Chapter 1

OVERVIEW, MOTIVATIONS, AND KEY CONTRIBUTIONS

1.1. Historical Background

An amorphous solid is a solid in which there is no long-range order of the positions of the atoms. The term "metallic glasses" refers to amorphous metallic alloys. Unlike conventional crystalline metals, metallic glasses must be cooled rapidly from the liquid state to freeze their random atomic structure in place before crystallization occurs due to the nucleation and growth of crystal grains. Consequently, the forming of metallic glasses can be realized by solidification of liquid alloys at cooling rates sufficiently high to suppress the nucleation and growth of competing crystalline phases. As a result of developing rapid solidification techniques for chilling metallic liquids at high cooling rates of $\sim 10^6$ K/s, Duwez and coworkers at Caltech in 1960 reported the first Au-Si metallic glass [1]. Earlier, Turnbull predicted that when the ratio of glass transition temperature to the liquidus temperature (reduced glass transition temperature) approaches 2/3, the homogeneous nucleation of crystals in the undercooled melt should get very sluggish on the lab time scale [2, 3]. This criterion remains one of the best "rules of thumb" to date for predicting the glass-forming ability of a liquid [4].

The extremely high cooling rate required to suppress crystallization upon cooling restricts the material geometry to thin ribbons, foils, and powders of a dimension up to a few hundred micrometers. Therefore, the engineering interest in them focused mainly on their electronic and magnetic properties. To produce practical metallic glasses for structural applications, a lot of effort has been made both to improve the processing technology for higher achievable cooling rates and to search for good glass-forming alloy systems with lower critical cooling rates.

The first finding of millimeter-diameter glassy rods was achieved by Chen and coworkers in the early 1970s using simple suction casting methods at significantly lower cooling rates (in the range of 10^3 K/s) in the Pd-Cu-Si ternary system [5]. This was the success of pushing the size of cast metallic glass from the micron to the millimeter range and these Pd-Cu-Si ternary amorphous alloys were likely the first examples of "bulk" metallic glasses (BMGs). Using boron oxide fluxing methods, Turnbull and coworkers demonstrated the formation of ~1 cm vitrified ingots of a Pd-Ni-P alloy with a reduced glass transition temperature of ~ 2/3 at cooling rates below 100 K/s [6, 7].

During the late 1980s, exceptional glass-forming ability in the rare-earth-rich alloys was found by Inoue and coworkers. They studied La-Al-Ni, La-Al-Cu, and La-Al-Cu-Ni materials and developed alloys to form glasses with critical casting thicknesses ranging toward 1 cm [8-10]. Shortly after, Mg-Cu-Y bulk-glass-forming alloys and a family of multi-component Zr-Cu-Al-Ni alloys were also developed [11-16]. These multi-component glass-forming alloys illustrated that bulk glass formation was not confined to

exotic Pd-based alloys, and opened the door to the development of other broad classes of BMGs.

In 1993, Johnson and Peker developed a family of highly processable BMGs based on Zr, Ti, Ni, Cu, and Be, which remains among the best glass-forming alloy systems discovered to date [17, 18]. One extensively studied example of this glass family is Vitreloy 1 ($Zr_{41.2}Ti_{13.8}$ -Cu_{12.5}Ni₁₀Be_{22.5} (at. %)), which has a critical cooling rate of ~ 1 K/s and can be cast in rods with a diameter of up to 5 cm. Vitreloy 1 has been utilized commercially to produce items including sporting goods and electronic casings.

Bulk glass formation in multi-component alloys was primarily attributed to the chemical complexity of these systems [4, 19]. In 1996, Johnson summarized that nearly all the discovered bulk metallic glasses can be described as pseudo-ternary alloys of the form ETM-LTM-SM, where ETM stands for early transition metals or Lanthanide-group metals such as Zr, Ti, Nb, and La; LTM is an abbreviation for late transition metals such as Fe, Co, Ni, and Cu; and SM refers to simple metals such as Al, Be, or Mg [20, 21]. Empirical factors in the formation of multi-component BMGs include: (1) a composition which favors a deep eutectic in the phase diagram; (2) significant differences in atomic sizes and chemical differences among the main constituent elements; and (3) an alloy composition containing at least three elements. Over the past decade, much attention has been paid to the development of multi-component alloy systems with high glass-forming ability and exceptional stability with respect to crystallization. To date, scores of cm-sized BMGs in a variety of alloy systems have been documented (see Table 1.1 and Figure 1.1) [22-24].

