

**Thermodynamic limits of crystallization and the prediction of glass formation tendency**Yongxin Yao,<sup>1</sup> R. Napolitano,<sup>2</sup> C. Z. Wang,<sup>1</sup> and K. M. Ho<sup>1</sup><sup>1</sup>*Ames Laboratory, USDOE and Department of Physics, Iowa State University, Ames, Iowa 50011, USA*<sup>2</sup>*Ames Laboratory, USDOE and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA*

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We have calculated the  $T_0$  curves for several Al-rare-earth binary alloys to assess the importance of the transport-based resistance to crystallization in the overall glass formation process and the general effectiveness of thermodynamic prediction of glass-forming ability. Our results show that the experimentally observed glass-forming compositions for Al-(Ce, Gd, Ho, Nd, Y, Dy) alloys strongly correlate with the composition range bounded by the  $T_0$  curves associated with the relevant crystalline phases. This indicates that sluggish material transport, together with the tendency for clustering and other types of ordering at medium-range scale, is a key factor governing glass formation in these systems.

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Metallic alloys which resist crystallization in their undercooled states sufficiently well to become amorphous solids or “metallic glasses” have emerged as a very interesting and potentially useful class of materials. However, the criteria for glass formation in metallic systems are still poorly understood. Unlike traditional topological or network glass systems where structural frustration promotes the formation of the glass state, metallic glasses are only found in multicomponent alloy systems. This indicates that restriction of material transport is a dominant factor in the glass formation process.

To date, a great deal of effort has been concentrated on (i) the quantification of the diverse and unusual physical and mechanical properties afforded by glass-forming metallic alloys, (ii) the identification of compositional ranges that give rise to amorphous solids in various alloy systems, and (iii) the development of alloys and processing techniques capable of yielding glassy alloys in quantities or geometries that permit engineering application, i.e., “bulk” metallic glasses. A number of excellent reviews<sup>1-3</sup> are available, and we forego a comprehensive discussion of these topics here.

More fundamentally, considerably less effort has been devoted to understand the thermodynamic and kinetic implications of the glassy state exhibited by many metallic systems. Differing substantially from the more common oxide glasses, where directional bonding constraints may lead to static glassy network structures, glass formation in metallic systems cannot be reasonably justified in terms of simple topological considerations. Clearly, the transition to the glassy state in a metallic system must be described as kinetic in nature, where relaxation to an energetically favorable crystalline state becomes sufficiently sluggish to effectively prevent its existence. Thus, the fundamental question to be answered with regard to this transition is “what are the critical kinetic contributors which limit the crystallization process in a metallic system, and how are these influenced by temperature and chemical composition?” Indeed, a substantial amount of work has been reported pursuant to the second part of this question, and composition ranges where glass formation is practically achievable have been experimentally determined for a number of metallic systems. However, the more fundamental, first part of the question has not been sufficiently addressed, and the suppression of structural and

chemical relaxation processes contributing to the kinetic transition have not been distinguished or well described.

Following the earliest observations of amorphous or “glassy” phase formation, reported in 1960 for a rapidly quenched Au-Si alloy<sup>4</sup> and in 1965 for a Pd-Si alloy,<sup>5</sup> researchers looked to quantify the inherent glass formation tendency, commonly termed *glass-forming ability* (GFA), for metallic systems. Various relationships were proposed, suggesting that parameters such as the melting temperature, the cohesive energy, the Debye temperature, the reduced liquidus temperature, and linear combinations of pure component melting temperatures may correlate with the glass transition temperature,  $T_g$ .<sup>6-11</sup> Such correlations offered only limited utility but reasonable success was achieved for several systems through the use of GFA maps constructed with two thermodynamic parameters. For example, Giessen and Whang<sup>12</sup> compared the GFA for several binary alloys by plotting the heat of formation for the liquid phase versus the atomic radius ratio of the two alloy components. Also, plots of reduced liquidus temperature [ $T_{LR} = (\bar{T}_L^0 - T_L) / \bar{T}_L^0$ , where  $T_L$  is the liquidus temperature and  $\bar{T}_L^0$  is a linear combination of the pure component melting temperatures] versus reduced eutectic composition [ $(C_e - C_s) / C_e$ , where  $C_e$  is the eutectic composition and  $C_s$  is the solidus composition for the solvent-rich phase at the eutectic temperature] were employed by Whang<sup>13</sup> to compare the GFA for Ti, Zr, Si, and Al alloys.

