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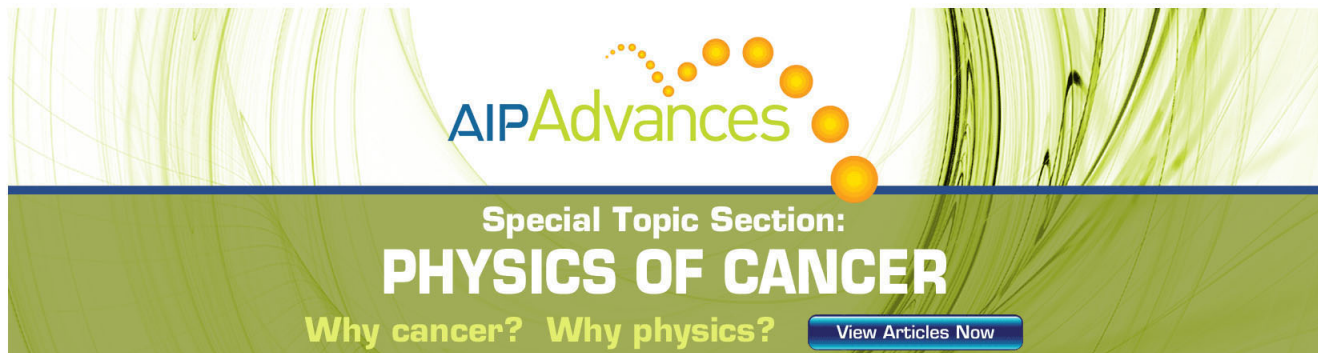
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## A “universal” criterion for metallic glass formation

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We have established a generally applicable criterion for the critical cooling rates  $R_c$  needed for the formation of metallic glasses, based on thermodynamic and kinetic properties of ten categories of metal-based alloys ranging from binary to multicomponent systems.  $R_c$  is found to depend on several fundamental properties of materials including the glass transition temperature (normalized with respect to the liquidus temperature), entropy of fusion, and kinetic fragility. Such a relation reproduces the experimental  $R_c$  values of 43 metallic glasses remarkably well with a  $R^2$  value of 0.94. The explanation of  $R_c$  provides guidance in search of metallic glasses. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4731881>]

A better understanding of glass forming ability (GFA) in metals and alloys is crucial to exploit new bulk metallic glasses (BMGs) applicable for melt-quenching at low cooling rates. Since the first preparation of metallic glasses, the understanding of GFA has been greatly improved with a number of criteria pioneered by Turnbull on the basis of classical crystal nucleation and growth theory from melts. These criteria point to the importance of two fundamental properties, namely the glass transition temperature  $T_g$  and the liquidus temperature  $T_l$ , or a reduced glass transition temperature defined by  $T_{rg} = T_g/T_l$ .<sup>1</sup> Empirical rules in multi-component alloys were also established emphasizing constituent features and have been proven useful in guiding compositional selections for the search of BMGs,<sup>2,3</sup> suggesting that certain fundamental quantities are significant in determining glass formation of alloys. Developing a criterion for glass formation relating to fundamental material properties is therefore taken as one of the ultimate goals for the understanding of glass formation in metals and alloys.<sup>4</sup> Although a complete explanation for the GFA remains to be clarified, a common recognition justified by theoretical and experimental views points to that glass formation is governed by the balance of thermodynamic and kinetic contributions, and various rules found from these two aspects have been applied for the prediction of glass forming regimes in alloy systems.<sup>5,6</sup> In this paper, we seek experimentally accessible properties that govern glass formation of metallic alloys based on thermodynamic and kinetic considerations. We find that four fundamental quantities can be used to effectively explain GFA of a large number of metallic alloys.

