A Polymer Model for Metal Alloy Glasses

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Some phenomenological parallels between certain metal alloy glasses, namely, those composed of pure metal and pure network-forming elements which are formed by melt quenching, are examined from the viewpoint of a polymer model. The applicability of the description of certain amorphous metal alloys in terms of polymer chains, backbones, side groups, and plasticizers is presented, and the role of the pure metal both as side group of, and as plasticizer to, the polymer-like chains is discussed. The available structural data, as well as the relevant data for thermodynamic and viscoelastic properties of the liquid and glassy states of these particular glass-forming metal alloys, are shown not to be inconsistent with the predictions of the model. Correlations of the glass temperature and of the efficiency of glass temperature depression with atomic size for glass-forming binary metal alloys appear to be predictable from analogies to plasticizer effects in polymer chemistry.

I. Introduction

Metal alloys which can be melt quenched to the glassy state are generally composed of mostly noble or transition metals (henceforth denoted by M and referred to as pure metals) in combination with small concentrations of semimetal or metalloid elements (henceforth denoted by N and referred to as network formers) which are characterized by high valences and strong directional bonding. Their glass formation requires extremely fast cooling rates ($\sim 10^6$ K/s), and the glasses themselves exhibit interesting mechanical, electrical, magnetic, and surface properties, all of which have been reviewed.[1] Some examples of metal alloy glasses are listed in Table I.

Theories thus far presented to account for the properties of metal alloy glasses and for the physical basis for their glass formation from the melt are based on models such as the dense random packing model for a system of hard spheres[2,3] and the nearly-free-electron model for metals.[4] The structure of metal alloy glasses, as well as the effects of composition and atomic size on the glass temperature (T_g), have been extensively analyzed from the viewpoint of the hard sphere model.[2,3] A recent investigation into the existence of a glass transition for a system of hard spheres indicates, however, that the hard sphere model is probably not adequate for the explanation of many aspects of the observed glass formation in metal alloys.[5,6]

The thermodynamic and viscoelastic behavior of the type of glass-forming metal alloys mentioned above in the region of the supercooled liquid are qualitatively identical with the corresponding behavior of many other glass-forming liquids, for which the molecular basis for glass formation is believed to derive from the characteristics of molecular asymmetry and/or chain stiffness.[11] Studies of viscosity[7,8] and of mechanical relaxation[9] for these particular metal alloys in the region of the glass transition reveal properties which are very similar to those of glass-forming liquids. Furthermore, the heat capacity difference between equilibrium liquid and crystal for these alloys is, as for glass-forming liquids, an increasing function of the degree of supercooling (see Figure 1A). This increased difference in the heat capacity can in fact be attributed to the loss of configurational entropy in the supercooled liquid[10] (see Figure 1B).

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TABLE I: Composition and T_g Values for Various Metal Alloy Glasses[a]

M	N	T_g, K
$Au_{0.77}$	$Ge_{0.14}Si_{0.09}$	294
$Au_{0.81}$	$Si_{0.19}$	290
$Pd_{0.80}$	$Si_{0.20}$	655
$Cu_{0.66}$	$Zr_{0.34}$	762
$Pt_{0.80}$	$P_{0.20}$	483
$Ni_{0.80}$	$P_{0.20}$	618
$Pt_{0.64}Ni_{0.16}$	$P_{0.20}$	483
$Ni_{0.75}$	$P_{0.16}B_{0.06}Al_{0.03}$	698
$Fe_{0.60}Co_{0.15}$	$P_{0.16}B_{0.06}Al_{0.03}$	735

[a] References 2, 7, 10, 20, 21, and 22.

As the Gibbs–Dimarzio theory for the glass transition postulates the vanishing of the configurational entropy as the factor responsible for glass formation in liquids,[11] the fact that these metal alloys appear to exhibit the same entropic basis for glass formation as do glass-forming liquids could be significant. It indicates the possibility that the physics which underlie glass formation in glass-forming liquids and in these particular metal alloy glasses could be qualitatively similar.

