} alone cannot infer relative GFA for BMGs while the new parameter γ , defined as $T_x/(T_g + T_1)$, has a much better interrelationship with GFA than T_{rg} . An approximation of the critical cooling rate and critical section thickness for glass formation in bulk metallic glasses is also formulated and evaluated. © 2002 Published by Elsevier Science Ltd on behalf of Acta Materialia Inc.

Keywords: Casting; Metallic glasses; Differential thermal analysis; Glass-forming ability; Order-disorder phenomena

1. Introduction

Glass-forming ability (GFA), as related to the ease of devitrification, is very crucial for understanding the origins of glass formation and also important for designing and developing new bulk metallic glasses (BMGs). The glass-forming ability of a melt is evaluated in terms of the critical cooling rate (R_c) for glass formation, which is the minimum cooling rate necessary to keep the melt amorphous without precipitation of any crystals during solidification. The smaller R_c , the higher the GFA of a system should be. However, R_c is a parameter that is difficult to measure precisely. A great deal of effort has therefore been devoted to searching for a simple and reliable gauge for quantifying GFA for metallic glasses. As a result, many criteria have been proposed to reflect relative GFA among BMGs on the basis of the characteristic temperatures measured by differential thermal calorimetry or/and differential thermal analysis (see [1] for a summary). Nevertheless, the most extensively used are the reduced glass transition temperature T_{rg} (glass transition temperature T_g over liquidus temperature T_1) and the supercooled liquid region ΔT_{xg}

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(the temperature difference between the onset crystallization temperature T_x and the glass transition temperature T_g). As shown by Lu et al. [2,3], the reduced glass transition temperature T_{rg} shows a better correlation with GFA than that given by T_g/T_m for BMGs (T_m : melting point).

Although both ΔT_{xg} and the ratio T_g/T_1 are used as indicators of the GFA for metallic glasses, they did show contrasting trends versus GFA in many alloy systems. Waniuk et al. [4] recently confirmed that T_g/T_1 correlated well with GFA in Zr–Ti–Cu– Ni-Be alloys whereas the supercooled liquid range ΔT_{xg} has no relationship with GFA in the least. Those glassy compositions with the largest ΔT_{xg} are actually the poorest glass formers in the system. Inoue et al. [5,6] also proved that the bulk glass-forming ability is more closely associated with T_{g}/T_{l} values in Cu–Zr–Ti and Cu–Hf–Ti ternary systems rather than ΔT_{xg} . On the other hand, it was found that the ratio T_g/T_1 is not reliable enough to infer relative GFA in $Pd_{40}Ni_{40-x}Fe_xP_{20}$ $(20 \ge x \ge 0)$ [7], Fe–(Co,Cr,Mo,Ga,Sb)–P–B–C [8] and $Mg_{65}Cu_{15}M_{10}Y_{10}$ (M = Ni, Al, Zn and Mn) [9] alloy systems. On the contrary, ΔT_{xg} was claimed to be a reliable and useful gauge for the optimization of bulk glass formation in these systems.

Hence, further investigation is necessary to obtain a better and more precise criterion to reflect the GFA of bulk metallic glasses. A literature search for critical cooling rates and critical thicknesses for glass formation in various metallic glassy systems, as well as for characteristic temperatures T_g , T_1 and T_x , has been carefully conducted. On the basis of all available data, a new criterion for glass formation has been proposed in this study. Its correlation with GFA will be discussed and compared with the reduced glass transition temperature T_g/T_1 as well as the supercooled region ΔT_{xg} . A estimation of critical cooling rate $R_{\rm c}$ and the critical thickness $Z_{\rm c}$ (the least dimension of the sample) for glass formation in metallic glasses will also be formulated in the light of this new parameter. Furthermore, this new criterion for glass formation will be applied to the Pd-Fe-Ni-P system in which T_g/T_1 and ΔT_{xg} showed opposite trends with GFA.

2. Theoretical analysis

As mentioned previously, R_c is a most effective gauge for glass-forming ability in metallic glasses but it is very difficult to measure experimentally. Moreover, $R_{\rm c}$ can only be determined once the composition for glass formation is known. It is thus necessary to establish a simple and reliable parameter that correlates well with GFA and can be calculated using more easily experimentally measured quantities such as $T_{\rm g}$ and $T_{\rm x}$. In return, such a criterion can then be utilized as a guideline for exploring new bulk glassy compositions. In the following, the factors that associate with GFA will be analyzed from the perspectives of both devitrification and amorphization. As a result, a simple indicator for representing the relative GFA will be proposed.