Work by Lu *et al.*<sup>14</sup> suggests that the reduced glass transition temperature ( $T_{rg} = T_g / T_L$ ) may be a reasonable indicator of the GFA in Zr, La, Mg, Pd, and rare-earth alloys (all containing at least three components) while other experimental reports suggest that the freezing range,  $\Delta T_{xg}$ , is a more reliable indicator in several multicomponent Fe-based, Mg-based, and Pd-Ni-based alloys.<sup>15-19</sup> Lu and Liu<sup>20</sup> examined this issue and proposed a parameter, defined as  $\gamma = T_x / (T_g + T_L)$ , that describes the ease of devitrification for a metallic glass and correlates with GFA better than both  $T_{rg}$  and  $\Delta T_{xg}$ . They go on to relate this parameter to a critical-cooling rate,  $R_c$ , and an associated critical section thickness.<sup>20,21</sup>

Beyond these rudimentary correlations, several approaches have been used for describing the behavior of undercooled metallic liquids and predicting glass formation in

metallic alloys.<sup>22</sup> Beginning with Cohen and Turnbull<sup>23</sup> in 1959, free volume theories have been used with reasonable success to describe some aspects of molecular motion and the associated glass transition.<sup>8,23–25</sup> Continuum mode-coupling theories<sup>26,27</sup> have been useful in describing high-temperature behavior of liquids but these break down at lower temperatures where atomistic mechanisms become important for transport processes.<sup>22</sup> Egami used local topological considerations to explain how the glass transition may occur at the nanoscale, giving rise to glassy clusters.<sup>22</sup> By modifying a treatment for oxide glasses, Takeuchi and Inoue<sup>28</sup> calculated critical-cooling rates,  $R_c$ , for glass formation in Ni-, Co-, and Pd-Cu-based alloys, showing a dramatic reduction in  $R_c$  with increasingly negative enthalpy of mixing in the liquid and with increasing atomic radius mismatch. Fecht and Johnson<sup>29</sup> have summarized the requirements for the formation of bulk metallic glasses (i.e.,  $R_c \geq 1$  K/s) with the following five conditions: (i) steep liquidus boundaries meeting at a low-temperature eutectic, (ii) atomic radius mismatch  $>15\%$ , (iii) reduced driving force for crystallization, (iv)  $T_{rg} > 0.65$ , and (v) complete miscibility in the liquid at the relevant temperatures. While structural “confusion” must play a role in suppressing the kinetics of crystallization,<sup>3</sup> these general conditions suggest that observed glass formation tendency is fundamentally linked to the thermodynamic properties of the system.

In this Brief Report, we use Al-rare-earth (Al-RE) alloys, which exhibit marginal glass-forming tendency, to examine the hypothesis that the dominant mechanism for confusion in metallic glass formation comes from the limitation of material transport at the compositional scale and that the reduced diffusional burden associated with partitionless crystallization provides a temporally competitive avenue for relaxation. Thus, the  $T_0$  criterion represents both a fundamental thermodynamic and kinetic limit to the glass formation range. Recently the composition range bounded by the relevant  $T_0$  curves has been compared with glass-forming ability for Al-La, Cu-Mg, and Al-Sm binary systems with good agreement.<sup>30</sup> Here we examine the general utility of the  $T_0$  criterion by employing a solution thermodynamics approach to compute the chemical limits of partitionless crystallization for several Al-RE binary alloys, chosen because their glass formation compositions have been well characterized by experiment and because reported glass formation ranges deviate substantially from the eutectic composition. More specifically, we calculate the  $T_0$  temperature as a function of composition ( $T_0$  is defined as the temperature for which the liquid phase and the crystalline phase have equal Gibbs free energies) and assert that glass formation is unlikely for compositions where  $T_g < T_0$ , suggested by Boettinger<sup>31</sup> since the partitioning and chemical transport requirements for crystallization vanish below this temperature.

