

Thermodynamics and Kinetics of Bulk Metallic Glass

R. Busch, J. Schroers, and W.H. Wang

Abstract

Bulk metallic glasses (BMGs) are multicomponent alloys with typically three to five components with large atomic size mismatch and a composition close to a deep eutectic. Packing in BMG liquids is very dense, with a low content of free volume resulting in viscosities that are several orders of magnitude higher than in pure metal melts. The dense packing accomplished by structural and chemical atomic ordering also brings the BMG-forming liquid energetically and entropically closer to its corresponding crystalline state. These factors lead to slow crystallization kinetics and consequentially to high glass-forming ability. This article highlights the thermodynamic and kinetic properties of BMGs and their contributions to extraordinarily high glass-forming ability. Some possible links with mechanical properties are also suggested.

Introduction

Liquids that can yield bulk metallic glasses (BMGs) are multicomponent eutectics or close-to-eutectic alloys with large negative heats of mixing. BMG-forming liquids thus have very low melting points compared with each constituent element, indicating that the melt is thermodynamically quite stable and highly favored with respect to the competing crystalline phases. Even in the supercooled (undercooled) liquid state, they show high thermal stability (i.e., resistance to crystallization). For some BMGs, this stability enables measurements of specific heat,^{1,2} diffusion,³⁻⁵ viscosity,⁶⁻⁸ local atomic motion,⁹ and emissivity¹⁰ in a temperature region that was previously not accessible. The stability of the supercooled liquid also enables experimental determination of the crystallization process,¹¹ which was found to change from a nucleation-controlled mechanism at high temperatures (low undercoolings) to a growth-controlled process at low temperatures.¹² Figure 1 shows the experimentally determined time-temperature-transformation (TTT) diagram for crystallization of the supercooled liquid for $\text{Zr}_{41.2}\text{Ti}_{13.6}\text{Cu}_{12.5}\text{Ni}_{10.0}\text{Be}_{22.5}$ (Vitreloy 1, or V1).^{11,13} It shows the typical “nose” shape, which is the result of increasing driving force for crystallization and decreasing atomic mobility upon

supercooling. The time at the nose is about 60 s, which is amazingly long, even if compared with phase transformations within the solid state such as the austenite-pearlite transformation in steels. By separating the kinetic and thermodynamic

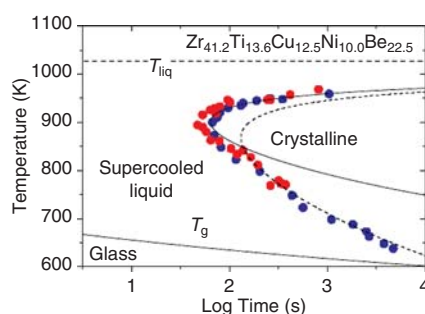


Figure 1. Time-temperature-transformation diagram for the primary crystallization of Vitreloy 1. Data obtained by electrostatic levitation (●)¹¹ and processing in high-purity carbon crucibles (●)¹³ are included. Calculated times for a crystalline volume fraction of $x = 10^{-4}$, using $D_{\text{eff}} \propto \eta^{-1}$ (solid curve) and $D_{\text{eff}} \propto \exp(-Q_{\text{eff}}/kT)$ (dashed curve). The lines labeled T_{liq} and T_g indicate the liquidus temperature and the glass-transition temperature, respectively.

contributions to glass-forming ability (GFA), it is found that BMGs show both unusually high viscosities and low driving forces for crystallization.

Thermodynamics of Supercooled BMG Liquids

The driving force for crystallization is approximated by the Gibbs free energy difference ΔG between the supercooled liquid and the crystal. An experimental assessment of ΔG requires determination of the heat of fusion ΔH_m and of the difference in the specific heat capacity $\Delta c_p(T)$ between supercooled liquid and crystal. Figure 2 shows examples of the specific heat capacity c_p of several glass-forming alloys as a function of temperature in the supercooled liquid state. The c_p of the liquid at the melting temperature is higher than that of the crystalline state and increases further with supercooling. For the good BMG-formers in this comparison, Vitreloy 1,² $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ (Vitreloy 4),¹⁴ and Mg-Cu-Y ,¹⁵ the curves are much shallower than for the other two alloys that have lower GFA. As will be discussed later, the BMG-forming systems show typical “strong” liquid behavior in which the configurations of the system change more slowly as the glass transition is approached on cooling.