2.1. Consideration from devitrification perspective

It is well known that $T_x - T_g$ is an indication of the devitrification tendency of a glass upon heating above $T_{\rm g}$. A large $T_{\rm x} - T_{\rm g}$ value may indicate that the supercooled liquid can exist in a wide temperature range without crystallization and has a high resistance to the nucleation and growth of crystalline phases [10]. Since crystallization is actually a competitive process with respect to glass formation, a large $T_x - T_g$ would lead to a high GFA. In this sense, this temperature interval is somewhat related to GFA. In order to make possible comparisons between various glasses showing different T_{s} , this temperature interval should be weighted by $1/T_{\rm g}$ leading to the factor $(T_{\rm x}-T_{\rm g})/T_{\rm g}$ [= (T_x/T_g) -1], which is dimensionless [11]. As such, GFA is proportional to the factor T_x/T_g based on the glass stability upon the reheating process of a glass.

2.2. Consideration from amorphization perspective

When a liquid is cooled from above the liquidus temperature T_1 to a temperature below T_g at a constant cooling rate R, the time-dependent volume

fraction of crystalline phase *X* can be given based on the non-isothermal crystallization kinetics[12,13]:

$$X(T) = \frac{4\pi}{3R^4} \int_{T_1}^{T_g} I(T') [\int_{T'}^{T_g} U(T') dT']^3 dT'.$$
 (1)

Here *I* and *U* are the steady-state nucleation frequency and the crystal growth rate, respectively. If one selects $X < 10^{-6}$ as a criterion for glass formation, then the critical cooling rate R_c can be derived from Eq. (1) as:

$$R_{\rm c}^4 = \frac{4\pi}{3 \times 10^{-6}} \int_{T_1}^{T_{\rm g}} I(T') [\int_{T'}^{T_{\rm g}} U(T') {\rm d}T'']^3 {\rm d}T'.$$
(2)

According to the common crystallization theory, the nucleation frequency and crystal growth rate can be estimated by the following equations [14,15]:

$$I = \frac{10^{35}}{\eta} \exp\left[\frac{-16\pi}{3} \cdot \frac{\Delta S_{\rm f} \alpha_{\rm m}^3 T^2}{N_{\rm A} k (T_{\rm I} - T)^2}\right]$$
(3)

and

$$U = \frac{kT}{3\pi a_0^2 \eta} \left[1 - \exp\left(-\frac{(T_1 - T)\Delta S_f}{R_g T}\right) \right].$$
 (4)

Here η , k, $\alpha_{\rm m}$, a_0 , $N_{\rm A}$, $\Delta S_{\rm f}$ and $R_{\rm g}$ are viscosity, the Boltzmann constant, a constant of 0.86, mean atomic diameter, Avogadro's number, the molar fusion entropy and the gas constant, respectively. From Eqs. (2), (3) and (4), one can know that the critical cooling rate R_c decreases with increasing viscosity of the supercooled liquid, activation energy for viscous flow, fusion entropy, and with decreasing liquidus temperature T_1 . When a glass is reheated with a constant heating rate β from a certain temperature T_0 up to a temperature T, as is the case with differential scanning calorimetry (DSC) heating experiments, the fraction X(T) of precipitated phases in amorphous solids could also be calculated from crystallization kinetics based on the non-isothermal transformation theory [16,17]:

$$X(T) = \frac{4\pi}{3\beta^4} \int_{T_0}^{T} I(T') [\int_{T'}^{T} U(T') dT'']^3 dT'.$$
 (5)

The nucleation frequency I and crystal growth rate U can also be computed based on Eqs. (3) and (4), respectively. It should be noted that Eq. (5) is only valid when X(T) is small compared with unity. This is the reason why T_x was defined as the onset temperature of crystallization. Based on Wakasugi et al.'s analysis [17], the T_x/T_1 ratio increases with increasing viscosity of the supercooled liquid, fusion entropy, activation energy of viscous flow, heating rate β and with decreasing T_1 . The dependence of the T_x/T_1 ratio on the magnitudes of liquid parameters such as viscosity of the supercooled liquid, fusion entropy, activation energy for viscous flow and liquidus temperature T_1 is quite similar to those of critical cooling rate R_c . In a nutshell, $T_{\rm x}/T_{\rm 1}$ is a reasonable indication of GFA based on the crystallization process of an undercooled liquid. The system with a larger T_x/T_1 ratio could have a lower R_c and thereby a higher GFA.