Thermodynamic studies on the glass formation in multi-component alloys are generally centered around the Gibbs free energy difference (or the enthalpy and entropy contributions) between liquids and various concomitant metastable and stable crystalline phases with which some empirical rules are established in searching for the best glass forming region. Examples are the mixing enthalpy<sup>7</sup> and the  $T_0$  lines where the Gibbs free energy of a liquid equals to that of the solid solution based on partitionless solidification.<sup>8</sup> The most direct thermodynamic argument for vitrification is the Gibbs

free energy difference  $\Delta G$  between an undercooled liquid and its equilibrium crystals, known as the thermodynamic driving force of the phase transition,<sup>9</sup>  $\Delta G = \Delta H - T\Delta S$ , where  $\Delta H$  and  $\Delta S$  are the difference in enthalpy and entropy. It is widely accepted that a small  $\Delta G$  at undercooling conditions thermodynamically favors glass formation.<sup>9</sup> Recent studies<sup>10</sup> show that  $\Delta G$  can be quantitatively addressed by only three independent variables,  $\Delta S_m$ ,  $T_l$ , and kinetic fragility, based on a correlation between the properties involved in glass transition and melting,  $m \propto \Delta C_p(T_g)T_g/\Delta H_m$  where  $\Delta C_p(T_g)$  is the liquid-crystal heat capacity difference at  $T_g$  and  $\Delta H_m$  is enthalpy of fusion.<sup>11</sup> The kinetic fragility represents how rapidly the structural relaxation kinetic properties (such as viscosity) vary with temperature near  $T_g$  and is defined by  $m = (d\log x/dT_g/T)|_{T=T_g}$ ,<sup>12</sup> where  $x$  denotes viscosity or relaxation time of a liquid. Liquids are accordingly divided into strong and fragile categories with the definition. Consequently,  $\Delta S_m$ ,  $T_l$ , and  $m$  are the fundamental experimental readily measurable parameters connecting to the thermodynamics of glass formation.

Kinetically, glass formation mainly concerns with the viscosity of alloy melts at  $T_l$  or near the fast crystallization temperature called the nose temperature in temperature-time-transformation plots.<sup>13</sup> High viscosity favors glass formation due to sluggish crystallization, as described in the classical nucleation and growth theory. The temperature dependence of viscosity of most glass forming liquids in the undercooled liquid region is usually described by a non-Arrhenius Vogel-Fulcher-Tammann (VFT) equation,  $\log \eta = A + B/(T - C)$ , where  $A$ ,  $B$ , and  $C$  are material-specific constants. Since liquid viscosities at  $T_g$  generally approach  $10^{12}$  Pa s,<sup>12</sup> the viscosity of an alloy melt at  $T_l$  is therefore determined by two factors, namely the temperature range of the undercooling liquid region,  $T_l - T_g$  or  $T_g/T_l$ , and how fast the viscosity changes with variation in temperature, i.e., kinetic fragility. The VFT equation can be therefore rewritten as  $\log \eta = A + (12 - A)^2/[m(T/T_g - 1) + 12 - A]$ . Here  $A$  denotes the logarithmic liquid viscosity at the high temperature limit, usually assigned to  $-5$  (with the unit of Pa s), corresponding to a relaxation time of  $10^{-13}$  s.<sup>12</sup> Naturally,  $m$  and  $T_g/T_l$  are two key kinetic parameters in

determining liquid viscosity at  $T_l$ . High  $T_g/T_l$  together with low  $m$  would kinetically favor glass formation.

We extract four experimentally accessible parameters,  $T_g/T_l$ ,  $\Delta S_m$ ,  $m$ , and  $T_l$  from a large number of glass forming alloys from the literatures to establish a criterion for glass formation based on the thermodynamic and kinetic analyses. In order to examine how individual properties are correlated with the GFA of materials, Fig. 1 depicts the dependences of these properties on critical cooling rate ( $R_c$ ) for glass formation. Except for  $T_l$ , all other three parameters of  $\Delta S_m$ ,  $m$ , and  $T_g/T_l$  is found to be somewhat correlated with  $R_c$ ; however, large uncertainty is also evident for each correlation, implying that none of the properties can be used alone in determining independently the GFA of metallic alloys. The fragility data used here are from two different measurements, namely viscosity and calorimetric measurements, and are plotted with different symbols.