The configurational entropy theory of the glass transition, first presented by Gibbs and Dimarzio,[11] identifies the point of vanishing of the configurational entropy as a sort of ground state of the amorphous phase. This point (usually designated as T_2) is the suggested lower limit to T_g, this lower limit only being reachable in experiments performed infinitely slowly. For those cases in which a theoretical calculation of T_2 has been possible, the location of T_2 has been found to vary with polymer chain length in a fashion similar to the variation of T_g.[11] Gibbs and Dimarzio also found similar correlations in the variation of theoretically predicted T_2 with experimentally determined T_g when other properties (extent of dilution with low molecular weight solvent,[12] copolymer composition,[13] etc.) were varied.

Adam and Gibbs[14] showed how the qualitatively plausible idea that relaxation times τ are strongly influenced by configurational entropy S_c (when the latter is in short supply) might be used to derive the equation

$$1/\tau = A \exp(-C/(TS_c(T))) \tag{1}$$

which is a generalization of the empirical Fulcher (or WLF) equation

$$1/\tau = A \exp(-B/(T - T_0)) \tag{2}$$

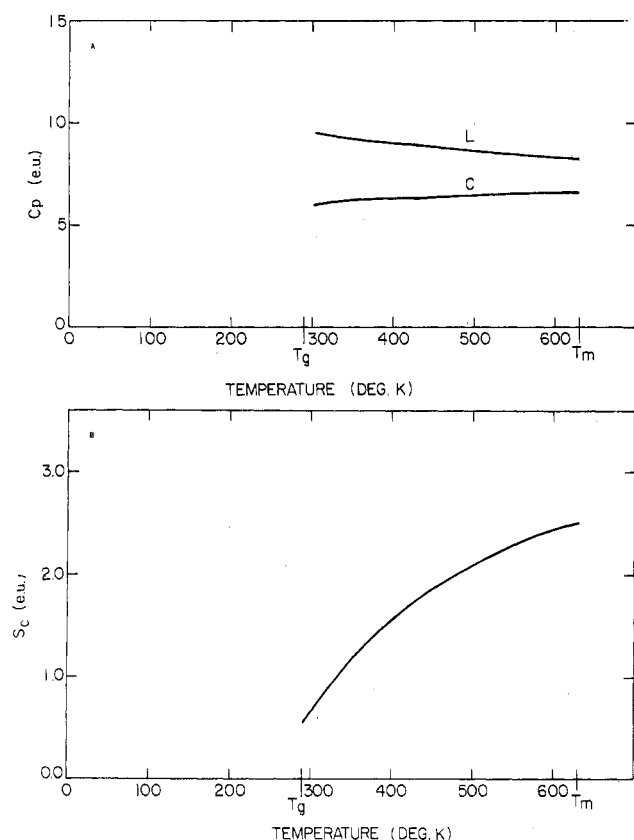**Figure 1.** Heat capacity at constant pressure (A) and configurational entropy (B) as functions of temperature for the metal alloy $Au_{0.81}Si_{0.19}$ (data from ref 23). Curves L and C in (A) represent the heat capacity for the equilibrium supercooled liquid and the intermetallic crystal, respectively. The melting and glass temperatures are denoted by T_m and T_g, respectively. Curves of this type have been found for the other glass-forming metal alloys for which heat capacity measurements have been made.[21]

with A, B, and C being constants. In the reduction of the Adam–Gibbs equation (eq 1) to the Fulcher equation (eq 2), the identification

$$T_0 = T_2 \qquad (3)$$

is established. Whereas T_0 is defined as a temperature chosen empirically to enable eq 2 to fit kinetic data, T_2 is defined by the extrapolation of thermodynamic entropy data. In the small number of cases for which both viscoelastic (or dielectric) relaxation data and specific heat data are available, eq 3 is well satisfied.[15]

It is hence particularly interesting that for the one metal alloy ($Au_{0.7690}Ge_{0.1365}Si_{0.0945}$) for which the determination of both T_0 (from a fit of the Fulcher equation to viscosity data) and T_2 (from the available calorimetric data) have been made, T_0 and T_2 are approximately equal.[7,16]

