Identify the best glass forming ability criterion

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Understanding glass formation and predicting glass forming ability (GFA) are vitally important and they are long-standing challenges in the metallic glasses community. Recently, a number of criteria have been developed to evaluate GFA, based mainly on fitting the experimental data of the critical cooling rate for glass forming. In this study, physically accepted boundary conditions have been imposed to evaluate the GFA criteria, and their combination with statistical analysis result in identifying the best GFA criterion useful for various glass forming systems, including oxide glasses, cryoprotectants, and metallic glasses.

1. Introduction

The first formation of Au–Si metallic glasses by quenching from the molten state in 1960 [1], and the fabrication of multi-component bulk metallic glasses (BMGs) with a critical diameter larger than 1 mm by slow cooling methods in 1988 [2] are two key milestones in the development of metallic glass materials. Over the past 50 years, significant progress has been made in exploring alloy systems with good glass forming ability (GFA), understanding the structure of metallic glasses on an atomic scale, improving their mechanical properties especially the ductility at temperatures below glass transition temperature (Tg) and also revealing the mechanisms of plastic deformation and fracture that are responsible for the poor ductility of BMGs. Awkwardly, even by now the search for BMG formers is mainly based on try and error experiments which are time consuming and costly, although a few empirical guides have been proposed and verified for certain particular systems [3–5]; however, there exist no justified theories or scientific rules to design alloys with excellent GFA. Even worse, for the existing BMGs, a simple and unified criterion that can characterize the GFA is still controversial.

The critical cooling rate, Rc, i.e., the minimum cooling rate to obtain fully amorphous solid from melts, and the critical size, Dc, i.e., the maximum attainable size a sample can be in fully amorphous structure, are commonly accepted as criteria of GFA [6]: the smaller Rc and the larger Dc, the better GFA is. Between Rc and Dc, Rc is more suitable to represent GFA as Dc is dependent on factors other than alloy composition, e.g., on the fabrication method [7,8]. However, measurement of Rc requires a series of continuous cooling experiments and is practically impossible for marginal glass former with very high Rc. Fortunately, it is found that Rc could be correlated to the characteristic temperatures (Tg, crystallization onset temperature; Tl, liquidus temperature) [7,9,10] and criteria based on these characteristic temperatures can be used to evaluate the GFA of available metallic glasses. These characteristic temperatures can be easily determined from the differential scanning calorimetry (DSC) or differential thermal analysis (DTA), which partially explains why there currently exist so many GFA criteria based on Tg, Tl and T through different combination of them [10,11], such as Tg=(Tg/Tl), DTg(=Tg–Tl), γ=(Tg/(Tl+Tg)), γm=(2Tg–Tl)/Tl, ΔTg(=(Tg–Tl)/(Tl–Tg)), β(=Tl–Tg)/(Tl–Tg), α(Tg/Tl), β(Tg/Tl+Tl) and α(=Tg/Tl–2Tg/(Tl+Tg)). The existence of so many GFA criteria, however, results in a profound confusion in the metallic glasses community.

The way to decide the reliability of the GFA criteria is mainly based on the linear regression analysis and hence the correlation of these criteria to the corresponding Rc or Dc. The larger the coefficient of determination, R2 (the better correlation of them to Rc or Dc), the better the GFA criterion is. However, several important points related to the statistical analysis are often ignored. First, the data source on characteristic temperatures and especially on Rc need to be reliable, i.e., Rc should come from reliable measurements or reasonable estimations. Second, a good GFA criterion should reflect the GFA of the whole range of metallic glasses, no matter whether their GFA is good or bad. Some proposed GFA criteria are effective for only a few alloys systems [6], indicating they are not universally applicable. Third, among the available data on Rc, most of them are from the BMG forming systems, which makes the R2 determined mainly by the BMGs and less by the marginal glass
formers, as is the nature of the least square method used in the regression analysis. The danger here is that, the regression might be mathematically meaningful but not physically, as the boundary conditions (two extreme ends of glass forming systems) are not met. In this paper, we introduced boundary conditions to examine the physical meaning of the existing GFA criteria and identified the best GFA criterion based on two considerations: good correlation to \( R_c \) and satisfying the boundary conditions.

