ELABORATION OF AMORPHOUS METALS AND GLASS TRANSITION - FORMATION AND CHARACTERIZATION OF AMORPHOUS METALS

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ELABORATION OF AMORPHOUS METALS AND GLASS TRANSITION.

FORMATION AND CHARACTERIZATION OF AMORPHOUS METALS

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ABSTRACT

This review deals with the definition of amorphous and glassy metals; the principal methods for their preparation by atom-by-atom deposition, rapid liquid quenching and particle bombardment; criteria for their formation, especially ready glass formation (RGF) and its alloy chemical foundations; and their classification. This is followed by a discussion of their elastic and plastic properties (Young's modulus and microhardness) and thermal stability (glass transition and crystallization temperatures), with emphasis on the correlation and composition dependence of these properties and without special reference to technically important glassy alloys.

INTRODUCTION

Glassy metals are presently the subject of intense fundamental and applied studies. The former now cover virtually all physical phenomena displayed by crystalline solids, including their structure, electronic properties, strength, etc., as well as properties specific to the glassy state, such as glass formation, glass-liquid transition, structure modelling, and thermal stability. Application-oriented work has been stimulated primarily by technically interesting properties such as their magnetic softness combined with high permeability, their outstanding corrosion resistance properties and their high specific mechanical strength.

DEFINITION OF AMORPHOUS AND GLASSY METALS

To define the glassy state, we turn to Fig. 1 (after Ref. 2) which shows the change of a property such as the volume or heat content with temperature. When a liquid is supercooled (in constrained equilibrium) below the equilibrium melting point $T_m$, the viscosity $\eta$ and with it the relaxation time $\tau$ increases until at a certain temperature, designated the (fictive) glass transition temperature $T_g$, the time available at temperature $T_g$ becomes smaller than the relaxation time $\tau(T_g)$ and the alloy leaves internal equilibrium, changing at this temperature from a supercooled liquid to a glass. Upon subsequent reheating of the glass beyond $T_g$, the regime of the supercooled liquid state is entered again, (unless crystallization intervenes before $T_g$ is reached).

In addition, relaxation processes generally occur before $T_g$, which alter the glass and lower its glass transition temperature; $T_g$ is thus a function of the quenching and heating history of the glass.

Figure 1

Metallic glasses are amorphous solids, however, the latter term has wider meaning and includes also noncrystalline materials whose internal configurations do not correspond to those of any supercooled liquid. As an example we mention amorphous alloys produced by irradiation methods (either from the crystalline state or a liquid quenched glass); they lack the high degree of short-range order typically present in liquid quenched glassy metals. Such amorphous solids should not be designated as glassy according to the present usage of this term. It should be apparent from the above discussion that formation of an amorphous material requires either bypassing of the crystallization process (e.g. by atomic deposition or rapid liquid quenching) or,
alternately, destruction of the crystallinity of a solid (by methods such as particle bombardment). Experimental approaches designed to accomplish this are reviewed in the next section.

PREPARATION METHODS

Amorphous metals can be prepared by a variety of methods, which can be divided into three main categories according to their main principle: atom-by-atom deposition; rapid liquid quenching; particle bombardment methods. (Probably some of the techniques based on the third principle actually also involve rapid liquid quenching as the active mechanism.) Operationally, the preparation methods based on these principles can be classified further as shown in Table 1. Due to space limitations, these methods cannot be described here in detail; instead, some salient aspects of their operation are reviewed briefly.

<table>
<thead>
<tr>
<th>Table 1 PREPARATION METHODS FOR AMORPHOUS METALS</th>
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<tbody>
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<td>1. Atom-by-Atom Deposition</td>
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<td>a) From the Gas Phase</td>
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<tr>
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<td>3) Salt Bath Quenching</td>
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<td>b) Batch Quenching Methods</td>
</tr>
<tr>
<td>1) Melthtagging</td>
</tr>
<tr>
<td>2) Electromagnetic field quenching</td>
</tr>
<tr>
<td>3) Flowing</td>
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<tr>
<td>&quot;CAGE COOLING&quot; by Laser beam</td>
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<tr>
<td>4) Laser quenching by different beam</td>
</tr>
<tr>
<td>3. Particle Bombardment Methods</td>
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<tr>
<td>a) Ion Bombardment Methods</td>
</tr>
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<td>3) Ion Implantation of Glass forming Chemos</td>
</tr>
<tr>
<td>4) Metal Working (Arc Ion Bombardment)</td>
</tr>
</tbody>
</table>

