Amorphous Metallic Alloys

Amorphous metallic alloys or metallic glasses have emerged as a new class of engineering materials after vitrification of metallic alloys by using the technique of ultra-rapid quenching of molten alloys has become possible. These materials, which do not have any long range crystalline order but retain metallic bonding, exhibit several interesting properties emanating from their unique structure which is isotropic and homogeneous in the microscopic scale. Extremely high hardness and tensile strength, exceptionally good corrosion resistance and very low magnetic losses in some soft magnetic materials are some of the attractive properties associated with amorphous metallic alloys. Usually poor tensile ductility - prevents structural applications

There are three technologically important classes of amorphous alloys, namely,
1. the metal - metalloid alloys, such as Fe-B, Fe-Ni-P-B and Pd-Si,
2. the rare earth - transition metal alloys, such as La-Ni and Gd-Fe,
3. the alloys made up of a combination of early and late transition metals such as Ti-Cu, Zr-Cu, Zr-Ni and Nb-Ni.

Important issues:
• glass forming abilities
• diffusion mechanisms
• modes and kinetics of crystallization
• formation of bulk metallic glasses
Glass Formation

3D lattice arrangement of atoms in a crystalline solid is destroyed as it melts.
In the liquid state, the long range order both translational and orientational of the crystalline solid is not retained as the atoms vibrate about positions which are rapidly and constantly interdiffusing. A low viscosity, which is essentially the inability to resist a shear stress, characterizes the liquid state.

Vitrification (or glass formation) of a liquid is possible only when the liquid is cooled at a rate sufficiently rapid to escape a significant degree of crystallization so that the ‘disordered’ atomic configuration of the liquid state is frozen in. Glass formation is easy in a number of nonmetallic systems such as silicates and organic polymers. The nature of bonding in these systems places severe limits on the rate at which crystalline order can be established during cooling. Thus the melt solidifies into a glass even at low cooling rates (often less than $10^{-2}$ K/s).

Metallic melts, in contrast, have non-directional bonding which allows a very rapid rearrangement of atoms into the crystalline state. Hence, very high cooling rates need to be imposed for forming metallic glasses by avoiding crystal formation. Cooling rates exceeding $10^5$ K/s are necessary for the formation of glasses in metallic alloys. Recent years several Zr based alloys with a number of components have been found to be amenable to vitrification at substantially slower cooling rates (Inoue 1998) – formation of bulk metallic glasses.
The process of **vitrification of a liquid under nonequilibrium cooling** can be compared with the equilibrium crystallization process in plots of viscosity, $\eta$, and thermodynamic quantities such as specific volume, $V$, and specific heat, $C_p$, against temperature.

While the liquid to crystal transformation is accompanied by a step change in these properties, **a progressive change in viscosity and enthalpy precedes the vitrification event as the liquid is undercooled below the equilibrium melting temperature, $T_m$**. It is evident from these plots that vitrification is possible only if the equilibrium crystallization process is avoided. **Cooling rate needs to be sufficiently high, so that insufficient time for nucleation and/or growth does not permit the formation of the crystalline phase to a detectable level.**

*Phase Transformations*
Although the driving force for nucleation continuously increases with the extent of undercooling, the rapid increase in viscosity is responsible for decreasing atomic mobility and thereby effecting the kinetic suppression of crystallization. Eventually, the atomic configuration of the liquid becomes homogeneously frozen at the glass transition temperature, \( T_g \). This structural freezing to the amorphous state is, by convention, considered to occur when the viscosity reaches a value of \( 10^{13} \) poise.

Atomic configuration of the amorphous state does not correspond to a unique equilibrium structure

- \( T_g \) and the glass structure are both cooling rate dependent
- variations in the latter resulting in glasses with different states of structural relaxation
**Thermodynamic Factors**

Pure metals - extremely difficult to vitrify under the conditions of rapid solidification (cooling rate \(~10^6\) K/s)

Thin sections of splat quenched foils of Ni with dissolved gaseous impurities to a level of about 2% have been reported to vitrify - *cooling rate \(~10^9 - 10^{10}\) K/s*, only for thin sections (< 100 nm) of splats.

**Why is the vitrification of pure metals difficult?**

- Poor stability of the amorphous phase with respect to the equilibrium crystalline structure
- **Crystalline phase requires very little structural adjustment and consequently a very low thermal activation**
- From the assessment of *glass forming abilities (GFA)* of a number of alloys it has been observed that **GFA is enhanced substantially in several systems with increasing additions of solute elements in certain composition ranges**

Alloy systems with strong glass forming ability typically exhibit either

- *one or more deep eutectics*
- *or a steep decrease in the liquidus temperature*
Thermodynamic Factors Influencing Glass Formation

The G-c (same as G-X) plots for the liquid and the \(\beta\) crystalline phase intersect at a point where the integral molar free energies of these phases are equal (see figure below) - marks the composition limit up to which partitionless solidification is thermodynamically possible - \(T_0(c)\) line the shaded area below which designates the region of stability of the \(\beta\) phase with respect to the liquid phase under the condition of partitionless solidification.

Rapid Solidification does not permit partitioning of the alloying elements between the parent liquid and the crystalline product - \(T_0(c)\) curve can, therefore, be considered as the polymorphic melting curve of a multicomponent system.
The addition of solute atoms to a pure metal, specially in the case where the solute and the solvent atoms differ in size and in chemical character, makes the diffusive rearrangement of atoms a necessary step during solidification into a crystalline phase - glass formation becomes easier. $T_g$ generally increases with solute concentration.

