Estimation of Gibbs free energy difference in Pd-based bulk metallic glasses

*Cai Anhui1,2, Xiong Xiang1, Liu Yong1, Tan JingYing2, Zhou Yong2, An WeiKe2

(1. State Key laboratory of Powder Metallurgy, Central South University, Changsha 410083, China; 2. Department of Mechanical and Electrical Engineering, Hunan Institute of Science and Technology, Yueyang 414000, China)

Abstract: A new thermodynamic expression for Gibbs free energy difference \( \Delta G \) between the under-cooled liquid and the corresponding crystals of bulk metallic glasses was derived. The newly proposed expression always gives results in fairly good agreement with experimental values over entire temperature range between the fusion temperature \( T_m \) and the glass transition temperature \( T_g \) of Pd\(_{40}\)Ni\(_{10}\)P\(_{20}\), Pd\(_{40}\)Cu\(_{10}\)Ni\(_{10}\)P\(_{20}\), and Pd\(_{40}\)Cu\(_{10}\)Ni\(_{10}\)P\(_{20}\), which possess different heat capacities. However, the TS and KN expressions cannot always provide results in good agreement with the experimental values. In addition, the deviations between the experimental values and the \( \Delta G \) calculated by the proposed expression at \( T_g \) are smaller than those given by other expressions for all the bulk metallic glasses studied.

Key words: thermodynamic; Gibbs free energy difference; bulk metallic glasses

1 Physical background

The bulk metallic glasses (BMGs) have drawn a lot of interest because of their superior physical and chemical properties compared to their crystal counterpart. Bulk glass formed from multi-component metallic alloys has widened the possible technical applications of metallic glasses. Many multi-component glass forming alloys, i.e., La\([1]\), Zr\([12,13]\), Pd\([14,15]\), Mg\([16,17]\), Cu\([18,19]\), Fe\([14,16]\), Ti\([17]\), Ni\([18,19]\), Pr\([20]\), Co\([21]\), Ca\([22]\) and Ce-based alloys\([23]\), possess excellent glass-forming ability. The Gibbs free energy difference (\( \Delta G \)) of crystallization of these multi-component under-cooled systems is an important parameter in nucleation processes. The nucleation frequency has an exponential dependence on \( \Delta G \), and hence the estimation of \( \Delta G \) is often critically important when analyzing nucleation phenomena. The Gibbs free energy change has played an important role in predicting the glass-forming ability of the multi-component metallic alloys. The temperature dependences of \( \Delta G \) in the under-cooled region can be obtained if the temperature dependences of the heat capacities of the liquid and crystalline phases of the multi-component alloys are known. However, the meta-stable nature of the under-cooled phase makes it difficult to obtain experimental heat capacity data accurately, although many attempts have been made\([24]\). Therefore, in the absence of experimental data the functional dependence of \( \Delta G \) must be estimated theoretically. However, there is no universal applicable expression for \( \Delta G \), although many attempts have been made to derive analytical expressions for \( \Delta G \) of different materials, such as

\[
\Delta G = \Delta H_m \left( \frac{2T(T_m - T)}{T_m(T + T_m)} \right)
\]

(TS expression),

\[
G = \Delta H_m \left( \frac{T_m - T}{T + T_m} \right)^2 \frac{2T}{3(T + T_m)^2}
\]

(KN1 expression) and

\[
\Delta G = \Delta H_m \left( \frac{4T^2(T_m - T)}{T_m(T + T_m)^2} \right)
\]

(KN2 expression)\([24]\). The aim of this work was to derive a new \( \Delta G \) expression for bulk metallic glasses. And then, the proposed expression was compared with TS, KN1 and KN2 expressions by applying them on Pd-Ni-(Cu)-P bulk metallic glasses, such as Pd\(_{40}\)Ni\(_{10}\)P\(_{20}\), Pd\(_{40}\)Cu\(_{10}\)Ni\(_{10}\)P\(_{20}\), and Pd\(_{40}\)Cu\(_{10}\)Ni\(_{10}\)P\(_{20}\), which possess different heat capacity. The proposed expression works well for these BMGs. However, the TS, KN1 and KN2 expressions are not always suitable for all the BMGs studied.