It may further be noted that for those glass-forming metal alloys for which quantitative determinations of the viscosity of the supercooled liquid in the vicinity of the glass transition have been made, eq 2, an empirical equation which has proven useful in the description of the behavior of glass-forming liquids in the vicinity of their glass transitions, is applicable, and determinations of T_0 have been made.[8] The view that the configurational entropy theory can be applied toward the interpretation of the behavior of this particular class of metal alloy glasses has been substantiated by experimental studies that have employed this theory toward the successful phenomenological interpretation of the flow behavior in metal alloy glasses,[17] and toward the successful interpretation of the composition dependence of the glass temperature, T_g.[18]

The purpose of this paper is to present a polymer model from which some phenomenological parallels between certain metal alloy glasses and polymer solutions may be established. The strength of the model will be shown to be its ability to predict some of the thermodynamic properties of metal alloy glasses as well as the effects of composition and atomic size on the glass temperature from analogies to amorphous polymers.

II. Polymer Model for Metal Alloys

In the formulation and development of the polymer model, only the type of binary (M–N) alloys described in section I are considered. Since the complex nature of interactions and structure in higher-order alloys is beyond the scope of the considerations presented in this paper, the observations and predictions presented below are restricted to binary (glass-forming) alloys, for which the effects of variations in composition and molecular size of one of the components can be isolated. Any extension of the model to higher-order alloys would require a more detailed analysis, so that with regard to the correlations cited below and in Tables II, IV, and VI, comparisons of data from higher-order alloys with binary alloys would not be in order.

The proposed picture for these metal alloy glasses is a polymer-like one of linear and/or branched chains for which the backbone is composed of alternating M and N atoms; the side groups consist of M atoms bound to N atoms; and the remaining (excess of) M atoms serve as space filler. The structure would be akin to a polymer-like chain that could be represented by the formula

$$\begin{array}{ccc} M & & M \\ | & & | \\ \cdots-M-N-M-N-\cdots \\ | & & | \\ M & & M \end{array}$$
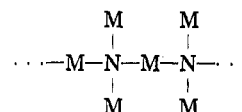
The alloying process would involve the network-forming element N (a liquid with a significant degree of ring-closing bonds) undergoing a ring-opening process in which the pure metal atoms "open" the ring structures. Such a process would clearly involve a considerable increase in entropy.

The high percentage of pure metal (low percentage of network former) required for the achievement of glass formation would furthermore not be inconsistent with the proposed polymer model since the chainlike structures would consist of a maximum of 25% network former. For many of the type of glass-forming alloys which have been studied herein, the concentration of pure metal is sufficiently large so as to be in excess of the concentration required for the formation of such polymeric chains (i.e., greater than the concentration required for saturation). For concentrations of pure metal below saturation, the addition of pure metal would alter the chemical composition of the polymeric chain. For concentrations of pure metal above saturation, however, the excess pure metal would act as an independent chemical component. In analogy to a well known phenomenon in polymer chemistry, the excess pure metal would act as a plasticizer (a concept discussed at greater length in section III).

In consideration of the experimental observations for these metal alloys, it is first noted that the polymer model would predict a vanishing of the configurational entropy and a consequent increase in relaxation times upon cooling the supercooled liquid for the same reasons they occur in amorphous polymers and other glass-forming liquids. As noted in section I, behavior of this sort is indeed observed for these glass-forming metal alloys.

TABLE II: Plasticizing Effect of Excess Pure Metal[a]

alloy	dT_g/dx	range of x
$Au_x Si_{1-x}$	−150	0.73–0.79
$Fe_x C_{1-x}$	−300	0.73–0.79
$Fe_x Si_{1-x}$	−1600	0.73–0.79
$Co_x Si_{1-x}$	−1600	0.73–0.79
$Ni_x Si_{1-x}$	−1600	0.73–0.79
$Fe_x P_{1-x}$	−800	0.73–0.79
$Co_x P_{1-x}$	−800	0.73–0.79
$Ni_x P_{1-x}$	−800	0.73–0.79
$Pd_x Si_{1-x}$	−500	0.80–0.84

[a] In each case, T_g decreases with increased concentration of excess pure metal (plasticizer), i.e., $dT_g/dx < 0$.[20,21]