System	Composition	Critical Size, D _c (mm)	Method	Year	Ref.
Pd-based	$Pd_{40}Ni_{40}P_{20}$	10	Fluxing	1984	[7]
	$Pd_{40}Cu_{30}Ni_{10}P_{20}$	72	Water quenching	1997	[25]
Zr-based	Zr ₆₅ Al _{7.5} Ni ₁₀ Cu _{17.5}	16	Water quenching	1993	[15]
	$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	25	Copper mold casting	1996	[17]
	$Zr_{44}Cu_{40}Ag_8Al_8$	15	Copper mold casting	2006	[26]
	$Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$	15	Copper mold casting	2007	This thesis
Mg-based	$Mg_{65}Y_{10}Cu1_5Ag_5Pd_5$	12	Water quenching	2001	[27]
	$Mg_{54}Cu_{26.5}Ag_{8.5}Gd_{11}$	25	Copper mold casting	2005	[28]
	Mg65Cu7.5Ni7.5 Zn5Ag5Y5Gd5	14	Copper mold casting	2005	[29]
RE-based	$Y_{36}Sc_{20}Al_{24}Co_{20}$	25	Water quenching	2003	[30]
	La ₆₂ Al _{15.7} Cu _{11.15} Ni _{11.15}	11	Copper mold casting	2003	[31]
Cu-based	$Cu_{46}Zr_{42}Al_7Y_5$	10	Copper mold casting	2004	[32]
	$Cu_{49}Hf_{42}Al_9$	10	Copper mold casting	2006	[33]
	$Cu_{44.25}Zr_{35}Ti_5Ag_{14.75}$	10	Copper mold casting	2006	[34]
Fe-based	$Fe_{48}Cr_{15}Mo_{14}Er_2C_{15}B_6$	12	Copper mold casting	2004	[35, 36]
	$(Fe_{44.3}Cr_5Co_5Mo_{12.8}Mn_{11.2})$	12	Copper mold casting	2004	[37]
	$C_{15.8}B_{5.9})_{98.5}Y_{1.5}$				
	$Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$	16	Copper mold casting	2005	[38]
Ca-based	$Ca_{65}Mg_{15}Zn_{20}$	15	Copper mold casting	2004	[39]
Pt-based	Pt _{57.5} Cu _{14.7} Ni _{5.3} P _{22.5}	20	Water quenching	2004	[40, 41]
Ti-based	$Ti_{40}Zr_{25}Cu_{12}Ni_{3}Be_{20}$	14	Copper mold casting	2005	[42]
Co-based	$Co_{48}Cr_{15}Mo_{14}C_{15}B_6Er_2$	10	Copper mold casting	2006	[43]

Table 1.1: Summaries of bulk metallic glass alloys with critical Size \geq 10 mm.



Figure 1.1. Record-size bulk metallic glasses (BMGs) developed in various alloy systems and the year of their discovery. The first metal (e.g., Zr in ZrTiCuNiBe) is the base element in each alloy. Alloy systems in which the BMG diameter has not reached 1 cm in copper mold casting are not included. (Reproduced from Ref. [22]. Copyright 2007 Materials Research Society.)

1.2. Mechanical and Rheological Aspects of BMGs

BMGs usually have very high yield strength, at least double that of ordinary commercially used crystalline materials, and high elastic strain limit of roughly 2% in tension or compression, due to their disordered atomic structure [4, 19]. They exhibit the best performance index σ^2/E and good values of the index $\sigma^2/\rho E$ (see Figure 1.2), where σ , ρ , and E are respectively the yield strength, density, and Young's modulus [44]. Cobalt-based Co-Fe-Ta-B and Co-Fe-Ta-B-Mo BMGs achieved record compressive fracture strength (σ_f) of 5.2 and 5.5 GPa at room temperature, approaching the theoretical strength. Fe-based BMGs exhibit σ_f of ~ 4 GPa, Ni-based show ~ 3 GPa, and both Zr-and Cu-based show ~ 2 GPa. Unfortunately, the Achilles heel of metallic glasses is their rather limited ductility and low resistance to the propagation of a crack. In tension, metallic glasses fail catastrophically on one single or a few dominant shear bands, exhibiting little overall plasticity [45-47].

