Thermodynamic Properties of Amorphous Solids
—Glass Formation and Glass Transition—

(Overview)

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Glasses are generally produced from the highly undercooled liquid state by rapid quenching methods or quasi-statically at slow cooling by the effective control of potent heterogeneous nucleation sites. For metallic systems the latter method recently has led to the development of bulk metallic glass with a complex multicomponent chemistry and advanced engineering properties. Besides the formation of "deep eutectics" due to the strongly varying atomic size of the constituents an enhanced oxygen solubility is necessary in order to control heterogeneous nucleation and produce a bulk metallic glass.

As long as crystallization can be avoided the relevant thermodynamic properties of the metastable glassy and undercooled liquid phases can be measured below and above the glass transition temperature, respectively. The obtained data give new insight into the nature of the glass transition suggesting that it is not a phase transition in the classical sense but kinetic freezing triggered by an underlying entropic instability. However, different types of glasses distinguished as "fragile" and "strong" exhibit different densities of configurational states. Therefore, the thermodynamic and transport properties become dependent on the time scales of their exploration.

Furthermore, glass formation can be achieved by solid-state-processing without passing through the liquid state. This crystal-to-glass transition is observed under a number of different experimental conditions when a sufficiently high energy level is reached and kinetic conditions prevent the establishment of equilibrium. In some instances it can be shown that basically the same glassy state can be reached approaching it from the liquid or the solid state. In both cases the stability of the undercooled liquid and the non-equilibrium solid against glass formation is limited by an isotropic condition. Conceptually, the formation of the glassy state from the liquid and the solid can then be understood within a thermodynamic framework under appropriate kinetic constraints resulting in a universal phase diagram with a pseudo-critical point.

(Received February 7, 1995)

Keywords: thermodynamic properties, nucleation, nanocrystalline material, bulk metal glass, crystal-to-glass transition, phase stability

I. Introduction

Glasses have been manufactured from silica and related oxides for thousands of years. Recently, more and more advanced materials have been produced in an amorphous form due to the considerable technological promises including directionally bonded, macromolecular and metallic systems. Glasses are generally formed if upon cooling of a melt below the glass transition temperature, \( T_g \), crystal nucleation and/or growth are avoided. At \( T_g \) the liquid freezes to a rigid solid, however devoid of crystalline order. Thus, glasses—and amorphous solids in general—are structurally characterized by the total absence of long range atomic order. But a short range order is still present and may be similar to that found in the crystalline counterpart.

A glass exhibits a glass transition manifested by a change in the thermodynamic properties, such as specific heat and thermal expansion coefficient during heating or cooling. Whether the glass transition is a real phase transition or just kinetic freezing is still a matter of controversy. From a theoretical point of view and analyzing selected experimental data obtained from different materials, the glass transition is considered to be either a first order, second order or third order phase transition. For example, the entropy theory of Gibbs concentrates on the stiffness of macromolecular polymer chains, whereas the free volume theories relate to the atomic mobility in a certain volume. Apparently, related relaxation and transport processes depend on the cohesive energy and the type of chemical bond. Just considering the dynamical aspects the glass transition has been described as a localization phenomenon with power law singularities of relevant relaxation times and viscosity based on mode-coupling theories. Further experimental results point to the kinetic nature. Therefore, no theory proposed as yet can account for all experimental observations which are mostly obtained for non-metallic systems.

Only three decades ago the synthesis of glasses was extended to metallic systems by Duwez et al. For this first generation of metallic glasses the cooling rates required to avoid heterogeneous nucleation were relatively high, typically \( 10^6 \) K/s. In general, these high cooling rates have been obtained by quenching the liquid alloys
on a cold metallic substrate which generally limited the sample geometries to thin sheets of metal typically 50 to 100 µm in thickness.

Other methods which have been developed to prepare glassy surface coatings by laser pulse heating, electrodeposition or physical vapor deposition methods can in general result in even higher cooling rates. Due to the nature of these processes however, the sample geometries here are also confined to thin sheets or thin film coatings. More recently, Perepezko demonstrated that the critical condition for glass formation in metallic alloys is not the cooling rate itself but the level of liquid undercooling which can be reached for the metastable liquid state\textsuperscript{(11)}. Here, droplets of about 10 µm diameter of liquid Cu-Te alloys have been cooled through their entire undercooled regime and frozen to a glass at cooling rates as low as 0.2 K/s without any detectable crystallization. These undercooling experiments have been extended to produce large glassy samples by containerless processing\textsuperscript{(12)}, applying special surface coatings\textsuperscript{(13)} or preventing the crystallization in multicomponent alloys by choosing complex chemical compositions\textsuperscript{(14)}. Extending the composition range to complex multi-component alloys with typically five elements, a second generation of metallic glasses has been developed in Japan by Inoue, Masumoto et al. and in the U.S.A. by Johnson et al. These samples can now be produced with dimensions of several cm\(^3\) by conventional casting or zone melting techniques. For a number of pseudo-eutectic Mg\textsuperscript{(15)}, Al\textsuperscript{(16)} and Zr\textsuperscript{(17,18)} based alloys cooling rates as low as 1–100 K/s are sufficient to obtain high levels of undercooling and produce a bulk glass.

These new alloys are excellent advanced engineering materials due to their excellent wear properties\textsuperscript{(19)}, low coefficient of friction, almost theoretical strength and excellent corrosion resistance. Furthermore, these alloys are sufficiently stable against crystallization to explore the highly undercooled liquid up to about 100 K above \(T_g\) and give new insight into the kinetics and thermodynamics of the highly undercooled liquid state of metals. From this point of view, glass formation is inherently coupled to the limited stability range of the more stable crystalline phases or phase mixtures. On the other hand, these crystalline phases can be destabilized by a wide variety of different methods and resulting in a crystal-to-glass transition\textsuperscript{(20)}. Such a crystal instability has been observed for example during hydriding of intermetallic compounds\textsuperscript{(21)}, thermal annealing of multilayered thin film specimen\textsuperscript{(22)} or metastable crystalline bulk samples\textsuperscript{(23)}, intense mechanical deformation\textsuperscript{(24)}, mechanical alloying of powder particles\textsuperscript{(25)} or thin metal sheets\textsuperscript{(26)}, ion beam\textsuperscript{(27)}, electron beam\textsuperscript{(28)} or ultraviolet irradiation\textsuperscript{(29)}, compression\textsuperscript{(30)} and decompression\textsuperscript{(31)} besides further chemical methods.

As such, there is ample experimental evidence that the glassy state can be reached by cooling a liquid or by destabilizing and “melting” a crystal to a glass. The underlying thermodynamic principles and kinetic constraints will be discussed in the following together with experimental observations on the properties of the metastable state of the undercooled liquid and non-equilibrium solids.

II. Nanostructured Materials

1. Nanocrystalline material versus glass

Nanocrystalline material has attracted considerable scientific interest recently due to their unusual physical and chemical properties. They are structurally disordered in comparison with a single crystal but exhibit atomic order on a length scale of several nanometers. As such, the distinction between an amorphous structure, a nanocrystalline structure and a glass can sometimes become difficult.

Nanocrystalline materials can be prepared by the same methods as glasses, i.e. from the liquid, gas or solid state at different kinetic conditions or different chemical composition (for a review see\textsuperscript{(32)}). Their structural and resulting physical properties are inherently different from glasses (short range atomic order on a scale of less than 2 nm) and conventional polycrystals (grain size larger than µm). Nanocrystalline materials are characterized by their small crystallite-size in the range of a few nanometers which are separated by high-angle grain or interphase boundaries and, consequently, by their large volume fraction of disordered regions, the grain boundaries. In contrast, the structure of an amorphous solid or glass can be described by a continuous random network of atoms or uniform hard spheres thus lacking translational symmetry\textsuperscript{(33)}. This structural difference is schematically shown in Fig. 1 for a nanocrystalline solid and a hard-sphere glass. Furthermore, a distinction between a glass and an amorphous solid is generally made in the sense that a glass exhibits a glass transition (to the undercooled liquid).

