Chapter 1

Introduction

1.1 Background and Origin of Study

The unique chemical and physical properties of transition metals and their alloys make them useful in various industrial, scientific, and technological applications. [1–3] Transition metals, such as iron, nickel, and platinum, exhibit catalytic properties due to their easy electron exchangeability. Some transition metals, say, iron, cobalt, and nickel show ferromagnetic properties. Transition metals are often alloyed with other metals or elements to improve their properties for structural, thermal, and electronic applications. Alloys of transition metals exhibit enhanced mechanical properties such as hardness, ductility, and tensile strength. Stainless steels, the alloys that contain iron, chromium and nickel, are valued for their corrosion resistance in harsh environments such as chemical processing, marine engineering, and biomedical devices. When metallic liquid alloys are rapidly quenched to form glasses-disordered solids that lack long-range order and grain boundaries, their mechanical properties (strength, hardness, elasticity), corrosion and wear resistance, magnetic properties, and catalytic properties become superior to their crystalline counterparts. [3–10] However, the necessity of high cooling rates ($10^5 - 10^6$K/s) for stabilising binary liquid alloys against crystallisation in the supercooled region severely restricted the physical dimensions of the produced metallic glasses; limiting their use in actual applications. [1, 11] Thin films/ribbons or wires of metallic glasses with a thickness/diameter of a few μm could be produced using splat

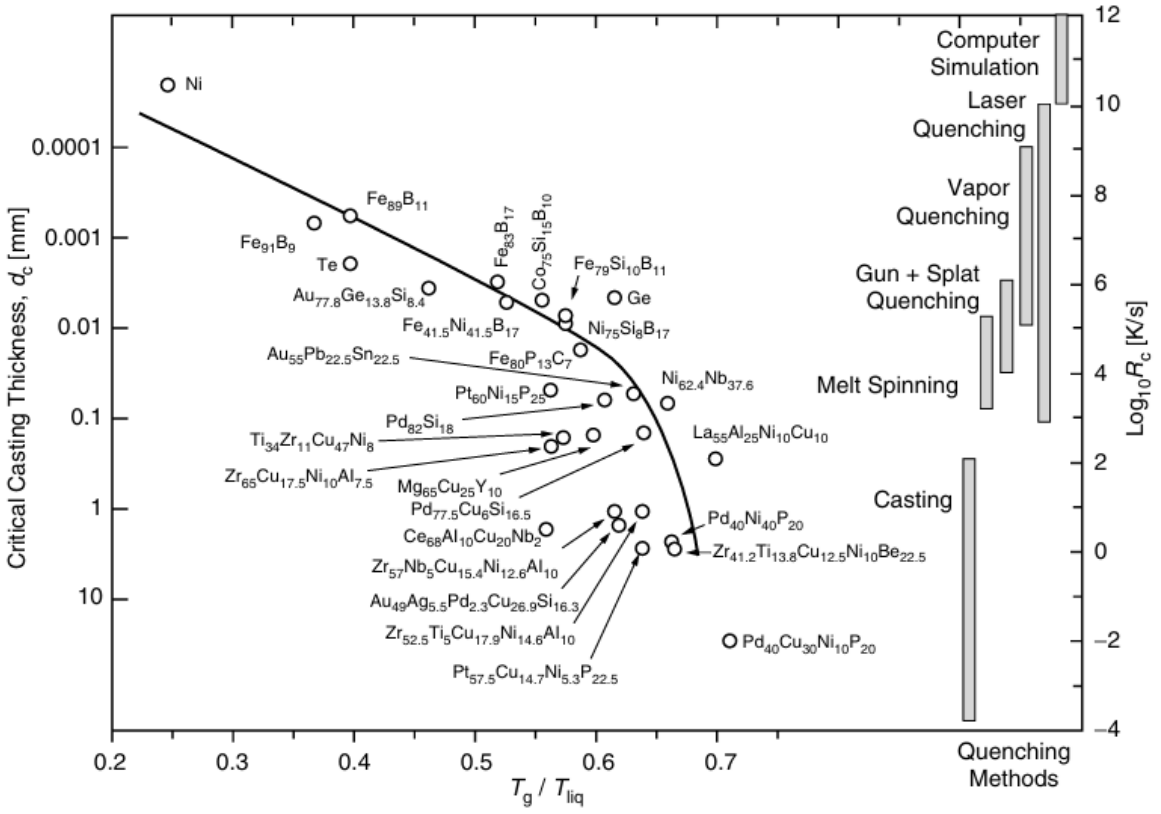

Figure 1.1: Critical casting thickness, critical cooling rate and reduced glass transition temperature correlation for various metallic glasses produced by different rapid quenching techniques. Reprinted with permission from Taylor and Francis Group LLC, Copyright 2007 Ref. [14]