The  $T_0$  calculations are performed using the calculation of phase diagrams (CALPHAD) methodology, with missing parameters generated by *ab initio* calculations. Thus, each phase is treated as a solution whose Gibbs free energy is expressed analytically over a certain composition and temperature range. In our treatment, binary solution phases are modeled with a single sublattice, with a molar Gibbs free energy given as

$$G^\Phi = (1-x)^0 G_{Al}^\Phi + x^0 G_{RE}^\Phi + RT[(1-x)\ln(1-x) + x \ln x] + {}^{xs}G^\Phi, \quad (1)$$

where  ${}^0G_i^\Phi$  is the molar Gibbs free energy of the pure element in structure  $\Phi$ , taken from Dinsdale.<sup>32</sup> The excess Gibbs free energy  ${}^{xs}G^\Phi$  is expressed as

$${}^{xs}G^\Phi = (1-x)x \sum_{j=0}^n {}^jL_{Al,RE}^\Phi (1-2x)^j, \quad (2)$$

where the  ${}^jL_{Al,RE}^\Phi$  interaction parameters take the form  ${}^jA^\Phi + {}^jB^\Phi T$ , including both enthalpic ( ${}^jA^\Phi$ ) and entropic ( $-{}^jB^\Phi$ ) contributions to each mixing term.

Typically, binary intermetallic phases are described using a two-sublattice model, with each component occupying one sublattice without mixing. The Gibbs free energy has the form

$$G^{Al_aRE_b} = a {}^0G_{Al}^\Phi + b {}^0G_{RE}^\Phi + A^{Al,RE} + B^{Al,RE}T, \quad (3)$$

where  $A^{Al,RE}$  and  $B^{Al,RE}$  represent the enthalpy and entropy of formation for the stoichiometric  $Al_aRE_b$  compound. (For the Al-RE alloys studied in this Brief Report, the coefficients  $A$  and  $B$  are taken from Refs. 33–35. Some of the model coefficients have been tested in ternary systems.<sup>34,35</sup>)

We treat the intermetallic phases as solutions, rather than simple stoichiometric compounds assumed in usual CALPHAD calculations. We approximate the Gibbs free energy of the intermetallic solution as

$$G^{Al_{(1-x)}RE_x} = (1-x) {}^0G_{Al}^\Phi + x {}^0G_{RE}^\Phi + \Delta H^{Al_{1-x}RE_x}, \quad (4)$$

where the formation enthalpy is estimated by interpolating *ab initio* total-energy calculation results for alloys at selected nearby compositions. We ignore the formation entropy, assuming that its contribution is relatively small in the temperature range where the metallic glasses usually form. In fact, for all the intermetallic compounds under investigation, the contribution of the formation entropy is one order smaller than that of formation enthalpy near 500 K, based on fitted experimental data. Furthermore, the formation entropy is negative in all the intermetallic compounds investigated, which would only raise the corresponding intermetallic Gibbs free energy at the particular composition, forcing the  $T_0$  curve to be steeper. This would not affect our conclusions.

The first-principles calculations were done using VASP (Ref. 36) with a plane-wave basis set. Projector-augmented wave potentials<sup>37</sup> were employed and the exchange-correlation potential was based on the generalized gradient corrections by Perdew *et al.*<sup>38</sup>

The calculated  $T_0$  curve results, plotted with the truncated Al-rich part phase diagrams for Al-Ce, Al-Gd, Al-Ho, Al-Nd, Al-Y, and Al-Dy, are shown in Fig. 1. The compositional dependence of structure for the corresponding rapidly solidified Al-RE binary alloys are also shown as insets. Two right-side  $T_0$  curves are shown for Al-Ce and Al-Nd since there exist two competing phases with similar compositions. The shaded regions are the experimentally observed glass-forming composition ranges.<sup>2</sup> Though the glass transition temperature,  $T_g$ , is not given, it is reasonable to assume that it is above 300 K. Down to 300 K, the partitioning zone