The Gibbs free energy of the supercooled liquid with respect to the crystal, $\Delta G(T)$, can be calculated by integrating $\Delta c_p(T)$ and taking H_m into account. This has been done, for example, for Pd-Ni-P,¹ Pd-Ni-Cu-P,¹⁶ Pt-Ni-Cu-P,¹⁷ Zr-Ti-Cu-Ni-Be,^{2,14} Mg-Cu-Y,¹⁵ ZrCuNiAlTi,¹⁸ and ZrCuNiAlNb.¹⁸

In Figure 3, ΔG is plotted as a function of supercooling a selection of glass-forming systems. The temperatures are normalized to the alloy melting temperatures. Qualitatively, the GFA, indicated by a low critical cooling rate, scales inversely with the driving force for crystallization, a correlation originating mainly from BMG systems having smaller entropies of fusion and therefore smaller gradients in ΔG at the melting point. A low value of entropy in the liquid indicates a small free volume and significant short-range order at the melting point and in the supercooled liquid. In fact, for Vitreloy 1, the fractional free volume at the melting point is only 1%.^{13,19} These findings are consistent with the high viscosity of BMG-forming liquids at the melting point and upon supercooling.

Viscosity of the Undercooled Liquid and Strong Liquid Behavior

Besides thermodynamic considerations, the viscosity of the liquid is the key kinetic

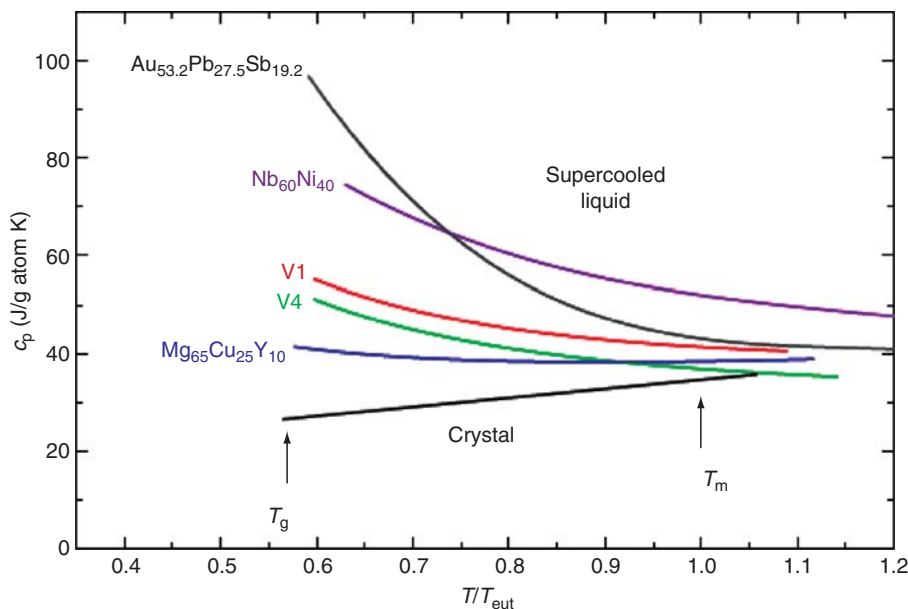


Figure 2. Specific heat capacities in the supercooled liquid for several alloys. Data on Au-Pb-Sb are from Reference 35, on Nb-Ni from Reference 36. For the other data, see References 2, 14, and 15. Good bulk metallic glasses show a shallow specific heat capacity (c_p) curve, indicative of strong liquid behavior.