quenching and single-roller melt-spinning[1–3] techniques. Therefore, the thrust of research on metallic glasses in the decades following their first production in 1960 by Klement et al [12] mainly remained on the production of bulk metallic glasses (BMG) with thickness/diameter of several mm to cm at the cooling rates as low as 1 K/s. [3, 7, 8] BMG formation has been reported in $Pd_{40}Cu_{30}Ni_{10}P_{20}$ alloy with the lowest critical cooling rate of 0.10 K/s and the maximum sample thickness as large as about 5 cm. [13] Fig. 1.1 depicts the critical casting thickness of various metallic glasses using different rapid quenching methods and its correlation with the reduced glass transition temperature defined as T_g/T_l. [14]

Amidst a developing theoretical understanding of the physics of glass formation in these systems, Inoue's research group's heuristic approach to the search for

bulk metallic glass-forming alloys led to the discovery of several families of BMG-forming alloys.[6, 11] This led Inoue [6] to propose the well-known empirical rules for BMG formation in metallic alloys that necessitate, (1) the presence of more than three elements in the alloy; (ii) an atomic size mismatch of 12% or more among the main constituent elements and; (iii) a negative heat of mixing among the constituent elements. These rules are the most practical guideposts for explaining glass formation in metallic alloys. However, glass formation in metallic alloys is a complex process governed by several structural, thermodynamic and kinetic factors that exhibit a significant variation over a wide range of composition of the alloys. [3, 5–7, 15–37] Therefore, prediction of the glass-forming ability (GFA) of the metallic alloys and finding the best glass-forming composition remains the most challenging task. Several empirical parameters, based on the characteristic temperatures such as the glass transition temperature (T_g), liquidus temperature (T_l), onset crystallisation temperature (T_x) etc. and the Gibbs free energy, enthalpy and, entropy of mixing etc. have been proposed to predict the GFA of metallic alloys. [20, 22, 38–49] Fig. 1.2 gives an overview of a few of GFA measures for the metallic alloys proposed in the early years of the development of bulk metallic glasses. [6] With the advancements in the experimental techniques and the computer simulation methods for the study of the materials, several investigations on the metallic glasses have reported the correlation of GFA with the structural parameters such as the structure factor, short-range order, density, packing fraction etc.[23, 27, 30–32, 36, 50–53] Thus, investigating the structure, dynamics and thermodynamics is central to understanding the glass formation in metallic alloys.

1.2 Objectives and Organization of Thesis

A common fact emerging from the literature survey on the families of metallic glass-forming alloys is that the transition metals are inevitable constituents of these alloys. The interactions among these constituents in the liquid state are key to the short- and