In order to clarify whether thermodynamic and kinetic factors can work together in explaining glass formation more efficiently, a number of glass forming alloys are investigated. Although many systems have some properties available from the literature, systems with complete datasets of four properties are relatively few. We found 43 complete systems from ten categories of metal-based alloys ranging from binary to septenary metallic alloys covering Au-, Cu-, Fe-, La-, Mg-, Ni-, Pd-, Pt-, and Zr-based alloys, as summarized in Table S-I.<sup>14</sup> Data processing was performed with various mathematical functions by using a combination of  $T_g/T_l$ ,  $\Delta S_m$ ,  $m$ , and  $T_l$  as independent invariables, and optimization was made by comparing the correlation coefficients. Fig. 2 shows dependence of critical cooling rate  $R_c$  on a combined parameter  $k$ , imposed by the four properties,  $k = (1 - T_g/T_l)^{3.8}(T_g/T_l)^3 \exp(0.4\Delta S_m/R)m^{0.8}$ . Fig. 3 plots the correlation of  $R_c$  values

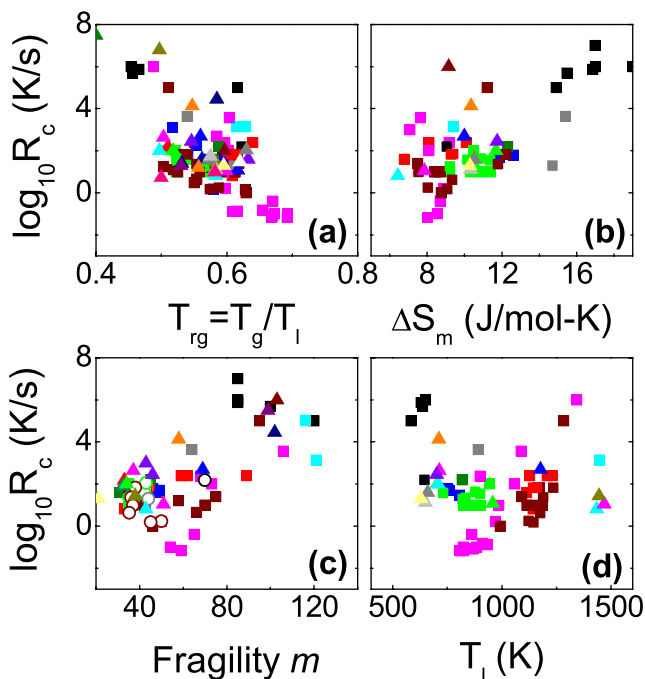


FIG. 1. Dependence of critical cooling rates  $R_c$  on four experimentally accessible properties of reduced glass transition temperature  $T_{rg}$ , entropy of fusion  $\Delta S_m$ , kinetic fragility  $m$ , and liquidus temperature  $T_l$  of metallic glass forming alloys.

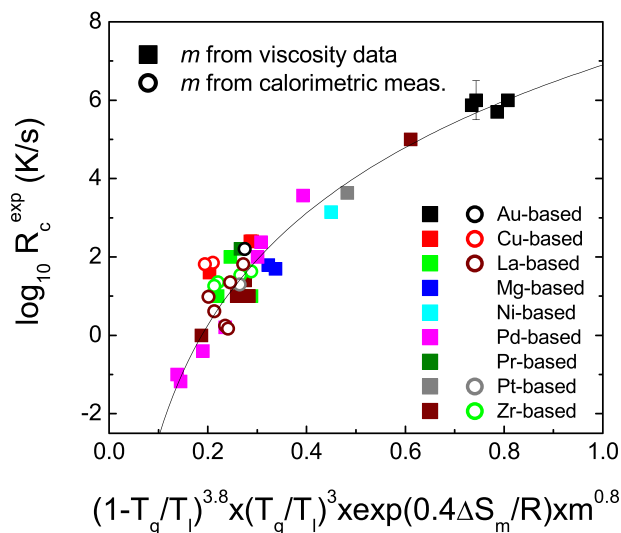


FIG. 2. Dependence of critical cooling rates  $R_c$  on a combination of four experimentally accessible properties listed in Fig. 1 in terms of certain partitioning function for ten metal-based glass forming alloys ranging from binary to septenary. Remarkable correlation suggests that the four properties can explain glass formation of metallic alloys. The solid curve is a fit to the data.

between the recorded values in literatures and the fitted ones according to the following relation:  $\log R_c^{cal} = 9.5 \log k + 6.9$ . A correlation coefficient of  $R^2 = 0.94$  was achieved. This remarkable correlation suggests that the four properties are able to interpret the glass forming ability satisfactorily. Somewhat surprisingly,  $T_l$  does not independently appear in the above relation, instead it works in a manner of  $T_g/T_l$ .

