Study of Interacting Interactions, Dynamics and Thermodynamics in Transition Metals and its Alloys

An Executive Summary

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EXECUTIVE

SUMMARY

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Chapter 1: Introduction

The transition metals are widely used in the production of materials like metallic alloys and metallic glasses. The defining characteristics of metallic glasses, compared to conventional metallic materials, are their lack of crystallinity, and associated lack of macro-structural features such as phase and grain boundaries [1]. On account of the absence of crystal planes, metallic glasses possess very high physical strength (e.g., elastic modulus). These characteristics make the metallic glasses superior materials for corrosion- and wear-resistant coatings in luxurious products like laptop & mobile cases as well as for medical applications such as surgical blades, tooth and knee implants. Metallic glasses are also used to manufacture gears and other mechanical parts of miniature devices. Owing to the absence of magnetic domains, unlike crystalline alloys, these glasses exhibit very small hysteresis loss. So, the metallic glasses (in the form of ribbons or thin sheets) are widely used in high power transformer cores to reduce the hysteresis losses.

Metallic glasses are mainly obtained by rapid quenching of the melt with practically achievable rates as high as 10^7 K/s. During the liquid to glass transition, crystallisation of the melt is bypassed to yield a kinetically metastable liquid state i.e., supercooled liquid. The dynamics of the metallic-glass forming liquids exhibits a non-Arrhenius temperature dependence in the supercooled region below the melting temperature (T_m). The structural

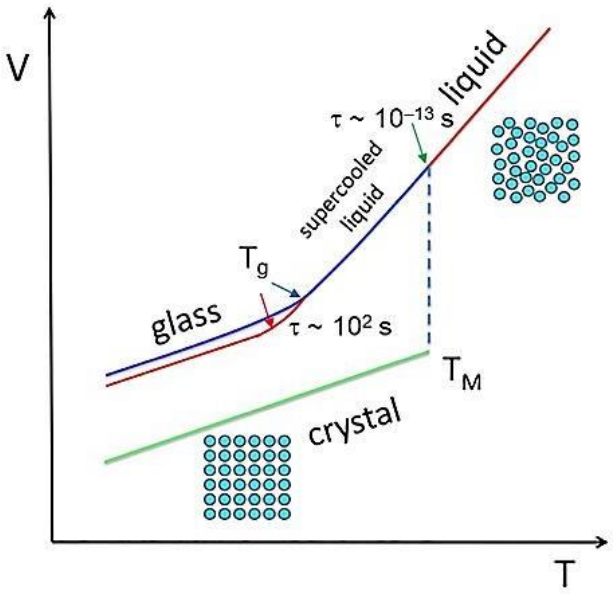

Figure 1: Schematic diagram demonstrating the change in thermodynamic variables during cooling of liquids and relevant timescales of atomic dynamics (ref. [2])

relaxation time, which is of the order of 10^{-12} s at T_m, rapidly increases. At temperature characterized as the glass transition temperature (T_g), it diverges to an extremely large value compared to the timescale for experimental measurements. (Fig. 1) The translation degrees of freedom of the atomic motion are nearly frozen at T_g and the liquid solidifies into the amorphous state. Thus, the dynamics of metallic liquids above T_m would have a significant bearing on the process of glass formation and the properties of the glasses produced by rapid quenching. Therefore, theoretical and experimental investigation of interatomic interactions, dynamics and thermodynamics in transition metals and their alloys are important to provide a better understanding of the dynamic, thermodynamic properties and its correlation with the glass-forming ability (GFA) of metallic glass-forming liquids.

Objectives of the Thesis

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.

Chapter 2: Study of Single Particle Dynamics in Liquid Metals

The Glass and Rice (GR) [3] theory is revisited to find any shortcomings in its formulation which, if addressed adequately, would provide better quantitative results and hence, a better description of the molecular motion liquids. Apparently, the first shortcoming is the assumption of the friction coefficient (β) to be independent of time. [4] It is questionable when the mass of a Brownian particle is similar to the surrounding particles. It also misses capturing the possible effects of the dynamic correlations on molecular friction. In fact, GR themselves suggested the possible extension of their approach to include the dynamical friction for the case where the period of oscillation of the long-range, rapidly fluctuating soft forces is not sufficiently short [5]. We show that the incorporation of time-dependent friction in GR theory leads to an equation of motion in terms of VAF with its solution encompassing three possible physical scenarios for the dependence of molecular friction.