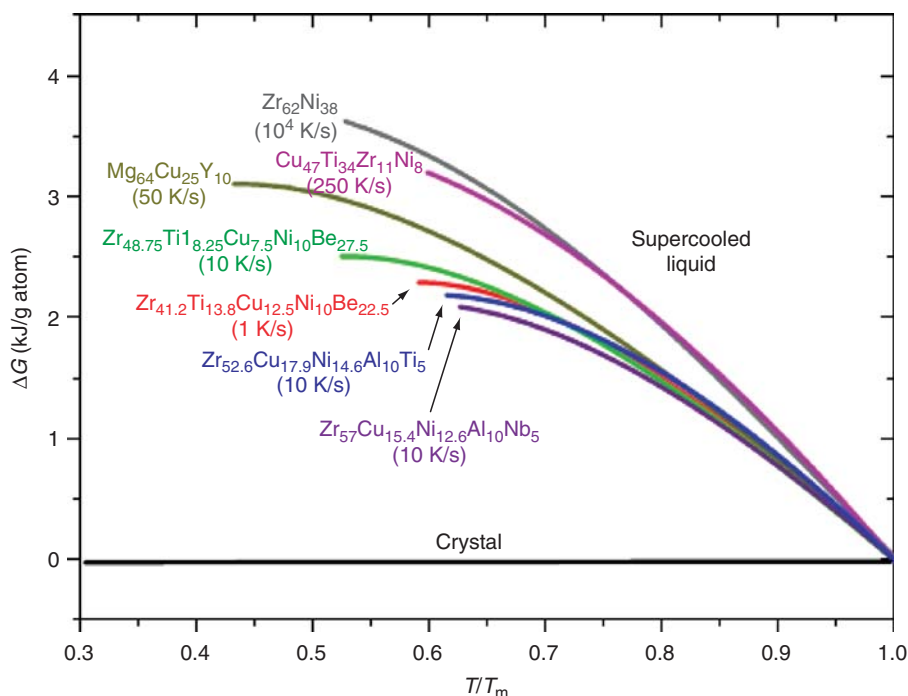


Figure 3. Difference in Gibbs free energy between the liquid and the crystalline state for glass-forming liquids. Data on Zr-Ni are taken from CALPHAD calculations; for the other alloys, see References 2, 15, and 18. The critical cooling rates for the alloys are indicated in the plot as K/s values beneath the composition labels.

parameter that determines the GFA of an alloy. The increasing viscosity on cooling reflects the decreasing atomic mobility observed in all supercooled liquids, whether metallic or nonmetallic. Figure 4 shows a “fragility plot” in the form proposed by Angell²⁰ in which the viscosities of different glass-forming liquids are compared in an Arrhenius plot for which the inverse temperature axis is normalized with respect to glass-transition temperature T_g . On this normalized scale, the melting point is at ~ 0.6 . All the curves meet at 10^{12} Pa s, corresponding to the viscosity at T_g . Two extreme cases are distinguished: kinetically “strong” liquids such as SiO_2 show near-Arrhenius behavior (straight line)²⁰ and have high viscosities. On the other hand, kinetically “fragile” liquids such as o-terphenyl exhibit a dramatic temperature-dependence of viscosity just above T_g and viscosities that are up to eight orders of magnitude lower than those of the strongest liquids.²⁰ The term “fragile” refers to this drop in viscosity with increasing temperature and does not indicate a mechanical behavior.

All pure metals,²¹ most metallic alloys, and water have liquid viscosities at the melting point of $\sim 10^{-3}$ Pa s; they are kinetically very fragile. The equilibrium viscosity data measured in the supercooled liquid can be described well with the Vogel-Fulcher-Tammann (VFT) relation

$$\eta = \eta_0 \times \exp [D^* \times T_0 / (T - T_0)]. \quad (1)$$

Equation 1 represents a formulation of the VFT equation according to Angell²⁰ in which η is the viscosity and the pre-exponential factor η_0 is the viscosity at infinite temperature. The VFT equation includes the parameter D^* , which is a measure of the kinetic fragility of the liquid, and the VFT temperature T_0 , where the barriers with respect to flow would go to infinity. For the most fragile liquids, D^* is on the order of two and reaches 100 for the strongest glass-former, SiO_2 . An interesting feature of the fragility plot is that the viscosity curves for all liquids would meet at infinite temperature. Therefore the pre-exponential factor η_0 can be kept constant for all materials, and reliable fits are possible even if data are available only in the vicinity of T_g . Figure 4 includes the viscosity data and VFT fits for several metallic-glass-forming alloys. The strongest among them have viscosities more than four orders of magnitude higher than the pure metals. The strong liquid behavior is the single most important contribution to the high GFA of BMG-forming alloys, because it drastically retards crystal nucleation and especially growth kinetics.^{22–24}