As discussed above, GFA of metallic glasses associates with two factors, T_x/T_g and T_x/T_l , from the perspective of crystallization processes during both reheating and cooling of the undercooled liquid. Their relationship can be expressed as follows:

$$GFA \propto \left(\frac{T_x}{T_g}, \frac{T_x}{T_1}\right).$$
(6)

The above correlation can be rewritten as:

$$GFA \propto \left(\frac{T_g}{T_x}, \frac{T_1}{T_x}\right)^{-1}.$$
(7)

For simplicity, we introduce a single parameter, which is an average of the two factors T_g/T_x and T_1/T_x , i.e. $1/2[(T_g + T_1)/T_x]$. Then Eq. (7) predicts:

$$GFA \propto \left(\frac{T_{x}}{T_{g} + T_{l}}\right).$$
(8)

Hence, we define a new parameter γ for inferring the relative GFA among BMGs as:

$$\gamma = \frac{T_{\rm x}}{T_{\rm g} + T_{\rm l}}.\tag{9}$$

It should be pointed out that indicators in other formats could also be derived from Eq. (6). However, the ratio in Eq. (9) is the simplest and most reliable based on experimental data. In the following sections, we shall show the strong correlation between γ and GFA by analyzing the readily available experimental data.

3. Calculation of GFA indicators

Table 1 shows the glass transition temperature $T_{\rm g}$, onset crystallization temperature $T_{\rm x}$ and liquidus temperature T₁ for Mg-, Zr-, La-, Pd- and Ndbased bulk metallic alloys. The data for recently developed Cu- and Ti-based glassy alloys are also included. It is necessary to point out that T_{g} , T_{x} and T_1 were defined as the inflection point of glass transition, the onset crystallization temperature and the offset fusion temperature, respectively. Note that all of these characteristic temperatures can be easily determined from single DSC measurements. Table 2 summarizes these characteristic temperatures for some typical conventional metallic glasses. The majority of the data in Table 1 were obtained from Refs. [2,3], and most of them were measured using differential thermal calorimetry (DSC) or/and differential thermal analysis (DTA) at a heating rate of 20 K/min. Since these temperatures are dependent on heating rate, it is important to utilize the same heating rate for the measurements.

Table 3 presents the summary of $\Delta T_{xg} (T_x - T_g)$, $T_{rg} (T_g/T_l)$ and γ calculated based on the data in Table 1, together with the critical cooling rate R_c and the critical section thickness Z_c for glass formation in these alloy systems. Table 4 tabulates the corresponding values for the conventional metallic glasses listed in Table 2. For BMGs, the newly defined γ value is in the range of from 0.350 to 0.500, while ΔT_{xg} ranges from 16.3 to 117 K and T_{rg} varies from 0.503 to 0.690.

4. Discussion

4.1. The correlation between γ and GFA

The relationship between the γ value and the critical cooling rate for glass formation in representative metallic glasses is shown in Fig. 1. A linear

interrelationship is observed between γ values and $\log_{10}R_c$, as demonstrated by the solid line. This relationship is expressed in an approximation formula:

$$\log_{10} R_{\rm c} = (21.71 \pm 1.97) - (50.90 \pm 0.71)\gamma.$$
(10)

Thus the critical cooling rate can be derived from the above equation:

$$R_{\rm c} = 5.1 \times 10^{21} \exp(-117.19\gamma), \tag{11}$$

where R_c is in K/s and γ is dimensionless. In order to reveal how closely the estimated values for the regression line correspond to the actual experimental data, the statistical correlation parameter, R^2 , was also computed using a readily available regression program. The R-squared value, also known as the coefficient of determination, is an indicator that ranges in value from 0 to 1. The higher the R^2 value, the more reliable the regression line should be. As is clear in the graph, the R^2 value is as high as 0.91 for this fit, suggesting that there is a solid correlation between the critical cooling rate R_c and the novel parameter γ . The predicted error band in Eq. (10) obtained at 95% confidence interval is shown in Fig. 1 as two dashed lines. This prediction interval, which was also computed by the common regression program, describes the range where the data values will fall a percentage of the time for repeated measurements. A narrower band at a fixed confidence level (normally 95%) implies less scatter of the experimental data and a stronger correlation between independent variables.

