Abstract

for the Doctoral Thesis entitled

Study of Interatomic Interactions, Dynamics and Thermodynamics in Transition Metals and its alloys

Submitted by:

Margi K. Patel

Reg. No. FOTE/946, Reg. Date: November 02, 2017

Applied Physics Department

Faculty of Technology and Engineering

The Maharaja Sayajirao University of Baroda

Vadodara, Gujarat

December 2024

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. The summary of the work and the key findings are given below:

1. Single-particle dynamics in monatomic liquids and liquid transition metals

   A microscopic theory of molecular motion in classical monatomic liquids is revisited and extended to incorporate the dynamic friction in the Brownian description of the atomic diffusion in a meantime- dependent harmonic force field. A modified, non-Markovian Langevin equation is utilized to derive an equation of motion for the velocity autocorrelation function with time-dependent friction coefficient. This equation gives excellent account of the velocity correlations in a broad range of liquid densities where the physical scenario changes from binary collision-dominated short-time dynamics to the one with significant many-body cooperative effects. It has been shown that the dynamic friction decays exponentially at low and moderate liquid densities whereas it exhibits exponential growth in high-density liquids like liquid metals. The results for high-density liquids, especially the observed negative molecular relaxation rates (α), intuitively hint at the existence of imaginary eigenmodes (unstable modes) in the density of states of the INMs in accordance with Zwanzigs disordered-solidlike picture of short-time dynamics. Amidst the growing interest and efforts to understand the molecular origin of the dynamic friction and its implications on microscopic transport properties, our findings about the dynamic friction in liquids provides a different outlook to the Brownian description of atomic dynamics in liquids.

2. Thermodynamics of glass formation and GFA of Zr-based metallic glasses

   A combined theoretical and computer simulation investigations 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 are presented. The atomic packing fraction (ξ), derived from the classical MD simulations and subsequent analysis of 3D atomic level structure. ξ being the essential input parameter in the analytical approach based on the equation of state for the mixture of hard spheres is used to derive different entropic terms. As we have used composition dependent ξ, our results for the different entropic terms are much more realistic compared to similar studies on binary and ternary alloys where ξ 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.

Estimation of the Gibbs free energy difference (ΔG) for the metallic alloys in the supercooled liquid region yet remains relevant in the theory of nucleation and growth processes. Thermodynamic behavior of $Zr_{56-x}Co_{28}Al_{16}Y_x$ (x = 0, 2, 7, 10 at. %) bulk metallic glassforming 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 ΔC_p in the supercooled liquid region. The study is focused on understanding the effect of yttrium (Y) doping on the thermodynamics of the alloys in the supercooled region and on the glass-forming ability (GFA) of these alloys. The analytical approach has been found to give estimates of ΔG

in a wide supercooled liquid region which is in excellent agreement with the experimental results. Estimated ΔG values are found to be minimum for Y concentration of 7% and 10% which is consistent with the observed high GFA for these compositions. Fundamental elemental properties such as atomic size, electronegativity, the heat of mixing have been found to play an important role in governing the thermodynamics of the alloys in the supercooled liquid region.

3. Kinetics of glass transition and thermal stability of ZBLAN glass.

   Kinetics of gslass transition and thermal stability of a technologically important ZBLAN glass are examined using differential scanning calorimetry (DSC) and thermal analysis methods. The heating rate dependence of glass transition temperature T_g, has been analyzed using the Kissinger and, the Augis - Bennett methods to derive the activation energy (E) of glass transition. The fragility index (m) - a measure of GFA of a system derived using the two methods indicates ZBLAN glass to be a kinetically "fragile" system. 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.