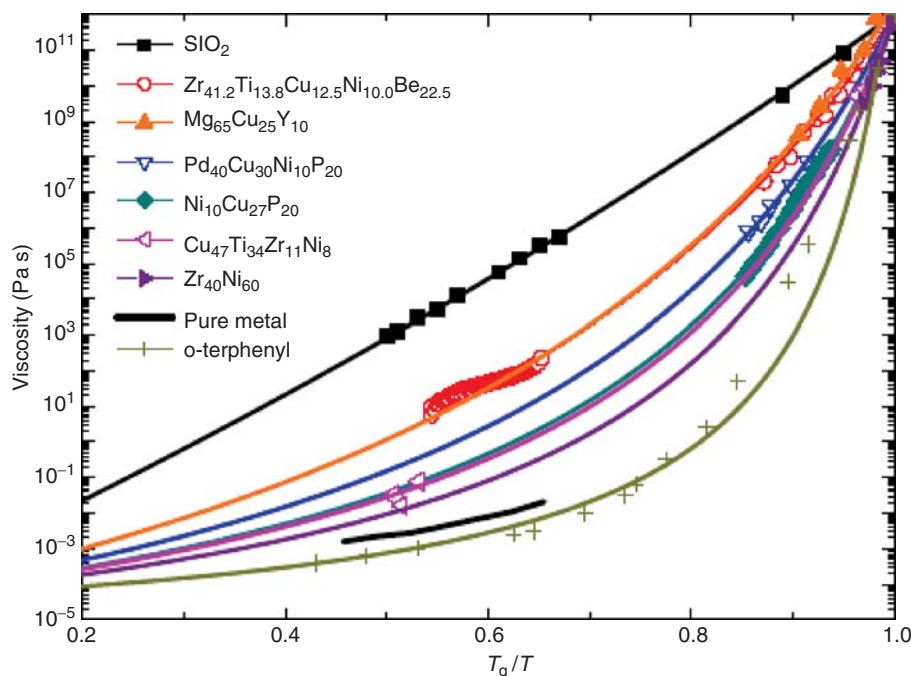


Figure 4. Angell plot comparing the viscosities of different types of glass-forming liquids.^{6–8,15,37} Data on the nonmetallic liquids are taken from Reference 20.

Correlation between Kinetics and Thermodynamics

The strong liquid nature is not only represented by the Arrhenius-like temperature dependence of the viscosity but is also reflected by the shallower c_p curves of the BMG-forming liquids close to T_g as compared with the curves of more fragile glass-formers (Figure 2). As noted in the previous section, the structural changes are more gradual as T_g is approached, which can be quantified in terms of configurational entropy. The Addam–Gibbs equation,

$$\eta = \eta_0 \times \exp \left[\frac{C}{TS_c(T)} \right], \quad (2)$$

connects the viscosity with the configurational entropy S_c , where T is temperature, C is a free enthalpy barrier to cooperative rearrangements, and S_c is the configurational entropy.²⁵ Angell and co-workers²⁶ introduced a thermodynamic fragility by plotting the entropy change for different liquids as a function of supercooling normalized to the respective entropy of fusion and the melting point. This works very well for liquids where the T_0 in Equation 1 and the Kauzmann temperature T_K are close together. The Kauzmann temperature T_K is where the entropy difference between supercooled liquid and crystal vanishes. However, as

pointed out by Tanaka,²⁷ the ratio T_K/T_0 becomes substantially larger than unity in the case of strong and especially metallic liquids, meaning that T_0 is found below T_K (see also References 2, 6, 7, 15, and 18). If one accepts that S_c in Equation 2 vanishes at a temperature below T_K , a consistent picture emerges in which both Equations 1 and 2 describe the viscosity equally well, thus connecting thermodynamics and kinetics.¹⁵ The high melt viscosities in multicomponent BMG-forming liquids as well as the small entropy differences between liquid and solid have a structural origin. Models for the underlying pronounced short- and medium-range order in BMG-forming liquids are discussed, for example, by Miracle et al. in this issue of *MRS Bulletin*.