Fig. 2 is a plot of the critical section thickness as a function of the parameter γ for typical bulk metallic glasses. A linear relationship between γ values and $\log_{10}Z_c$ is obtained with considerable scatter. The relationship can be expressed as follows:

$$log_{10}Z_{c} = (-6.55 \pm 1.07)$$
(12)
+ (18.11 ± 0.70) \gamma.

The critical section thickness for bulk metallic glasses can then be estimated using the formula below:

$$Z_{\rm c} = 2.80 \times 10^{-7} \exp(41.70\gamma), \tag{13}$$

where Z_c is in millimeters. The dashed line in Fig.

Table 1

The glass transition temperature (T_g) , crystallization temperature (T_x) and liquidus temperature (T_l) for representative BMGs. Most of data were obtained by DSC or/and DTA at a heating rate of 20 K/min

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$La_{55}Al_{25}Ni_5Cu_{10}Co_5$ 465.2541.8822.5[2,3] $La_{66}Al_{14}Cu_{20}$ 395.0449.0731.0[18]	
La ₆₆ Al ₁₄ Cu ₂₀ 395.0 449.0 731.0 [18]	
Pd- $Pd_{40}Cu_{30}Ni_{10}P_{20}$ 576.9 655.8 836.0 [2,3]	
$Pd_{s_1,s}Cu_{s_1,s_1,s_2}$ 633.0 670.0 1097.3 [2,3]	
$Pd_{70}Cu_2Si_{16,5}$ 635.0 675.0 1086.0 [2,3]	
$Pd_{775}Cu_{s}Si_{165}$ 637.0 678.0 1058.1 [2,3]	
$Pd_{77}Cu_6Si_{17}$ 642.4 686.4 1128.4 [2,3]	
$Pd_{735}Cu_{10}Si_{165}$ 645.0 685.0 1135.9 [2,3]	
$Pd_{71} \leq Cu_{12}Si_{16} \leq 652.0 = 680.0 = 1153.6 = [2,3]$	
$Pd_{40}Ni_{40}P_{20}$ 590.0 671.0 991.0 [31]	
Nd- Nd ₆₀ Al ₁₅ Ni ₁₀ Cu ₁₀ Fe ₅ 430.0 475.0 779.0 [2.3]	
$Nd_{61}Al_{11}Ni_8Co_5Cu_{15}$ 445.0 469.0 744.0 [2,3]	
Cu- $Cu_{60}Zr_{30}Ti_{10}$ 713.0 763.0 1151.0 [5]	
$Cu_{54}Zr_{27}Ti_9Be_{10}$ 720.0 762.0 1130.0 [19]	
Ti- $Ti_{34}Zr_{11}Cu_{47}Ni_8$ 698.4 727.2 1169.2 [2,3]	
$Ti_{50}Ni_{24}Cu_{20}B_1Si_2Sn_3$ 726.0 800.0 1310.0 [20]	

Alloys	<i>T</i> _g (K) [Ref.]	$T_{\rm x}$ (K) [Ref.]	T_1 (K) [Ref.]
Ni	425.0 [21]	425.0 [21]	1725.0 [21]
$Fe_{91}B_9$	600.0 [21]	600.0 [21]	1628.0 [21]
Pd ₉₅ Si ₅	647.0 [22]	647.0 [22]	1688.0 [23]
Pd ₇₅ Si ₂₅	656.0 [22]	656.0 [22]	1343.0 [23]
Zr ₆₅ Be ₃₅	623.0 [15]	623.0 [15]	1238.0 [24]
Ti ₆₃ Be ₃₇	673.0 [15]	673.0 [15]	1353.0 [25]
$Pd_{82}Si_{18}$	648.0 [22]	648.0 [22]	1071.0 [23]
Mg ₇₇ Ni ₁₈ Nd ₅	429.4 [2,3]	437.2 [2,3]	886.9 [2,3]
Mg ₉₀ Ni ₅ Nd ₅	426.2 [2,3]	449.0 [2,3]	918.8 [2,3]
$Au_{77.8}Si_{8.4}Ge_{13.8}$	293.0 [21]	293.0 [21]	629.0 [21]