Recently, it was reported that some BMGs can undergo surprisingly extensive plastic deformation under compression or bending tests [44]. Schroers and Johnson reported that large macroscopic compressive plasticity was observed in a Pt-based BMG, which was attributed to a high Poisson's ratio leading to suppression of crack nucleation and propagation [41]. Eckert and coworkers found a "work hardening effect" under compressive testing in a Cu-Zr-Al and a Ti-Cu-Ni-Zr-Sn metallic-glass-forming alloys [48, 49]. The work-hardening capability and ductility was attributed to a unique structure related to nano-scale inhomogeneity, leading to proliferation of shear banding, shear band-

material interactions, and multiplication of shear bands. Inoue and coworkers reported that as-cast 1 mm Cu-Zr binary glassy rods could sustain a compressive plastic strain of more than 50% at room temperature due to a dispersion of embedded nano-crystals [50]. In this 1 mm rod, strain softening caused by localized shearing was verified to be effectively inhibited by nano-crystallization produced by the plastic flow within the shear bands. This leads to large plasticity and strain hardening [51]. In 2007, Wang and coworkers found that by adjusting the composition to maximize Poisson's ratio in Zr-Cu-Ni-Al alloys, the resulting BMG could sustain high deformation without fracture both under compression and under bending tests [52]. Microstructural analysis indicated that this Zr-Cu-Ni-Al bulk metallic glass is composed of nano-scale hard regions surrounded by soft regions, which enabled arrest of shear bands and enhanced plasticity.

Other approaches to solve the problem of low plastic strain include developing in-situ and ex-situ metallic glass composites and amorphous foam structures [23]. For the in-situ case, the original glass-forming composition is varied toward that of the primary crystallizing phase. This ductile phase then crystallizes first as dendrites. The remaining liquid solidifies as a BMG matrix. This two-phase structure is effective in increasing shear band population and in hindering propagation of shear bands. This in turn results in a dramatic increase in the plastic strain to failure, impact resistance, and toughness of the metallic glass [53-71]. Two-phase composites can also be produced through the introduction of foreign particles into the liquid alloy, followed by quenching [72-82]. Usually, plastic strain is improved by sacrificing the yield strength. In this case, soft particles are even more effective in improving plastic strain [82]. Recent progress indicates that pores are also effective in preventing catastrophic failures resulting from shear band localization [83-93].



Figure 1.2. Elastic limit (strength σ_y) plotted against Young's modulus *E* for bulk metallic glasses and over 1500 conventional metals, alloys, and composites. The contours show the yield strain, σ_y/E , and the resilience, σ_y^2/E . (Reproduced from Ref. [94]. Copyright 2006 Elsevier B.V.)

Many research efforts have been devoted to understanding the deformation and fracture behavior of bulk metallic glasses. One interesting observation is that the properties of metallic glasses are remarkably well correlated with each other, which will lead to fruitful research opportunities. Johnson and Samwer analyzed the room-temperature elastic constants and compressive yield strength of ~ 30 bulk metallic glasses and discovered that an average shear limit $\gamma_c = 0.0267 \pm 0.0020$, where $\tau_y = \gamma_c G$ is the maximum resolved shear stress at yielding, and G the shear modulus (see Figure 1.3) [95]. A cooperative shear model, inspired by Frenkel's analysis of the shear strength of solids, is proposed. It reveals that the plastic flow barrier scales closely with shear modulus. This will be described in detail in the next section. In addition, the elastic moduli are closely correlated with the strong/fragile characteristics of the glass-forming liquid, possibly with the glass-forming ability, and with the toughness/brittleness of the glass [22]. Earlier research showed that the ductile behavior of BMGs is correlated with their Poisson's ratio, v [96]. For instance, the Pt-based BMG with high v of ~ 0.41 shows excellent compressive ductility and high fracture toughness, while the Fe-based BMG with low v of ~ 0.30 shows poor ductility and low fracture toughness [41, 97]. It was also reported that the "critical Poisson's ratio" for compressive plasticity in Fe-Mo-C-B-Ln BMGs is about 0.32, where an onset of plasticity was observed [97]. Novikov and Sokolov reported that Poisson's ratio v of a glass at room temperature is correlated with the fragility of glass-forming liquid at high temperature (see Figure 1.4 and 1.5) [98-100]. Wang also observed a rough correlation between the liquid fragility and elastic properties of the BMG (see Figure 1.6) [101]. Lewandowski and coworkers demonstrated a correlation between the critical fracture energy and the elastic