2. Analyses

2.1. Reliable database

To make the correlation between GFA criteria and \( R_c \) statistically robust, a database composed of many alloys with characteristic temperatures and \( R_c \) data is necessary. However, the size of the database is limited by available \( R_c \) data. In addition, the methods to obtain \( R_c \) need to be reviewed to decide whether they are reliable. Basically, five methods are commonly used to measure or estimate \( R_c \) in the literature.

1) Continuous cooling method. The melts are cooled with a range of cooling rates in a stepwise way until a fully amorphous structure is achieved [12,13]. \( R_c \) measured by continuous cooling is very reliable but practically it only works for excellent metallic glass formers with low \( R_c \).

2) Colmenero and Barandiaran (CB) method. Although the continuous cooling method is accurate, it is too laborious. Barandiaran and Colmenero [14] found a relationship that enables \( R_c \) to be estimated from a couple of thermal analysis by measuring \( T_l \) upon melting at a constant heating rate and onset temperature of solidification \( T_{xc} \) upon cooling at different cooling rates \( R_c \):

\[
\ln R = \ln R_c - \frac{b}{(T_l - T_{xc})^2} \tag{1}
\]

where \( b \) is a constant.

\( R_c \) can be determined from the \( R \) vs \( 1/(T_l - T_{xc})^2 \) plot. Wichard and Day [15] had confirmed that \( R_c \) estimated by the CB method agrees well with that from the continuous cooling method.

3) Time–temperature-transformation (TTT) curve method or the so-called "nose method" initiated by Ulhmann [16]. The idea is to construct a TTT curve that defines the time required at any temperature to form a particular volume fraction of crystallization of \( x \); by arbitrarily defining \( x = 10^{-6} \) (as the detectable limit of crystallization volume) and calculating the required time for forming a crystallization volume of \( x \) based on growth kinetics, the TTT curve can be obtained and a nose appears as the result of the competition between the driving force for crystallization and atomic mobility both depending on undercooling (temperature). \( R_c \) is given by the slope of the linear cooling curve that just avoids the nose of the TTT curve:

\[
R_c = \frac{T_m - T_n}{T_n - t_n} \tag{2}
\]

where \( T_m \) is the melting temperature, \( T_n \) and \( t_n \) are temperature and time corresponding to the nose of the TTT diagram.

4) Bridgeman method. Directional solidification is an effective way to prepare BMGs by controlling the velocity of solidification, \( V_c \), and the temperature gradient, \( G \), at the front of solid/liquid interface [18]. \( R_c \) of the glassy alloys made by Bridgeman method is the product of critical solidification velocity and temperature gradient:

\[
R_c = GV \tag{3}
\]

\( R_c \) measured using Bridgeman method is close but lower than \( R_c \) measured by CB method [19].

5) Critical size estimate method. Based on the thermal conductivity calculation, it is predicted that \( R_c \) is inversely proportional to the square of \( D_c \) [20]. However, as explained earlier, \( D_c \) is affected by many factors like alloy preparation route and the accurate value of \( D_c \) is hard to obtain, which can probably account for the weak correlation between \( D_c \) and the existing GFA criteria [7,10]. As a result, \( R_c \) estimated from the critical size is considered not reliable and excluded when establishing the database.

\( R_c \) data reported in the literature without mentioning affirmative source on the measurement/estimation method are also excluded to make sure that the GFA criteria are correlating to meaningful \( R_c \). After careful data collection and selection based on the above mentioned points, a reliable database is established and given in Table 1, together with the calculated values of the typical GFA criteria. It needs to point out that the database is established as a premise based on which the different GFA criteria are judged, and not the other way around.

2.2. Correlation of GFA criteria to \( R_c \)

GFA criteria based on the characteristic temperatures, which can act to evaluate the GFA of metallic glasses, need to be correlated to \( R_c \). Previous work has clearly indicated that the correlation between good GFA criteria and \( R_c \) is almost linear [7,9,10], which is also the reason using the linear regression and \( R^2 \) to evaluate the superiority of GFA criteria. This linear relationship between \( R_c \) and GFA criteria, \( g \), defined as:

\[
g = g(T_g, T_s, T_l) \tag{4}
\]

where \( A \) and \( B \) are constants.