Table 2 Summary of T_{g} , T_{x} and T_{1} for non-bulk metallic glasses

2 also shows the 95% prediction limits for this correlation, as expressed in Eq. (12). Compared with Fig. 1, the data in Fig. 2 are more scattered. The widely spread data result in a lower R^2 value of 0.57 and a larger prediction band. This can presumably be attributed to the large casting variations for glass formation and different approaches to the maximum casting sizes. For instance, there are many kinds of techniques involved in manufacturing BMGs such as water quenching, suction casting, injection casting, high-pressure die casting, etc. The use of various techniques can contribute to the large deviation in critical section size. Meanwhile, almost all reported maximum section sizes for different systems are in integer numbers, and this loose approach can also lead to a higher deviation in the data. However, Eq. (13) can still be used as an approximation of the maximum size achievable for the different amorphous alloys. As mentioned earlier, γ values for BMGs vary from 0.350 to 0.500. Substituting 0.500 into Eq. (13), we can predicate the maximum section size for BMGs to be around 320 mm. Additionally, the γ value for pure Ni is about 0.198 (see Table 4), and its maximum size is determined to be 1 µm. This is in good agreement with the fact that no glass for pure Ni can be formed even by the melt-spinning technique.

4.2. The comparison between γ , T_{rg} and ΔT_{xg}

Fig. 3 presents the relationship between T_{rg} and GFA for all of the metallic glasses listed in Table

1. In Fig. 3(a) is the critical cooling rate R_c as a function of $T_{\rm rg}$. The solid line is the best fit of the data. The corresponding equation of the trend line and the resultant R^2 value are indicated on the graph. Although R_c is somewhat dependent on T_{rg} , compared with the correlation displayed in Fig. 1, however, the current regression demonstrates a lower R^2 value of 0.74 and a larger prediction band implying that the new parameter γ correlates better with the critical cooling rate R_c than T_{rg} . Similarly, Fig. 3(b) depicts the relationship between T_{rg} and the critical section thickness Z_c. Compared with Fig. 2, it is clear that the new parameter γ also has a better correlation with Z_c than T_{rg} . This is in accordance with the lower R^2 value of 0.32 and the wider prediction band observed for the current $T_{\rm rg} - Z_{\rm c}$ correlation. It is therefore reasoned out that the presently proposed indicator γ has a stronger correlation with GFA than $T_{\rm rg}$.

The ratio T_g/T_1 was introduced for purely kinetic reasons associated with the need to avoid crystallization [37,48]. In the first place, T_g is typically assumed to be less dependent on composition, while T_1 often decreases more strongly. The interval between T_1 and T_g thus generally decreases and the value of T_{rg} increases with increasing alloying concentration so that the probability of being able to cool through this 'dangerous' range without crystallization is enhanced, i.e. GFA is increased [49]. This is probably reliable for conventional binary alloy systems. However, T_1 and T_g differ significantly for multicomponent systems as shown in Table 1. In this sense, T_{rg} values might not be