constants of metallic glasses [102]. Glasses with low B/G or v tend to be brittle, whereas those with high B/G or v are tough (see Figure 1.7). A rough conclusion that can be drawn from these correlations is that BMGs with low v in the glassy state tend to have higher glass-forming ability but lower ductility and toughness (see table 1.2) [103]. Based on these correlations, the assessment of elastic properties can assist in selecting alloying components to guide BMG designs [101-104].

The link between thermodynamic, kinetic, elastic, and plastic properties of metallic glasses is remarkable, and seems to provide predictability for these disordered systems at a level that exceeds that for their ordered crystalline cousins [22]. The challenge now is to understand these correlations, and to employ such understanding to develop new glass compositions with good-glass forming ability and mechanical toughness.

Table 1.2. Expected qualitative correlations of values of selected properties with the kinetically stron	g oi
fragile behavior of the supercooled liquid in bulk-metallic-glass-forming systems.	

Glass characteristic	Viscosity	Glass-Forming Ability	Fracture Toughness	Poisson Ratio	Gibbs Free Energy
Kinetically strong	High	High	Low	Low	Small
Kinetically fragile	Low	Low	High	High	High



Figure. 1.3. Experimental shear stress at yielding, $\tau_y = \sigma_y/2$, vs. shear modulus *G* at room temperature for 30 bulk metallic glasses. (Reproduced from Ref. [95]. Copyright 2005 American Physical Society.)



Figure. 1.4. Angell plot comparing the viscosities of different types of glass-forming liquids. (Reproduced and corrected from Ref. [103]. Copyright 2007 Materials Research Society.)



Figure. 1.5. Correlation between fragility of liquids *m* and the ratio of instantaneous bulk to shear modulus *K/G* of respective glasses. Circles--data for nonmetallic glass formers; triangles--data for metallic glass formers; solid lines--linear fits, Eqs. $m = (7 \pm 2)K/G + (24 \pm 10)$ (BMG) and $m = (29 \pm 2)K/G - (12 \pm 5)$ (nonmetals). (Reproduced from Ref. [100]. Copyright 2006 American Physical Society.)



Figure. 1.6. The correlation between m and B/G for metallic glasses. (Reproduced from Ref. [101]. Copyright 2006 American Institute of Physics.)



Figure. 1.7. The correlation of fracture energy with Poisson's ratio for all the collected data on metallic glasses (as-cast and annealed). (Reproduced from Ref. [102]. Copyright 2005 Taylor and Francis.)

1.3. Potential Energy Landscape Theory and Cooperative Shear Model

The concept of "potential energy landscape (PEL)" was first proposed by Goldstein in 1968 to provide a description of the flow process in viscous liquids [105]. In his paper, Goldstein formulated dynamics in terms of the 3N-dimensional PEL as a function of all the atomic coordinates of an N-atom system. The potential energy surface that represents the liquid or the glassy region has a large number of absolute minima of varying depths. At low temperatures, a glass configuration is at or near a potential energy minimum. As temperature is raised, sufficient thermal energy will allow transitions to occur over potential barriers, which separate the minima. Progress towards understanding glasses and liquids has been made using this picture. Stillinger, Weber, Debenedetti, Sastry, and coworkers formulated an exact thermodynamic theory based on partitioning the PEL into basins of attraction surrounding local minima. The basins are called inherent structures (IS) [106-118]. They mapped each liquid configuration to an IS via steepest descent minimization by molecular dynamics (MD) simulations. They were able to evaluate the thermodynamic Helmholtz free energy, equation of state, and other thermodynamic quantities of the system. The connection between fragility and PEL was studied and constructed [98, 119-121]. Wales and coworkers used catastrophe theory to describe the surface geometry changes of the PEL with parameters in the interatomic or intermolecular potential, and provided universal scaling relations among barrier heights, path lengths and vibrational frequencies [122-133]. The landscape picture provides a natural separation of low-temperature motion into sampling of the distinct potential energy minima, and vibration within each minimum. It is therefore possible to separate formally the

corresponding configurational and vibrational contributions to a liquid's properties [111, 134-144]. Lacks and coworkers investigated the volume dependence of the PEL, shear-induced changes in the PEL, and how these changes are related to flow fracture and shear avalanches in disordered systems [145-151].