As such, the thermal stability during heating of a glass is eventually characterized by nucleation and growth of crystallites which occurs at a rather well defined temperature typical for the activation energy of crystallization. In comparison, nanocrystalline materials will experience overall grain growth of the crystallites smeared over a broad range of temperatures. This behavior has been observed for a number of materials. For example, the thermal response of a nanocrystalline Zr-sample is shown in Fig. 2(a) typically for grain growth and in comparison for a Zr–Al metallic glass in Fig. 2(b) typical for crystallization. Other methods of distinguishing glassy and nanocrystalline structures are based on electron diffraction (comparison bright-field and dark-filed imaging) and other diffraction methods and often cannot clearly distinguish an amorphous structure from a nanocrystalline structure.

2. Nanostructure-property correlations

Decreasing the grain size of a material to the nanometer range leads to a drastic increase of the number of grain boundaries reaching typical densities of \(10^{10}\) interfaces per cm\(^3\). The large number of atoms located in the
Fig. 1 A schematic representation of the structure of the nanocrystalline (a) and glassy state (b) using a single element hard sphere model.

Fig. 2 Thermal stability and exothermic response as a function of temperature of nanocrystalline Zr exhibiting grain growth (a) and a glassy Zr-Al alloy exhibiting crystallization to the more stable intermetallic compounds (b).

Fig. 3 The stored enthalpy $\Delta H$ as a function of the average reciprocal grain diameter $1/\langle d \rangle$ for Ru powder prepared by mechanical attrition.

Metals and can reach values up to typically 30% of the enthalpy of fusion. The excess specific heat capacity $\Delta c_p$ exhibits a linear dependence with the stored enthalpy $\Delta H$ when given as a percentage of the heat of fusion ($\Delta H/\Delta H_f$). According to an analysis by Chen and Spaepen the stored enthalpy of a nanocrystalline material relates with the interfacial energy $\gamma$ according to the following relationship:

$$\Delta H = \frac{2 \gamma_H gV}{\langle d \rangle}$$  

where $\gamma_H$ is the enthalpic part of the grain boundary energy, $\langle d \rangle$ the mean grain diameter, $g$ a geometric factor of typically 1.3 and $V$ the molar volume. As an example, Fig. 3 shows the stored enthalpy $\Delta H$ as a function of the average reciprocal grain diameter $1/\langle d \rangle$ for Ru powder prepared by mechanical attrition for different periods of time. In the nanocrystalline regime the stored enthalpy shows a distinct $1/\langle d \rangle$ dependence according to eq. (1) and the enthalpic contribution to the grain boundary energy can simply be obtained from the slope in Fig. 3 and is estimated to be about $2.5 J/m^2$.

The excess specific heat as a function of reciprocal average grain size exhibits a $1/\langle d \rangle$ dependence as well as shown in Fig. 4. The measured increase in specific heat $\Delta c_p$ scales with the volume fraction of grain boundaries and the specific heat of the grain boundaries $c_p^{gb}$ can be obtained from the slope of Fig. 4 with

$$\Delta c_p = \frac{36 \gamma_H}{\langle d \rangle}.$$  

As such, it is concluded that the atoms located within the grain boundaries have a specific heat typically double of that of the atoms located within the crystalline regions. Thus, in comparison with a glass the disorder in nanocrystalline materials is localized within the interface regions which have in general a different atomic structure and a larger excess free volume than the glass.
Fig. 4  Specific heat increase $\Delta C_p(\%)$ at room temperature in comparison to the unmilled state as function of the stored enthalpy $\Delta H$ (given as a percentage of $\Delta H$) for bcc and hcp nanocrystalline metals.

III. Liquid Undercooling

1. Phenomenology

A liquid can be cooled below its equilibrium melting point if appropriate kinetic measures are taken to control the onset of crystallization. The metastability of the undercooled liquid phase is finally terminated by the transformation to a solid phase, i.e. either a crystal or a glass.

Liquid undercooling can be achieved either dynamically by rapid quenching or quasi-statically by carefully controlling the most potent nucleation sites. Experimentally, the catalytic effects of active nucleants may be restricted to a small fraction of the overall sample by dispersing the liquid into a large number of small droplets. This method is based on the ideas of Turnbull\textsuperscript{38} and Perepezko\textsuperscript{39}. Alternatives to undercool bulk samples are found by fluxing techniques where the liquid is encased in inorganic glasses\textsuperscript{40} or by containerless processing\textsuperscript{41}. Here, the removal of active nucleation sites involves a chemical treatment to deactivate possible catalytic sites or a physical separation of the sites from a container.

The experience derived from the application of these methods has provided a basis to interpret the solidification response during splat quenching and melt spinning where direct and accurate measurement of the properties of the undercooled liquid and the initial phase selection during solidification is difficult or impossible.

2. Crystallization kinetics

The kinetics controlling the rate of crystal nucleation in undercooled liquids have been discussed in terms of classical nucleation theory\textsuperscript{42-44}. The nucleation rate increases precipitously with increasing undercooling down to temperatures well below the melting point.

Homogeneous nucleation provides an intrinsic limit to glass formation. In most glass forming alloys, however, copious homogeneous nucleation can only be avoided by applying high cooling rates. Some metallic glasses have a reduced glass transition temperature $T_g/T_m$ high enough to avoid homogeneous nucleation and/or growth of post-critical nuclei\textsuperscript{45}. In these cases, the only limiting factor to glass formation is heterogeneous nucleation above $T_g$. Elimination of heterogeneous nucleation sites (sites for nucleation catalysis in the melt, at the gas/liquid interface or on container walls) then allows large undercooling and glass formation at much lower cooling rates, and thus the synthesis of "bulk" glassy materials.

In order to describe the crystallization from an undercooled liquid theories have been developed which are basically adopting the Volmer-Weber\textsuperscript{46} and Becker-Döring\textsuperscript{47} approach and describing the formation of liquid droplets in a supersaturated vapor\textsuperscript{48}. The homogeneous nucleation rate per unit volume is then simply the collision frequency of single atoms with clusters of critical size resulting in a nucleation rate:

$$J_n = n_v \exp \left[ \frac{-\Delta G_A}{kT} \right] \exp \left[ \frac{-16\pi \sigma_d^2}{kT} \right]$$

where $n_v =$ number of atoms per unit volume, $v =$ a frequency factor equal to the Debye-frequency $10^3$ s\(^{-1}\), $\Delta G_A =$ activation energy for an atom addition to a cluster, $\sigma_d =$ interfacial energy between the crystalline nucleus and liquid, $\Delta G_c =$ chemical driving force per unit volume. In general the prefactor in eq. (3) can be lumped together and corresponds to $W_c = 10^{10} \eta^{-1}$ cm\(^{-3}\) s\(^{-1}\) with $\eta$, the liquid shear viscosity in poise, often approximated by\textsuperscript{49}

$$\eta = 10^{-3.3} \exp \left[ \frac{-3.34 T_m}{T - T_g} \right].$$

An alternative to the classical approach of postulating an a priori distribution of subcritical crystalline configurations has recently been suggested by Desrè et al.\textsuperscript{50}. Here, it is assumed that nuclei of critical size are formed inside zones of density fluctuations of appropriate amplitudes by a diffusionless transformation. In these zones polytetrahedral liquid-like structural units form critical size crystalline nuclei resulting however in a similar nucleation barrier as in the classical approach.

