Evaluation of glass forming ability of alloys

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Abstract: Key step of exploiting a new type BMG (Bulk Metallic Glass) is quickly judging GFA (Glass Forming Ability) of the alloys. The mole melting heats of BMGs are calculated using the weighted averages principle. The reliability and limitation of $T_c$ criterion for GFA are discussed. The reason why $T_c$ of BMGs is larger than 0.5 is discussed. Two new criteria for GFA, $\Delta H_{mg}$ and $\Delta G_{f}$, are proposed. GFA sequence of BMGs is calculated using the $\Delta H_{mg}$ criterion, the result agrees with that of A. Inoue and the $R_i$ criterion. Furthermore, as an example, the $R_i$ of the alloys developed by Chuang DONG et al is calculated using the $\Delta H_{mg}$ and $\Delta G_{f}$. The ascending sequence of these alloys calculated with the $\Delta H_{mg}$ criterion agrees with that of Chuang DONG et al. On the contrary, the result by the $\Delta G_{f}$ criterion is in contrary with Chuang DONG et al, indicating that the $\Delta H_{mg}$ criterion is better and more convenient than the $\Delta G_{f}$ criterion. Calculation showed that the optimum $\Delta H_{mg}$ is -15.16 kJ/mol.

Keywords: bulk metallic glasses; glass forming ability; weighted averages principle; GFA criterion

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1. Introduction

Bulk metallic glasses (BMG) have been one of the hotspots in material fields because of their excellent properties in physics, chemistry, optics, magnetism and mechanics. The glass forming ability (GFA) parameters were extensively researched at the point of thermodynamics, kinetics and physical structure. Two initial GFA parameters were the super-cooled liquidus region $\Delta T = T_c - T_a$ ($T_a$ and $T_c$ are the onset crystallization temperature and the glass transition temperature) and the reduced glass transition temperature $T_{rg} = T_a/T_g$ ($T_a$ is the onset-melted temperature). Subsequently, on the base of $T_{rg}$, P. LU et al. proposed a new parameter, the reduced glass transition temperature, i.e. $T_{rg} = T_a/T_g$ ($T_g$ is the glass transition temperature). Recently, Takeuchi Akira et al. reported a function for multi-component alloys combining $\Delta H$ and $S/k_B$, and successfully obtained two critical values of typical multi-component metallic glasses, i.e. 15 kJ/mol and 0.1 respectively, and found that more negative the $\Delta H$ was and the bigger the $S/k_B$ was, the stronger the GFA of the alloys was. In addition, A. Inoue proposed of three empirical rules for BMG. However, those GFA parameters needed to determine many parameters. Among those, some can be obtained only after BMGs have been obtained, and some even cannot be obtained. Therefore, to research criteria quickly and exactly evaluating GFA of the alloys has been a concerned problem.

In this paper, total 35 alloys of 7 groups are used in this study. The reliability and limitation of $T_c$ criterion for GFA are discussed. Two new criteria for GFA, $\Delta H_{mg}$ and $\Delta G_{f}$, for the evaluation of the GFA of the alloys are proposed and discussed. And the GFA sequence of BMGs is calculated by using the $\Delta H_{mg}$ criterion, and the result agrees with that of A. Inoue's. In addition, as an example, the $R_i$ of the alloys (Zr-Al-Cu-Ni) developed by Chuang DONG et al. is calculated by use of the new criteria. The ascending sequence of GFA of these alloys calculated by the $\Delta H_{mg}$ criterion agrees with that of Chuang DONG et al. On the contrary, the result by the $\Delta G_{f}$ criterion doesn't accord with that of Chuang DONG et al, indicating that the $\Delta H_{mg}$ criterion is better and more convenient than the $\Delta G_{f}$ criterion.

2. Physic background and calculation methods

The Gibbs free energy ($G$) of the super-cooled melt is higher than that of the crystal, so there is a tendency of crystallization in super-cooled melt. The difference in the free energy ($\Delta G$) between solid and liquid is a force of crystallization. The larger the $\Delta G$ is, the bigger the force is. The force is a critical factor influencing formation of crystal nucleus and nucleation rate, the critical radius of crystal nucleus, crystal nucleus growth and growth rates from solidification theory point of view. Therefore, the $\Delta G$ directly influences the formation of BMG.