Outstanding Issues on the Correlation between Thermodynamics, Kinetics, Elastic Constants, and Mechanical Behavior

It has been suggested recently that the kinetic fragility of a glass-forming liquid is intimately linked to the elastic properties of the corresponding glass, in particular, the ratio of bulk modulus B_∞ to shear modulus G_∞ or, equivalently, to the Poisson ratio ν .²⁸ When comparing a wide range of different glass-formers, the authors found a linear relationship, $m = 29(B_\infty/G_\infty - 0.41)$,

with the steepness index m as a measure of fragility. This steepness index is defined as the slope of the viscosity curve in the fragility plot (Figure 4) at T_g (see, e.g., Reference 29). When metallic-glass-formers are considered,²⁹ a similar correlation is found, but with a different slope, $m = 11(B_\infty/G_\infty - 0.27)$. The difference has been attributed to the contribution of the free electron gas to the bulk modulus in metallic glasses.³⁰ There are still only very few BMG-formers for which the kinetic fragility and elastic constants (B/G or ν) are known, and the correlation between these parameters remains controversial.^{30,31} While it seems that BMGs with higher ν tend to have higher kinetic fragility of the supercooled liquid^{28,29} and therefore lower GFA, more data are needed to establish clearly the nature of the correlation.

There is a more well-established correlation between elastic constants and toughness for metallic glasses. Glasses with low B/G or ν are brittle, whereas those with high B/G or ν are tough.^{32,33} This correlation, observed for a wide range of BMGs, is reviewed, for example, by Yavari et al. in this issue of *MRS Bulletin*. It thus seems that a BMG composition with low ν in the glassy state should tend to have a higher GFA but a lower toughness. Thus, these correlations^{22–24,28,29,32,33} could lead to the awkward conclusion that BMGs with better GFA are intrinsically more likely to be brittle. In particular, it excludes the possibility that there could be a BMG alloy combining good GFA with large fracture toughness.

The noble-metal-metalloid glass formers, in particular the Pt-based BMGs, as supercooled liquids are kinetically relatively fragile compared to the metal-metal compositions like the Zr-based BMGs,¹⁷ yet they have excellent GFA. Kinetically fragile glasses are mechanically tougher than kinetically strong glasses. This suggests that there is hope to combine toughness and good GFA in one alloy, although for these particular alloys their cost is a barrier to widespread applications. The elastic constants of metallic glasses can often be surprisingly well estimated from the elastic constants of their constituent elements.^{29,34} Because many inexpensive metals, in particular iron, zinc, and magnesium, have low Poisson ratios, the development of an inexpensive and tough BMG alloy will be an interesting challenge.

Given its correlation with a range of properties, the Poisson ratio is expected to be a useful guide in designing new BMG alloys with good GFA, high fracture resistance, and low cost.

Table I: Expected Correlations of Values of Selected Properties with the Kinetically Strong or Fragile Behavior of the Supercooled Liquid in Bulk-Metallic-Glass-Forming Systems.

Glass Characteristic	Viscosity, η	Glass-Forming Ability	Fracture Toughness	Poisson Ratio	Gibbs Free Energy, ΔG
Kinetically strong	High	High	Low	Low	Small
Kinetically fragile	Low	Low	High	High	High

Conclusions

Bulk-metallic-glass-forming liquids are densely packed, and as a consequence, they show high viscosity and sluggish crystallization kinetics. Different BMG compositions nonetheless show significant differences in their temperature-dependent viscosities; they can be classified on a spectrum ranging from strong to fragile. These fragility characteristics are often reflected in other properties of the supercooled liquid and the corresponding glass (Table I), and these correlations pose interesting challenges for the development of new BMGs combining the desired characteristics of good glass-forming ability, high toughness, and low cost.

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