Heterogeneous nucleation involves the formation of a nucleus on an energetically favorable catalytic surface. The interaction between the nucleus and the catalytic site is taken into account in the nucleation rate expression through a variation of the interfacial tension $\sigma$ between the crystalline nucleus and the catalytic substrate. The contact angle $\theta$, between the nucleus and substrate, can vary from $180^\circ$ (non-wetting) to $0^\circ$ (perfect wetting). Thus, the interfacial term is modified by multiplying $\sigma$ with the wetting function $f(\theta)$ which for a spherical cap nucleus on a planar substrate corresponds to:

$$f(\theta) = 0.25(2 - 3 \cos \theta + (\cos \theta)^2).$$

In principle, the wetting behavior results from the energy of the heterophase boundary being formed between the nucleus and a substrate, typically a metal/non-metal interface. This interfacial energy relates to the inter-
facial atomic structure and can be evaluated based on the static distortion wave concept\(^{31,32}\). This energy is minimized when the reciprocal lattice vectors of both lattices are equal and the epitaxial strain energy is negligibly small. Thus, the lock-in energy is gained when both crystallites are properly oriented, resulting in a corresponding reduction of the activation energy for heterogeneous nucleation. In case of heterogeneous nucleation, the prefactor term \(W_s\) can vary by several orders of magnitude depending on how well the thermodynamic properties of the undercooled liquid are known\(^{33}\). Often it is assumed to be about \(W_s = 10^{32} \text{cm}^{-1} \text{s}^{-2} \text{mol}^{-1}\). Thus, the nucleation frequency for heterogeneous nucleation is given as

\[
J_s = W_s \exp \left[ -\frac{\Delta G^* f(\theta)}{kT} \right].
\]

The nucleation rate is a relatively steep function of temperature with a magnitude determined principally by the exponential term involving \(\Delta G^*\) and to a lesser degree by the prefactor term. Consequently, the most important parameters for determining the crystallization rate and hence the maximum level of undercooling and the tendency for glass formation are \(\sigma_a\) and \(\Delta G^*\). The interfacial tension \(\sigma_a\) between undercooled liquid and a crystalline nucleus is often taken as proportional to the enthalpy\(^{35}\) or entropy of fusion, such as\(^{36}\):

\[
\sigma_{al} = \alpha_{al} \frac{\Delta S_f T}{(N V^1)^{1/3}}
\]

where \(\alpha_{al}=\) structure dependent constant, \(\Delta S_f=\) entropy of fusion, \(N=\text{Avogadro number}\), \(V=\text{molar volume}\). Thus, according to this model the interfacial tension is proportional to the temperature with the proportionality coefficient including the entropy of fusion and the molar volume. Such an approach is valuable close to the melting point, i.e. at low undercooling. However, at high undercooling the deviations in the entropy difference between liquid and crystal probably exhibit large deviations.

The second important factor in the analysis of the kinetics of crystallization at high undercooling is the Gibbs free energy difference per unit volume \(\Delta G\) and its temperature dependence. \(\Delta G\) depends primarily on the heat capacity difference between metastable liquid and crystalline solid and can be described as:

\[
\Delta G = \frac{\Delta H_f \Delta T}{T} - \int_T^{T_m} \Delta C_p \, dT + \int_T^{T_m} \frac{\Delta C_p}{T} \, dT
\]

with \(\Delta H_f\) being the enthalpy of fusion, \(\Delta T\) the temperature difference between the melting point, \(T_m\), and the nucleation temperature of crystallization, \(T_N\), and \(\Delta C_p\) the heat capacity difference between undercooled liquid and the corresponding crystalline solid. Here it becomes evident that the thermodynamic properties of the undercooled liquid and, in particular, the specific heat at high undercooling is an important measure for the tendency of crystallization or glass formation.

3. Thermodynamic properties

The experimental studies of the thermodynamic properties of liquid metals have been confined usually to the stable liquid range of temperature and pressure. The results suggest that the values for \(C_p\) near the melting point for most liquid main group metals amount to about 30 J K\(^{-1}\) mol\(^{-1}\). This value is close to the value for the crystal at the melting point which corresponds to the sum of the vibrational contribution (\(3R = C_v\)) and the dilatational contribution (\(C_p = C_v - C_s = \alpha^2 V T / k T\) where \(\alpha\) is the thermal expansion coefficient, \(k\) is the isothermal compressibility) and the additional contribution from equilibrium point defects\(^{37}\). Any deviations from these values are caused by strong anharmonicity of atomic vibrations or electronic contributions. Above the melting point \(C_p\) first decreases with temperature, passes through a minimum and then rises to values up to 8–10 R\(^{37}\). From a theoretical point of view\(^{39,60}\) the existence of crystal-like clusters in the liquid is generally postulated. These clusters give an additional contribution to \(C_p\). With increasing temperature these clusters dissolve and reduce the contribution to the specific heat, thus explaining the decrease of \(C_p\) with temperature. Chapman\(^{61}\) showed that \(C_i\) of several liquid metals (Na, K, Hg, In, Sn, Pb) is a universal function of only two dimensionless parameters and decreases steadily with temperature.

By pseudopotential and thermodynamic perturbation theories, the undercooled liquid and amorphous state of several metals have been studied and compared with the measured \(C_p\) data\(^{62}\). By calculating the entropy \(S(T, P)\) along the line of constant normal pressure in the phase diagram and taking its temperature derivative the specific heat was estimated to be within about 20% of the experimental values. In addition, a comparison of the experimental data with predictions for the specific heat from the so-called “hole theory”' a similar temperature dependence is obtained\(^63\). Within such a model the liquid state is described as a quasicrystalline lattice containing a considerable fraction of vacant sites or holes.

Reviewing the literature for measured specific heat data of undercooled liquids, it becomes obvious that only very few systematic studies are available. In Fig. 5 experimental results of specific heat measurements for pure metals as well as glass forming alloys are shown as a function of reduced melting temperature \(T/T_m\). Here it is sufficient to consider the difference in specific heat \(\Delta C_p\) between the undercooled liquid and the corresponding crystalline stable solid. For pure metals with melting points <900 K, i.e. Bi, Sn and In\(^64\), and Au–Pb–Sb–alloys in the glass forming composition range\(^65\), specific heat values have been measured by Perepezko and coworkers over a maximum undercooling range of about 0.4\(T_m\). For other glass forming alloys the specific heat has been measured close to the melting point at low levels of undercooling by standard calorimetric measurements on undercooled bulk samples or by drop calorimetry with undercooling levels of less than 10%. Alternatively, more or less rapidly quenched amorphous samples representing relatively
stable metallic glasses can be heated above the glass transition temperature into the undercooled liquid regime from below\(^{(69)}\). These data are included in Fig. 5 for the glass forming composition range of the alloys NiPd\(^{66}\), MgCu\(^{68}\), PdCuSi\(^{68}\), MgLaNi\(^{69}\), AuSi\(^{70}\) and TiCr\(^{71}\). Despite the large scatter of experimental data, it is apparent that for the glass forming alloys, the crystal/liquid specific heat difference is relatively large at the eutectic temperature whereas for pure metals at the melting point it is small in comparison.

At least for the systems selected here, the change in the specific heat in comparison with the values at the melting point can be roughly approximated by\(^{(72)}\)

\[
\Delta C_p(T) - \Delta C_p(T_m) = 20 - 20 \frac{T}{T_m} \quad (J/g \cdot \text{at K}) \quad (9)
\]

For the specific heat increase near the eutectic composition, i.e. in the glass forming composition range, three possible reasons have been considered\(^{(73)}\):

1. a change in the vibrational spectrum due to a change in the type of bonding during melting;
2. a decrease in non-random association between unlike atoms with increasing temperature, and
3. changes in configurational entropy from the multiplicity of atomic positions which also causes the temperature variation. To evaluate these relationships further, in particular in the high temperature regime where no accurate data exist up to now for the undercooled liquid, improved experiments are being designed\(^{(76)}\).