Atom-by-atom methods are probably the most powerful ones for producing amorphous metals. By techniques such as vapor deposition or sputtering, alloys with which do not form glasses by any other method have been obtained in the amorphous state, such as alloys with compositions corresponding to high melting intermetallic phases. Further, thick samples usable for bulk processes can be obtained, e.g., by sputtering. On the other hand, the process is expensive and alloys produced by it are generally not ductile. Some liquid quenching methods, especially continuous melt flow methods such as melt spinning, have been engineered to industrial maturity and are capable of producing technologically important alloys as rapidly quenched glasses relatively cheaply and in large amounts; with the product having the thin sheet shape desirable for some applications such as magnetic sheets for use in transformers or as brazing foils.

Other liquid quenching methods such as those based on surface heating (glazing) and ion bombardment or implantation offer promise for the production of glassy metal surfaces showing desirable corrosion or wear resistance; ion implantation is presently much studied as a means of producing surface property improvements and it was found recently that the alloys formed from a base material by this technique become amorphous when certain critical alloying compositions are reached.

GLASS FORMATION

The following discussion is directed primarily at glass formation from a liquid.

Fundamental Parameters Determining Ready Glass Formation (RGF): Upon supercooling a liquid below its liquidus temperature $T_m$, a glass will form at the glass transition temperature $T_g$ if crystallization of the melt into one or more crystalline phases is avoided in the interval from $T_m$ to $T_g$. Operationally, the important parameter is thus $(T_m - T_g)/T_m$, i.e., the temperature interval $T_m - T_g$, normalized by the melting temperature $T_m$. This parameter is a function of the reduced glass temperature $T_g = T_g/T_m$ which thus plays a fundamental role in characterizing the glass forming ability of an alloy which scales with $T_g$.

Assuming that homogeneous nucleation is the mode of crystallization of the liquid and using pertinent expressions for the rates of nucleation and growth as functions of supercooling, the critical cooling rate leading to crystallization of, e.g., $<5\%$ of the liquid can be calculated and T-T-T curves such as those shown e.g. in Fig. 2 of Ref. 2 can be obtained, with $T_g$ as the sole parameter. To retain a glass, the cooling process must be conducted such that the "nose" of the pertinent T-T-T curve is avoided. Calculations using such diagrams show that the critical cooling rate $R_c$ increases with decreasing $T_g$, as shown in Fig. 3 of Ref. 13. One often defines as "readily glass forming" such alloys for which $R_c < 10^5$ K/sec corresponding to $T_g > 0.60$. In binary alloys, $T_g$ varies monotonically and slowly with composition $X$ over wide ranges of
X; in its variation with $X$, $T_{gr}$ therefore depends more strongly on $T_m$ (which shows much larger changes with composition) than on $T_l^g$. The RGF composition ranges are therefore primarily defined by $T_m$. Zr-Cu is shown in Fig. 2 as a typical binary system with a wide RGF composition range.

![Figure 2](image)

**Ab Initio Calculations of Glass Forming Ability:** Knowledge of the liquidus lines (i.e., features of the equilibrium phase diagram) and the glass transition temperatures thus suffice to determine the RGF properties of an alloy; generally these quantities must be obtained experimentally and are not easy to predict. However, recently considerable progress has been made in obtaining the energetics of liquid alloys of simple metals from first principles; in connection with calculations of the energies of the crystalline phases involved, this allows construction of the phase diagram, and hence derivation of $T_m$, the principal quantity controlling the variation of $T_{gr}$ with $X$. Theoretical calculations of $T_g$ do not yet exist; however, $T_g$ could be derived e.g., from calculations of the viscosity $\eta$ as a function of temperature (using the fact that $T_q$ can be defined at the temperature at which $\eta \sim 10^{13}$ Pa s), yielding $T_{gr}$ and hence $R_C$. It is therefore likely that in the near future theoretical ab initio calculations of $R_C$ for binary alloys will be made and that the degree of glass forming ability of known glass forming alloys can then be confirmed and subsequently predicted for other, new compositions.

**Operational Parameters Relating RGF Ability:**

As such calculations are not yet available, a number of operational parameters or alloy properties have been used for the prediction of RGF ability. The more important known parameters determining RGF ability are listed in Table 2 of Ref. 3. Some of these characteristics (such as the melting point and the type of intermetallics present) are phase diagram features requiring knowledge of the phase diagram or its ab initio calculation by a hypothetical, systematic program involving the calculation and comparison of the structural energies of all possible intermetallic phases for all compositions.