According to thermodynamic theory, the Gibbs free
energy of system is expressed as,

\[ G = U - TS + PV = H - TS \]  

(1)

When one mole melt crystallizes, which leads to the change of \( \Delta G_g \), i.e., the change of chemical potential of system is as follows:

\[ \Delta G_g = \Delta H_g - T \Delta S_g \]  

(2)

Where, \( \Delta G_g \), \( \Delta H_g \) and \( \Delta S_g \) are the differences for \( G \), \( H \) and \( S \) between solid and liquid when one mole melt crystallizes respectively.

Since the melt and crystal are in equilibrium at melting point \( T_m \), therefore, there is the following expression.

\[ \Delta G_{mg} = \Delta H_{mg} - T_m \Delta S_{mg} = 0 \]  

i.e.,

\[ \Delta S_{mg} = \Delta H_{mg} / T_m \]  

(3)

Where, \( \Delta G_{mg} \), \( \Delta H_{mg} \) and \( \Delta S_{mg} \) are the difference of \( G \), \( H \) and 5 between solid and liquid phases when one mole melt crystallizes at the melting point respectively.

When the melt is cooled slightly down under \( T_m \) the crystallization can happen immediately. Because of the small super-cooling, \( \Delta H_{mg} = \Delta H_{ng} \) and \( \Delta S_{mg} \approx \Delta S_{ng} \) are of the adequate approximation. Hence, the difference in the mole free energy of solid and liquid is:

\[ \Delta G_s = \Delta H_{mg} - T \Delta S_{mg} = \Delta H_{mg} (T_m - T) / T_m \]  

(4)

However, at large super-cooling, supposing that the \( \Delta G \) and the \( \Delta H \) change linearly with temperature \([13,14]\), as the first approximation, the following equation is proposed.

\[ \Delta G_g = \Delta H_{mg} \left( \frac{T - T_m}{T_m} \right) \]  

(5)

When the melt transforms to the metallic glass, let \( T = T_g \), the expression (5) is rewritten as the following expression,

\[ \Delta G_g = \Delta H_{mg} (1 - T_g / T_m) \]  

(6)

According to Ziman liquid theory and supposing that the melt is an ideal solution, the \( \Delta H_{mg} \) can be calculated by using the following expression:

\[ \Delta H_{mg} = \sum_{i=1}^{n} (x_i \Delta H_{mi}) \]  

(7)

Where, \( x_i \) is the mole percent of \( i \)-th component, \( n \) is component number, \( \Delta H_{mi} \) is the mole melting heats of \( i \)-th component.