4. Metastable phase equilibria and kinetics

A metastable phase equilibrium is a true reversible equilibrium\(^{(79)}\) though the free energy of a metastable phase is above that of the equilibrated stable phase. It can be regarded as an extension of stable equilibria due to a change in temperature or pressure under the constraint that one or more of the stable phases are absent due to an effective kinetic hindrance in their formation.

In contrast to samples rapidly quenched to low temperatures where the atomic mobility is frozen, measurements on droplet samples can be conducted below the melting temperature \(T_m\) under reversible metastable equilibrium conditions\(^{(76)}\). For example, Pb–Sn alloys form a simple eutectic phase diagram under stable equilibrium conditions. Here, three different metastable phase diagrams have been experimentally determined under reversible metastable equilibrium conditions\(^{(77)}\), namely (i) \(\alpha_m + L^*\), (ii) \(\beta_m + L^*\), and (iii) a peritectic reaction involving a metastable tetragonal \(\alpha_l\)-phase as shown in Fig. 6. Based on the thermodynamic information only the prediction of the kinetics of crystallization for a given composition and the corresponding solidification path would be impossible. With controlled undercooling experiments of eutectic alloys however two different solidification paths can be clearly distinguished.

Figure 7 depicts the free energy functions as function of undercooling below \(T_E\) for the eutectic composition.
From this energetic hierarchy of possible crystallization products, it is evident that the most stable phase is the \( \alpha\)-Pb/\( \beta\)-Sn mixture at all temperatures. However, it is possible to create the \( \alpha\)-Pb/\( \beta\)-Sn mixture by different intermediate steps from the undercooled liquid. In order to minimize the Gibbs free energy function \( G \) of the undercooled liquid, there are four different possibilities: \( L \rightarrow \alpha A + L' \), \( L \rightarrow \alpha A + L'' \), \( \rightarrow \beta A + L'' \), or \( L \rightarrow \alpha + \beta \) which are distinguished by different energy levels together with an increase in driving force. For eutectic alloys two principal solidification paths have been identified for eutectic alloys, indicated by A (low undercooling) and B (high undercooling), whereas nucleation of \( \alpha \) or \( \beta \)-Sn directly from the undercooled melt has not been observed.

For type A samples at low undercooling, the solidification path indicates that metastable states can be kinetically favored over the stable states. This is consistent with Ostwald's step rule stating that a system evolves through the succession in the order of decreasing energy of available metastable states\(^{179}\). This statement is equivalent to Turnbull's description of phase evolution noting that the more general tendency in structural evolution appears to be toward formation of the available state with the entropy \( S = \frac{\partial G}{\partial T} \) closest to that of the initial one\(^{178}\).

In contrast, type B samples exhibit higher levels of undercooling than type A samples and crystallize to the stable \( (\alpha + \beta) \) mixture without formation of the intermediate metastable \( \alpha A \)-phase.

Thus, it is seen that the solidification response is complex even in simple alloys. When these crystallization steps can be kinetically suppressed the undercooled liquid will freeze to a glass below the glass transition temperature.

5. \( T_g \)-concept

Unlike for pure metals, melting and crystallization of a binary alloy is accompanied by the redistribution of solute between the crystalline and liquid phases. Therefore, the kinetics of crystallization and melting depends in this case on the applied heating and cooling rates, respectively.

In general, crystal nucleation requires compositional fluctuations within the undercooled liquid. Thus, it is assumed that a critical nucleus relating to the maximum driving force is being formed which has a composition different from the average composition of the liquid. When at high undercooling of an alloy concentration fluctuations are kinetically suppressed, the formation of a critical nucleus can be avoided. In particular, for eutectic alloys with a relatively high viscosity of the melt\(^{180}\) and a predominance of heteroatomic bonding such compositional fluctuations can be suppressed.

On the other hand, composition-invariant single phase nucleation of a metastable crystalline phase represents a valuable competition, however, with reduced driving force. Thus, during rapid cooling, it is often observed that partitionless crystallization is kinetically favored over solidification involving solute partitioning. When partitionless crystallization is avoided the alloy will be trapped in the amorphous state as a glass.

Furthermore, alloys with "deep" eutectics have a strong tendency for glass formation due to the attractive heteroatomic interactions in the liquid. In determining the composition dependence of the liquidus lines the molal exchange energy of solid and liquid is essential. For metallic systems it is generally a positive quantity nearly equal to the elastic strain energy which results from the atomic size differences between the solvent and solute atoms in the solid solution\(^{181}\). Thus, the \( T_g \)-temperature has been defined as the temperature where for a certain composition the Gibbs free energies of crystal and liquid are equal. The \( T_g \)-temperature therefore represents a limit to the partitionless or polymorphous crystallization for binary crystalline solid solutions\(^{182,183}\). A schematic representation of these relationships is given in Fig. 8.

Similar deviations from equilibrium have been observed for the melting transition. When heating a solid solution of Sn–Bi alloys above its solidus temperature at sufficiently high heating rates partitionless melting is observed to occur close to the estimated \( T_g \)-temperature\(^{184}\). This partitionless crystallization or melting transition can be described as a function of pressure, temperature and composition by the generalized Clapeyron equations given in reference\(^{185}\).

This has important consequences for the phase diagrams of most metallic glass formers which are characterized by deep eutectics and thus, steeply plunging \( T_g \)-lines\(^{186}\). For such alloys a generic non-equilibrium phase diagram can be developed neglecting the stable kinetically excluded intermetallic compounds and illustrating the possible thermodynamic states of a metastable system constrained to be a single phase. For alloys with large negative slopes for the \( T_g \)-lines, the \( T_g \)-line (\( \Delta G = 0 \)) must cross the isentropic temperature \( T_s \) (\( \Delta S = 0 \)) at a certain composition \( c^* \). Under this condition, a triple point \( c^*, T^* \) is defined between supersaturated crystal, undercooled liquid and ideal glass with

\[
\Delta G = \Delta H - T\Delta S = 0
\]

![Fig. 8](image.png)  
*Fig. 8 The schematic Gibbs free energies and definition of the polymorphous condition.*
as depicted in Fig. 9. With regard to the isentropic condition Kauzmann already pointed out that with progressive undercooling, the entropy of a liquid tends towards the entropy of the crystalline state as indicated by the increase of $\Delta C_p$ during cooling\(^{87}\). Since the entropy difference between liquid and crystal relates to

$$\Delta S = \int_{T_a}^{T} c_p(\text{liq}) - c_p(\text{cryst}) \, \frac{dT}{T}$$

\[ (11) \]

one would be faced with Kauzmann’s paradox that, at temperatures below $T_{go}$, the entropy of the ordered, thermodynamically most stable crystal would exceed that of the disordered liquid. This situation is averted by the occurrence of the glass transition. Thus, the compositional induced disorder reduces the melting point of the crystalline solid solution to an ideal glass transition temperature $T_{go}$. The slope of the $T_c$-line, which corresponds to

$$\frac{dT_c}{dc} = -\frac{\Delta \delta G}{\Delta S}$$

\[ (12) \]

approaching infinity at $(c^*, T^*)$. Using appropriate fitting parameters for the CALPHAD method\(^{88}\) and including appropriate corrections for the heat capacities of the undercooled liquid realistic extrapolations for the location of this triple point can be made. For example, the triple point for hexagonal Zirconium supersaturated with Ni is predicted at 638 K and 11.5 at% Ni\(^{80}\).