The Gibbs free energy difference between the liquid and crystalline phases is given by

\[
\Delta G = \Delta H - T \Delta S
\]

(1)

Where,

\[
\Delta H = \Delta H_m - \int_{T_m}^{T} \Delta C_p \, dT
\]

(2)

\[
\Delta S = \Delta S_m - \int_{T_m}^{T} \Delta C_p \, dT
\]

(3)

Where, \( T_m \) is the melting temperature, \( \Delta S_m \) is the entropy of fusion and \( \Delta H_m \) is the enthalpy of fusion. They are related to each other by the following relation

\[
\Delta S_m = \frac{\Delta H_m}{T_m}
\]

(4)

The \( \Delta C_p \), defined as \( C_p(l) - C_p(g) \), is the difference between the specific heat of the under-cooled liquid \( C_p(l) \) and the specific heat of the crystalline phase \( C_p(g) \). Thus, if we have experimental...
specific heat data available for the under-cooled liquid and the crystalline phase of a material, the experimental $\Delta G$ values can be calculated by Eqs. (1)–(3). In the absence of $\Delta C_p$ data, one must estimate the value by choosing an expression that satisfactorily explains the temperature dependence of the $\Delta C_p$.

According to the definition of $C_p$:

$$C_p = \frac{\partial H}{\partial T}$$

(5)

And $\Delta H$ could be expressed by:

$$\Delta H = \Delta H_m \frac{T - T_g}{T_m - T_g}$$

(7)

Where $T_g$ is the isenthalpic temperature when $\Delta H = 0$.

Substituting Eq. (7) into Eqs. (1)-(3)

$$\Delta C_p = \frac{\partial \Delta H}{\partial T} = \frac{\Delta H_m}{T_m} \frac{T - T_g}{T_m - T_g}$$

(8)

Substituting Eq. (8) into Eqs. (1)-(3)

$$\Delta G = \Delta H_m \frac{T_g(T - T_g)}{T_m(T_m - T_g)} + \frac{T}{T_m - T_g} \ln \left( \frac{T_m}{T} \right)$$

(9)

Let $T_g = \alpha T_m (0 \leq \alpha < 1)$, we obtain

$$\Delta G = \Delta H_m \left[ \frac{\alpha (T - T_g)}{(1 - \alpha) T_m^2} + \frac{T}{(1 - \alpha) T_m} \ln \left( \frac{T_m}{T} \right) \right]$$

(10)

### 2 Results and discussion

Table 1 gives the change in specific heat $\Delta C_p$ of the under-cooled liquid and the crystal, glass transition temperature $T_g$, fusion temperatures $T_m$ and the heats of fusion $\Delta H_m$ for Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$, Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ with different heat capacities $^{[4-6]}$. The $\Delta C_p$ data were used to calculate the experimental $\Delta G$ using Eqs. (1)–(3) in the temperature range between $T_m$ and $T_g$. The expressions, i.e. TS, KN1, KN2 and Eq. (10), are used to obtain the calculated $\Delta G$. Figures 1–6 show the plot of $\Delta G$ as function of temperature for these BMGs. As shown in Figs. 1–6, the proposed expression in this study always gives the results in better agreement with the experimental values over the entire temperature range between $T_m$ and $T_g$ on the condition of the suitable $\alpha$ values. However, the TS, KN1 and KN2 expressions do not always provide good agreement with the experimental values. As shown in Fig.1, Fig.2 and Fig.5, the TS and KN1 expressions both provide good agreement with the experimental values over the entire temperature range, but the KN2 expression gives results deviated far from the experimental values. However, as shown in Fig.3 and Fig.6, the KN2 expression succeeds in providing good agreement with the experimental values over the entire temperature range, but the TS and KN1 expressions both deviates far from the experimental values. Moreover, in Fig.4 the TS, KN1 and KN2 expressions give poor results in the temperature range between $T_m$ and $T_g$. Meanwhile, results given by Eq. (10) nearly overlaps with the experimental values. Results obtained from TS, KN1 and KN2 expressions vary with the heat capacity data even though the same type of BMG is considered. For example, as for Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$, the KN2 expression can provide good agreement with the experimental values in Fig.3, but it gives poor results in Fig.4. However, as for Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$, the TS and KN1 expressions both succeed in providing reasonable agreements. On the contrary, the KN2 expression gives poor results in Fig.6. It indicated that the $\Delta G$ expression depends on the multi-component metallic glass itself. As shown in Table 2, although the calculated Gibbs free energy differences given by TS and KN1 expressions deviated from the experimental values at $T_g$ are 0.3% and 0.5%, respectively, for Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ with $\alpha=0$, the deviation given by Eq.(10) (expression proposed in this study) is only 0.2%, smaller than those given by other expressions for all the bulk metallic glasses studied, and its maximum deviation is only 1.2%. Therefore, the application of Eq.(10) is more general and more accurate than the TS, KN1 and KN2 expressions. It is a good choice in selecting $\Delta G$ expression for the multi-component glass-forming alloys.