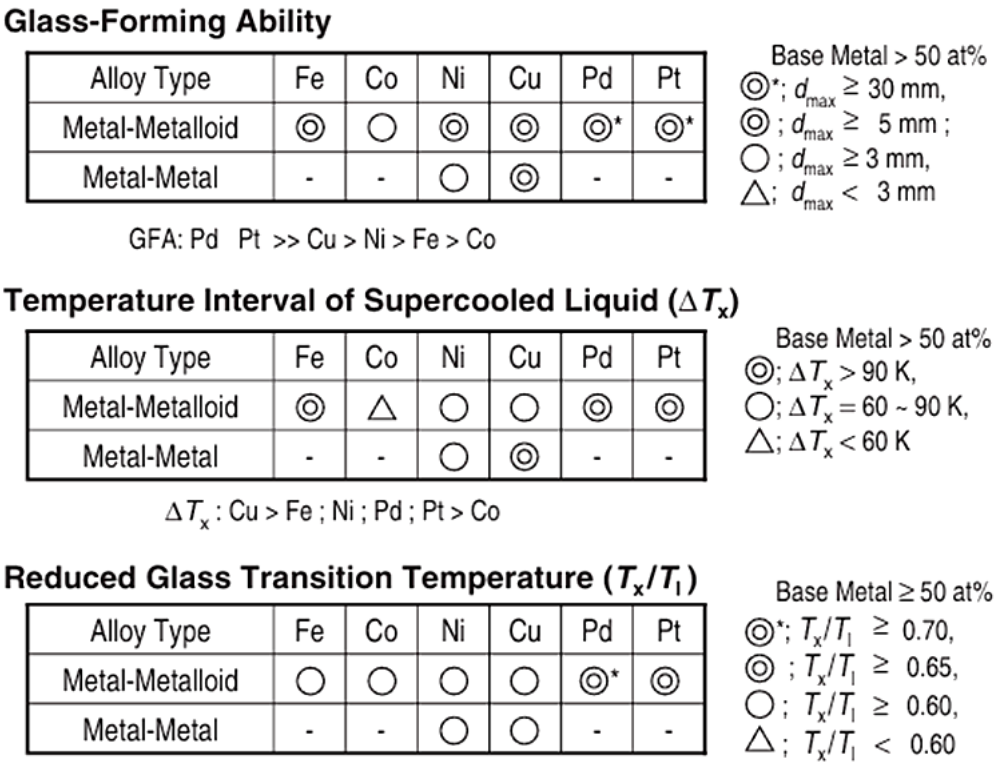

Figure 1.2: Overview of different Glass-forming ability measures, (a) the maximum casting thickness (d_{max}), (b) supercooled liquid region (ΔT_x) and, (c) reduced glass transition temperature for late transition metal-based bulk glassy alloys. Adapted from Ref. [6]

medium-range order and different dynamical features such as dynamic heterogeneity that evolves remarkably in the supercooled region in the metallic alloys. The partially filled d-orbitals in transition metals significantly influence their bonding. Even in the liquid state, transition metals exhibit short-range order, where atoms tend to retain a preferred coordination number. [54] This is often related to the local packing and bonding preferences seen in the solid phase. This thesis reports theoretical and experimental investigations of some liquid transition metals and transition metal-based multicomponent alloys. The studies broadly encompass some fundamental aspects such as (a) interatomic interactions and atomic dynamics, (b) thermodynamics of glass formation and GFA and, (c) kinetics of glass transition and thermal stability. While the detailed investigations, results and discussions are covered in chapters 2 - 5 of the thesis. Introduction of the key ideas and motives of each is given in the following discussion.

The study of the interatomic interactions and atomic dynamics in liquid transition metals is one of the objectives of the present work. A simple liquid picture of the liquid metals is usually considered for modelling the interaction potentials where the atoms interact via spherically symmetric and pairwise additive forces. [55, 56] Unlike the simple liquids described by the Lennard-Jones (LJ) potentials, the situation is more complicated in liquid metals due to the presence of conduction electrons and, the interaction potentials manifest softer repulsive forces and long-range oscillatory tail.[57] However, since its advent in the early 1960s to tackle the electronic structure calculations in metals, the pseudopotential formalism has become the bedrock for modelling the interatomic interactions in metals for theoretical investigations and simulation studies using the modern density functional theories. The replacement of the actual interaction of the atomic cores (the tightly bound core electrons to the nucleus) with the (nearly free) valence electrons by a model local pseudopotential representing a weak ion-electron interaction facilitates derivation of the effective pair potentials through the second-order perturbation theory. [58–61] The effective pair potentials along with the liquid state theories have been successful in giving a good description of the structural and thermodynamic properties of liquid metals.[62–70] The d-band electrons in transition metals contribute to the overall electron density and affect the interaction potentials. A pseudopotential-based approach proposed by Wills and Harrison(WH) for the interionic interaction in transition metals takes into account the d-electron effects and the s-d hybridization effect.[64, 71, 72] The WH formulation and its modified versions[71] have been successfully employed in many theoretical and computer simulation studies of structural, dynamical and thermodynamic properties of liquid transition metals and alloys.[64, 66, 67, 69, 73–80] As our primary objective is to study the atomic dynamics in the liquid transition metals, we have adopted the WH approach to derive the effective pair potentials which are further used to obtain

the necessary input parameters for the theoretical calculation of the velocity autocorrelation function (VAF). VAF is the simplest time correlation function that describes the dynamical correlation in the atomic motion in liquids. It is often used to extract transport coefficients such as the self-diffusion coefficient and other dynamical variables like vibrational density of states (VDOS), mean-square displacement, dynamical structure factor etc. The WH framework for the effective pair potential and the details of the MD simulations are summarized in Appendices A and B, respectively in Chapter 2.