Alloy	$T_{\rm x} - T_{\rm g}$	$T_{\rm g}/T_{\rm l}$	$T_{\rm x}/(T_{\rm g}+T_{\rm l})$	$R_{\rm c}$ (K/s)	<i>Z</i> _c (mm)
$Mg_{80}Ni_{10}Nd_{10}$	16.3	0.517	0.353	1251.4 [26]	0.6 [26]
$Mg_{75}Ni_{15}Nd_{10}$	20.4	0.570	0.379	46.1 [26]	2.8 [26]
$Mg_{70}Ni_{15}Nd_{15}$	22.3	0.553	0.373	178.2 [26]	1.5 [26]
$Mg_{65}Ni_{20}Nd_{15}$	42.1	0.571	0.397	30.0 [27]	3.5 [26]
$Mg_{65}Cu_{25}Y_{10}$	54.9	0.551	0.401	50.0 [28]	7.0 [29]
ZreeAloNize	35.6	0.537	0.368	66.6 [30]	
$Zr_{66}Al_8Cu_7Ni_{19}$	58.4	0.552	0.387	22.7 [30]	
$Zr_{66}Al_8Cu_{12}Ni_{14}$	77.4	0.559	0.401	9.8 [30]	
$Zr_{66}Al_9Cu_{16}Ni_9$	79.5	0.561	0.403	4.1 [30]	
$Zr_{c5}Al_{75}Cu_{175}Ni_{10}$	79.1	0.562	0.403	1.5 [32]	16.0 [32]
$Zr_{57}Ti_5Al_{10}Cu_{20}Ni_8$	43.3	0.591	0.395	10.0 [33]	10.0 [34]
$Z_{r_{29}} = T_{145} = 100 = 200 = 100$	48.0	0.628	0.415	1.4 [4]	
$Zr_{20,00}Ti_{10,2}Ti_{20,0}Cu_{12,2}Zr_{20,0}$	57.0	0.625	0.420	1.4 [4]	
$Zr_{44} = Ti_{12} = Cu_{12} = Si_{10} = Be_{22} = C$	49.0	0.626	0.415	14[4]	50.0 [35]
$2r_{41,2}r_{13,8}cu_{12,5}r_{10}bc_{22,5}$	89.0	0.589	0.413	50[4]	50.0 [55]
Zr. Ti. Cu. Ni. Bear	114.0	0.518	0.404	12 5 [4]	
$Zr_{44}r_{11}cu_{10}r_{10}bc_{25}$ Zr Ti Cu Ni Be	117.0	0.513	0.404	17.5 [4]	
$Z_{145.38} = 1_{9.62} C_{18.75} = 1_{10} D_{26.25}$	105.0	0.505	0.357	28 0 [4]	
$\Sigma_{146.25} \Pi_{8.25} Cu_{7.5} \Pi_{10} Dc_{27.5}$	105.0	0.525	0.402	28.0 [4]	
La55Al25Ni20	64.3	0.521	0.388	67.5 [36,37]	3.0 [38]
La ₅₅ Al ₂₅ Ni ₁₅ Cu ₅	67.6	0.526	0.394	34.5 [36]	
$La_{55}Al_{25}Ni_{10}Cu_{10}$	79.8	0.560	0.420	22.5 [36]	5.0 [38]
La ₅₅ Al ₂₅ Ni ₅ Cu ₁₅	60.9	0.523	0.389	35.9 [36]	
$La_{55}Al_{25}Cu_{20}$	38.9	0.509	0.366	72.3 [36]	3.0 [38]
$La_{55}Al_{25}Ni_5Cu_{10}Co_5$	76.6	0.566	0.421	18.8 [36]	9.0 [38]
$La_{66}Al_{14}Cu_{20}$	54.0	0.540	0.399	37.5 [18]	2.0 [18]
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	78.9	0.690	0.464	0.1 [39]	72.0 [39]
$Pd_{81.5}Cu_2Si_{16.5}$	37.0	0.577	0.387		2.0 [40,41]
$Pd_{79,5}Cu_4Si_{16,5}$	40.0	0.585	0.392	500.0 [42]	0.75 [43]
$Pd_{77,5}Cu_6Si_{16,5}$	41.0	0.602	0.400	100.0 [43]	1.5 [44]
$Pd_{77}Cu_6Si_{17}$	44.0	0.569	0.388	125.0 [45]	2.0 [40,41]
Pd_{73} 5Cu ₁₀ Si ₁₆₅	40.0	0.568	0.385		2.0 [40.41]
$Pd_{71} Cu_{12}Si_{16} S$	28.0	0.565	0.377		2.0 [40,41]
$Pd_{40}Ni_{40}P_{20}$	63.0	0.585	0.409	0.167 [31]	25.0 [42]
Nd ₆₀ Al ₁₅ Ni ₁₀ Cu ₁₀ Fe ₅	45.0	0.552	0.393		5.0 [46]
$Nd_{61}Al_{11}Ni_8Co_5Cu_{15}$	24.0	0.598	0.394		6.0 [46]
$Cu_{60}Zr_{30}Ti_{10}$	50.0	0.619	0.409		4.0 [5]
$Cu_{54}Zr_{27}Ti_9Be_{10}$	42.0	0.637	0.412		5.0 [19]
$Ti_{34}Zr_{11}Cu_{47}Ni_8$	28.8	0.597	0.389	100 [35]	4.5 [35,47]
$Ti_{50}Ni_{24}Cu_{20}B_{1}Si_{2}Sn_{3}\\$	74.0	0.554	0.393		1.0 [20]