### 3 Conclusions

A new thermodynamic expression for the calculation of Gibbs free energy difference $\Delta G$ between the liquid and the crystal of bulk metallic alloys was proposed. The new expression always gives results in good agreement with the experimental values over the entire temperature range from $T_g$ to $T_m$ for Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$, Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ and Pd$_{40}$Cu$_{30}$Ni$_{10}$P$_{20}$ with different heat capacities. However, other expressions (such as TS and KN) do not always provide good agreement with the experimental values.

### Table 1 $\Delta C_p$ of the under-cooled liquid and the crystal, glass transition temperature $T_g$, fusion temperatures $T_m$ and the fusion heats $\Delta H_m$ for Pd-Cu-Ni-P bulk metallic glasses

<table>
<thead>
<tr>
<th>Bulk metallic glasses</th>
<th>$\Delta C_p$ J mol$^{-1}$ K$^{-1}$</th>
<th>$T_g$ K</th>
<th>$T_m$ K</th>
<th>$\Delta H_m$ kJ mol$^{-1}$</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$<em>{40}$Ni$</em>{10}$P$_{20}$</td>
<td>39.9608 – 0.035112 $T$</td>
<td>575</td>
<td>892</td>
<td>7.95</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>42.6208684 – 0.0370802 $T$</td>
<td>582</td>
<td>884</td>
<td>10.42</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td>14.57 + 0.0285 $T$ – 1.46 $\times 10^4$ $T^2$</td>
<td>575</td>
<td>804</td>
<td>4.84</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>35.22361 – 0.0280168 $T$</td>
<td>578</td>
<td>798</td>
<td>6.82</td>
<td>[5]</td>
</tr>
<tr>
<td></td>
<td>0.0332 $T + 4.89 + 106$ $T^2 – 5 + 10^5$ $T^2$</td>
<td>576</td>
<td>790</td>
<td>7.2</td>
<td>[4]</td>
</tr>
<tr>
<td></td>
<td>31.1147 – 0.01902 $T$</td>
<td>585</td>
<td>802</td>
<td>7.01</td>
<td>[5]</td>
</tr>
</tbody>
</table>
Table 2 Calculated Gibbs free energy difference deviation (%), compared with experimental values, at $T_g$ of the bulk metallic glasses using TS, KN1, KN2 expressions and Eq.(10) of this study.

<table>
<thead>
<tr>
<th>Bulk metallic glasses</th>
<th>$\alpha$ values</th>
<th>TS expression</th>
<th>KN1 expression</th>
<th>KN2 expression</th>
<th>Eq.(10) of this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$<em>{40}$Ni$</em>{40}$P$_{20}$</td>
<td>0.30</td>
<td>10.2</td>
<td>11.9</td>
<td>13.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Pd$<em>{40}$Ni$</em>{40}$P$_{20}$</td>
<td>0.15</td>
<td>2.9</td>
<td>4.4</td>
<td>18.4</td>
<td>0.05</td>
</tr>
<tr>
<td>Pd$<em>{40}$Cu$</em>{30}$Ni$<em>{10}$P$</em>{20}$</td>
<td>0.76</td>
<td>76.8</td>
<td>77.7</td>
<td>54.5</td>
<td>0.04</td>
</tr>
<tr>
<td>Pd$<em>{40}$Cu$</em>{30}$Ni$<em>{10}$P$</em>{20}$</td>
<td>0.45</td>
<td>15.0</td>
<td>18.0</td>
<td>3.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Pd$<em>{40}$Cu$</em>{30}$Ni$<em>{10}$P$</em>{20}$</td>
<td>0</td>
<td>0.3</td>
<td>0.5</td>
<td>16.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Pd$<em>{40}$Cu$</em>{30}$Ni$<em>{10}$P$</em>{20}$</td>
<td>0.52</td>
<td>23.3</td>
<td>24.3</td>
<td>3.9</td>
<td>0.5</td>
</tr>
</tbody>
</table>
values. The deviations of $\Delta G$ from the experimental values at $T_1$ given by Eq.(10) are smaller than those given by the other expressions for all the bulk metallic glasses studied. The application of the newly proposed expression is more general and more accurate than the TS, KN1 and KN2 expressions.

Acknowledgement

The project was supported by Scientific Research Fund of Hunan Provincial Education Department (06B038) and Postdoctoral Science Foundation of Central South University.

References