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Short Communication

Correlation between glass transition temperature and melting temperature in metallic glasses

C.R. Cao [a], D.W. Ding [a], D.Q. Zhao [a], E. Axinte [b], H.Y. Bai [a], W.H. Wang [a,*]

[a] Institute of Physics, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Gheorghe Asachi Technical University of Iasi, Faculty of Machine Manufacturing & Industrial Management, 700500 Iasi, Romania

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ABSTRACT

We report that the glass transition temperature (T_g) of a variety of metallic glasses (MGs) correlates with the eutectic or peritectic temperature of two main components corresponding stoichiometric proportion in their binary phase diagram. The correlation suggests that the T_g of MGs is mainly determined by their solvent of two base components, which have composition close to the eutectic and peritectic points in the binary phase diagram and the weakest link in amorphous structure. The results have implications for understanding the structure and glass transition in MGs and for predicting and designing metallic glasses with a desirable T_g.

1. Introduction

In contrast to conventional metallic alloys, metallic glasses (MGs) are macroscopically isotropic and homogeneous, and microscopically liquid-like disordered structure containing short-range orders (SRO) and medium-range orders (MRO) [1,2]. The structure of the MGs is regarded to inherit from their liquid state. The SRO is modeled as the solute-centered clusters, and the MRO is the highly structured superclusters consisting of interconnected smaller clusters and the packing of the SRO [1–3]. The MRO have been found to closely correlate with the features and properties of MGs [1–5]. Ma et al. showed that the elastic moduli of some MGs inherit from their solvent components [6], and the elastic properties, the plasticity, some physical properties, and glass transition in some MGs are found to inherit from the base components [5]. The pressure-induced polyamorphism in lanthanide-based MGs related to the electronic structure of 4*f* electrons is also found to be inherited from its lanthanide-solvent constituent and the results suggest that the electrical properties of MGs might inherit from their base components as well [7]. On the other hand, Poisson's ratio, which is physical parameter for characterize the solid, is found to correlate with the viscous characteristic of its liquid [8], and the glass transition of MGs has the characteristics of melting [9–11]. This demonstrates that the glass transition in MGs might have the similar family traits [4] and could relate to the melting temperature of their base components which also correlates with the glass-forming ability in glass-forming alloys [12–19].

In this paper, the relationship between the glass transition temperature (T_g) and the temperature of the eutectic or peritectic point [$T_{m(AxBy)}$] of two base components in their binary phase diagram in various MGs is investigated. It is found that the T_g shows a better linear relationship with the $T_{m(AxBy)}$ than that of the base element melting temperature in various MGs. The results confirm that there exist the weakest link and inhomogeneous structure in MGs, and close relationship among the glass transition, melting and microstructural characteristics in glass-forming alloys.

2. The theories

The studied bulk MGs samples exhibit a wide range of glass transition temperature, T_g, and significantly difference in physical and mechanical properties [3,8]. Both the elastic moduli C and the T_g of MGs show the similar "rule of mixtures" [11,20],

$$C^{-1} = \sum \left(f_i \cdot \frac{1}{C_i} \right), \tag{1}$$

$$T_g = 0.385 \sum f_i (T_m)_i, \tag{2}$$

where C_i and $(T_m)_i$ is the modulus and melting temperature of constituent element *i*; f_i is the atomic percent of element *i*.

The T_g of various MGs has a close correlation with the elastic moduli [21]:

$$T_g = 2.5E, \tag{3}$$

$$T_g \propto MG, \tag{4}$$

* Corresponding author. Tel.: +86 10 82649198.
E-mail address: whw@iphy.ac.cn (W.H. Wang).

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where E is the Young's modulus, M is the molar mass of MG, and G is the shear modulus. According to the Lindermann melting criterion, the melting temperature T_m of a solid is related to Debye temperature θ_D [22] which is closely related to the elastic modulus. In MGs, the relationship between T_g and θ_D is [9]

$$T_g = aM\theta_D^2, \tag{5}$$

here a is a constant. The MGs can also inherit the feature and the properties from the base component [2,3,5].

Based on previous research results (Eqs. (1)–(5)), it is expected that the MGs might inherit their glass transition temperature from their base components. According to Eq. (5), the T_g of base component correlates with its T_m. The data of T_g of various MG systems and the melting temperature [$T_{m(base)}$] of their base components are then surveyed, and the data are listed in Table 1. Fig. 1 shows the T_g vs. $T_{m(base)}$ of various MGs listed in Table 1. One can see that the T_g and $T_{m(base)}$ do not show a clearly linear relationship, and this indicates that unlike the moduli inheritance the T_g and T_m of the base component in MGs have no clear correlation.