3. Results and discussion

Total 35 alloys of 7 groups are used in this study. Their critical cooling rates \( R \) \([9-11]\) and calculated \( \Delta H_{mg} \) and \( \Delta G_g \) using above equation \([6]\) are all listed in Table 1. Their average values of the critical cooling rates \( R \) \([9-11]\), \( \Delta H_{mg} \) and \( \Delta G_g \) are also calculated and shown in Table 2.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>( \Delta H_{mg} ) [kJ·mol(^{-1})]</th>
<th>( T_m )</th>
<th>( \Delta G_g ) [kJ·mol(^{-1})]</th>
<th>( R ) [K·s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(_3)Ni(_3)Nd(_1)</td>
<td>-10.1437</td>
<td>0.57</td>
<td>-2.4862</td>
<td>46.1</td>
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<td>Mg(_3)Ni(_3)Nd(_1)</td>
<td>-10.5113</td>
<td>0.571</td>
<td>-2.5748</td>
<td>30</td>
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<tr>
<td>Mg(_3)Ni(_3)Nd(_1)</td>
<td>-10.0530</td>
<td>0.553</td>
<td>-2.485</td>
<td>178.2</td>
</tr>
<tr>
<td>Mg(_3)Cu(_2)Y(_1)</td>
<td>-10.8930</td>
<td>0.551</td>
<td>-2.6949</td>
<td>50</td>
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<tr>
<td>Nd(_3)Fe(_3)Al(_15)</td>
<td>-9.9250</td>
<td>0.617</td>
<td>-2.3454</td>
<td>12</td>
</tr>
<tr>
<td>Nd(_3)Al(_3)Cu(_3)Fe(_5)</td>
<td>-9.7886</td>
<td>0.552</td>
<td>-2.4207</td>
<td></td>
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<tr>
<td>Nd(_3)Al(_3)Cu(_3)Co(_2)Cu</td>
<td>-9.6976</td>
<td>0.598</td>
<td>-2.3313</td>
<td></td>
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<tr>
<td>Pd(_3)Cu(_3)Si(_3)</td>
<td>-21.2312</td>
<td>0.602</td>
<td>-5.0869</td>
<td>100</td>
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<td>Pd(_3)Cu(_3)Si(_17)</td>
<td>-21.1687</td>
<td>0.569</td>
<td>-5.1914</td>
<td>125</td>
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<td>Pd(_3)Cu(_3)Si(_15)</td>
<td>-21.0477</td>
<td>0.577</td>
<td>-5.1371</td>
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<tr>
<td>Pd(_3)Cu(_3)Si(_15)</td>
<td>-20.9187</td>
<td>0.568</td>
<td>-5.1329</td>
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<tr>
<td>Pd(_3)Cu(_3)Si(_15)</td>
<td>-21.0188</td>
<td>0.585</td>
<td>-5.1028</td>
<td>500</td>
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<td>Pd(_3)Cu(_3)Si(_15)</td>
<td>-20.8827</td>
<td>0.565</td>
<td>-5.1324</td>
<td></td>
</tr>
<tr>
<td>Pd(_3)Cu(_3)Ni(_3)P(_20)</td>
<td>-12.0682</td>
<td>0.69</td>
<td>-2.5814</td>
<td>0.1</td>
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<td>Pd(_3)Cu(_3)Ni(_3)P(_20)</td>
<td>-13.4726</td>
<td>0.585</td>
<td>-3.2708</td>
<td>0.167</td>
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<tr>
<td>La(_3)Al(_3)Ni(_3)Cu(_10)</td>
<td>-13.1519</td>
<td>0.56</td>
<td>-3.2406</td>
<td>22.5</td>
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<td>La(_3)Al(_3)Ni(_3)Cu(_10)</td>
<td>-12.9136</td>
<td>0.523</td>
<td>-3.2216</td>
<td>35.9</td>
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<tr>
<td>La(_3)Al(_3)Ni(_3)Cu(_10)</td>
<td>-13.6157</td>
<td>0.521</td>
<td>-3.3979</td>
<td>67.5</td>
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<tr>
<td>La(_3)Al(_3)Ni(_3)Cu(_10)</td>
<td>-12.9724</td>
<td>0.54</td>
<td>-3.2233</td>
<td>37.5</td>
</tr>
<tr>
<td>La(_3)Al(_3)Ni(_3)Cu(_10)</td>
<td>-13.3856</td>
<td>0.526</td>
<td>-3.3374</td>
<td>34.5</td>
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</table>
Using the data in Table 1 a three-dimensional graph for $\Delta G_g$, $T_g$ and $\Delta H_{mg}$ is shown in Fig.1. It is seen from Fig.1 that when $T_g$ is fixed, $\Delta G_g$ increases with the increase of $\Delta H_{mg}$. When $\Delta H_{mg}$ is invariable, there exists a minimum position or critical point, $T_g=0.5$. When $0.5 \leq T_g \leq 1$, the absolute value of the $\Delta G_g$ decreases with the increase of $T_g$, which is the forming region of BMG. In addition, it could be the reason why $T_g$ of BMG is larger than 0.5 presently. In addition, the larger the $\Delta G_g$ is, the bigger the driving force is for the melt to crystallize. Normally for forming BMG, $\Delta G_g$ should be as small as possible, and $\Delta G_g$ value reflects the GFA of BMG.

Fig.2 shows the curves between $\Delta G_g$ and $T_g$ for two $\Delta H_{mg}$: -1 kJ·mol$^{-1}$ and -2 kJ·mol$^{-1}$ respectively. It is seen from Fig.2, for an alloy with large $T_g$, a larger $\Delta G_g$ can be found for large $\Delta H_{mg}$, its GFA is weaker. This shows that although $T_g$ of the alloy is high, its GFA may not be always strong. $T_g$ has a certain limitation for the GFA.
criterion.

For the six groups (except for Nd-based) of MGF alloys the fitted coefficients for the equations between $R_c$ and $\Delta H_{mg}$ or $\Delta G_g$ (using regression equation $R_c = A + B_1 X + B_2 X^2$, $X$ represents $\Delta H_{mg}$ or $\Delta G_g$) and their minimal values are calculated and shown in Table 3. The relationships between $R_c$ and the three parameters ($T_{rg}$, $\Delta H_{mg}$ and $\Delta G_g$) are shown in Fig.3. It is seen that the relationships between $R_c$ and $\Delta H_{mg}$ and $\Delta G_g$ are simple parabolic, but the relationships between $T_{rg}$ and $R_c$ is quite complicated, indicating $T_{rg}$ is not a very good GFA criterion.