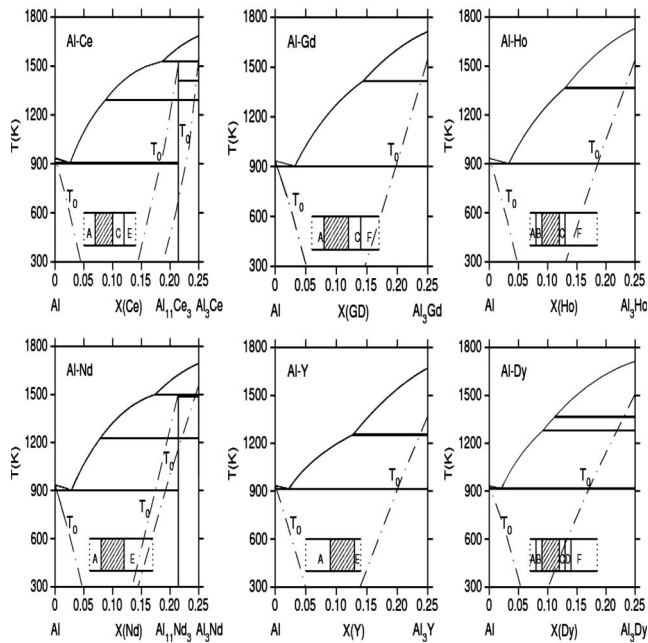


FIG. 1. Calculated  $T_0$  curves with the truncated Al-rich part phase diagrams for Al-Ce, Al-Gd, Al-Ho, Al-Nd, Al-Y, and Al-Dy. Inset: compositional dependence of structure in the corresponding rapid solidified Al-RE binary alloys taken from Ref. 2. Shaded regions: amorphous, A: Al solid solution, B: amorphous+Al, C: amorphous+X (unidentified phase), D: Al+X (unidentified phase), E: Al+Al<sub>11</sub>RE<sub>3</sub>, and F: Al+Al<sub>3</sub>RE.

defined as the composition range bounded by the relevant  $T_0$  curves matches very well with the experimentally observed glass-forming range. For comparison, GFA predicted by  $T_{rg}$  and  $T_{LR}$  is peaked around the eutectic composition while Takeuchi's  $R_c$  criterion<sup>28</sup> favors the composition near 40 at. % of RE. Thus only our  $T_0$  criterion gives a reasonable prediction in the systems investigated here. We emphasize that this crucial result should not be very sensitive to model thermodynamic parameters in use. Only Gibbs free-energy function values are needed to determine  $T_0$  curves. In contrast, the calculation of equilibrium phase diagram involves the common tangent construction, where the derivatives of the Gibbs free-energy functions are used. Thus the error in determining the  $T_0$  curve is much smaller than that in the usual phase diagram calculation. Therefore some variation in the  $T_0$  curves due to the inaccuracy of the fitted Gibbs free-energy functions will not affect our main conclusion. It should also be pointed out that the above-mentioned  $T_{rg}$ ,  $\Delta T_{xg}$ , and  $\gamma$  criteria are generally not useful for GFA prediction since  $T_g$  and  $T_x$  are unknown for new systems, although GFA could still be predicted by assuming that the compositional dependence is dominated by  $T_L$ .

Considering that partitionless crystallization requires only short-range atomic motion and that such a transition may occur at extremely high rates,<sup>39</sup> we view the  $T_0$  criterion as an upper bound (i.e., a zero-driving force) temperature limit for partitionless crystalline solidification, and, therefore, view the two relevant  $T_0$  curves in an eutectic system as operational inner bounds for the glass formation range. Accordingly, we offer the present analysis as a means for as-

sessing the importance of chemical partitioning in the resistance to crystal phase formation. Instead of the traditional eutectic composition, around which it is often presumed that the glass-forming ability is particularly high, our results suggest that the partitioning range, bounded by the  $T_0$  curves, may offer a more relevant thermodynamic criterion for metallic glass formation tendency. It is interesting to note that the partitioning ranges for the systems we investigated here are all clearly off the eutectic compositions. Our theoretical predictions agree well with experiment that glass-forming ranges have been generally shifted to hypereutectic compositions.