From Eq. (4), candidates of \( g \) need to satisfy at least two requirements. First, \( g \) is unitless. Based on this concern, \( J_T \) is not suitable as a GFA criterion. Actually, it has been well known that \( J_T \) does not have a strong correlation to GFA of metallic glasses if put on a wide scope of alloy systems. Second, \( g \) increases as \( R_c \) decreases. This is physically meaningful as a larger \( g \) means better GFA, which is reflected by the smaller \( R_c \). From this viewpoint, \( g \) is not a suitable criterion as, with decreasing \( R_c \), \( g \) also decreases [10,21].

2.3. Further consideration on GFA criteria

The reason for the solid correlation between the GFA criteria (based on the characteristic temperatures) and \( R_c \) is that, these criteria catch the thermodynamic process of the glass formation, and can also reflect the kinetics of this process through the kinetic dependence of \( T_g \) and \( T_s \). The previous regression analysis has demonstrated that the GFA criteria composing three characteristic temperatures have a better correlation to \( R_c \) as compared to those composed of two [11]. Thus, the solidification \( (T_l) \), glass transition
Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Tg(K)</th>
<th>Tx(K)</th>
<th>Tl(K)</th>
<th>Txg</th>
<th>α</th>
<th>γ</th>
<th>R(K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgMoSi2NdTi</td>
<td>545.3</td>
<td>501.4</td>
<td>804.9</td>
<td>0.571</td>
<td>0.623</td>
<td>0.794</td>
<td>0.675</td>
</tr>
<tr>
<td>Mg82Co15Y10</td>
<td>424.5</td>
<td>479.4</td>
<td>770.9</td>
<td>0.551</td>
<td>0.622</td>
<td>0.802</td>
<td>0.693</td>
</tr>
<tr>
<td>Mg75Co25Ge10</td>
<td>406.0</td>
<td>478.0</td>
<td>755.0</td>
<td>0.540</td>
<td>0.633</td>
<td>0.822</td>
<td>0.726</td>
</tr>
<tr>
<td>Mg65Co15AgPd5Ge4</td>
<td>430.0</td>
<td>472.0</td>
<td>748.0</td>
<td>0.575</td>
<td>0.631</td>
<td>0.802</td>
<td>0.687</td>
</tr>
</tbody>
</table>

Characteristic temperatures, Tg, Tx, Tl (measured at heating rates of 10–40 K/s), R, and typical GFA criteria for a wide range of metallic glasses. Data for SiO2 is also included to represent the best glass former.

Notes:
- a: R, measured by continuous cooling.
- b: R, measured by Bridgeman.
- c: R, measured by TTT curve.
- d: R, measured by CB.
- e: R, measured by continuous cooling.

(Ts) and crystallization (Tc) all affect the glass formation and hence the GFA criterion expression. An obvious question here: on which condition a glass is extremely easy to form? The following extreme conditions might not be realistic, but at least they can help to test the validity of these GFA criteria.

**Condition 1:** Tg = Tc = Tg is the liquid transforms to glassy state immediately upon cooling from the molten state. At this condition the glass is extremely easy to form and the value of GFA criterion should reach unity or unity after normalization. Seen from Table 2, only criteria Tg, γ, γm and α can satisfy this “lower extreme condition”.

**Condition 2:** Tc = Tc = 0 (K). The crystallization is doomed to happen above the absolute zero temperature, and no stable glass can exist. It should correspond to an extremely difficult condition to form glass. All the GFA criteria except β equal to zero at this condition, satisfying the “lower extreme condition”.

Only those satisfying both extreme conditions can be considered as candidates for the GFA criterion, i.e., only Tg, γ, γm and α are qualified. Their superiority can then be judged by the R2 and the newly proposed boundary conditions introduced later in this paper. Another point worth mentioning here is that, as R2 is commonly used as the benchmark to judge the superiority of GFA criteria, it is tempting to mathematically manipulate the combination of Tg, Tc and Tg to achieve a larger R2, exemplified by the expression β = Tg0.141 [22]. There is no doubt that more expressions with adjustable parameters can be created (or are creating) to improve the statistical satisfaction between themselves and Rc. However, these expressions lack physical meaning, and the logic behind deducing them is problematic: they are based on pre-supposed and unjustified models and the adjustable parameters are determined from the fitting to data (Rc); however, it is the fitting of these expressions to data that should decide which one is better correlated to Rc and hence a better GFA criterion. Therefore, these mathematically determined expressions should not be considered as reliable GFA criteria.

