SUMMARY

This thesis describes some investigations on diffusion and oxidation behaviours of a few iron based and zirconium based metallic glasses.

Metallic glasses have emerged as a new class of materials which have drawn the attention of research scientists because of their amorphous nature and many attractive properties. CHAPTER I of this dissertation gives a brief overview of the nature and properties of metallic glasses. Not many investigations on diffusion in and oxidation of these materials have been reported to date in the literature, hence the present study was undertaken.

CHAPTER II presents an extensive literature survey on diffusion and oxidation studies carried out in metallic glasses. The diffusion of Au, Sb, Pb, Cu, Al, Bi, Fe and Ni was studied in binary metal-metalloid (Fe$_{62}$B$_{18}$, Fe$_{80}$B$_{20}$) and metal-metal (Zr$_{1-x}$Ni$_x$, x = 33, 35 and 39 at %) glasses. These studies were carried out on three different structural states of the alloy specimens, namely, as-quenched (Q'), relaxed (R) and crystallized (C). In the beginning of CHAPTER III, the specimen preparation methods for diffusion studies have been described. The major problem pertaining to diffusion studies in metallic glasses is related to their incipient crystallization during annealing. Hence, the annealing time and temperature are limited and permissible values of these parameters lead to small diffusion distances $\sim$ a few hundreds of Å. Diffusion studies in metallic glasses thus necessitates the use of experimental techniques with good depth resolution (typically $\sim200\AA$). In the present work, diffusion measurements were carried out by using the techniques of Rutherford backscattering spectrometry (RBS) and Auger Electron Spectroscopy (AES). The basic principles of these techniques are described in CHAPTER III. The diffusion studies were carried out by depositing a thin film (100-2000Å) of the diffusing species by the vacuum evaporation technique and determining the compositional depth profiles before and after diffusion annealing treatment by the above mentioned techniques. The values of the diffusion coefficients were evaluated by using the
thick film solution of the diffusion equation wherever applicable and by solving it numerically in other cases. The procedure for data analysis is described in detail in CHAPTER III. The oxidation studies were carried out on three commercial iron-based metallic glasses - Fe$_{80}$B$_{20}$, Fe$_{81}$B$_{13.5}$Si$_{13.5}$C$_2$ and Fe$_{67}$Co$_{18}$B$_{14}$Si$_{1}$. Oxidation in air atmosphere at room temperature (native oxide) as well as at high temperatures (air oxidation) and in an aqueous medium, containing 0.5 M K$_2$SO$_4$ adjusted to a pH 4.0 by the addition of H$_2$SO$_4$, was investigated. The oxide films formed were analysed by X-ray photoelectron spectroscopy (XPS) and AES. The basic principles of XPS and data analysis procedure are described in the end of CHAPTER III.

In the beginning of CHAPTER IV the method of evaluating $D$ has been illustrated in a few typical cases. The results are later tabulated in the same chapter. Important features observed in each case have also been indicated. The last section of this chapter is devoted to a discussion on these results. Some of the main points pertaining to the diffusion studies could be summarized as follows:

(i) An error of $\sim \pm 50\%$ in $D$ was estimated in our measurements. The errors in the frequency factor, $D_0$, and the activation energy, $Q$, were calculated on the basis of linear regression analysis.

(ii) The $D\nu$ diffusion measurements were made by using RBS as well as AES and the two sets of results showed a reasonably good agreement.

(iii) The $D$ values obtained compared fairly well with those reported in literature.

(iv) A comparison of the measured $D$ values with the extrapolated values for self and impurity diffusion in crystalline solids indicated that the former are generally higher than the latter by a few orders of magnitude.

(v) The structural relaxation treatment was found to have an insignificant effect on diffusivity values. Diffusion in pre-crystallized specimens was faster as compared with that in amorphous specimens in some instances. However, the opposite trend was also noticed in some cases.

(vi) A reasonably good agreement was found between the diffusivity values
obtained in this work and those reported in literature on the basis of crystal growth data.

(vii) The temperature dependence of the $D$ values could be described satisfactorily by the Arrhenius law.

(viii) A correlation of diffusion data with other parameters suggested that the value of $D$ decreases with increasing atomic size of the diffusing species. The quantity $Q/kT_m$ was found to be constant (within ±15%) at 12.28.

(ix) The possible mechanism of diffusion involves cooperative movement of atoms.

CHAPTER V deals with the presentation and the interpretation of results of the oxidation and corrosion studies on iron-based commercial metallic glasses carried out in atmosphere and in an aqueous medium. XPS and AES analysis indicated the following:

(i) Native oxide analysis revealed that iron was present in both $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ states on the outermost surface. The boron enrichment in the form of boron oxide was found at and near the interface. In case of cobalt containing glass ($\text{Fe}_{67}\text{Co}_{18}\text{B}_{14}\text{Si}_{1}$), $\text{Co}^{2+}$ was likely to be present at and near the interface as $\text{CoO}$.

(ii) The air oxidation studies carried out in the temperature range 423-613K showed the enrichment of the metalloids B and Si as their respective oxides in all cases. In fact, the relative concentration of B in the oxide film showed a decrease at higher temperatures ($>483K$). Amongst all the glasses, $\text{Fe}_{61}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_{2}$ (2605 SC) glass had the thinnest oxide film and therefore a superior oxidation resistance. It was observed that the oxide film formed was thinner on amorphous specimens than on the corresponding crystallized specimens. The thickness of the oxide film on 2605 CO glass in atmosphere at room temperature was comparable to that formed on 2605 SC. However, at higher temperatures, this alloy had the highest film thickness. XPS analysis of oxide film formed at 573 K, 300 min indicated the formation of $\text{Fe}_2\text{O}_3$ on the surface.
(iii) The corrosion studies in 0.5 M $\text{K}_2\text{SO}_4$ solution adjusted to pH 4.0 by addition of $\text{H}_2\text{SO}_4$ showed that the glass $\text{Fe}_{67}\text{Co}_{16}\text{B}_{14}\text{Si}_1$ displayed superior corrosion resistance in this medium as compared to other metallic glasses, namely, $\text{Fe}_{80}\text{B}_{20}$ and $\text{Fe}_{81}\text{B}_{13}\text{Si}_{3.5}\text{C}_{2}$. This was attributed to the formation of Co $(\text{OH})_2$ in addition to FeOH and Fe$_2$O$_3$ in the oxide film. The maximum corrosion rate was found for the case of $\text{Fe}_{80}\text{B}_{20}$ on the basis of weight loss measurements.