**Pertinent Characteristics not requiring knowledge or calculation of the phase diagram include:**

(a) the size ratio $r/R$ of the components, which is $<0.85$ for most RGF alloys and (b) the heat of formation $\Delta H_M$ of the liquids, which is $<10$ Kcal/mole for most RGF alloys and can be obtained experimentally or theoretically by semiempirical approaches such as that of Miedema who utilizes the electronegativities and electron concentrations of the constituent elements to obtain $\Delta H_M$.

**RGF Maps:** Used singly, neither $r/R$ nor $\Delta H_M$ suffices to predict RGF ability. Together, however, they have been found to provide a useful criterion. Ready-glass-formation plots (RGF maps) can be constructed which show that binary elemental combinations with size ratios $r/R < 0.85$ and $\Delta H_M < 10$ Kcal/mole generally possess RGF ability. As an example, a partial RGF map for Ni is given in Fig. 3; it shows good division between elements readily forming glasses with Ni and those that do not. It should be noted that these maps do not indicate the position and extent of the RGF composition range which is determined by the phase diagram features such as low liquidus temperatures and competing stable intermetallic phases.
A different, alloy chemical approach to the prediction of RGF for binary alloys is based on the type of intermetallics occurring in the system. In this approach the glass is considered somewhat like a (noncrystalline) alloy phase; in the same way in which the equilibrium alloy phase in homologous systems are often identical or structurally related Hume-Rothery phases, Laves phases, or related tetrahedrally-close-packed phases, interstitial phases, etc. the glass may be correlated with crystalline alloy phases by structure (based e.g. on similar short-range order or coordination number) or electronic considerations. Table 2 gives a listing of alloy phases that have been found to be connected with RGF in binary systems. Generally these phases have compositions lying in or near the RGF composition range; however, if Laves-Friauf phases of composition AB₂ or related phases exist in an RGF system the glass tends to occur in the "opposite" region of the diagram where the larger element A is the majority component. Presence of both an RGF glass and a Laves phase in the same system is so frequent that one might designate these glasses in view of their composition as "anti"-Laves phases.

In the context of considering the glass as an alloy phase, Turnbull's concept is of interest according to which there may be a number of alloy compositions for which the glass (formed by infinitely slow cooling) is the single phase with the lowest free energy compared to all possible isostoechiometric crystalline single phases; it is thus the single phase ground state for this composition. (Among organic glasses, there is at least one documented instance for which \( T_g > T_m \), i.e., where the glass forms upon cooling at a temperature above \( T_m \) and where the glass transition thus is an equilibrium reaction rather than a constrained equilibrium reaction.)

It is not known whether this glass can also be prepared from the terminal crystalline phases as the product of a solid-state reaction between them.

CLASSIFICATION

Glassy metals can be classified on the basis of their constituents. In the light of the preceding discussion of formation, especially the RGF maps, it is clear that ready glass formation is not possible if the constituent elements are alloy chemically too similar; for RGF to occur they must differ in size by >15% combined with a negative heat of mixing of >-10 Kcal/mole (due to electron concentration and electronegativity difference). On the other hand, there are probably also upper limits to the size difference and negative heat of mixing which are consonant with RGF; this point has not yet been established.

A brief listing of major and minor families of readily glass forming alloy combinations is given in Table 3 (after Ref. 3).