Atomic motion in dense liquids like liquid metals differs from a simple diffusion process in gases. It is often described as a short-time vibrational motion of the atoms in their nearest-neighbour cages followed by a diffusive motion on the cage relaxation due to cooperative rearrangement of the cage atoms. Theories of the atomic motion in liquids are invariably linked directly or indirectly to the Brownian motion. The Langevin theory of Brownian motion is a fundamental approach in statistical mechanics to describe the motion of particles suspended in a fluid, subject to random collisions with the molecules of the surrounding medium. While the Langevin theory provides a good approximation for Brownian particles in thermal equilibrium, it assumes instantaneous relaxation of the random force correlation, which may not hold in all systems. For cases where memory effects (non-Markovian dynamics) are significant, the theory can be extended with generalized Langevin equations that incorporate memory kernels.[81, 82] Alternatively, Glass and Rice (GR) used a modified Langevin equation to derive an equation of motion in terms of VAF by assuming Brownian particles diffusing in a mean-time-dependent field.[83] While the GR approach was mainly proposed for low-density fluids like liquid argon, its generalized versions [84, 85] for high-density liquids like liquid metals fail to give a complete account of the VAF in these systems. Therefore, to overcome the limitations of the GR approach such as the consideration of time-independent (static) friction, we have revisited the GR theoretical framework and extended it to

incorporate the dynamic friction in the Brownian description of the atomic diffusion in a mean-time-dependent harmonic force field. A modified, non-Markovian Langevin equation is utilized to derive an equation of motion for the VAF with a time-dependent friction coefficient. The numerical solution of the equation gives an excellent account of the VAF in Lennard-Jones liquids, liquid alkali, and transition metals over a broad range of density and temperature. Derivation of the equation of motion leads to a self-consistent expression for the time dependence of friction coefficient. Our results demonstrate that the nature of the time dependence of the friction coefficient changes dramatically with the liquid density. At low and moderate densities, the dynamic friction decays exponentially whereas it increases exponentially at high liquid densities. Our findings provide an opportunity for a different outlook on the Brownian description of atomic dynamics in liquids. The theoretical framework, results and discussion are elaborated in Chapter 2.

Because of the significant contribution of d-electrons, many-body interactions are important in liquid transition metals. These interactions go beyond simple pair potentials and, require more complex models like the embedded-atom model (EAM) which accounts for the influence of surrounding atoms on the potential felt by a particular atom. To ensure the validity of our approach for the transition metals, we have performed classical molecular dynamics (MD) simulations for the studied liquid metals using well-established EAM potentials reported in the literature. The MD trajectories have been analysed to obtain the VAF. The equation of motion derived in the present work was solved numerically to fit the VAF from MD. The necessary initial estimates of the input parameters were obtained using the effective pair potentials calculated in the WH formulation. The WH framework for the effective pair potential and the details of the MD simulations are summarized in Appendices A and B, respectively in Chapter 2.

Random close-packing of atoms in liquids is a fundamental paradigm for describing the liquid structure. The Percus-Yevick approximation [86] for the hard-sphere model of the liquids, in terms of packing fraction (η), has been successfully

employed in many theories for the investigation of the structural, transport and thermodynamic properties.[56, 63, 73, 87–92] Several structural models,[21, 50, 93–95] based on dense random-packing of atoms, have been proposed to account for short and medium-range order in metallic glasses and, the compositional dependence of GFA. These models highlight the role of efficient atomic packing in governing the kinetic and thermodynamic factors that stabilize the metallic alloys in the supercooled liquids against crystallization. For example, a low free volume in a liquid of high packing density corresponds to low atomic mobility which imposes a strong kinetic constraint on the nucleation and growth of crystals in the supercooled region. [51] An experimental investigation of CuZr alloy over a broad composition range has shown that the density of the metallic glass correlates with the GFA and suggests that the densest liquids are also the best glass formers.[51] Detailed investigations of the atomic-level structure and the atomic packing efficiency of the polytetrahedral clusters in Cu-Zr metallic glasses reveal that the packing efficiency strongly correlates with the GFA. [27, 52] The packing efficiency (η) is also an important input parameter in the approach proposed by Mansoori et al[96] for the equilibrium thermodynamic properties of the mixture of hard spheres. This approach is often used to calculate the excess entropy in the metallic alloys. The excess entropy, the mixing enthalpy and mismatch entropy estimated from the hard-sphere model are useful in exploring the glass-forming composition range.[35, 48, 97] However, in the absence of knowledge of the actual packing efficiency in the hard-sphere mixtures of different compositions, such studies usually consider the value of η equal to 0.64. An MD study on Cu-Zr metallic glasses reports estimates of the η over a wide composition range and its correlation with GFA. It motivated us to obtain the excess entropy and mismatch entropy for $Cu_xZr_{100-x}(46 \leq x \leq 70)$ using the analytical thermodynamic approach proposed by Mansoori et al. To extend the study further, we conducted a MD study on $Cu_{50}Zr_{50-x}Al_x(5 \leq x \leq 40)$ alloys and computed the packing efficiency for studying the composition dependence of different entropy terms. Chapter 3 of the thesis reports the details of these investigations.

