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 \( T_s - T_g \) could reflect the stability of glass-forming liquids at the equilibrium and undercooled state, respectively, while the onset crystallization temperature \( T_c \) could indicate the crystallization resistance during glass formation. Thus, a modified \( \gamma \) parameter, defined as \( \gamma_m = (2T_s - T_g)/T_l \), has been established. This parameter shows an excellent correlation with the GFA of bulk metallic glasses, with the statistical correlation factor of \( R^2 = 0.931 \). 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.\(^2\)\textsuperscript{-21} Based on the nature of glass formation, coupled with physical metallurgy considerations, Lu and Liu\(^2\textsuperscript{-4}\) have recently proposed a simple GFA parameter \( \gamma = T_s/(T_g + T_l) \), which has been confirmed to have a better correlation with GFA than all other GFA indicators.\(^22\textsuperscript{-24}\)

Following the previous argument by Lu and Liu,\(^2\textsuperscript{-4}\) 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.\(^25\textsuperscript{-27}\) 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:

\[
\text{GFA} \propto \frac{1}{T_l}.
\] (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 \( \Delta T_s = (T_s - T_g) \) determined upon devitrification is a quantitative measure of the stability of the supercooled liquid. A large \( \Delta T_s \) 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,\(^28\textsuperscript{-30}\) as expressed as follows:

\[
\text{GFA} \propto (T_s - T_g).
\] (2)

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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 onsets crystallization temperature \( T_c \) 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 \( T_c \) value suggests a higher crystallization resistance (i.e., the larger GFA). Thus, the relationship between the GFA and \( T_c \) can be described as follows:

\[
\text{GFA} \propto 1/T_c. \tag{3}
\]

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

\[
\gamma_m = \frac{2T_c - T_g}{T_l}. \tag{4}
\]

In order to compare the efficiency of the currently proposed GFA criteria \( \gamma_m \) with previous parameters such as \( \Delta T_g/T_l \), \( \alpha = (T_g - T_c)/T_l \), \( \Delta T_g - T_{cr} \), \( T_g/(T_c - T_g) \), and \( (T_c - T_g)/(T_r - T_g) \), they are all plotted against the \( R_c \), the critical cooling rate for glass formation, for a variety of metallic glasses in the literature.\(^{2,3,5,7,77} \) Figure 1 shows the relationship between \( \gamma_m \) 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 \( \gamma_m \) can be expressed as

\[
\log R_c = 14.99 - 19.441 \gamma_m. \tag{5}
\]

\( \gamma_m \) gives 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 I compares the \( R^2 \) values for \( R_c \) with various GFA parameters. It is evident from Table I that the newly proposed \( \gamma_m \) 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 \( \gamma_m \), defined as \( (2T_c - T_g)/T_l \), is proposed in the present study. The \( \gamma_m \) parameter also reflects the effects of \( T_c \), \( T_g \), and \( T_l \) which are basically measured upon devitrification of glassy samples, the same as the previous \( \gamma \) parameter. However, the present result shows that the \( \gamma_m \) 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 \( \gamma_m \) parameter can be calculated simply by data on \( T_c \), \( T_g \), and \( T_l \), the current parameter is a simple and user-friendly indicator.

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\begin{table}[h]
\begin{center}
\caption{Comparison between different GFA parameters using the data in Refs. 2 and 3.}
\begin{tabular}{cccccc}
\hline
GFA criteria & \( \gamma_m \) & \( \gamma \) & \( \alpha \) & \( \Delta T_g \) & \( T_g/T_l \) & \( T_c - T_g/T_r - T_g \) \\
\hline
\( R^2 \) & 0.931 & 0.91 & 0.88 & 0.32 & 0.73 & 0.72 & 0.69 \\
\hline
\end{tabular}
\end{center}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{The correlation between the critical cooling rate and the parameter \( \gamma_m \) for metallic glasses. Data were taken from Refs. 2 and 3.}
\end{figure}