### Table III. Readily Glass Forming Alloy Systems Based on Chemical Classification of Constituents (Ref. 3)

<table>
<thead>
<tr>
<th>Group</th>
<th>Representative Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major Systems</td>
<td></td>
</tr>
<tr>
<td>T² (or noble) metal + metalloid [I]</td>
<td>... ... ... Fe-Co, Co-P, Fe-P-C, Ni-P-Be</td>
</tr>
<tr>
<td>T¹ metal + T² metal (or Cu)</td>
<td>... ... ... Zr-Cu, Ti-Zr, Nb-Ni</td>
</tr>
<tr>
<td>A metal + B metal</td>
<td>... ... ... Cu-Co, Fe-Co, In-P</td>
</tr>
<tr>
<td>Lanthanide + ? (or B metal)</td>
<td>... ... ... La-Ni, Ce-Ni</td>
</tr>
<tr>
<td>Actinide + ? metal</td>
<td>... ... ... U-Cr, Pu-Be</td>
</tr>
<tr>
<td>Miscellaneous Systems</td>
<td></td>
</tr>
<tr>
<td>T¹ metal + A metal</td>
<td>... ... ... Ti-(Zr)-Be</td>
</tr>
<tr>
<td>A metal + T¹ metal</td>
<td>... ... ... Cu-Co, Fe-Be</td>
</tr>
<tr>
<td>A metal + T² metal</td>
<td>... ... ... Cu-Co, Fe-Be</td>
</tr>
<tr>
<td>A metal + Cu, Zn, Al groups; metalloid</td>
<td>... ... ... Cu-Co, Fe-Be</td>
</tr>
<tr>
<td>A metal + Si, Ge, P, Na, Mg groups; T¹ metal + early transition metal (Ni, Fe, Co, Ni groups); B metal</td>
<td>... ... ... Cu-Co, Fe-Be</td>
</tr>
</tbody>
</table>
MECHANICAL PROPERTIES

In this survey, we have space only to discuss two sets of properties: elasticity, represented by the Young's modulus $E$, and plasticity, represented by the Vicker's microhardness $H_v$. We survey the correlation of these properties with each other and their variation with composition for some representative glassy alloy systems.

**Elasticity:** The Young's moduli $E$ of many metallic glasses have been accurately determined using dynamic methods such as the pulse echo technique which is suitable for melt-spun ribbons of $>10$ cm length or the impulse-induced resonance technique appropriate for short samples of $\sim 1$ cm length such as those typically obtained by arc-furnace hammer-and-anvil quenching. Typically, the compositional variations of $E$ across metal-metal and metal-metalloid binaries A-B show approximately linear increases of $E$ with increasing alloying element content $X_B$ over a broad range of $X_B$. As an example, $E$ for Zr-Cu glasses is shown schematically in Fig. 2. In metal-metal glass systems with a sufficiently broad glassy composition range, a maximum of $E$ is often found, generally at a composition rich in the smaller component $B$, as seen also in the plot of Zr-Cu. The occurrence of a sharp maximum of $E$ and its near-linear change with composition over a wide range of $X_B$ are features not expected from simple quasichemical theories of elastic property variation. Correlations of the position of $E_{\text{max}}$ with alloy chemical features of the equilibrium phase diagram have been noted.

The Young's moduli of elemental metallic glasses have been predicted to be 20-30\% lower than the values of the corresponding crystalline elements by calculations of the corresponding Debye frequencies; however, at present few experimental data are available for comparisons of glasses and crystals. For elements the "crystalline" $E$ values are known but elemental glasses are hard to prepare and measure; for alloys where $E$ has been measured for the glasses, the values for the corresponding crystalline phases are not yet known. Preliminary data show that the changes of $E$ for the crystalline phases across the Zr-Cu diagram roughly follow those for the corresponding glasses.

**Plasticity:** Due to the absence of work hardening in glassy metals, they fail shortly after the onset of plastic deformation in tension; accordingly, tension stress-strain measurements cannot be used as an indicator of plastic strength. In compression, however, high strength values as measured, e.g., by the Vicker's microhardness $H_v$ can be realized; this strength measure is therefore widely used. $H_v$ has been shown to have a remarkably consistent correlation with the elasticity as measured by the Young's modulus $E$.

For many metalloid-free metal-metal glasses varying over a wide range of strength values from soft glasses such as Ca-Zn to high strength glasses such as Ta-In there is a linear correlation between $H_v$ and $E$, implying that for all of these glasses, regardless of the nature of their interatomic interactions, size ratio, etc., the yield strain $e_y$ is approximately constant, according to the relation

$$e_y = \frac{\sigma_y}{E} = \frac{H_v}{E}.$$

This result differs drastically from the situation for crystalline alloys, for which the theoretical yield strain is rarely reached due to dislocation movements; it implies that metallic glasses, due to the apparent absence of analogous defects promoting plastic deformation, "live up to" their full elastic strength potential more than crystalline materials.

It may be noted that for metalloid containing glassy metals a somewhat different $H_v$ vs. $E$ curve exists, with a narrow band of values corresponding to somewhat differing $e_y$ values; Chen has suggested that $e_y$ depends on the differing Poisson ratios $\nu$ of these glasses.