Based on the experiment data survey, it is reported that a linear relationship between the T_g and the absolute value of the mixing enthalpy ΔH^{chem} for MGs can be described as [23]:

$$T_g \approx T_a + k|\Delta H^{chem}| \tag{6}$$

where T_a and k are constants. To estimate the ΔH^{chem} of the multicomponent MGs, the binary eutectic compositions are often used as the starting points [18,24]. The two base elements in their binary eutectic or peritectic compositions always have a greatest contribution of mixing entropy for a multicomponent MGs. The close correlation between the mixing enthalpy and T_g mainly depends on the interaction intensity between the base binary eutectic compositions for different MGs [23], this indicates that the T_g for various MGs might be mainly contributed to the interaction intensity between the two base components in their eutectic compositions in phase diagram. The MGs are typically formed either by liquid quenching near the deep-eutectic [19] or in the vicinity of multiple quasi-peritectic points [25]. From these results, it is inferred that T_g have a close relation with the interaction of two base elements in their eutectic or peritectic compositions.

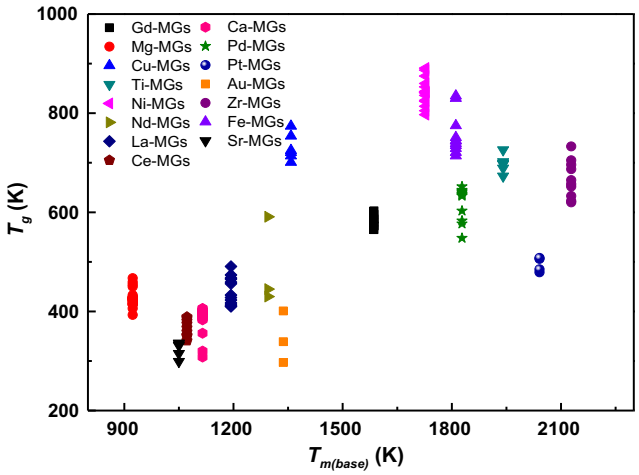

Fig. 1. Glass transition temperature (T_g) vs. the melting temperature [$T_{m(base)}$] of their base components of various metallic glasses. The statistical analysis R-square is about 0.35.

Table 1
The values of $T_{m(base)}$, $\langle T_m \rangle$, and $T_{m(AxBy)}$ for a variety of metallic glasses.

Composition of MG	$T_{m(base)}$ (K)	$\langle T_m \rangle$ (K)	$T_{m(AxBy)}$ (K)
$Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$	1337	1405	636
$Au_{55}Cu_{25}Si_{20}$	1337	1412	636
$Ca_{65}Mg_{8.54}Li_{9.96}Zn_{16.5}$	1115	963	664
$Ca_{55}Mg_{25}Cu_{20}$	1115	1115	718
$Ca_{55}Mg_{20}Cu_{25}$	1115	1137	755
$Ce_{70}Al_{10}Cu_{20}$	1072	1112	697
$Ce_{68}Al_{10}Cu_{20}Nb_2$	1072	1145	697
$(Ce_{80}La_{20})_{68}Al_{10}Cu_{20}Co_2$	1072	1146	697
$Cu_{60}Zr_{29}Ti_{10}Sn_1$	1358	1630	1163
$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	1358	1676	1248
$Cu_{50}Hf_{43}Al_7$	1358	1786	1253
$Fe_{61}Mn_{10}Cr_4Mo_6Er_1C_{15}B_6$	1811	2254	1426
$Fe_{70}Mo_5Ni_5P_{12.5}C_5B_{2.5}$	1811	1791	1321
$Gd_{40}Y_{16}Al_{24}Co_{20}$	1586	1499	1148
$Hf_{48}Cu_{29.25}Ni_{9.75}$ Al_{13}	2423	1850	1243
$La_{60}Al_{20}Co_{20}$	1193	1256	820
$La_{55}Al_{25}Cu_{10}Ni_5Co_5$	1193	1200	823
$Mg_{65}Cu_{25}Y_{10}$	923	1119	825
$Mg_{65}Cu_{25}Tb_{10}$	923	1103	825
$Mg_{64}Ni_{21}Nd_{15}$	923	1145	779
$Nd_{60}Al_{10}Ni_{10}Cu_{20}$	1283	1307	793
$Nd_{60}Fe_{20}Al_{10}Ni_{10}$	1283	1398	958
$Ni_{45}Ti_{20}Zr_{25}Al_{10}$	1726	1789	1343
$Ni_{60}Nb_{35}Sn_5$	1726	2020	1539
$Pd_{40}Cu_{40}P_{20}$	1828	1431	1051
$Pd_{39}Ni_{10}Cu_{30}P_{21}$	1828	1485	1051
$Pd_{77.5}Cu_6Si_{16.5}$	1828	1780	1083
$Pt_{60}Ni_{15}P_{25}$	2041	1563	861
$Pt_{57.5}Cu_{14.7}Ni_5P_{22.8}$	2041	1532	861
$Sr_{60}Li_5Mg_{15}Zn_{20}$	1050	930	642
$Sr_{60}Mg_{20}Zn_{15}Cu_5$	1050	986	699
$Ti_{40}Zr_{20}Ni_3Cu_{12}Be_{20}$	1933	1724	1253
$Ti_{50}Ni_{24}Cu_{20}B_1Si_2Sn_2$	1933	1700	1250
$Zr_{50}Cu_{50}$	2128	1743	1201
$Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$	2128	1813	1268
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	2128	1834	1238
$Zr_{45}Cu_{45}Al_7Gd_3$	2128	1682	1201
$Zr_{46.75}Ti_{8.25}Cu_{10.15}Ni_{10}Be_{27.25}$	2128	1887	1238
$Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$	2128	1870	1268
$Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$	1337	1405	636