Since the interfacial energy $\sigma_{il}$ between crystal and liquid (or glass) is mainly entropic in origin according to Spacapan\(^{91}\) with $\sigma_{il} = \Delta S(T_a)$, the nucleation barrier for melting or amorphization would vanish at the triple point. Thus, also from the kinetics of the transition the composition $c^*$ represents the maximum solubility of a crystalline solid solution which can be obtained.

### IV. The Liquid-to-Glass Transition

#### 1. Glass forming ability

From the above discussion and, in particular, the analysis of crystallization kinetics, it is evident that the probability to form either a crystal or a glass strongly depends on composition. In particular eutectic alloys are favored in terms of glass formation\(^{89,90}\). Mostly elastic (topological) and electronic contributions to the free energy of crystalline solid solutions due to atomic size mismatch set a limit to their stability. Thus, when the crystal solubility is small glass formation becomes favored.

Since glasses are generally not in thermal equilibrium glass formation can only be discussed relative to appropriate time scales. During the measurement of a certain physical quantity of the glass a time average is performed which in general is equivalent to an ensemble average over only a limited region of phase space. This behavior is described as broken ergodicity\(^{91}\).

For non-metallic glasses measurements in the undercooled liquid regime above the glass transition temperature are possible over a wide temperature range in comparison with metallic glasses. Since a true internal equilibrium though metastable can be achieved, important conclusions can be drawn for the glass formation. For example, the viscosity of non-metallic highly undercooled liquids exhibits a distinct temperature dependence which can either be of the Vogel-Fulcher type or Arrhenius type. As such, often a distinction is made between “strong” network glass-forming liquids, such as SiO$_2$, GeO$_2$ or BeF$_2$, and “fragile” liquids, such as ionic systems (Ca(NO$_3$)$_2$) and organic materials (o-terphenyl)\(^{92}\). Thus, there should be a connection between the topology of the potential energy hypersurface of the system and the time scale for its exploration\(^{93}\). Consequently, “fragile” liquids exhibit a high density of configurational states characterizing the potential energy surface. As a function of temperature the configurational degeneracy is large leading to rapid thermal excitations. This results in a high heat capacity with a pronounced maximum at $T_g$ and consequently steep entropy curves. Here the vanishing entropy problem is most eminent and a “fragile” glass behaves similar to a Nernst solid with a vanishing entropy at 0 K (third law). For “strong” glasses the specific heat change is small as the relaxation times cross the experimental time scale and consequently, the deviation from the “ideal” behavior is more pronounced\(^{87}\).

In comparison, the accessibility of the undercooled liquid state for metallic glasses has been rather limited. Only recently with the advent of bulk glass forming alloys attempts have been made to investigate metallic systems above $T_g$ with respect to the discussion above. In the following two examples are described which seem to be typical for “fragile” and “strong” behavior.
2. "Fragile" metallic glasses

Au–Pb–Sb alloys have been found to undercool extensively at rates of $10^{-3}$ K/s by droplet techniques and vitrify at rates of $10^{-3}$ K/s by drop tube processing leading to the formation of mm-sized glassy spheres. The specific heat of eutectic Au$_{53.2}$Pb$_{27.4}$Sb$_{19.2}$ samples obtained from rapidly quenched samples near the glass transition temperature and from droplet samples near the eutectic melting temperature is shown in Fig. 10. A peak in the specific heat close to $T_g$ can be clearly distinguished typical for a "fragile" liquid.

From these measurements the entropy and enthalpy functions have been obtained for the stable crystalline state and the metastable undercooled liquid state. The results are shown in Fig. 11 for the enthalpy and entropy difference $\Delta H$ and $\Delta S$, respectively. An extrapolation of the entropy function of the highly undercooled liquid gives an isentropic temperature (ideal glass transition temperature) $T_{g0}=276$ K.

The experimental glass transition temperatures $T_g$ obtained from calorimetric measurements are shown in Fig. 12(a) as function of the heating rate $R=dT/df$ on a logarithmic scale. Here $T_g$ is taken as the onset of the slope change in the specific heat (heat flow) signal extrapolated back to the baseline. Apparently, this plot is non-linear a behavior which is typically observed for a wide range of oxide glasses, polymers and metal/transitonal metal alloys. At the slowest heating rate the glass transition occurs within about 20 K of the estimated Kauzmann temperature.

A fit of the data according to a suggestion by Saslow demonstrates that the associated temperature dependent relaxation time $\tau$ is consistent with a Vogel-Fulcher law for the slowing down of relaxation processes. The relaxation times have been obtained by numerical integration of the experimental data shown in Fig. 12(a) and are presented in Fig. 12(b). This approach can be based on a standard Landau free energy expansion similar to spin ordering of a ferromagnet above its critical point. The experimental results in Fig. 12(b) can be fitted to the equation

$$\tau^{-1}(T) = \tau_0^{-1} \exp \left( -\frac{E}{T-T_c} \right)$$

with $\tau_0=1.48 \times 10^{-2}$ s, $E=78.9$ K (corresponding to 7 meV) and $T_c=276.4$ K. It turns out that, according to this fit, the ordering temperature $T_c$ extrapolated to zero heating rate corresponds to the Kauzmann temperature $T_{g0}$ obtained from the specific heat data. However, the $T_g$ results for heating rates larger than 100 K/min are usually lacking the accuracy required for DSC measurements. Thus neglecting these data the measured results at medium heating rates can be equally well fitted to a linear function of $T_g$ versus log $R$ as indicated in Fig. 12(b).
Therefore, an enthalpy measurement (caloric evaluation of $T_g$) in general can not be used to clearly distinguish between Arrhenius and Vogel-Fulcher type behavior.

Thus, the question naturally arises if the viscosity shows Vogel-Fulcher behavior. The viscosity of these samples heated through the glass transition has been measured using a dynamic mechanical analyzer as described in detail elsewhere\textsuperscript{109}. For the lowest applied stress of $1.4 \times 10^5$ Pa the most dramatic viscosity change is obtained at the glass transition. Figure 13 exhibits the measured viscosity near the glass transition temperature which amounts to $2.5 \times 10^{11}$ Poise\textsuperscript{109}.

Figure 13 shows the viscosity data as a function of temperature measured for the glass and highly undercooled liquid just above the glass transition temperature together with literature values for the viscosity of the stable liquid\textsuperscript{101}. Altogether the viscosity behavior is Vogel-Fulcher-like. In an attempt to compare thermodynamic data with kinetic measurements Ramachandran-Rao suggested the functional dependence\textsuperscript{102}:

$$\ln \eta(T) = a + \frac{b}{(\Delta H(T) - \Delta H_k)} \quad (14)$$

Here, $a$ and $b$ are fit parameters ($a = -16.05$, $b = 1.03 \times 10^3$), $\Delta H$ corresponds to the enthalpy difference and $\Delta H_k$ to the enthalpy difference at the Kauzmann temperature. Since the enthalpy values have been measured over a broad range of temperature (see Fig. 11) the fit according to eq. (14) is included in Fig. 13 for the undercooled regime (solid line).

Thus, despite the problems of accurate $T_g$ measurements using calorimetric methods the inverse relaxation times and, in particular, the viscosity of Au–Pb–Sb alloys are consistent with a Vogel-Fulcher law and a vanishing residual entropy coinciding with $T_g$ and $\Delta H_k$ in eqs. (13) and (14), respectively. As such, this behavior is suggestive of an underlying entropic instability to cause the glass transition.

