

# Chapter 1

## Introduction

The first metallic glass was reported by Klement and Duwez at the California Institute of Technology in 1960 [1]. The first metallic glass system,  $\text{Au}_{75}\text{Si}_{25}$ , was found during an effort to increase the solid solubility of the Au Si system in which the system was cooled at a rate of  $10^5$ – $10^6$  K/s. As it turned out this cooling rate was sufficient to bypass crystallization resulting in a metallic glass. These initial glasses were only available in thin strips and splats which severely limited the uses to which they could be applied. The first Bulk Metallic Glass (BMG), a glass capable of being cast into sections greater than 1 mm, was developed by Chen in 1974 [2]. The composition was based on the Pd-Cu-Si alloy system.

When creating a metallic glass it is necessary to cool the liquid quickly enough to bypass the nose on the Time-Temperature-Transformation (TTT) diagram for crystallization. The nose of the TTT diagram corresponds to the temperature at which the material crystallizes the fastest. If the cooling rate is fast enough to avoid crystallization at the nose the material will form a glass. BMGs have a lower thermodynamic driving force towards crystal nucleation and growth than ordinary metallic glasses, resulting in the nose of the TTT diagram being pushed out to longer times. When the nose of the TTT diagram is pushed out to longer times the critical cooling rate is lowered, and thicker sections of material can be cast amorphous. Therefore, due to their increased liquid stability, BMGs have an increased glass forming ability [3, 4]. One example of a BMG is

commercial Vitreloy 1 which has a critical cooling rate of 1 K/s, compared to the  $10^5$ – $10^6$  K/s needed for the original metallic glasses [5].

In a normal metal the atoms are arranged in an orderly crystalline arrangement. In a metallic glass the liquid has been rapidly undercooled to the point at which nucleation and growth of crystals has been arrested. Therefore, the amorphous structure of the liquid is retained even at room temperature, resulting in a glass. The deformation mechanisms that exist in normal metals, such as dislocations, do not occur in metallic glasses. This is due to the random nature of the glass inhibiting the formation of preferential directions for deformation. Instead, highly localized shear bands account for the deformation seen in metallic glasses. This difference in deformation mechanisms leads to a lower Young's Modulus and a higher yield strength than are found in normal metals. Additionally, the lower Young's Modulus and higher yield strength result in increased elasticity for metallic glasses when compared to conventional metals [6, 7]. At low temperatures metallic glasses fail by a single catastrophic shear band, since the matrix is unable to dissipate the stored energy on the time scale of the deformation [3]. The fracture surfaces associated with metallic glasses exhibit vein-like patterns indicating a decrease in the glass viscosity during failure [8]. From high-strain-rate experiments it has been proposed that local melting occurs during unstable fracture and is what gives rise to the observed fracture surfaces [9-11].

The kinetics of metallic glasses are intimately tied to the absolute temperature of the material. Metallic glasses are shown to undergo glass transition and crystallization phenomenon in contrast to the melting associated with crystalline metals. The glass transition is traditionally defined as the temperature at which the viscosity is equal to  $10^{12}$

Pa-s, which corresponds to a laboratory time scale. Crystallization in metallic glasses is a kinetically governed stochastic process in which crystal nuclei form and then grow.

Therefore, as the metallic glass is heated to higher temperatures, the kinetics of the material continue to increase until the kinetics are fast enough for crystallization to occur.

Crystallization in metallic glasses is dominated by a high number density of formed nuclei and slow-growth kinetics, and is very history dependent [12-18]. If large numbers of nuclei have formed during a previous processing stage of the material it will exhibit a lower crystallization temperature and reduced performance in comparison to a fully amorphous sample.

Metallic glasses flow plastically in between the glass transition and crystallization temperatures due to a decrease in the viscosity of the material. The liquid viscosity will continue to decrease as the temperature increases until crystallization occurs. Due to the increased thermal stability of BMGs it has become possible to apply plastic processing to a metallic glass system. Most plastic processing experiments have been done below the nose of the TTT diagram. In this procedure material is plastically deformed at a temperature between the glass transition and crystallization temperatures. When plastically processed in this manner metallic glasses are capable of surface feature replication on the size scale of 1  $\mu\text{m}$  [19-21]. Furthermore, it is possible to do net shape forming with appropriately engineered molds. Micro-forming techniques have also been applied to these materials in an effort to utilize the enhanced ductility of these materials at small length scales for use in micro-nano devices [22-25]. Another plastic processing route may be attempted if the heating rate is fast enough, or if a liquid melt is supercooled [14]. In this method, crystallization is avoided by processing above the nose of the TTT

diagram at greatly reduced viscosities. After processing the material must be quenched to room temperature quickly enough to again avoid crystallization at the nose.

If metallic glasses are to be used as engineering materials it is necessary to be able to measure and predict their properties. Furthermore, it is necessary to know how those properties will change during deformation and relaxation. The objective of this dissertation is to develop and validate an analytical model capable of predicting the flow behavior of metallic glasses. Additionally, this dissertation will identify the processes controlling both the transient and steady-state responses of metallic glasses. In Chapter 2 a model is put forward linking the isoconfigurational shear modulus of the material with the viscosity during deformation. In Chapter 3 rheological data for  $\text{Pt}_{57.5}\text{Ni}_{15.3}\text{Cu}_{14.7}\text{P}_{22.5}$  is presented and the model of Chapter 2 is applied to it. Chapter 4 investigates the fragilities of glass-forming systems using the model presented in Chapter 2. Chapter 5 establishes that elastic softening in metallic glasses is governed by a unique functional relationship between the isoconfigurational shear modulus and configurational enthalpy. In Chapter 6 the relaxation processes of metallic glasses are investigated using the changes in material properties associated with the transient stress strain response of specimens subjected to isothermal deformation. Additionally, the criteria for shear localization and the barrier height controlling flow are investigated using the steady-state flow properties of the material at different strain rates. Chapter 7 will summarize the current work, and Chapter 8 will present possible future work.

## References

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