Table 3 Summary of ΔT_{xg} ($T_x - T_g$), T_{rg} (T_g/T_l), $\gamma [T_x/(T_g + T_l)]$, critical cooling rate R_c and critical section thickness Z_c for typical BMGs

able to judge the dangerous temperature interval T_1-T_g for all systems. Secondly, T_{rg} theory arises from the requirement that viscosity must be large at temperatures between T_1 and T_g [50]. Generally,

the viscosity of glasses at $T_{\rm g}$ is 10^{12} Pa s; the higher the ratio $T_{\rm rg}$, the more viscous the melt becomes before it is ever undercooled and the more difficult crystallization becomes, thus enhancing GFA. Yet

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$T_{\rm x} - T_{\rm g}$	$T_{\rm g}/T_{\rm l}$	$T_{\rm x}/(T_{\rm g}+T_{\rm l})$	$R_{\rm c}$ (K/s) [Ref.]	
_	0.246	0.198	3.00×10 ¹⁰ [21]	
_	0.369	0.269	2.60×10 ⁷ [21]	
_	0.383	0.277	5.00×107 [22]	
_	0.488	0.328	1.00×10 ⁶ [22]	
_	0.503	0.335	1.00×10^7 [15]	
_	0.497	0.332	6.30×10 ⁶ [15]	
_	0.605	0.377	1.80×10^3 [21]	
7.8	0.484	0.332	4.90×10 ⁴ [26]	
22.8	0.464	0.334	5.30×10 ⁴ [26]	
-	0.466	0.318	3.00×10 ⁶ [43]	
	$ \frac{T_x - T_g}{T_x - T_g} $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$T_x - T_g$ T_g/T_1 $T_x/(T_g + T_l)$ - 0.246 0.198 - 0.369 0.269 - 0.383 0.277 - 0.488 0.328 - 0.503 0.335 - 0.497 0.332 - 0.605 0.377 7.8 0.484 0.332 22.8 0.464 0.334 - 0.466 0.318	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 4 Summary of ΔT_{xa} $(T_x - T_a)$, T_{xa} (T_a/T_1) , $\gamma [T_x/(T_a + T_1)]$ and critical cooling rate R_c for some typical non-BMGs



Fig. 1. The correlation between the newly defined parameter γ and critical cooling rate R_c for representative metallic glasses.

the temperature variation of viscosity is different from system to system, depending on the classification (fragility concept) as defined by Angell [51,52]. T_g alone does not give any information about the temperature–viscosity relationship and hence the crystallization tendency. Therefore, T_g/T_1 theory might not hold for some systems.

Fig. 4 shows the relationship between ΔT_{xg} and GFA for bulk BMGs. ΔT_{xg} values for some alloys even exceed 100 K, implying those glasses are rather stable upon reheating. As a whole, GFA



Fig. 2. Critical section thickness Z_c as a function of the new parameter γ for typical bulk metallic glasses.

nevertheless shows very weak dependence on ΔT_{xg} , particularly critical section thickness Z_c as plotted in Fig. 4(b). Apparently, $\Delta T_{xg} (T_x - T_g)$ is a quantitative measure of glass stability which is defined as the resistance of glasses towards devitrification upon reheating above T_g . However, GFA is specified as the ease by which melts can be cooled to form amorphous alloys without any crystal formation. It is well known that GFA and glass thermal stability are related but independent properties. Weinberg [53] demonstrated theoreti-



Fig. 3. Critical cooling rate (a) and critical section thickness (b) as a function of T_g/T_1 for metallic glasses.

cally that an increasing GFA is not always accompanied by enhanced stability as measured by a difference $T_x - T_g$ of the same magnitude. Therefore, GFA and thermal stability are akin concepts but they can be different for some systems. It is more likely that $T_x - T_g$ is just a reflection, or a corollary, rather than a cause of GFA. As such, it is inappropriate to utilize ΔT_{xg} alone as a gauge of GFA for BMGs.

4.3. Application of γ in bulk glass formation of Pd–Ni–Fe–P system

Shen et al. [7] have investigated the effect of the addition of Fe on GFA in the bulk Pd–Ni–P alloy



Fig. 4. The correlation between $\Delta T_{xg} (T_x - T_g)$ and critical cooling rate (a) as well as critical section thickness (b) for some bulk metallic glasses.

system. The addition of Fe is supposed to improve GFA in this system according to the empirical rules framed by Inoue et al. [54] and Johnson [55]:

- 1. Iron has very low heats of mixing with both Pd and Ni,
- 2. The molar volumes of Fe and Ni differ by 7.7%,
- 3. The addition of Fe will increase the complexity of the alloy system.