3. "Strong" metallic glasses

The current generation of zirconium-based "bulk metallic glass" forming alloys has created considerable scientific and technological interest because of the relatively easy accessibility to the metastable glass state and the exceptionally high stability against crystallization\textsuperscript{103,104}. These alloys present the unique opportunity to produce bulk metallic glasses (i.e. volumes greater than typically 1 cm\textsuperscript{3}) within the temperature and time constraints of industrial processing. Deep eutectic phase equilibria are thought to facilitate glass formation in undercooled metastable liquids by the favorable convergence of physical properties such as reduced interfacial tension, high viscosity, increased solid versus liquid specific heat difference resulting in a decrease of the driving force for crystallization and high reduced glass transition temperature. One of the most stable metallic glasses has been found by Johnson et al. in Zr–Ti–Ni–Cu–Be alloys at cooling rates of less than 10 K/s. The specific heat of the pseudo-ternary $(Zr_{83}Ti_{17})(Cu_{47}Ni_{53})Be_{2}$ alloy is shown in Fig. 14 for the stable crystal, the fully relaxed glass, the undercooled liquid and the stable liquid obtained at a heating rate of 8 K/min. The glass transition can be clearly distinguished and the data in the undercooled liquid can be interpolated as indicated by the dashed line to the eutectic temperature. In comparison with the "fragile" Au–Pb–Sb alloy the peak in the specific heat close to $T_g$ is missing. The absolute $c_p$ values on the other hand are comparable. Varying the heating rate between 0.5 K/min and 250 K/min results in a shift of the experimentally determined reduced glass transition temperature from 0.65 to 0.70$T_m$. These data can be fitted within the accuracy of the measurement according to eq. (13) with the Kauzmann temperature equivalent to $T_g$. However, the remarks made above on the reliability of enthalpic measurements for the definition of $T_g$ apply here as well. Further measurements of the viscosity indicate rather an Arrhenius type behavior which leads us to conclude that this new generation of metallic glasses is rather "strong"\textsuperscript{105}. In order to quantify the glass forming ease of these "strong" glass formers we have compared their thermodynamic properties with those of metallic elements\textsuperscript{106}. For the purpose of analyz-

![Fig. 13 Measured (triangles) and modeled data (open circles, solid line) for the viscosity of Au$_{25}$Pb$_{27.5}$Sb$_{28.5}$ alloys as a function of temperature.](image1)

![Fig. 14 Specific heat $c_p$ of Zr$_{83}$Ti$_{17}$Cu$_{47}$Ni$_{53}$Be$_2$ alloys in the glassy, undercooled liquid, stable liquid and crystalline state as a function of temperature.](image2)
Fig. 15 The crystal/liquid specific heat difference $\Delta c_p$ as a function of reduced temperature for several pure metals and bulk glass forming alloys.

In order to compare the thermodynamic properties of the elements with the "strong" eutectic glass formers, the corresponding entropy $\Delta S$ (integration over $c_p / T$), enthalpy $\Delta H$ (integration over $\Delta c_p$) and Gibbs free energy functions $\Delta G = \Delta H - T \Delta S$ have been calculated and exhibited in Fig. 16. The results are presented as a percentage of the entropy and enthalpy of fusion, respectively. Two examples characteristic for metallic elements and bulk metallic glasses are being compared: Indium representing a typical example of a pure metal with an entropy of fusion of 7.62 J/g·atomK (dashed line) and Zr$_2$Ti$_3$Cu$_{13}$Ni$_{19}$Be$_{23}$ as a typically example of bulk glass formation having an entropy of fusion of 8.72 J/g·atomK (full line). It is interesting to note that the entropy of fusion of the "strong" glass corresponds to about half of that of the "fragile" glass Au–Pb–Sb (see Section IV.2).

The liquid-solid entropy difference is shown in Fig. 16(a). If the entropy values are extrapolated beyond the experimentally determined range an isentropic temperature $T_K$ is found at about 0.37 $T_m$ for the metallic element ($T_K^m$) and at 0.52 $T_m$ ($T_K^b$) for the bulk metallic glass ($T_K^b$). Further experimental results varying the heating rate over two decades indicate that this isentropic condition at 561 K (see Fig. 14) corresponds to the glass transition temperature for indefinitely slow heating (ideal glass transition temperature $T^b_{g0}$) [807]. As such, for "strong" glasses the isentropic temperatures sets a limit to the maximum level of undercooling as well. However, in comparison with the "fragile" glass the isentropic instability can not approached as closely. Based on the same specific heat data the enthalpy difference $\Delta H$ is obtained and shown in Fig. 16(b). It is obvious that enthalpy is frozen out during undercooling. Due to the smaller specific heat the enthalpy reduction for the elemental metal is much less than for the bulk glass with increasing undercooling.

The excess enthalpy for the Zr-based alloys at the ideal glass transition temperature $T^b_{g0}$ corresponds to 0.26 of the enthalpy of fusion $\Delta H_f$ and represents the smallest value a fully relaxed glass with zero residual entropy could have. Experimentally, larger values for the heat of crystallization have been measured in agreement with the estimate (Fig. 16(b)). The crystallization in these alloys occurs at temperatures typically 150 K above $T^b_{g0}$, e.g. at approximately 0.75 $T_m$ depending on the heating rate. These considerations appear to be of general relevance and indicate the deviation from the state of an ideal glass when enthalpies of crystallization are measured.

A further important parameter is the Gibbs free energy difference $\Delta G$ shown in Fig. 16(c) as a fraction of the en-
enthalpy of fusion $\Delta H_f$. Since the entropies of fusion, i.e., the slopes of the $\Delta G$ curves at $T/T_m = 1$, for the bulk glass is only slightly reduced in comparison with the pure elements the main contribution to the reduction in the Gibbs free energy results from the different specific heat values.

At high undercooling, for the metallic element the driving force for crystallization is reduced to about half of the enthalpy of fusion. For the bulk glass former the driving force is reduced by another factor of two in comparison with the element. Thus, the resistance to crystallization of bulk glasses is inherently coupled with a reduction of the driving force for crystallization $\Delta G$ and is reflected in the corresponding increase in excess specific heat.

Since the ease of metallic glass formation is generally related to the formation of eutectic alloys further conclusions can be drawn about the principles of formation of "strong" bulk glasses. For example, by comparing the average melting temperature of the $Zr_{64}Ti_{15}Cu_{15}Ni_{10}Be_3$ alloy with its measured eutectic temperature a reduction in the melting point from 1832 to 937 K obviously has been achieved due to a eutectic reaction. The eutectic temperature of this "strong" glass forming alloy corresponds to approximately half of the melting point of the constituent elements as indicated in the schematic phase diagram given in Fig. 17. The estimated ideal glass transition temperatures $(0.3T_m$ for the elements and $0.52T_m$ for the bulk metallic glass) indicate approximately the temperature range of glass formation as given by the dotted line.

Thus, it becomes obvious that the glass transition temperature seems to be rather weakly dependent on composition. This has been observed experimentally in many instances. In comparison, the melting temperature (liquidus line or $T_v$-line depending on kinetic constraints) exhibits a much more pronounced composition dependence. As such, it is concluded that the glass transition temperature and the glass transition is controlled by the cohesive energy of the alloy whereas the melting transition is rather controlled by the elastic energy of the crystal and stabilization of the liquid due to the chemical enthalpy of mixing. These relationships become even more obvious in the following when discussing the crystal destabilization and the formation of an amorphous solid by externally driven solid state processes.

V. Crystal-to-Glass Transition

1. Thermodynamics and kinetics

Amorphous solids and glasses can be also produced from the solid state by a variety of experimental methods including hydriding of intermetallic compounds, thermal annealing of multilayered thin film specimen or metastable crystalline bulk samples, intense mechanical deformation, mechanical alloying of powder particles or thin metal sheets, ion beam, electron beam or ultraviolet irradiation, compression and decompression besides further chemical method. For this transition to occur both thermodynamic conditions and kinetic constraints must be satisfied with (i) the crystalline phase being prepared in or driven to a non-equilibrium state energetically above that of the amorphous state, and (ii) the formation of crystalline equilibrium phases or phase mixtures often stoichiometric intermetallic compounds-being frustrated by the kinetic constraints imposed at the low reaction temperatures. Then an amorphous structure is found to be formed instead of the stable phase or phase mixture.