Chapter 3: Correlation between Entropy and Glass-forming Ability of Cu-Zr and Cu-Zr-Al alloys

The study of the effect of topological packing on the excess entropy, the configurational entropy, and the mismatch entropy in Cu-Zr and Cu-Zr-Al alloys have been investigated using an analytical approach based on the equation of state for the mixture of hard spheres.

The essential input parameter for this approach, the atomic packing fraction (η), has been derived from the classical MD simulations and subsequent analysis of 3D atomic level structure. As we have used composition dependent η, our results for the different entropic terms are much more realistic compared to similar studies on binary and ternary alloys where η is uniformly assumed to be equal to 0.64 for all the alloy compositions. The mismatch entropy and the change in the excess entropy of mixing show good correlation with the GFA in Cu-Zr alloy in a wide composition range. It suggests that the analytical approach based on hard sphere mixture model is appropriate for the description of the thermodynamic properties of Cu-Zr alloys. For Cu-Zr-Al alloys, however, this approach is effectively applicable in the limited composition range with Al < 10% due to dominant chemical-short range ordering on account of increasing Al%. The composition dependence of the different entropic terms for both binary and ternary alloys, in general, indicates that the contributions of all the entropy terms to the total entropy should be maximum for better GFA. It is consistent with the entropy maximization in process of glass formation.

Chapter 4: Theoretical Investigation on Glass-Forming Ability of Zr-based Metallic Glasses

The estimation of the Gibbs free energy difference (ΔG) between the supercooled liquid and the corresponding crystalline state of the multicomponent Zr-based metallic glass-forming liquids has been investigated in this chapter. ΔG is an important parameter in nucleation processes. The nucleation frequency has an exponential dependence on ΔG, and hence its estimation is often critically important when used in the analysis of nucleation phenomena. [6] It is well-known fact that the mixing of solute the atoms of the host element leads to the formation of local atomic clusters with five-fold symmetry which is incompatible with the three-dimensional packing. The resultant geometrical frustration promotes glass formation in an alloy. However, the presence of impurity atoms such as carbon, oxygen etc. adversely affects the GFA of an alloy. In case of mixing of rare-earth/transition metal elements, a large amount of charge transfer occurs due to the difference in their electronegativity. The doping of rare-earth elements also helps to remove the impurities to yield better GFA [7]. Therefore, the concentration of rare-earth elements in transition metal-based multicomponent alloy plays a dominant role in controlling the fundamental factors like the atomic packing and heat of mixing that affect GFA. In the present work, the effect of yttrium (Y) doping on the thermodynamics of the Zr56-xCo28Al16Yx (x = 0, 2, 7, 10 at. %) alloys in the supercooled region and GFA. Thermodynamic behaviour of these alloys has been studied using an analytical approach where

some of the key thermodynamic quantities such as ΔH, ΔS and ΔG have been estimated using a hyperbolic temperature dependence of specific heat difference ΔCp in the supercooled liquid region. [8] The primary data of thermodynamics provide an estimate of the Kauzmann temperature and fragility parameter. [9,10] Fundamental elemental properties such as atomic size, electronegativity, the heat of mixing have also been calculated and found to play an important role in governing the thermodynamics of the alloys in the supercooled liquid region.

Chapter 5: Experimental Study of Glass-Transition Kinetics and The Glass-Forming Ability of a Fluorozirconate Glass-ZBLAN

This chapter includes the experimental investigations on a commercially important heavy metal fluoride glass known as ZBLAN glass. It possesses high thermal stability and excellent property as a transmitting material. [11] The current study examines the thermal properties of ZBLAN glass utilizing Differential scanning calorimetry (DSC) at various heating rates. The glass transition temperature, Tg, is observed to vary with heating rate, indicating its kinetic nature. Through the use of Kissinger [12] and Augis-Bennett methods [13] and the heating rate dependence of Tg, the activation energy (E) has been determined. These methods have also been used to obtain the fragility index (*m*), which can be used to evaluate the glass forming ability (GFA) of the system. The fragility index found is greater than 16, indicating that the ZBLAN glass is "fragile".

Finally, important conclusions drawn out the investigations presented in the thesis will be summarized in *Chapter 6.* Also, the possible extensions of the present work will be discussed as future scope for further work.

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