However, the authors found that the ternary $Pd_{40}Ni_{40}P_{20}$ (x = 0) glass is easiest to form among

all alloys. The maximum size for amorphous $Pd_{40}Ni_{40}P_{20}$ alloy is around 1 in. but all quaternary alloys can only form 7 mm glassy rods. In fact, the addition of Fe demoted the GFA in this system.

It was also found that this phenomenon cannot be interpreted by applying T_g/T_1 theory, although ΔT_{xg} coincidentally correlates well with the GFA in this alloy system. Table 5 tabulates the characteristic temperatures T_g , T_x and T_1 as well as T_{rg} values for bulk $Pd_{40}Ni_{40-x}Fe_xP_{20}$ ($20 \ge x \ge 0$) alloys from Ref. [7]. As is seen, the ratio of T_g/T_1 shows a maximum at about 7.5 at% Fe. This observation alone would suggest that this composition should have the highest GFA among these alloys. However, it contradicts the fact that the ternary alloy containing no Fe has the highest GFA.

In addition, according to the so-called 'confusion principle' [56], a large number of solutes help improve GFA since it is harder for the concentrations of all elements to simultaneously satisfy the composition requirements of crystalline nuclei. The crystalline process will require severe solute partitioning and long-range diffusion. Thus, the addition of the fourth element iron into the $Pd_{40}Ni_{40}P_{20}$ alloy should facilitate glass formation. Therefore, the 'confusion principle' has difficulties in clarifying the effect of Fe additions in the Fe– Ni–P system as well.

Nevertheless, the new parameter γ that was calculated in Table 5 can solve this theory paradox and effectively gauge GFA among these alloys. As shown, the Pd₄₀Ni₄₀P₂₀ alloy has the highest γ value of 0.429 among all alloys, which is compat-

ible with its largest Z_c . The addition of iron to the Pd–Ni–P system only resulted in a decrease in γ value for all quaternary alloys, suggesting that iron is detrimental to GFA in this system. This agrees with the experimental results described previously.

5. Conclusions

A new parameter γ , defined as $T_x/(T_g + T_l)$, for judging GFA among metallic glasses has been proposed from the perspectives of both amorphization and devitrification processes. Regardless of alloy system, the relationship between γ and the critical cooling rate R_c as well as critical section thickness Z_c has been formulated as follows:

$$R_{\rm c} = 5.1 \times 10^{21} \exp(-117.19\gamma)$$

and

$$Z_{\rm c} = 2.80 \times 10^{-7} \exp(41.70\gamma).$$

Note that these two equations can be utilized to estimate R_c and Z_c when γ is measured readily from DSC/DTA measurements. Also, it was found that ΔT_{xg} alone cannot effectively reflect the relative GFA for metallic glasses. Although the GFA of metallic glasses is somehow dependent on T_{rg} , parameter γ showed a stronger correlation with GFA than T_{rg} . This was confirmed by a higher R^2 value and a narrower prediction band for the $\gamma - (R_c, Z_c)$ relation than those of $T_{rg} - (R_c, Z_c)$. The newly defined gauge γ has been successfully

Table 5

The characteristic temperatures $T_{\rm g}$, $T_{\rm x}$, $T_{\rm l}$ and calculated $T_{\rm rg}$ as well as γ values for bulk amorphous ${\rm Fe}_{40}{\rm Ni}_{40-x}{\rm Fe}_{x}{\rm P}_{20}$ ($0 \le x \le 20$) alloys [7]

Fe content, x (at%)	<i>T</i> _g (K)	<i>T</i> _x (K)	<i>T</i> ₁ (K)	$T_{ m rg}$	γ
0.0	572	675	1001	0.571	0.429
2.0	593	669	1013	0.585	0.417
5.0	614	671	1024	0.600	0.410
7.5	618	676	1020	0.606	0.413
10.0	611	686	1016	0.601	0.422
12.5	607	689	1022	0.594	0.423
15.0	602	672	1033	0.583	0.411
17.5	600	664	1039	0.577	0.405
20.0	600	653	1056	0.568	0.394

applied to glass formation in the bulk Fe–Nd–P alloy system.

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