Such a transformation to a non-equilibrium state of matter can be described by thermodynamic methods when the kinetic constraints are defined appropriately. Within such a framework, a thermodynamic scenario is developed relating the crystal-to-glass transition to regular melting (crystal to liquid) and to the glass transition itself (liquid to glass). Basically, the destabilization of the crystalline lattice can be obtained by the incorporation of non-equilibrium lattice defects, such as vacancies, antisite defects and interstitials or by the extension of the solid solubility beyond the equilibrium limit far into the supersaturated regime typical for mechanical deformation and bombardment of crystals with high energy particles or chemically driven interdiffusion reactions of crystalline matter, respectively. All of these processes have in common the fact that they lead to static disordering of the parent crystalline material characterized by large defect concentrations and steep concentration gradients. Thus, it is not evident in all cases that local internal equilibrium can be attained. Thus, the use of thermodynamic potentials cannot be generally justified. However, under most experimental conditions where solid state amorphization has been observed, the thermal chemical diffusivity is frequently suppressed in the solid state. Thus, polymorphous conditions prevail which allow an extrapolation of the melting behavior of solid solutions deep into the metastable regime which can be summarized by generalized Clapeyron equations.

The nucleation of the amorphous phase can be treated similar to the crystallization from an undercooled eutectic liquid where the phase selection during crystallization plays a significant role. As indicated schematically in Fig. 18 a driving force for amorphous phase formation...
develops when the α-solid solution is supersaturated beyond cα, i.e. the composition of the α-crystal corresponding to the two-phase metastable equilibrium with the amorphous phase of composition cγ. For concentrations larger than cα a driving force $\Delta G_m$ for amorphous phase formation develops and can be obtained by the parallel tangent construction$^{(109)}$ approximated by$^{(110)}$

$$\Delta G_m = \frac{d^2G^\alpha}{dc^\alpha} \cdot (c^\alpha - c^\gamma) \cdot \Delta c^\gamma$$  \hspace{1cm} (15)$$

where $G^\alpha$ represents the Gibbs free energy of the α-solid solution and $c^\alpha$ and $c^\gamma$ the actual compositions of the amorphous solid (to be formed) and α-solid solution, respectively. Thus, the driving force for the solid-state-amorphization process $\Delta G_m$ increases with increasing supersaturation $\Delta c^\gamma$ of B-atoms. It is expected that the nucleus of the new phase most likely to form is the one with the lowest free energy barrier $\Delta G^*$. This barrier is a function of the driving force $\Delta G_m$, the interfacial energy $\sigma_{ab}$ between crystal and amorphous phase to be formed and the nucleus’ radius $r$. Because the interfacial energy and the radius are only weakly dependent on composition it is expected that a nucleus forms with a composition corresponding to the maximum driving force. Thus, large concentration fluctuations of B-atoms in the α-crystal are essential. Such fluctuations are generally small in the crystalline state but can be greatly enhanced by the presence of high angle grain boundaries$^{(111)}$. When the composition of the solid solution reaches the polymorphic condition at $c_0$ the Gibbs free energies of crystalline and amorphous phases become equal and a transformation to the glassy phase becomes possible without change of composition.

Measuring the enthalpies of transformation for mechanically alloyed Zr–Al alloys indeed indicates an energy cusp at 17 at% Al and demonstrates polymorphic constraints controlling the non-equilibrium phase transition$^{(112)(113)}$.

Figure 19 shows a sequence of X-ray diffractograms for Zr$_{0.75}$Al$_{0.25}$. After 2 h mechanical alloying (see Fig. 19(a)) the (111) Bragg peak related to fcc Al at 38.47° for 2θ is still detectable. Further processing leads to the disappearance of the (111) Al Bragg peaks, indicating that Al has been dissolved completely in Zr after 8 h MA (Fig. 19(b)). In addition, it is found that the Bragg peaks related to α-Zr are shifted towards higher angles when compared with the Bragg peaks of pure Zr. This implies that Al atoms are dissolved in the hexagonal Zr crystal, causing the lattice parameter of α-Zr to shrink. The experimentally determined atomic volume is still larger than that of the corresponding stable phases by 2.5%. This excess volume is comparable to that required for glass formation of ion bombarded Zr$_{1}$Al$_{4}$ (+3%) suggesting a similar underlying mechanism of elastic instability$^{(114)}$. Consequently, during mechanical alloying for more than 12 h the sharp Bragg peaks disappear and the broadened X-ray diffractogram typical for amorphous samples is obtained and shown in Fig. 19(c).

Thus, to form a metallic glass it is necessary to include chemical disorder in the Zr crystal, which can be achieved by alloying with a number of elements having a negative heat of mixing with Zr, such as for example Ni, Cu, Co, Al, Fe, etc. (It should be noted however that in general a negative enthalpy of mixing is not a necessary condition for solid-state amorphization to occur.) Measuring the enthalpy of crystallization of the glass formed by solid-state-amorphization corresponds to 4.3 ± 0.5 kJ/g-at for Zr$_{0.75}$Al$_{0.25}$ (see Fig. 1(b)). With regard to the above discussion (see for example Fig. 16) the enthalpies of crystallization of a metallic glass formed from the solid solid state or from the liquid state seems comparable. However, the exact values depend on the heating rates and the level of structural relaxation of the glass. In general however, it is obvious from a thermodynamic point of view that the energy stored in the crystal must increase above that of the corresponding glassy state in order for glass formation to proceed. This energy can be
estimated for typical laboratory time scales based on the specific heat evaluations discussed earlier.

Whether a crystal to glass transition occurs from a kinetic point of view seems to depend on different conditions, i.e. (i) whether the accumulated elastic strains can be released by the formation of grain boundaries or by a transition to the amorphous structure and (ii) whether recovery processes and atomic re-ordering occurring at the prevalent temperatures prevent the nucleation of the amorphous state. When the kinetic conditions are favorable the crystal-to-glass transition can be analyzed further by a comparison with melting.

2. Relationship with melting

Both, the crystal-to-glass transition and melting are topological order to disorder transitions. The structural similarities of the starting and end phase and the disappearance of long range translational symmetries at the transitions suggest that they are the same\(^{115}\). However, they are distinguished in their kinetics since the atomic mobility is controlled by different time scales.

All melting theories are based on some form of instability or catastrophe which are either vibrational\(^{116}\), elastic\(^{117}\), isochoric\(^{108,109}\), defective\(^{120}\) or entropic\(^{121}\) in nature. In general, these melting theories rely on a homogeneous melting process throughout the entire crystal, even though it is a well known experimental fact that melting starts at lattice defects, such as surfaces and internal interfaces. Thus, it is observed experimentally that regular melting occurs at \(T_m\), i.e. before an instability develops and, as such, represents a first order phase transition as indicated by a well-defined crystal/liquid interface and an entropy of fusion on the order of \(1k_B\). If the effective heterogeneous nucleation sites for the formation of a liquid nucleus can be eliminated, considerable crystalline superheating can be achieved as shown for a variety of materials including oxides\(^{122}\), pure metals\(^{123}\), semiconductors\(^{124}\) and solid Helium\(^{125}\).

Furthermore, as mentioned above a hierarchy of inner instabilities has been developed describing the maximum undercooling. This has also been extended to the melting transition. Thus, for melting as well as liquid undercooling a succession of catastrophe barriers exists including a thermodynamic barrier (equilibrium melting and crystallization), a kinetic barrier (glass formation and shear instability for melting) and finally an entropic barrier (Kauzmann points)\(^{118}\). The locations of these barriers can be estimated based on specific heat and thermal expansion data in addition to the thermodynamic functions measured in the equilibrium state\(^{126,127}\).

