Conclusion and Scope for the Future Work

The thesis entitled "***Study of Structure, Thermodynamics and Phase Transformation in Zr-Based Amorphous Alloys***" incorporates both, experimental as well as theoretical, aspects of glass formation in amorphous alloys.

The experimental aspect comprises of:

(i) Study of kinetics of crystallization of $Ti_{20}Zr_{20}Cu_{20}$ metallic glass.

(ii) Understanding the heating rate dependence of crystallization temperatures.

The non-isothermal crystallization kinetics of $Ti_{20}Zr_{20}Cu_{60}$ metallic glass was studied by using non-linear heating rate employed by modulated Differential Scanning Calorimetry (MDSC). MDSC thermo-grams for $Ti_{20}Zr_{20}Cu_{60}$ metallic glass clearly indicated a two-step crystallization process. The analysis of the MDSC thermograms, by using modified expressions for iso-conversional methods for non-linear heating rates, revealed that both crystallization events were multiple mechanism processes. The activation energy of crystallization was calculated for various degree of conversions by linear integral iso-conversional methods i.e., Ozawa-Flynn-Wall (OFW), Kissinger-Akahira-Sunose (KAS), and also with Friedman method which is a linear differential iso-conversional method. The term that is expected to cause non-linearity, i.e., $(A_T\omega/2\beta)^2$ is almost constant for all heating rates. Thus, the non-linear heating rate does not change the nature of different linear iso-conversional methods. The linear behavior of the various expressions remain intact. Hence, MDSC can be conveniently used for studying kinetics of crystallization of metallic glasses.

Further, the variation of onset of crystallization temperature (T_x) and peak crystallization temperature (T_p) with heating rate (β) was studied. It was found that both (T_x and T_p) varies in a power law behavior with heating rate (β) for $Cu_{60}Zr_{20}Ti_{20}$ metallic glass and shows a linear variation for $Cu_{60}Zr_{40}$ metallic glass. The power law relation, expressed as T_x (or T_p) = T_0 $[\beta]^y$; where, β is the normalized heating rate, T_0 is the T_x (or T_p) at a heating rate of 1^0Cmin^{-1}, was found to be an appropriate theoretical explanation of the variation of crystallization temperature (T_x or T_p) with β for $Cu_{60}Zr_{20}Ti_{20}$ metallic glass. It was further observed that the characteristics temperatures shift towards higher values with increase in number of components. Hence, in addition to heating rate, the composition of a metallic glass also affects its crystallization temperature.

Theoretical analysis includes the study of thermodynamic aspect of glass formation in metallic glasses along with the determination of their glass forming ability (GFA). The thermodynamic parameters i.e. Gibbs free energy difference (ΔG), entropy difference (ΔS) and enthalpy difference (ΔH) were calculated for an Au-based metallic alloy in its undercooled region. The calculations of ΔG was done on the basis of various expressions available in literature depending upon different variations of specific heat difference (ΔC_p) with temperature. Gibbs free energy difference is the driving force for the crystallization. A smaller value of ΔG indicates greater GFA of metallic glasses. Hence, in order to understand the GFA of metallic glasses precisely and to design new glasses with better properties, the true determination of ΔG is important. The ΔG values can be estimated if the experimental ΔC_p is known, which is very difficult due to the metastable nature of undercooled liquids. Therefore, various assumptions were made by researchers for explaining the temperature dependence of ΔC_p and based on them different expressions of ΔG were derived. On comparing the theoretically obtained values of ΔG with the experimental data for Au- based metallic glass, the expression of ΔG derived on the basis of hyperbolic variation of ΔC_p was found to explain the variation of ΔG with temperature, in its entire undercooled region, excellently well.

In addition to the thermodynamic aspect, the GFA of glassy alloys can also be studies on the basis of various GFA parameters available in literature. Chapter 4 reports a study made on evaluation of best GFA parameter by correlating them with the experimental parameter, critical size (Z_{max}). It was clearly visible from the results that ΔG is the best GFA criterion.

Further the effect of micro-alloying on the GFA of metallic glasses was studied using various GFA parameters and ΔG. It was found that minor addition of alloying elements increase the GFA of metallic glasses.

Apart from the crystallization kinetics and GFA of metallic glasses, this thesis also focuses on the study of bio-corrosion resistance of different metallic glasses. The bio-corrosion studies were performed by conducting potentiodynamic polarization experiments using a potentiostat. A potentiostat is an electronic device that conducts electrochemical reactions between the electrodes and the electrolyte. For studying the bio-corrosion resistance of a metallic glass, the electrochemical reactions were carried out in different simulated body fluids (SBFs), such as artificial saliva solution and artificial blood plasma. The potentiodynamic polarization experiments were conducted on Co-and Fe-based amorphous alloys. On comparing Co- and Fe-based metallic glasses with other orthopedic and dental alloys, available in literature, it was found that $Co_{66}Si_{12}B_{16}Fe_4Mo_2$ and $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ metallic glasses are better biocompatible material as compared to Sr-based, Ca-based BMG, conventional crystalline Mg-alloys, pure Mg, Cu-Al dental alloy, etc. Hence, superior corrosion resistance of $Co_{66}Si_{12}B_{16}Fe_4Mo_2$ and $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ metallic glasses under the influence of all four simulated body-fluids make them a potential candidate for orthopedic and dental implants.

In future, the research work carried out for this thesis can be extended by the utilizing the knowledge of Gibbs free energy difference (ΔG) in the undercooled region to plot Time-Temperature-Transformation (TTT) diagram. The value of critical cooling rate (R_c) can be obtained from the values of nose time (t_n) and temperature (T_n) of TTT diagram.

Also the oxidative stability and corrosion resistance of metallic glasses can be studied. The potentiodynamic polarization experiments can be performed to calculate the corrosion resistance of metallic glasses in various other biological media and chemical electrolytes. Amorphous alloy with high bio-corrosion resistance can be used as bio-implants and those having excellent corrosion resistance abilities can be used in other applications such as decorative items, fuel cell separators and other materials where minimum corrosion is required along with high strength. This in turn will provide us the insight to properly utilize the properties of different metallic glasses in various spheres of life.

The research on metallic glasses can further be extended by studying their electrical properties. Four probe method can be used to measure electrical conductivity of metallic glass samples. Further, studies can be extended to the formation of nano-crystallites in the amorphous matrix of a metallic glass. These microstructures tend to improve their hard and soft magnetic properties.

Hence, these studies will contribute towards improvement and utilization of the properties of metallic glasses in a more effective way.