Table 3 The parameters and fitted coefficients for equations between $R_c$ and $\Delta H_{mg}$ or $\Delta G_g$, their Minima for the six sub-groups and those of Zr-Al-Ni-Cu alloys (in bracket)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$A$</th>
<th>$B_1$</th>
<th>$B_2$</th>
<th>$R$</th>
<th>Minima (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_c$ and $\Delta H_{mg}$ [kJ/mol]</td>
<td>1304.13</td>
<td>176.19</td>
<td>5.81</td>
<td>0.788</td>
<td>-15.16</td>
</tr>
<tr>
<td>(27133.93)</td>
<td>(2752.75)</td>
<td>(69.82)</td>
<td>(0.992)</td>
<td>(-19.71)</td>
<td></td>
</tr>
<tr>
<td>$R_c$ and $\Delta G_g$ [kJ/mol]</td>
<td>1214.97</td>
<td>675.65</td>
<td>91.74</td>
<td>0.743</td>
<td>-3.68</td>
</tr>
<tr>
<td>(14278.82)</td>
<td>(5935.12)</td>
<td>(616.64)</td>
<td>(0.993)</td>
<td>(-4.81)</td>
<td></td>
</tr>
</tbody>
</table>

As shown in Table 3, the two correlation coefficients, $R_c$, are both larger than 0.74, indicating the regressed equations have relatively good reliability. And the relationships between $R_c$ and the two parameters ($\Delta H_{mg}$ or $\Delta G_g$) are similar to one another in Fig.3, which indicates the $T_{rg}$ influences not the tendency but the magnitude of the $\Delta G_g$. It is also shown that the $T_{rg}$ is not a good criterion. Furthermore, since the relationships all present the parabola, and then there is other BMGs whose GFA are better than the BMGs presented. Fortunately, it is testified, recently, by C. DONG et al. [15] developed other Zr-Al-Ni-Cu BMGs with better GFA. And the optimal values are calculated in terms of the fitted equations in Table 3, that of $\Delta H_{mg}$ and $\Delta C_g$ are $-15.16$ kJ/mol, -3.68 kJ/mol respectively. It is shown that when $\Delta H_{mg}$ is excessive large, it is unfavorable to the formation of BMG. Large $\Delta H_{mg}$ reflects the stronger bonding force and the cluster [16] is big but less, and if excessive heats exhausting in the solidification of melt cannot be carried about, obviously it will influence the formation of BMG. On the contrary, less heats leads to small and more clusters even though the exhaustion of heats is easy.

The comprehensive effects above-mentioned result in the decrease of GFA of BMG. And thus, only when $\Delta H_{mg}$ is moderate, it is favorable to the formation of BMG. Furthermore, GFA sequences are performed on seven subgroups. According to the $R_c$, the GFA ascending sequence is Pd-Cu-Si, Mg-based, La-based, Zr-Al-TM, Zr-Ti-TM and Pd-T-TM. According to $\Delta G_g$, that is Pd-Cu-Si, Mg-based, Zr-Al-TM, Pd-T-TM, Zr-Ti-TM and La-based. And according to $\Delta H_{mg}$ it will be Pd-Cu-Si, Mg-based, Zr-Al-TM, Zr-Ti-TM, Pd-T-TM and La-based. It is shown that the GFA ascending sequences in three cases agree with that of A. Inoue's [12] except for La-based. If the above-mentioned rules are correct, one can develop more BMGs with better GFA in La-based alloy system. In addition, the GFA of Nd-based was predicted by the use of two above-mentioned criteria, and the results of the predictions are that the GFA of Nd-based is in the vicinity of that of Mg-based. And furthermore, J. XU et al. [17] recently, reported Mg$_{65}$Cu$_{20}$Zn$_{5}$Y$_{10}$ BMGs with thickness up to 6 mm and its $R_c$ may reduce to 25 K/s. Particularly, the fitted equations between $R_c$ and the parameters ($\Delta H_{mg}$ or $\Delta G_g$) for Zr-Al-Ni-Cu alloys are tabulated in Table 3 (in bracket) and the corresponding relationships are shown in Fig.4 respectively. The minimum, i.e., optimum value, is -19.71 kJ/mol for the $\Delta H_{mg}$ and -4.81 kJ/mol for the $\Delta C_g$. And then, five Zr-Al-Ni-Cu BMGs [15] (shown in Table 4) developed recently are examined by means of $\Delta H_{mg}$ and $\Delta G_g$ criteria.
respectively. As in Table 4 and Fig.4, the $\Delta H_m$ and $\Delta G_s$ values are in the vicinity of -19.71 kJ/mol and -4.81 kJ/mol, which indicates that the GFA of these alloys is strong. Furthermore, as shown in Table 3, the correlation coefficients of the equation for Zr-Al-Ni-Cu base system between $R_c$ and the parameters ($\Delta H_m$ or $\Delta G_s$) are both larger than 0.99, indicating that these relationships are fairly reliable. And thus, the $R_c$ of the alloys developed by C. DONG et al[15], is calculated (shown in Table 4). From $\Delta H_m$ criterion, the GFA ascending sequence is Zr$_{65.5}$Al$_{5.6}$Cu$_{22.4}$Ni$_{6.5}$, Zr$_{65.3}$Al$_{6.5}$Cu$_{20}$Ni$_{8.2}$, Zr$_{65.5}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$, Zr$_{64.8}$Al$_{8.3}$Cu$_{1.55}$Ni$_{11.4}$, Zr$_{64.5}$Al$_{9.2}$Cu$_{13.1}$Ni$_{13.2}$, Zr$_{63.8}$Al$_{11.4}$Cu$_{17.2}$Ni$_{7.6}$.