3. Normalized GFA criteria

To facilitate the comparison between the “qualified” criteria based on Table 2, a numerical factor of 2 is used to time the γ criterion out of obvious reason. The linear regression of Tg, α, 2γ and γm to Rc is plotted in Fig. 1, with the parameters A and B in Eq. (4) and the R2 values given in Table 3. Apparently, γm shows the best correlation to Rc, with a R2 value as high as 0.892.

Larger R2 in Table 3 represents the better correlation of the GFA criteria to Rc, or the better linear relationship between g and Rc as reflected by Eq. (4). In other words, Rc could reliably be predicted from g based on this g–Rc linearity. However, due to the biased data distribution (more data in the excellent glass former systems with low Rc values) and the mathematical nature of the regression analysis (the least square method), the fitted g–Rc line might also be biased or deviate from the true condition. There is a simple way to check this deviation based on the boundary conditions. Earlier in this paper, two extreme conditions are hypothesized to exclude some GFA criteria that can not meet these extreme conditions. The two extreme conditions are, however, not realistic. As a result, the upper and lower limits for the GFA criteria are not 1 and 0, as shown in Table 1. If the real boundary conditions are known, i.e., the best glass former and the worst glass former are known, their corresponding g values can be used to normalize the GFA criterion in the individual definition. A normalized GFA criterion, g’ is hereby defined as:

\[ g' = \frac{g - g_{\text{min}}}{g_{\text{max}} - g_{\text{min}}} \]

where g_{max} and g_{min} are values of the GFA criterion for the best and worst glass formers.

The relationship between g’ and Rc is transformed from Eq. (4) into:

\[ g' = A' - B' \log_{10}R_c \]

where A’ and B’ are constants.

It is worth pointing out that the normalized GFA criterion, g’, does not change the physical meaning of the original GFA criterion (g). The correlation between g’ and Rc remains the same as that of g and Rc (same R2). The only purpose of the normalization is to simplify the compassion between the g’–Rc relationship based on the boundary condition (by normalizing, the boundary conditions would be unique: g’ = 0 and g’ = 1) and those comes from the regression analysis, as will be shown in Fig. 2.

Based on the literature, pure Ni has the most critical requirement on cooling rate to form glass with Rc = 10^10 K/s and this value is used as Rc for g’ = 0; the best glass former is SiO2 although it is an oxide glass and not a metallic glass. Lu and Liu have shown that Rc of oxide glasses can also be linearly correlated to the GFA criterion (γ in their paper) [9]. Hence, Rc = 10^-3 K/s for SiO2 can be assumed as Rc for g’ = 1. From these two boundary conditions, the g’–Rc relationship is reduced to:

| Table 2 |
| GFA criteria at two extreme conditions. |
| Condition | Tg | γ | γm | ΔTg | δ | β | φ | α | β |
| Tg - Tg = Tc | 1 | 1/2 | 1 | 0 | 0 | 0 | 1 | 2 |
| Tc - Tc = 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |

<p>| Table 3 |
| Fitting parameters A and B, and R2 from the linear regression of GFA criteria, Tg, α, 2γ and γm to Rc. |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>2γ</th>
<th>γm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg</td>
<td>0.613</td>
<td>0.687</td>
<td>0.853</td>
<td>0.761</td>
</tr>
<tr>
<td>γ</td>
<td>0.022</td>
<td>0.034</td>
<td>0.034</td>
<td>0.045</td>
</tr>
<tr>
<td>R2</td>
<td>0.626</td>
<td>0.833</td>
<td>0.874</td>
<td>0.892</td>
</tr>
</tbody>
</table>
from it being highly correlated to provides another consideration to select the GFA criterion: apart statistical deviations of the measured condition, which is also qualitatively confirmed by calculating the from the regression analysis as did for the fitted and physically meaningful, rather than mathematically obtained.

\[ g' = \frac{2}{3} - \frac{1}{T_0 \log_{10} R_c} \]  