Secondly, the change in entropy associated with the opening of ring-closing bonds and the formation of polymeric structures from the two pure components should be positive and in noticeable excess of the ideal entropy of mixing. The enthalpy of mixing, on the other hand, will depend on the relative strengths of the M–N, N–N, and M–M bonds, is not predictable a priori from the mechanism suggested above, and, depending on the bond strengths, may vary noticeably in magnitude and sign from one alloy to the next. In fact, large, positive excess entropies of mixing characterize M–N alloys whereas no such generalization is apparent for the enthalpy of mixing.[3,20]

Thirdly, the structure of the polymer model would not be inconsistent with the corresponding available structural data, neutron and X-ray scattering experiments,[19] from which a picture has emerged for the binary alloys, $M_x N_{1-x}$, for which each pure metal atom, M, has approximately ten other M nearest neighbors and two N nearest neighbors, and each network-forming atom, N, has approximately nine M nearest neighbors and no N nearest neighbors. The space-filling M atoms of the model could arrange themselves so as not to be inconsistent with the structural model of the dense random packing of hard spheres. The M atoms would also be able to satisfy the criterion that each have only two N nearest neighbors. There would also be an accounting for the fact that there are no N–N nearest neighbors.

III. Consequences of the Polymer Model

A. The Pure Metal as Plasticizer. The role of excess pure metal (i.e., in excess of the quantity required for saturation of the network former) in metal alloy glasses appears to be similar to the role of plasticizer in polymer glasses. Just as the addition of (low molecular weight) plasticizer molecules to polymer glasses results in the depression of the glass temperature, so the increased concentration of pure metal in the type of (already saturated) M–N alloys discussed herein also results in the depression of the glass temperature (see Table II).

The analogy to plasticization can be taken one step further with the consideration of the dependence of the efficiency of the plasticizer (i.e., the magnitude of dT_g/dx) on the size of the plasticizer molecule. As predicted by the configurational entropy theory and as evidenced by the available experimental data,[12] increasing the volume of an inflexible plasticizer molecule decreases the plasticizer efficiency. (The example of the plasticizer efficiency of relatively small inflexible organic molecules in plasticizing polystyrene is presented in Table III.) The determination of dT_g/dx (summarized in Table II) for these binary metal alloy glasses provides data with which to test this observation. The metal alloy glasses cited in Table II are particularly well suited to such a test since the pure metal is a good example of an inflexible plasticizer molecule and since the concentration of plasticizer (excess pure

TABLE III: Plasticizer Efficiency of Small Inflexible Organic Molecules in Plasticizing Polystyrene[a]

plasticizer molecule	molar vol, cm^3/mol	dT_g/dv[b]
CS_2	60.3	−674
$CHCl_3$	79.7	−485
CCl_4	96.5	−426
CH_5NO_2	102.8	−386
$C_6H_5CH_3$	106.3	−346

[a] Reference 11. [b] For low concentrations of plasticizer. v is the volume fraction of plasticizer.

TABLE IV: A Regrouping of the Examples of Table II to Show the Effect of Atomic Size on the Effectiveness of Plasticization

alloy	dT_g/dx	
$Au_x Si_{1-x}$	−150	↑ increasing atomic size for the pure
$Pd_x Si_{1-x}$	−500	metal (M)
$Fe_x Si_{1-x}$	−1600	
$Co_x Si_{1-x}$	−1600	
$Ni_x Si_{1-x}$	−1600	
$Fe_x C_{1-x}$	−300	↓ increasing atomic size for the network
$Fe_x P_{1-x}$	−800	former (N)
$Fe_x Si_{1-x}$	−1600	

metal) is sufficiently large that dT_g/dx should not be a rapidly varying function of x.

First, for the alloys $M_x N_{1-x}$ in which the size of M is approximately the same and the identity of N is the same (namely, $M_x Si_{1-x}$ and $M_x P_{1-x}$ where M = Fe, Co, Ni), the plasticizer efficiency (dT_g/dx) is the same.

Secondly, for alloys in which the identity of N is the same and the size of M is varied ($M_x Si_{1-x}$ with M = Au, Pd, Fe, Co, Ni, see Table IV), the plasticizer efficiency is seen to decrease with the increased size of M (plasticizer molecule).