Indeed the concept of purely thermodynamic criteria for glass formation is not a new one.<sup>40</sup> However, the  $T_0$  criterion for metallic glass formation has not been thoroughly investigated partly because previous solution-based models have not been adequate for accurate prediction of the  $T_0$  temperature for metallic alloys. Our present study demonstrates that by combining a CALPHAD approach with first-principles methods for reliable computation of energies, more accurate and comprehensive description of alloy phases can be achieved.

While rudimentary thermodynamic treatments have shown promise in this regard, it should be noted that the above analysis does not account for the kinetics of partitionless solidification. Several investigators have combined thermodynamic models with models for crystallization kinetics to assess critical-cooling rates<sup>41</sup> and composition ranges for glass formation.<sup>40,42</sup> Zhu *et al.*<sup>43,44</sup> incorporated existing thermodynamic treatments into analytical kinetic models to quantify nucleation and growth rates as a function of alloy composition for four Al-RE alloys. In each case, they assume equilibrium chemical partitioning and compute the time ( $\tau$ ) required for transformation of a "minimal" ( $10^{-6}$ ) volume fraction as a function of composition. For the Al-Ce and Al-Gd systems, their results for  $T=500$  °C show a strong correlation between long transformation times and experimental observation of glass formation. Less agreement is observed for Al-Y and rather poor agreement for Al-Nd. The good agreement between our results based on simple  $T_0$  considerations with these more elaborate calculations and the observed experimental glass formation compositions indicates that the dominant factor affecting glass formation is the limitation of material diffusion in the liquid in these systems. If this premise, supported here by our results for several Al-RE alloys, turns out to be true for a large class of materials, favorable glass formation composition ranges could be estimated using purely thermodynamic models. Extension of our calculations into alloys with more components would be very interesting to test this hypothesis.

In conclusion, while accurate modeling of crystallization kinetics will ultimately be essential for reliable prediction of glass formation tendency over wide ranges of composition, it is scientifically prudent to examine, more completely, the implications of thermodynamic treatments before attempting to apply rigorous kinetic models. Indeed, any reliable kinetic treatment must include accurate thermodynamic descriptions of the relevant phases, including the undercooled liquid, and must account for the formation of the crystalline phase(s) over a continuous range of permissible compositions. More-

over, we must recognize that relaxation kinetics are integrally linked to the phenomenon of phase selection itself and that the composition of the crystalline phase is a degree of freedom that nature may explore in her quest for more efficient transitions. Thus the  $T_0$  serves as a clearly defined and calculable value representing a transition point in the balance between high and low transport requirements, where nature may choose to pay the energetic penalty associated with non-equilibrium partitioning or even completely diffusionless crystallization. From a temporal viewpoint, the  $T_0$  condition defines a completely partitionless limit to this behavior where the requirement for long-range diffusion vanishes; i.e., it provides a limit in multicomponent systems beyond which the kinetics mimic that of single-component systems for which no glassy solids have been observed. Consistent with the Al-RE and several other glass-forming systems,<sup>1-3</sup> we note that the region bounded by the relevant  $T_0$  curves is quite naturally shifted toward the intermetallic phase, exhibiting the most severe increase in Gibbs free energy as phase

composition moves away from the equilibrium value. Thus, the observed hypereutectic shift in the Al-RE alloys can be attributed to the strong stoichiometric nature of the intermetallic phases, as compared to the Al(fcc) solution phase. We offer this simple criterion here as a fundamental limit in terms of both system thermodynamics ( $\Delta G=0$ ) and system kinetics, asserting that *accurate* calculation of such limits should precede more convoluted treatments, where the natural selection of the dynamical transformation path, itself, becomes a critical variable.

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