Equation (7) is plotted in Fig. 2 as the solid line. Note that this \( g'-R_c \) line is determined exclusively from the boundary conditions and physically meaningful, rather than mathematically obtained from the regression analysis as did for the fitted \( g'-R_c \) lines shown in Fig. 1. By normalizing the GFA criteria according to Eq. (5), and plotting the \( g'-R_c \) for each definition of GFA criterion in Fig. 2, their deviations to the true condition is immediately obvious. Fig. 2 clearly shows that the deviation from the fitted \( g'-R_c \) lines to the true \( g'-R_c \) line is quite large for some GFA criteria in the marginal glass former side (small \( g \) and large \( R_c \)). This is exactly what can be expected from the regression analysis based on the biased data distribution as discussed before. The merit of Fig. 2 is that it provides another consideration to select the GFA criterion: apart from it being highly correlated to \( R_c \) (large \( R^2 \)), the deviation of the fitted \( g'-R_c \) line to the true condition needs to be as small as possible. From Fig. 2, \( \gamma_m \) has the smallest deviation to the true condition, which is also qualitatively confirmed by calculating the statistical deviations of the measured \( g'(g_m') \) to the true \( g'(g') \), \( \sum (g_m' - g')^2 \), the deviations being 0.273, 0.653, 0.950 and 2.138, respectively for \( \gamma_m, \alpha, 2\gamma \) and \( T_{rg} \).

4. Discussion

Based on the criteria of both the high correlation to \( R_c \) and the agreement of the regression determined \( R_c \) to the boundary conditions, \( \gamma_m \) is clearly identified clearly as the best GFA criterion. The physical meaning of \( \gamma_m \) is briefly recapped here. \( \gamma_m = (2T_x - T_g)/T_I = (T_x - T_g)/T_I + T_x/T_I = \Delta T_x/T_x + T_x \). The reasoning behind \( \gamma_m \) is that GFA correlates to the stability of liquid, \( 1/T_I \) (the lower \( T_I \), the larger stability of the liquid is), the stability of the supercooled liquid, \( \Delta T_x := T_x - T_g \) the larger \( \Delta T_x \), the larger stability of the supercooled liquid is) and the resistance to crystallization, \( T_x \) (the higher \( T_x \), the higher resistance to crystallization is). It can well describe the glass forming process and the competition between the liquid and crystalline phase that controls the GFA.

The physical meanings of other GFA criteria are, however, not as strong as that of \( \gamma_m \) even they appear to have a decent regression coefficient of \( R^2 \). For example, \( \beta - 1 \)

\[ (= T_x/T_g + T_x/T_I - 1 = (T_x - T_g)/T_x + T_x/T_I \) or \( T_x/T_g - (T_I - T_g)/T_I \) the constant \( -1 \) is added to the original \( \beta \) expression to satisfy the “extreme conditions”, as given in Table 2 \) has a \( R^2 \) of 0.894, even higher than that of \( \gamma_m \). Assuming \( \beta - 1 = (T_x - T_g)/T_x + T_x/T_I \) this definition, two factors related to glass formation are included, the thermal stability of the glass, \( T_x - T_g/T_g \) and the glass forming tendency during cooling from the molten state, \( T_I/T_g \) (the reduced glass transition temperature). This definition of \( \beta - 1 \) has two shortcomings as a suitable GFA criterion. First, the resistance to crystallization is not reflected in the expression, although \( T_x \) is included in \( T_x - T_g/T_g \) which however, at the same time describes the stability of the supercooled liquid. Second, since \( T_g \) is not very sensitive to composition but \( T_I \) is \[23\], \( 1/T_I \) alone can effectively reflect the stability of liquid (so \( 1/T_I \) is not necessary), which is also the reason that most BMGs forming alloys are near the eutectic valley. Similarly, neither the other definition of \( \beta - 1 \) nor other GFA criteria can as comprehensively reflect the three aspects (stability of liquid, stability of the supercooled liquid and resistance to crystallization) attributable to the good GFA as \( \gamma_m \) does.

5. Conclusions

In summary, we critically reviewed the existing GFA criteria and judged their merits from physically accepted boundary conditions together the commonly used statistics concern. Our study has led to the identification of \( \gamma_m := 2T_x - T_g/T_I \) to be the best GFA criterion from both statistical and physical considerations. It can be used unambiguously in the future to index the GFA of metallic glasses as well as other amorphous materials.

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