Our study reveals that the compositional dependence of the entropies in Cu-Zr alloys shows a good correlation with the GFA. In Cu-Zr-Al alloys, the entropy variation with the composition does not indicate an unambiguous correlation with GFA. However, the study provides useful insights into the effect of the substitution of Zr by Al on the GFA.

After exploring the correlation between the structural and thermodynamic quantities with the GFA in binary and ternary metallic glasses in Chapter 3, we focus on another fundamental problem associated with the thermodynamics of glass formation in metallic alloys. The alloys in the supercooled liquid region are in a thermodynamically metastable state compared to the corresponding stable crystalline state. The knowledge of the differences in the enthalpy (ΔH), the entropy (ΔS) and the Gibbs free energy (ΔG) of the two states is important for understanding the kinetics of the nucleation and growth processes suppressing the crystallization in the supercooled region. ΔG is considered to be the driving force for crystallization and, the alloys with lower ΔG are expected to possess higher GFA. Experimental determination of ΔH, ΔS and ΔG requires the measurement of ΔC_p in the temperature range of interest i.e. the supercooled region between T_m and T_g in glasses. However, the experimental specific heat measurements in the entire supercooled region is severely constrained due to the thermodynamic metastability of the supercooled liquid state, especially for the metallic glasses with higher to moderate fragility (lower GFA). So, several analytical expressions for the estimation of the temperature dependence of ΔG in the supercooled liquid region have been proposed over the years. [98–107] As these expressions employ a variety of approximations for the temperature dependence of ΔC_p, their applicability to the different metallic glass-forming alloys is often debated. Chapter 4 of this thesis presents a case study of the thermodynamics of $Zr_{56-x}Co_{28}Al_{16}Y_x (x = 0, 2, 7, 10 at.\%)$ bulk metallic glass-forming alloys where, ΔH, ΔS and ΔG have been estimated using a hyperbolic temperature dependence of ΔC_p in the supercooled liquid region. The estimates of ΔG in a wide supercooled liquid region have been found to be in excellent agreement with the experimental

results. The study also provides an understanding of the effect of yttrium (Y) doping on the thermodynamics of the alloys in the supercooled region and the GFA. Fundamental elemental properties such as atomic size, electronegativity, and the heat of mixing have been found to play an important role in governing the thermodynamics of the alloys in the supercooled liquid region.

Apart from the theoretical and computer simulation investigations on monatomic transition metals, transition metal-based binary, ternary and quaternary alloys, experimental investigations of the kinetics of the glass transition process in a fluorozirconate glass - ZBLAN using differential scanning calorimetry (DSC) are included in Chapter 5 of the thesis. ZBLAN glass is a type of fluoride glass composed mainly of fluorides of zirconium (ZrF_4), barium (BaF_4), lanthanum (LaF_3), aluminium (AlF_3), and sodium (NaF). It has unique properties, such as low phonon energy, high infrared transmittance, and a low refractive index, making it valuable for infrared optics, fibre optics, and photonics applications. The main interest in these glasses stems from their broad optical transmission that extends from the UV to the mid-infrared spectrum and their extremely low OH contamination. [108] The superior optical characteristics of fluorozirconate glasses are attributed to their weak interionic bonding and the heavy mass of their constituent ions. However, such intrinsic properties also lead to these glasses' relatively poor thermal stability. Therefore, careful tailoring of the composition of these glasses plays an important role in attaining high thermal stability while retaining their desirable optical properties.[108, 109] Thermal characterization of the fluorozirconate glasses using DSC gives very useful information about their thermal stability and GFA, which is crucial for the large-scale commercial production of optical fibres of these glasses. The thermal analysis of ZBLAN glass using DSC is presented in Chapter 5. The heating rate dependence of the glass transition temperature is utilized to derive the activation energy of glass transition through the Kissinger [110] and Augis- Bennett [111] methods. The activation energy and the glass transition temperature are used to determine the fragility index for the studied ZBLAN glass.

Key findings and highlights of the investigations on monatomic transition metals and binary to quaternary alloys are summarized in Chapter 6. Possible extensions of the studies presented in the thesis and future scope is also discussed in this chapter.