PEL/IS theory of glass-forming liquids has been extensively used to rationalize and explain the thermodynamics, kinetics, and relaxation behavior of diverse liquids. To describe the yielding in metallic glasses, Johnson and Samwer developed a Cooperative Shear Model for the glassy states of BMGs [95]. The yielding strength of metallic glasses is thought to be determined by the cooperative shear motion of atomic clusters, termed shear transformation zones (STZs) [45-47, 152-163]. In the PEL/IS theory, the energy landscape of the system consists of a large population of basins associated with local minima that are configurational states of the liquid. The configurational states are separated by saddle points that constitute the barriers for hopping between configurations. Following Frenkel's calculation of the theoretical shear strength of dislocation-free crystals [164], the potential energy of an STZ can be described by a periodic stored elastic energy density function, $\phi(\gamma)$. It is assumed that the average potential energy as a function of shear strain in the vicinity of a basin is sinusoid. The total potential energy barrier for plastic shearing of an STZ, $W(\gamma)$, is the integral of $\phi(\gamma)$ over the effective volume of the STZ. The function $\phi(\gamma) = \phi_0 \sin^2(\pi \gamma / 4\gamma_c)$ is minimum at zero applied strain, and increases to a maximum at shear barrier of strain $2\gamma_c$ (see Figure 1.8).

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For an infinite elemental crystal, the periodic minima of $\phi(\gamma)$ correspond to a perfect crystal configuration since the atoms are indistinguishable. There is no configurational entropy. However, for the glassy liquid, there are many stable atomic configurations corresponding to the ISs of the glass. In the energy-density function, γ_c , is the yield strain limit of the material, which is found to be a universal constant based on the data of over 30 known BMGs. The critical yield stress is $\phi'|_{\text{max}} = \tau_c = \pi \phi_0 / 4 \gamma_c$. For the unstressed solid, $G = \phi''|_{\gamma=0}$, giving $\phi_0 = (8/\pi^2)G\gamma_c^2$. Therefore, the total potential energy barrier for an STZ is $W = \phi_0 \zeta \Omega = (8/\pi^2)G\gamma_c^2 \zeta \Omega$, where Ω is the actual volume of the STZ defined by the plastic core, and ζ is a "Eshelby" correction factor arising from matrix confinement of a dressed "STZ" [95, 165-167].

The Cooperative Shear Model constructs a scaling relationship among the shear flow barrier, a universal critical yield strain, and the isoconfigurational shear modulus G. The model reveals that for a fixed glass configuration, the barrier height for shear flow is proportional to the isoconfigurational shear modulus G. It is also found that G has a strong dependence on the specific configurational potential energy of the equilibrium liquid, and the temperature dependence of G in the liquid state is directly related to the fragility of the metallic-glass-forming liquid [166, 168]. In addition, based on the link between elastic softening and configurational changes, a rheology law of metallic-glass-forming liquids has been proposed and validated, in which G was identified to be the effective thermodynamic state variable controlling flow [165, 167]. The isoconfigurational shear modulus G plays a controlling role in understanding the yielding and rheological behavior of metallic glasses and liquids. Thus it can be utilized to design and develop rather fragile glass-forming systems with high ductility and toughness [104].



Figure. 1.8. Potential energy density function, $\phi/\phi_0 = \sin^2(\pi\gamma/4\gamma_c)$, in the vicinity of an inherent state, where ϕ is the barrier energy density and $4\gamma_c$ the average configurational distance.

