

New criterion of glass forming ability for bulk metallic glasses

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It has been confirmed that glass-forming ability (GFA) is related to not only liquid phase stability but also the crystallization resistance. In this study, it was found the liquidus temperature T_l and supercooled liquid region $T_x - T_g$ could reflect the stability of glass-forming liquids at the equilibrium and undercooled state, respectively, while the onset crystallization temperature T_x could indicate the crystallization resistance during glass formation. Thus, a modified γ parameter, defined as $\gamma_m = (2T_x - T_g)/T_l$, has been established. This parameter shows an excellent correlation with the GFA of bulk metallic glasses, with the statistical correlation factor of $R^2 = 0.931$. © 2007 American Institute of Physics. [DOI: 10.1063/1.2718286]

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 Based on the nature of glass formation, coupled with physical metallurgy considerations, Lu and Liu²⁻⁴ have recently proposed a simple GFA parameter $\gamma = T_x/(T_g + T_l)$, which has been confirmed to have a better correlation with GFA than all other GFA indicators.²²⁻²⁴

Following the previous argument by 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. The liquid phase stability should also contain two aspects: the stability of the liquid at the equilibrium state and at the supercooled state. It has long been recognized that the GFA of metallic glasses is inversely related to the liquidus temperature T_l which actually reveals, to what degree, the equilibrium liquid can exist against the solidification.²⁵⁻²⁷ Therefore, the liquidus temperature T_l can be used to indicate the relative stability of stable glass-forming liquids; the lower T_l the larger stability

of the liquid (i.e., the liquid can remain stable to a lower temperature with no formation of any solid phases). As such, the correlation between the GFA of metallic glasses and T_l can be expressed as follows:

$$\text{GFA} \propto \frac{1}{T_l}. \quad (1)$$

Meantime, 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 atomic clusters move more and more sluggishly. As the temperature is lowered to a certain value, the time scale for atomic cluster rearrangements becomes hopelessly long compared to that of the experimental observations. The structure of this material is "frozen" for practical purposes and the glass formation takes place. It is important to emphasize that the glass transition is a kinetic event which depends upon the crossing of an experimental time scale and the time scales for atomic cluster rearrangements. It is well known that the supercooled liquid region $\Delta T_x = (T_x - T_g)$ determined upon devitrification is a quantitative measure of the stability of the supercooled liquid. A large ΔT_x value may indicate that the undercooled liquid can remain stable in a wide temperature range without crystallization, thus leading 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 correlate reasonably well with the GFA of alloys,²⁸⁻³⁰ as expressed as follows:

$$\text{GFA} \propto (T_x - T_g). \quad (2)$$

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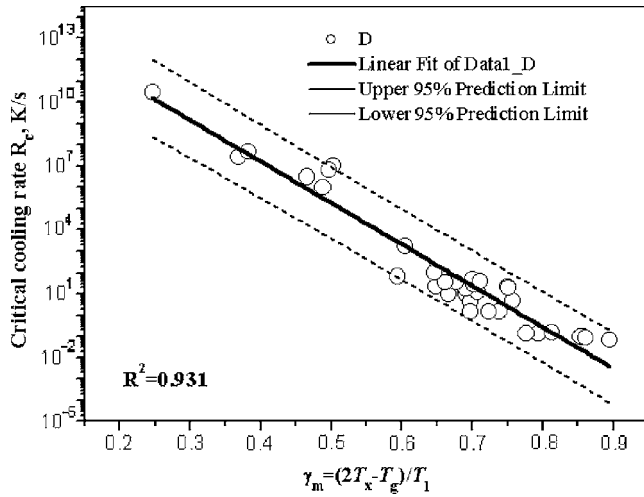


FIG. 1. The correlation between the critical cooling rate and the parameter γ_m for metallic glasses. Data were taken from Refs. 2 and 3.

It is to be noticed that, under no circumstance, the GFA of alloys can be attributed to the liquid phase stability alone. The crystallization resistance of glass-forming liquids must be considered as far as the GFA is concerned. 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. As elaborated previously, the onset crystallization temperature T_x could be used to roughly compare the crystallization resistance during glass formation for metallic liquids, although in some compositions the decisive competing solid phase during cooling might be different from that on devitrification.³¹ The larger T_x value suggests a higher crystallization resistance (i.e., the larger GFA). Thus, the relationship between the GFA and T_x can be described as follows:

$$\text{GFA} \propto T_x. \quad (3)$$

As discussed earlier, the overall liquid phase stability is positively related to the quantity of $(T_x - T_g)/T_l$ while the crystallization resistance is proportional to T_x . Combining Eqs. (1)–(3), one can simply define a modified parameter γ_m ,

$$\gamma_m = \frac{2T_x - T_g}{T_l}. \quad (4)$$

In order to compare the efficiency of the currently proposed GFA criteria γ_m with previous parameters such as $\gamma (=T_g/T_x + T_l)$, $\alpha (=T_x/T_l)$, ΔT_x , T_{rg} , $T_x/(T_l - T_g)$, and $(T_x - T_g)/(T_l - T_g)$, they are all plotted against the R_c , the critical cooling rate for glass formation, for a variety of metallic glasses in the literature.^{2,3} Figure 1 shows the relationship between γ_m and R_c . An excellent linear relation of R_c is clearly observed. A linear regression analysis shows that the relation between R_c with γ_m can be expressed as

$$\log R_c = 14.99 - 19.441 \gamma_m. \quad (5)$$

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

TABLE I. Comparison between different GFA parameters using the data in Refs. 2 and 3.

GFA criteria	γ_m	γ	α	ΔT_x	T_{rg}	$T_x/(T_l - T_g)$	$(T_x - T_g)/(T_l - T_g)$
R^2	0.931	0.91	0.88	0.32	0.73	0.72	0.69

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 I compares the R^2 values for R_c with various GFA parameters. It is evident from Table I that the newly proposed γ_m gives an R^2 value of 0.931 with R_c , which is the highest among all the GFA criteria.

In summary, a GFA parameter γ_m , defined as $(2T_x - T_g)/T_l$, is proposed in the present study. The γ_m parameter also reflects the effects of T_g , T_x , and T_l which are basically measured upon devitrification of glassy samples, the same as the previous γ parameter. However, the present result shows that the γ_m parameter exhibits the best correlation with GFA among all parameters suggested so far. 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 γ_m parameter can be calculated simply by data on T_g , T_x , and T_l , the current parameter is a simple and user-friendly indicator.

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