Point of intersection of the $T_0(c)$ and $T_g(c)$ lines indicates the minimum solute concentration limit for an alloy to vitrify. An alloy having a solute content exceeding this limit can not solidify into the crystalline solid through a partitionless solidification as it cools down to $T_g$, where the viscosity of the liquid rapidly rises to about $10^{13}$ poise. The thermodynamic basis of glass formation can thus be explained by considering the competition between the partitionless polymorphic solidification of the liquid to supersaturated $\beta$ on one hand and the liquid to glass transition on the other.
**Kinetic considerations**

For a glass to form, one of the following conditions has to be satisfied:

*a) complete suppression of nucleation of crystalline phases;*  
*b) limited nucleation of crystals but no significant growth of these, resulting in a distribution of quenched-in nuclei of crystals in an amorphous matrix;*  
*c) nucleation of a very few isolated crystalline nuclei which grow to relatively large sizes but the number density of these crystals embedded in the amorphous matrix is too low to be detected by X-ray diffraction (XRD).*

The condition (a) is rarely satisfied in metallic glasses including Ti and Zr based ones.  
Even in a process like laser glazing, where the cooling rate of the thin layer (< 10 µm) of the surface is very high, it is difficult to suppress the nucleation of crystals completely - *certain number density of quenched-in nuclei is invariably present and, therefore, glass formation is essentially controlled by the fact that these nuclei do not get an opportunity to grow.*  
In some instances, a limited number of large size crystals have been detected in metallic glass samples, suggesting that the condition (c) is operative in such cases.
Crystallization of Metallic Glasses

Crystallization of metallic glasses has been investigated by a number of experimental techniques - **most important of these have been DSC and TEM**

DSC - crystallization leads to distinct exothermic peaks
Area under the peak gives a measure of the heat of crystallization - usually of the order of ~ 40% of the heat of fusion
In addition to structural relaxation, heating of an amorphous alloy leads to several changes including glass-liquid transitions, phase separation, and, crystallization

*Instances have been reported of phase separation in metallic glasses prior to crystallization*, e.g. Pd$_{74}$Au$_{8}$Si$_{18}$ (Chou and Turnbull, 1975), Zr-24%Fe (Banerjee, 1979), and, Fe$_{40}$Ni$_{40}$B$_{20}$ (Piller and Haasen, 1982).

*Amorphous to crystalline phase transition is necessarily a first-order transition involving nucleation and growth*

- **No periodic arrangements of atoms in the parent amorphous structure, therefore no possibility of achieving a lattice correspondence between the parent and the product structures**
- **Crystallization is expected to occur essentially by diffusional atomic movements**
- Depending upon the diffusion distances involved in the crystallization process, one can broadly classify the mechanisms of crystallization into three broad categories, namely
  1. **polymorphic crystallization**
  2. **eutectic crystallization**
  3. **crystallization involving long range diffusion - primary followed by eutectic or primary followed by polymorphic crystallization**
These three modes of crystallization are schematically illustrated in Figure (previous page).

i) **Polymorphic crystallization (A→α):**

- Compositions of the parent amorphous phase and of the product crystalline phase are the same
- The crystallization process involves *diffusional atomic jumps across the advancing transformation front* - situation is analogous to `partitionless solidification' processes and is illustrated in figure above for the alloy composition c1. Koster and Herold (1980) have termed this type of crystallization as `polymorphic crystallization'.

  e.g. Ni$_{33.3}$Zr$_{66.7}$ alloy exhibits polymorphic crystallization to form the Zr$_2$Ni phase (see below). Activation energy for this crystallization process has been determined to be 320 kJ/mol (Dey et. al., 1986). Very closely spaced planar faults have been observed within the Zr$_2$Ni crystals (see below).
**ii) Eutectic crystallization** $(A \rightarrow \alpha + \beta)$:

- The partitioning of alloying elements into two crystalline phases (for the composition c3 in figure), which are forming simultaneously from the parent amorphous phase in a cellular transformation.
- Requires diffusion at or near to the transformation front.

Eutectic/eutectoid decomposition and cellular precipitation are the analogous phase transformations in crystalline systems.

Eutectic crystallization, which has been encountered in several systems such as Fe-B, Fe-Ni-B, Mo-Ni, and Zr-Fe occurs at a relatively low rate as compared to polymorphic crystallization.

Decomposition of an amorphous phase into a mixture of a crystalline and a second amorphous phase, in a cellular transformation mode, appears to be possible in a system in which the amorphous phase has a tendency towards phase separation (or unmixing).

*However, in the case of metallic glasses, such a transformation, which is analogous to the monotectoid reaction, has not been encountered.*
iii) Primary crystallization followed by eutectic or polymorphic crystallization:

• Formation of a crystal having a composition which is different from that of the parent amorphous phase, requires long range diffusion ahead of the transformation front – primary crystallization

• Kinetics controlled by the mechanism of long range atom transport in the amorphous matrix

• The composition of the matrix amorphous phase may finally transform via one of the many possible phase reactions. e.g. in case of Fe-B, primary crystallization of $\alpha$-Fe takes place followed by the amorphous matrix gradually attaining the Fe75B25 composition and then transforms into the Fe3B phase via a polymorphic crystallization process.

By analogy with various liquid-to-crystal phase reactions one can visualize many possible reactions, such as the following: Primary crystallization followed by an eutectic reaction

\[(A \rightarrow \alpha \text{ (primary)} + A' \rightarrow \alpha \text{ (primary)} + \alpha + \beta \text{ (eutectic)}) : A \text{ and } A' \text{ are amorphous phases having different compositions and are different crystalline phases as shown for composition c2. The appearance of more than one exothermic peak in DSC thermograms appears to originate from such successive phase reactions (Fig. 3.33).} \]