1.4. Motivations and Key Contributions

In 2004, simple binary glass-forming systems were brought to attention. Binary alloys had been previously considered as a forbidden area to form bulk amorphous alloys. The binary Cu₆₄Zr₃₆, Cu₄₆Zr₅₄, and Cu₆₄Hf₃₆ alloys were first reported to readily form bulk glasses by the Caltech Johnson Group [32, 169-171]. The discovery of bulk-glass formers in binary systems, from an engineering point of view, can provide important guidance in the search for exceptional glass-forming alloys. This can potentially improve the current alloy development efficiency. Also simple binary systems would open avenues towards better understanding of fundamental theoretical problems. The atomic-level short-range structures, thermodynamic modeling, and computer simulations become more readily tractable by avoiding the difficulties encountered in higher-order alloys where complex multi-component interactions are involved [171].

The Cooperative Shear Model predicts that the barrier height for shear flow for a given glass or liquid configuration should be proportional to the isoconfigurational shear modulus. For an equilibrium liquid near and above T_g , the IS configuration and corresponding configurational enthalpy depend on temperature. It is natural to inquire how the elastic constants of the liquid depend on the liquid configuration, or on configurational enthalpy. In the present thesis study, we combined molecular dynamics (MD) simulations and experiments to systematically investigate the Debye-Grüneisen thermal expansion effect, and the configurational potential energy dependence of elastic properties for glassy states. Furthermore, we utilized the correlation between elastic properties and fragility as a guiding tool to design and to develop novel bulk metallic glasses.

In Chapter 2 we fit the effective Rosato-Guillope-legrand (RGL)-type force field parameters for a binary Cu-Zr alloy system, carry out MD simulations, and study the glass transition and the atomic-level structure of this system. It is extremely important to create appropriate interatomic potentials, generate glassy configurations, and study the local atomic structures of the system before we advance to the next step. An effective tightbonding RGL-type n-body force field for the binary Cu-Zr alloy system is constructed and employed in our MD simulations. Partial radial distribution functions, coordination numbers, and Honeycutt Andersen (HA) indices have been calculated to analyze the local structures of Cu₄₆Zr₅₄ metallic glass. Chapter 3 reports the strong dependence of elastic properties on configurational changes in a Cu-Zr binary metallic glass assessed by molecular dynamics simulations. It is shown that the shear modulus' dependence on the specific configurational inherent state of metallic glasses is much stronger than the dependence on Debye-Grüneisen thermal expansion. The isothermal equation of state (EOS) in a wide range of temperatures and pressures obtained by MD simulations on a simple binary model metallic glass is described in Chapter 4. Pressure-induced cavitation is observed at varying temperatures from our simulations. The intrinsic origin of why and how Poisson's ratio or the ratio of G/B is involved in the deformation and fracture behavior of glasses is argued. The compositional dependence of thermal and elastic properties of Cu-Zr-Be ternary bulk-metallic-glass forming alloys is systematically studied in Chapter 5. Shear modulus, G, and Poisson's ratio, v, are very sensitive to changes in compositions. Low G, and relatively high v can be achieved with high Zr concentration by eliminating Ni and Ti. Chapter 6 discovers lightweight Ti-based bulk amorphous structural metals with more than double the specific strength of conventional titanium alloys. These amorphous

alloys exhibit good glass-forming ability, exceptional thermal stability, and high strength. The research results have important implications for designing and developing low-density bulk metallic glasses. In Chaper 7, we report a lightweight (ρ = 5.4 g/cc) quaternary glass-forming alloy, Zr₃₅Ti₃₀Cu_{8.25}Be_{26.75}, having the largest supercooled liquid region, (ΔT = 159 K at 20 K/min heating rate) of any known bulk-glass-forming alloy. The alloy can be cast into fully amorphous rods of diameter ~ 1.5 cm. The under-cooled liquid exhibits an unexpectedly high Angell Fragility of m = 65.6. Based on these features, it is demonstrated that this alloy exhibits "benchmark" characteristics for thermoplastic processing. Starting from the two binary bulk-glass formers in the Cu-Zr system, we systematically investigated the compositional dependence of glass formation, thermal, elastic, and mechanical properties in the Cu-Zr-Ag ternary alloys in Chapter 8. Both Cu_(50-x)Zr₅₀Ag_x and Cu_(64-x)Zr₃₆Ag_x series alloys show a good combination of high glass-forming ability and high Poisson's ratio.

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