3. Results and discussions

To confirm the idea, the data of T_g from the literatures [20,26–51], and the nearest eutectic or peritectic temperature [$T_{m(AxBy)}$] of the two base elements A and B from their binary alloy phase diagram [52] were collected, and the data are listed in Table 1. To determine the $T_{m(AxBy)}$, the following rules are followed: (1) for $Cu_xZr_yR_{1-x-y}$MGs (R is the third component), the Cu and Zr are two dominant base components, and CuxZry has a nearest eutectic or peritectic point in the Cu–Zr binary phase diagram. For example, for $Zr_{45}Cu_{45}Al_7Gd_3$ bulk MG, its $T_{m(AxBy)}$ is the eutectic temperature in CuZr binary diagram at Cu 50% or 50% Zr (atomic fraction); (2) for some MGs such as $Pd_{40}Cu_{30}Ni_{10}P_{20}$, their two base components Pd and Cu have no eutectic or peritectic point in their binary phase diagram, and then the temperature in the nearest eutectic point ($Pd_{66.7}P_{33.3}$) in their Pd–P phase diagram as the $T_m(Pd_{40}P_{20})$ is used; (3) for the MGs with several secondary base components which have same corresponding stoichiometric compositions, The one which has the highest mixing enthalpy with the base element is chosen. The obtained values of $T_{m(AxBy)}$ are also listed in Table 1.

Fig. 2 shows the relationship of T_g and $T_{m(AxBy)}$ for 163 different MGs including Au-based, Ca-based, Cu-based, rare earth-based, Fe-based, Mg-based, Ni-based, Pd-based, Pt-based, Sr-based, Ti-based, and Zr-based MGs. These MGs have markedly different glass-forming ability, mechanical, chemical and physical properties (the elastic moduli range from less than 20 GPa to more than 200 GPa, and T_g ranges from 297 K to 891 K) [20,26–51]. Although the data are from different literatures and were measured by different methods, it can be seen that the T_g and $T_{m(AxBy)}$ show a clear linear relationship in a form of $T_g = 0.55T_{m(AxBy)}$. Compare with the relation of

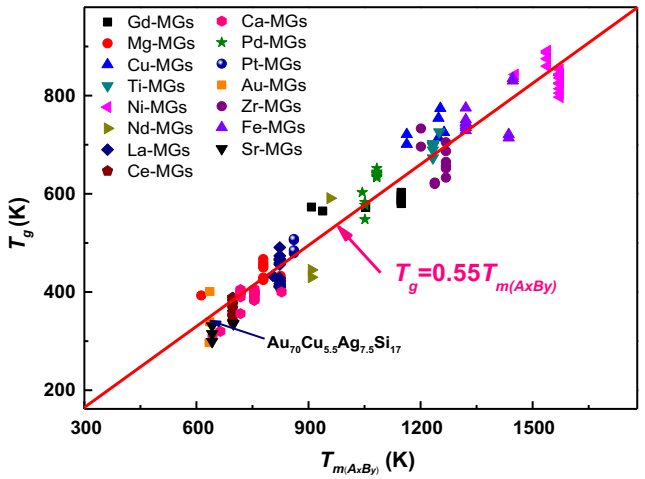

Fig. 2. The correlation between the T_g and the temperature[$T_{m(AxBy)}$] of the eutectic or peritectic point of two base elements in their binary phase diagram in MGs. They show a linear relationship of $T_g = 0.55T_{m(AxBy)}$. The statistical analysis R-square is about 0.94.