Thirdly, for alloys in which the identity of M is the same and the size of N is varied ($Fe_x N_{1-x}$ with N = C, P, Si, see Table IV), a case in which the plasticizing molecule appears progressively larger as the size of the network former, N, is decreased, the plasticizer efficiency is observed to increase with the increased size of N. In other words, plasticizer efficiency decreased with the increased size of the plasticizer molecule.

The above three observations are each consistent with the predictions of the configurational entropy theory and with the analogous effects of molecular size on plasticizer efficiency for amorphous polymers.[12]

B. Pure Metal as Side Groups. Effect of Atomic Size on the Glass Temperature. In the role of the pure metal as part of the proposed chain structure, the effect of the size of the pure metal on the glass temperature, which is most clear from considerations of metal alloys $M_x N_{1-x}$ in which the identity of N and the value of x are held constant and different M atoms are used, provides an analogy with a comparable effect in polymer chemistry. A common observation in polymer chemistry is that, for polymers in which the size of the side group is comparable to or larger than the size of the backbone molecules, an increase in the size of the side group results in a decrease in the glass temperature, with greater depressions of T_g produced by larger side groups. The reason for this effect is related to the ability of the larger side group to more effectively push apart the polymer chains and to create a situation in which the "flex energy" of the polymer (i.e., the difference in potential energy minima for internal rotation[11]) is decreased. An example of this effect is the substitution in poly(tetrafluoroethylene) for one F atom by Cl and by CF_3, respectively (see Table V).

TABLE V: Effect of the Size of the Side Group on $T_g{}^a$

polymer	T_g, °C
$(CF_2CF_2)_n$	126
$(CF_2CFCl)_n$	45
$(CF_2CFCF_3)_n$	11

^{a} The effect on T_g for the substitution in poly(tetrafluoroethylene) of one F atom by Cl and by CF_3. The substitution of a larger side group depresses T_g, with the greater depression of T_g occurring for the larger side group.[24]

TABLE VI: Effect of Atomic Size on T_g

alloy	$T_g{}^c$	atomic size
$Pt_{0.80}P_{0.20}$	increasing ↓	increasing ↑
$Pd_{0.80}P_{0.20}$		
$Ni_{0.80}P_{0.20}$		
$Au_{0.81}Si_{0.19}$	increasing ↓	increasing ↑
$Pd_{0.81}Si_{0.19}$		

^{a} References 21 and 22.

The effect of the size of relatively large side groups (it is emphasized that the side group considered prior to substitution must be relatively large) can also be observed in the binary metal alloy glasses. We consider metal alloys of the same composition for which the molecule of the polymeric backbone is the same (i.e., M_xN_{1-x}, $M_x'N_{1-x}$, $M_x''N_{1-x}$) and the size of the M atom is comparable to or larger than the network former, N (see Table VI). It appears that T_g correlates with the size of the M atoms in the same way that T_g correlates with the size of the side group for glass-forming polymers.

The assigned significance of such a correlation must be qualified, however, on two accounts. First, it must be assumed that the influence of different pure metals on the determination of T_g in their role as side group of the polymer chain is significantly greater than their influence as part of the chain backbone. Secondly, the observed correlation must be reconciled with the earlier observation of an apparently opposite correlation of plasticizer efficiency with atomic size. On the one hand, increasing the size of the pure metal decreased T_g, as described in the preceeding paragraph. On the other hand, increasing the size of the pure metal decreased its plasticizer efficiency and, hence, the degree to which it depresses T_g relative to smaller atoms of pure metal. Experimental studies of the composition dependence of T_g in binary metal alloy glasses have not been conducted over a sufficiently wide range of compositions so as to afford observations of the two competing effects cited above. The fact that T_g appears to correlate with the size of M atoms in metal alloy glasses in the same way that T_g correlates with the size of the side group for polymers would appear to indicate that the

magnitude of the size effect of M as side group of the polymeric backbone is significantly greater than the magnitude of the size effect of M as plasticizer. Were the size effect of M as plasticizer of significantly greater magnitude, a correlation opposite to that noted in Table VI would be observed, and were the two competing size effects of comparable magnitude, no correlation would be apparent.

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