It is generally agreed that thermally induced vibrations of atoms in solids play a major role in melting\(^{128}\). A simple vibrational model of Lindemann predicts a lattice instability when the root-mean-square amplitude of the thermal vibrations reaches a certain fraction \(f\) of the next neighbor distances. However, the Lindemann constant \(f\) varies considerably for different substances because lattice anharmonicity and soft modes are not considered, thus limiting the predictive power of such a law considerably. Furthermore, Born proposed the collapse of the crystal lattice to occur when one of the effective elastic shear moduli vanishes\(^{117}\). Experimentally, it is found instead that the shear modulus as a function of dilatation is not reduced to zero at \(T_m\) and would vanish at temperatures far above \(T_m\) for a range of different substances\(^{129}\). In addition, the role of equilibrium lattice defects is not negligible close to the melting point. Due to the entropy stabilization of vacancies at elevated temperatures the specific heat at constant pressure exhibits an increase in addition to the linear term by

\[
e_n^s = \frac{A(\Delta H)^2}{k_B T^2} \exp\left( \frac{\Delta H^*}{k_B T} \right)
\]

where \(\Delta H^*\) represents the heat of formation of a vacancy in the dilute limit and the prefactor \(A\) equals \(\exp(\Delta S^*/k_B)\), \(\Delta S^*\) being the activation entropy of a defect (about \(2k_B\))\(^{129}\). Vacancies in metals are strongly related with the cohesive energy and as such, the heat of formation of a vacancy \(\Delta H^*\) is related to the equilibrium melting point \(T_m\) by the following relationship\(^{131}\):

\[
\Delta H^* = 8 \times 10^{-4} \cdot T_m \text{ (eV / K-atom)}
\]

Extrapolations of measured heat capacity data into the superheated crystal regime allow to determine the thermodynamic properties of a superheated crystal as function of vacancy concentration. In analogy, non-equilibrium melting can simply be analyzed by the consideration of vacancies frozen in the crystal.

By comparing the Gibbs free energies of the undercooled liquid with that of the crystal containing point defects (non-equilibrium melting) the relative stability of such non-equilibrium structures can be evaluated. The virtual melting point of the defective crystal can be determined as a function of vacancy concentration by the equality of the crystal/liquid Gibbs free energies. Such an assumption is fully correct, especially at low temperatures, and with respect to the well known fact that gamma irradiation lowers the melting points of pure metals by an amount which is proportional to the dose, \(e.g.\) the number of point defects generated.

Consequently, a generic non-equilibrium phase diagram can be developed as shown in Fig. 20 indicating a decrease of the virtual melting point as a function of vacancy concentration\(^{132}\). The melting curve with the slope \(dT/dc_\text{v} = (\partial \Delta G / \partial c_\text{v}) / \Delta S_\text{v}\) corresponds to the \(T_m\)-lines in binary phase diagrams. The isentropic and isenthalpic temperatures are additionally included as function of vacancy concentration. It is seen that the melting line \((\Delta G = 0)\), isentropic temperature \((\Delta S = 0)\) and isenthalpic temperature \((\Delta H = 0)\) must intersect at the temperature \(T\) and vacancy concentration \(c_\text{v}^*\). At this condition, melting is reduced to an isentropic transition with \(\Delta G = \Delta S = \Delta H = 0\) (no latent heat).

3. A universal phase diagram

The phase diagrams of typical glass-forming metallic alloys are usually characterized by the formation of "deep" eutectics and thus by steeply plunging \(T_c\)-lines.
In analogy to a Lindemann-model the melting transition of a crystalline solid solution can be described by including the static disorder in addition to the temperature induced dynamic disorder. Computer simulations as well as analytical solutions can be based on the elastic energy contribution due to atomic size mismatch. As such, the uncertainty of atom position $w$ for a binary alloy with concentrations $c_1$ and $c_2$ and atomic radii $r_1$, $r_2$ corresponds to:

$$w^2 = \frac{\langle (\Delta r)^2 \rangle}{d_1^2} = \frac{\langle (\Delta r)^2 \rangle}{d_2^2} + \frac{4\langle (\Delta r_{12})^2 \rangle}{d_2^2}$$

(18a)

with

$$\langle (\Delta r_{12})^2 \rangle = c_1 c_2 (r_1 - r_2)^2$$

(18b)

and the melting temperature $T_m$:

$$T_m = \frac{M_k \theta_1 d_1^2 d_2^2}{9\hbar^2} x_m \left( 1 - \frac{4\langle (\Delta r_{12})^2 \rangle}{x_m^2 d_2^2} \right)$$

(19)

Good agreement between the prediction and experimental data for solid solutions with relatively flat $T_c$ lines and small atomic size difference is obtained for $x_m = 0.15$ for bcc, $x_m = 0.11$ for the fcc structure.

For glass forming alloys with steep liquidus curves a different approach has been chosen based on elasticity theory as described in Ref. (134). As a result, the energy rise necessary for solid-state amorphization to occur corresponds to 1.4% of the cohesive energy (or 40% of the enthalpy of fusion). The corresponding critical local atomic level volume strain $\varepsilon$ amounts to about 11%. In the case of Ni-Zr alloys the critical solubility of Ni in hex-Zr corresponds to 8 at% and of Zr in fcc Ni to 18 at%.

Further molecular dynamic studies have suggested the possibility of solid-state-amorphization to occur when the atomic size difference exceeds 0.83. In this simulation, amorphization occurs when both the volume and enthalpy of the crystalline solid solution become equal to those of the glass. Close to the expected pseudo-critical point the transition appears almost isenthalpic and isochoric with a vanishing "tetragonal" shear constant $(C_{11} - C_{12})/2$. Thus, the isentropic condition in Fig. 9 at $(e^*, T^*)$ and the shear rigidity criterion and the equal volume criteria degenerate into one limit for crystal stability when the crystal is sufficiently disordered.

Based on the approach presented here a first-order phase transition, such as melting, can be reduced to an isentropic transition and possibly to a second-order phase transition by the variation of the degree of crystalline disorder. Furthermore, the metastable phase diagram proposed for binary alloys distinguishing the metastable crystal, liquid and glass phases is of generic character. It applies for defect-systems as well. The phase diagram indicates the structural stability of non-equilibrium phases with strong similarities to the magnetic glass transition including the corresponding Nishimori lines. It is basically characterized by a general, tunable parameter, characteristic for the degree of crystal disorder or frustration which can correspond to alloy composition, defect concentration, pressure, excess free volume, reciprocal particle or grain size etc. Above a certain degree of frustration around the predicted instability point the ordered crystalline state becomes unstable against liquid-like heterophase fluctuations and the system collapses to a disordered glassy or liquid-like state. This describes the crystal-to-glass transition under polymorphous constraints.

When the same polymorphous constraints hold during undercooling of a liquid the glass transition becomes favored. Assuming that the eutectic composition $c_E$ lies outside of the $T_c$-condition ($c_E > c^*$) solidification to a polymorphic crystal would be strictly impossible since it lies outside of the stability range of that crystal (see for example Fig. 17). Thus, as long as compositional fluctuations are limited glass formation becomes favored and bulk glass formation possible.

Acknowledgments

The financial support by the Deutsche Forschungsgemeinschaft (Fe 313/8) as well as the German Space Agency (DARA 50-WH-9431-1) is gratefully acknowledged. The author would like to thank many coworkers and colleagues and, in particular, Prof. P. Desrê, Prof. H. Gleiter, Prof. W. L. Johnson, Dr. S. Klose, Prof. J. H. Perepeko, Prof. K. Samwer and Dr. R. Wunderlich for discussions and support over the years.

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