T_g and $T_{m(base)}$ of base component as shown in Fig. 1, the T_g and $T_{m(AxBy)}$ presents a much better linear relationship, which reveals the T_g of a MG mainly determined by the interaction intensity between the two base components.

It has been reported that the T_g has a relationship with average melting temperature $[\langle T_m\rangle = \Sigma f_i(T_m)_i]$ [10]. The relationship between $\langle T_m\rangle$ and T_g for these MGs is then also investigated, and the relationship between T_g and $\langle T_m\rangle$ are illustrated in Fig. 3. It can be seen that the T_g and $\langle T_m\rangle$ roughly follow the form of $T_g = 0.385\ \langle T_m\rangle$ [11] but show a larger scattering compared with that of T_g and $T_{m(AxBy)}$ as shown in Fig. 2. For example, for $Au_{70}Cu_{5.5}Ag_{7.5}Si_{17}$ [29] (as indicated in Fig. 3), its $T_{m(AxBy)}$ is 636 K and its $\langle T_m\rangle$ is higher than 1200 K, while its T_g is 339 K lower than the ultralow T_g systems of Ce- and La-based MGs which have the lower $\langle T_m\rangle$. Therefore, in general, the $T_g = 0.55T_{m(AxBy)}$ can more accurately reflect the relationship between T_g and the components in a MG, which is crucial for design a MG with desirable T_g. It is noted that a good correlation between the glass transition temperature and liquidus temperature in metallic glasses has also been recently reported by other groups [53].

Near the compositions of eutectic and peritectic points, and the temperatures, which are much lower than the pure element

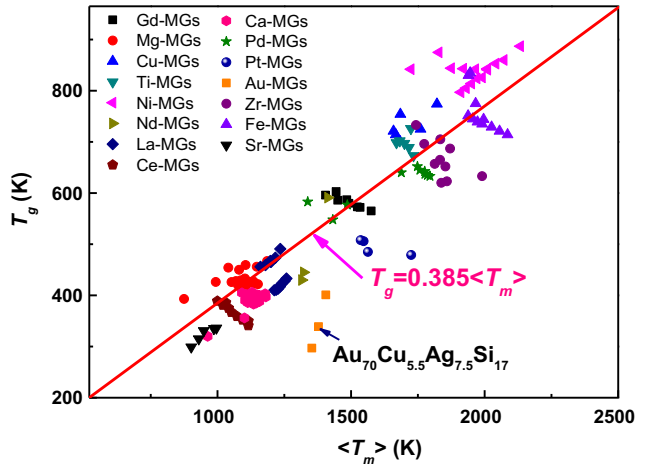

Fig. 3. The T_g vs. average melting temperature ($\langle T_m\rangle$) for the same MGs listed in Figs. 1 and 2. The statistical analysis *R*-square is about 0.82.

melting temperatures of their components, are at the valleys in phase diagrams. The correlation between T_g and eutectic and peritectic temperature of the two base components indicates that the two base components are solvent atoms in MGs, and the T_g is dominated by the bonding forces among the two solvents [4,5]. The results also indicate that the glass state to supercooled liquid state transition can be regarded as the broken or bonded of the weakest the solvent–solvent bonds among the solute-centered clusters in the MG, and the MGs can be regarded to consist of the solute-centered clusters, and the solvent atoms are mainly two base components, and the other components are solute atoms. The solvent–solvent junction bonding among the solute-centered clusters determine the characteristics of the glass transition and T_g of a MG. The correlation between T_g and eutectic and peritectic temperature of the two base components might also indicate that the bonds broken in the process of glass transition and A and B base components binary eutectic or peritectic melt is similar. This result may have implications for understanding that the best glass-forming ability is often near eutectic composition point.

4. Conclusions

The glass transition temperature of a variety of MGs shows a heredity from the eutectic or peritectic point $T_{m(AxBy)}$ which from the binary phase diagram of two base elements in MGs. The T_g and $T_{m(AxBy)}$ have a linear relationship of $T_g = 0.55T_{m(AxBy)}$. The correlation or inheritance suggests that the glass transition mainly determined by the solvent–solvent junction bonding among the solute-centered clusters. The finding might offer a simple means to predict and design MGs with desired glass transition temperature and properties.

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