The success in correlating critical cooling rates for glass formation with the thermodynamic and kinetic quantities therefore indicates that the four experimentally accessible properties are decisive regarding the glass formation of metallic alloys, and a proper combination of the parameters is required, although any simple criterion from either thermodynamics or kinetics alone does not explain satisfactorily the GFA of materials. Whereas the two quantities of  $T_g/T_l$  and  $m$  have been accepted in correlating with GFA of various materials,<sup>1,15</sup> as evidenced in Figs. 1(a) and 1(c), the dependence of GFA on  $\Delta S_m$  seems somehow more complex in the

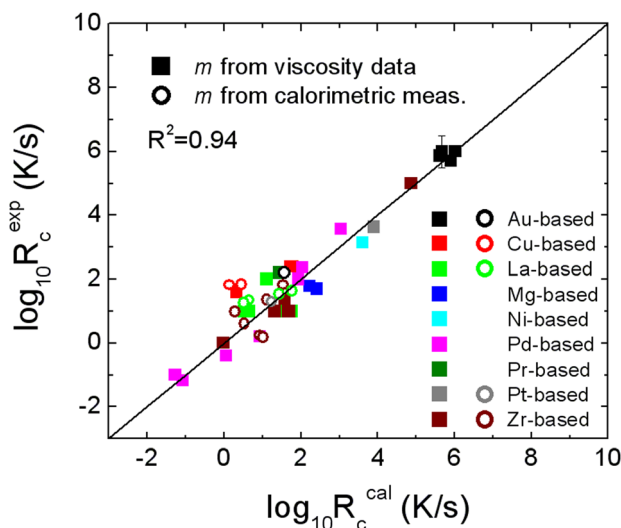


FIG. 3. Correlation of experimental critical cooling rates  $R_c^{exp}$  and calculated values  $R_c^{cal}$ . A correlation coefficient of 0.94 is reached.

sense that both high and low  $\Delta S_m$  values have been argued to work in determining GFA of materials.<sup>1,9</sup> Earlier nucleation theory emphasizes the importance of high  $\Delta S_m$  for vitrification as  $\Delta S_m$  scales with free-energy barriers for nucleation.<sup>1</sup> However, experimental measurements show that glass forming alloys usually have relatively low  $\Delta S_m$  resulting in a low liquid-solid Gibbs free energy difference.<sup>9,16</sup> Table S-I shows that alloys with increasing number of constituents generally have low values of  $\Delta S_m$ , in addition to enhanced GFA with low  $R_c$ . Hence a noticeable negative deviation in  $\Delta S_m$  of materials with high GFA is expected from the ideal mixing behavior among individual constituents.  $\Delta S_m$  has long been recognized as a crucial thermodynamic quantity in determining kinetic behaviors of materials. In addition to decreasing thermodynamic driving forces for crystallization in a liquid-solid transition, low  $\Delta S_m$  also reduces crystal growth rate<sup>17</sup> and interfacial tension<sup>18</sup> and steepens the profiles of liquidus lines in equilibrium phase diagrams which has an advantage in obtaining deep eutectics.<sup>19</sup> All of these support the notion that low  $\Delta S_m$  favors glass formation of metallic alloys.

Although it is believed that both thermodynamics and kinetics are involved in glass formation, a direct comparison of their contributions is rarely reported.<sup>13</sup> The found correlation in this letter offers an assessment to the individual contributions to GFA as quantified by  $R_c$  among glass forming metallic alloys.  $\Delta S_m$  of metallic alloys varies roughly from 7 to 19 J/mol-K, leading  $R_c$  to change in a scale of more than two orders of magnitude, provided other quantities remain unchanged. The  $m$  of metallic alloys is generally constrained in a range of 20–130, largely depending on the number of alloy components. This range of fragility would generate a change in  $R_c$  over seven orders of magnitude. The dependence of  $R_c$  on  $T_g/T_l$  is somehow intermediate and a change over five orders of magnitude is expected as  $T_g/T_l$  spans from 0.4 to 0.75. Naturally, one can reach a conclusion that the large span of GFA is largely weighted by the kinetic factors, namely kinetic fragility and  $T_g/T_l$ . This is consistent with recent studies of three Zr-based BMGs where dominant contribution from kinetics is emphasized.<sup>13</sup>