Obviously, Inoue alloy, i.e. Zr$_{65}$Al$_{7.5}$Cu$_{17.5}$Ni$_{10}$, don't own highest GFA in these alloys. This is in agreement with C. DONG et al.

However, from the $\Delta G_s$ criterion, the ascending sequence is contrary with the result of the $\Delta H_m$ criterion, indicating the $\Delta H_m$ criterion is better and more convenient than the $\Delta G_s$ criterion. Furthermore, it could be predicted that there will be another Zr-Al-Cu-Ni base alloys characterized by higher GFA.

### Table 4 The calculated parameters ($\Delta H_m$ and $\Delta G_s$) and predicted $R_c$ for the alloys developed by Dong Chuang et al.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$\Delta H_m$ [kJ/mol]</th>
<th>$\Delta G_s$ [kJ/mol]</th>
<th>$R_c$ [K/s]</th>
<th>$R_c$ [K/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr$<em>{65}$Al$</em>{5}$Cu$<em>{12.8}$Ni$</em>{6}$</td>
<td>-19.7863</td>
<td>-4.9342</td>
<td>0.39</td>
<td>6.67</td>
</tr>
<tr>
<td>Zr$<em>{65}$Al$</em>{5}$Cu$<em>{12.8}$Ni$</em>{6.2}$</td>
<td>-19.8218</td>
<td>-4.9253</td>
<td>0.53</td>
<td>5.38</td>
</tr>
<tr>
<td>Zr$<em>{65}$Al$</em>{5}$Cu$<em>{12.8}$Ni$</em>{11.4}$</td>
<td>-19.8741</td>
<td>-4.8655</td>
<td>0.572</td>
<td>-0.73</td>
</tr>
<tr>
<td>Zr$<em>{65}$Al$</em>{5}$Cu$<em>{12.8}$Ni$</em>{13.2}$</td>
<td>-19.9049</td>
<td>-4.8551</td>
<td>0.578</td>
<td>-1.35</td>
</tr>
<tr>
<td>Zr$<em>{65}$Al$</em>{5}$Cu$<em>{12.8}$Ni$</em>{17.2}$</td>
<td>-19.9646</td>
<td>-4.8599</td>
<td>0.582</td>
<td>-1.25</td>
</tr>
</tbody>
</table>

Note: $R_{ci}$ and $R_{gi}$ are the critical cooling rates calculated by the parameters of the $\Delta H_m$ and $\Delta G_s$ respectively.

### References


[13] S. C. Glade, R. Busch, D. S. Lee and W. L. Johnson. Thermodynamics of Cu_{47}Ti_{34}Zr_{11}Ni_{8}, Zr_{52.5}Cu_{17.9}Ni_{14.6}Al_{10}Ti_{5} and Zr_{50}Cu_{15}Ni_{12}Al_{10}Mb; bulk metallic glass forming alloys [J]. J. APPL. PHYSICS, 2000, 87(10): 7243-7248