**Thermal Stability:** Thermal effects of interest include, with increasing temperature, relaxation processes, the glass transition temperature (where observable), the crystallization temperature(s) and further transformation temperature(s). We do not address the relaxation effects here.

**Glass Transition Temperature $T_g$:** $T_g$ is generally regarded as the most fundamental measure of thermal glass stability since the two structural entities involved in the glass transition,
i.e., the glass and the super-cooled liquid, are very similar in their atomic arrangements and many electronic properties (unlike the phases involved in a glass \textarrow{\rightarrow} crystal transition), differing drastically in viscosity, specific heat, and associated properties. A model for the glass transition can be given in terms of the free volume theory in which the glass transition involves a cooperative rearrangeability of the free volume $V_f$. For an elemental glass of atomic mass $M$ it is therefore reasonable to model the glass transition process in analogy to the model for the melting process used in the derivation of the Lindemann expression for the melting point $T_m$.

$$kT_m \propto MV^{2/3} e^{\frac{2\alpha M V^{2/3} E_{cr}}{M}}$$

where $\theta_{D,cr}$ is the Debye temperature of the crystal and $E_{cr}$ is its Young's modulus and $V$ is the atomic volumes. This leads to

$$kT_m \propto MV^{2/3} e^{\frac{2\alpha M V^{2/3} E_{g}}{M}}$$

One expects that this relationship between $T_g$ and $E$ should be followed even more closely than the corresponding Lindemann relation for the melting point because of the much closer similarity between glass and liquid than between liquid and crystal. Assuming the Lindemann relation to be valid, one would expect

$$T_g = E_{cr} \cdot T_m$$

Unfortunately, these relationships for $T_g$ cannot be tested directly because elemental glasses always crystallize far below their glass transition. Measured $T_g$ values for glassy metal all refer to alloys rather than elements; unfortunately, as discussed above, for these compositions the relevant property values of the crystalline phases such as $E_{cr}$ or $\theta_{D,cr}$ are not yet available. In any case the Lindemann formula cannot be expected to hold for ordered intermetallics because the implied model for melting assumed for it may not agree with the melting mechanism for an ordered phase. Rather than attempting to make comparisons of the thermal properties of glasses with those of the crystalline phases at this time, we examine the relation between the thermal and elastic properties for glassy alloys. For the Zr-Cu system, e.g., $T_g$ and $E_g$ are proportional to composition over a wide composition range, with the relationship

$$T_g = aE_g + b$$

over the linear range of values. While a formula of this type can be understood readily in terms of the viscosity at $T_g$ and its temperature dependence, this expression obviously cannot hold for small values of $E_g$.

**Crystallization Temperatures:** The exothermic processes associated with equilibration may involve phase separation of a glass into two glasses, phase separation into a glass and a crystalline phase or crystallization into one or more phases; ordering reactions and recrystallization also occur. These complicated processes involving nucleation, growth, and other phenomena cannot be readily and solely associated with the elastic properties of the glassy alloys and any observed empirical correlations of the crystallization temperature with $E_g$, etc. could therefore be considered as coincidental; nonetheless, correlations involving $T_c$ are frequently made in the absence of observable glass transitions. Probably the most important precaution necessary in evaluating $T_c$ as a measure of thermal stability is to exclude "easy" crystallization processes from consideration such as those frequently taking place at the end of the glass forming range at low alloying element contents. An example of this situation is shown in Fig. 4 for the Ca-Al system, where elemental Ca crystallizes "easily" at low Al contents of 15-20 at.pct. Al, while above ~30 at.pct. Al the "intrinsic" stability of the glass with respect to crystallization dominates the process. In comparing glass stability as measured by $T_c$ for different systems, only glasses with high alloying content should therefore be considered and, secondly, only similar compositions can be compared meaningfully. If such precautions are taken, and identical, high-alloy-composition glasses are compared for chemically related systems, remarkably consistent correlations between $T_c$ and $E$, as well as between $T_c$ and the equilibrium melting points $T_m$ of the crystalline phases are sometimes observed, as demonstrated for a series of $T_b$-$T_g$ glasses (Fig. 5). Wang has attempted to correlate glass stability with the structural complexity of the corresponding
alloy phases.

On the basis of these observations it is apparent that, at least in first order elastic, plastic, and thermal stabilities of glasses scale together; in some cases, in addition, they are related to the corresponding properties of the crystalline equilibrium alloys.

Figure 4

Figure 5

ACKNOWLEDGEMENT

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