Structural consideration is also a critical aspect for glass formation and stability of undercooled alloy melts and has been scrutinized widely. Recent studies justified the importance of the existence of locally favored structures in undercooled liquids for the stability of undercooled liquids and glass formation,<sup>20–22</sup> arguing that the formation of ordered structures such as medium ranged ordering would effectively reduce liquid entropy.<sup>20</sup> Experimental studies on inorganic materials confirmed that low entropy of fusion provides a promising route to generate more ordered and correlated structures in liquids,<sup>23</sup> indicating that entropy of fusion is directly related to liquid structures. The formation of short-range ordering, in particular the icosahedral motifs, in multi-component metallic undercooled liquids is therefore expected to relate to the reduction in  $\Delta S_m$ . Additionally, structural studies in undercooled metallic alloys confirmed that the formation of icosahedral local structures would dramatically slow down relaxation dynamics in liquids with a decrease in kinetic fragility.<sup>24</sup> The structural contribution to glass formation can be manifested evidently by the thermo-

dynamic and kinetic properties identified in our present work.

Empirical rules for glass formation in metallic alloys emphasize the importance of negative mixing heat, multiplicity of the number, and size polydispersity of alloy constituents.<sup>3</sup> A direct consequence of the negative mixing heat is the formation of somehow strong interatomic bonding among unlike components<sup>25</sup> forming miscible alloy melts. Negative mixing heat is necessary for the formation of ordered atomic structures (or clusters), relating to a reduction in the configurational entropy of liquids.<sup>20</sup> Certain size ratio among the alloy constituents is proven capable of enhancing packing fraction<sup>26</sup> and decreasing kinetic fragility.<sup>27</sup> Kinetic fragility thermodynamically associates with the configurational and excess vibrational entropies in liquids, which contribute to the total excess entropy of liquids with regard to crystalline solids.<sup>12</sup> For the total excess entropy at melting points (i.e.,  $\Delta S_m$ ), approximately 17% is assessed to come from excess vibrational contribution for metallic alloys.<sup>28</sup> Studies show that the decrease in kinetic fragility is ascribed to the reduction in relative contribution from the excess vibrational entropy to the total excess entropy of liquids.<sup>29</sup> The decrease in both configurational and excess vibrational entropies in metallic alloy melts induced by structural ordering and dense packing predicts a decrease in  $\Delta S_m$ . An increase in the constituent number in alloys can reduce  $T_l$  and thus enhance  $T_g/T_l$  since  $T_g$  is not as sensitive as  $T_l$  to the change in composition. Our recent studies found that miscible mixing behaviors in liquids with negative heat generally produce a negative effect on liquid fragility, i.e.,  $m$  of the mixtures is smaller than the average from the fragility indexes of two pure components.<sup>30</sup> Multi-component alloys such as those listed in Table I generally have low  $m$  indexes, consistent with previous observations that liquid kinetic fragility decreases with increasing number of constituents in metallic alloys.<sup>31</sup> Hence, our empirical rule for glass formation in metallic alloys underlines the fundamental properties of materials with their correlation with GFA.

The finding of the universal criterion for evaluating the GFA of an alloy in terms of the four properties might point to effective routes to designing BMGs which can be produced at low cooling rates: Thermodynamic consideration is first used to recommend systems with low entropies of fusion as an initial selection of components. Then follow kinetic considerations by adding alloy elements with certain negative mixing heat, which assists in decreasing both liquidus temperature and kinetic fragility.

The critical cooling rates  $R_c$  for the glass formation of metallic alloys is explained in terms of the fundamental physical properties: the reduced glass transition temperature, entropy of fusion, and kinetic fragility. A remarkable agreement between the calculated and experimental values of  $R_c$  is presented. The rationalization of critical cooling rates may provide guidance for seeking metallic glasses. An extension of the relation to other glass forming materials such as inorganic oxides and molecular systems is reasonably expected.

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