5.1 Introduction

The corrosion behaviour of amorphous metallic alloys is important property to understand their chemical stability against corrosive environment, which is specially important for glasses, considered them as potential candidates for technological applications. Especially Fe-based metallic glasses having remarkable soft magnetic properties, combined with high resistivity and improved thermal stability have opened up new possibilities of their use in high frequency (>100 kHz) applications, where conventional magnetic alloys cannot be used due to excessive eddy current losses, in addition to their use in transformer cores, tape heads and magnetic shielding commercially. However, the application of these alloys for the above purposes is viable only when their chemical stability is guaranteed. It may be noted that glasses of certain compositions have far superior corrosion resistance compared to that of their
crystalline counterparts [1,2]. **During** the last two decades a great deal of effort has been made to characterize and understand the general corrosion behaviour of metallic glasses, in particular TM-Metalloid metallic glasses [1,3] which are considered to have applications in power transformers. While trying to improve corrosion properties of Fe-based glasses, it has been observed that an addition of elements like Cr or Mo makes these glasses relatively more corrosion resistant. Extensive studies in this direction have been made on Fe-Ni and Co based alloys with various combinations of several metal and metalloid elements. In this regard, the glass $\text{Fe}_{40}\text{Ni}_{18}\text{Mo}_{4}\text{B}_{18}$ [4] has been reported to have better magnetic properties and thermal stability over $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_{6}$. Further it is also found that substantial reduction in Ni with simultaneous addition of Si and a heat treatment can provide excellent properties. Thus $\text{Fe}_{75}\text{Ni}_{14}\text{Mo}_{16}\text{Si}_{2}$ and a series of alloys $\text{Fe}_{x+y}\text{Ni}_{x}\text{Mo}_{y}\text{B}_{18-x}\text{Si}_{z}$ [(0<x<12), (0<y<6) and (0<z<6)] show that when optimally heat treated provide an ac work loss of just 7-8 W/kg, exciting power of 13-14 VA/kg, effective permeability of $10^4$ at 50 kHz and at an induction of 0.1 T [5]. From the above literature it becomes clear that Fe-base alloys with less Ni content and no P are preferred for magnetic applications. Fe-Ni-Mo-B-Si metallic glasses seem to have electrical and magnetic properties suitable for high frequency applications [5], therefore a systematic investigation has been carried out to study the corrosion behaviour of the $\text{Fe}_{60-x}\text{Ni}_{14-x}\text{Mo}_{x}\text{Si}_{2}\text{B}_{10}$ ($x=0,1,2,3$ and 4) metallic glass system, the details of which are presented and discussed in this chapter.

Although strong influence of metalloids on the corrosion behaviour of metallic glasses has been noted [1,3] it is still not clear as to whether such effects are results of their glassy structure or metalloid composition. However, glasses being metastable thermodynamically tend to crystallise into one or more stable crystalline phases with different compositions so that it is not clear whether the superior corrosion resistance of such glasses is due to their amorphous structure or due to their chemical homogeneity. It will be generally difficult to dissociate these two aspects. The experimental results have indicated that high degree of homogeneity, both compositional and structural, confer greatly improved corrosion resistance on the glassy alloys. Also from electrochemical point of view, absence of crystalline defects such as grain boundaries, dislocations etc. in these metallic glasses results in the
absence of local electrochemical potential difference and hence minimization of the corrosion reactions. In addition, rapid quenching from liquid state to prepare amorphous alloys prevents solid state diffusion during quenching which generally causes segregation, precipitation and thereby reduces the localized corrosion attack. Thus, high corrosion resistance of metallic glasses has been attributed mainly to the chemical homogeneity of the amorphous phase coupled with the absence of crystalline defects inherent in metallic glasses and it has been further attributed to the high protective quality, the uniformity and the rapid formation of a passive film on the glassy substrate. However, composition also plays an important role in the determination of their corrosion behaviour [6,7]. Thus, further understanding of the relative importance of the amorphous structure and elemental composition in the corrosion resistance of amorphous metallic alloys will be useful.

Much interest has been centered on the effects of different alloying elements like metalloids P, B, Si, C and metals like Cr, Mo, W, Nb etc., on the corrosion resistance of Fe-based metallic glasses, due to their good soft magnetic properties. In particular, the effects of Phosphorous, P and Molybdenum, Mo (with or without Cr) on the promotion of stable passive films have been investigated by several authors [8-12]. The corrosion resistance of these glasses exposed to H₂SO₄ and HCl environments has been the object of many investigations, as these glasses show spontaneous passivation even in such aggressive environments. Therefore, amorphous alloys are suitable model systems to probe the influence of atomic structure and composition on the electrochemical interaction of alloys with their environment.

It is well known that addition of P in a metallic glass enhances its corrosion resistance [6]. The addition of Ni is considered to promote the formation of a passive film in the presence of Cr, thus providing good corrosion resistance [10]. In the absence of both these elements P and Cr, the corrosion resistance of these glasses significantly decreases. Hence it is thought worthwhile to examine the corrosion behaviour of Fe based metallic glasses free from P and Cr and having low Ni content, which are generally preferred for magnetic applications. Also, the role of Mo being a good corrosion resistant element, has been widely investigated in crystalline alloys [13-16]. Mo is found to reduce the critical and passivation current densities in several Cr-containing alloys. On the other hand, FeMo binary alloys (not containing Cr) do not
passivate in HCl, though a limited degree of passivation can be achieved in H$_2$SO$_4$ [13]. However, if P is one of the alloying elements of the glass, the passivation resulting from Mo, is found to be enhanced in HCl even in the absence of Cr.

As already much work has been reported on the effect of addition of P and Cr, in the present investigation, glasses free from P and Cr have been chosen to understand the role of Mo. Also, yet another advantage in studying the influence of Mo in these systems is that, in crystalline Fe-based alloys, as the solid solubility of Mo is less, addition of Mo beyond a critical limit will introduce additional phases resulting in the destruction of homogeneous single phase nature of these alloys. The latter will also influence the corrosion behaviour of the alloys in addition to Mo per se where as in amorphous alloys addition of alloying elements in wider range is possible, without the destruction of the homogeneous single phase.

Before discussing the results of the present investigation, an attempt has been made to explain some general concepts of corrosion theory.

### 5.2 Corrosion Principles

Corrosion is defined as the destruction or deterioration of a material due to a chemical or an electrochemical reaction with its environment. Corrosion behaviour of a material is mainly determined by its structure and composition. There are several ways of classifying corrosion. One method divides corrosion into low-temperature and high-temperature corrosion. Electrochemical corrosion reactions are conveniently divided into Dry corrosion which is mainly concerned with the oxidation of a dry metal surface and Wet corrosion in which the reactions occur in an environment which, under normal conditions, is predominantly composed of water.

The importance of corrosion studies is threefold:

(i) Economic factor which is the prime motive for much of the current research in corrosion

(ii) Improved safety in the design of the operating equipment.

(iii) Conservation of energy and resources

A corrosion engineer applies accumulated scientific knowledge in the choice of a material which in turn depends on many factors. Fig. 5.1 shows some of the
properties that determine the choice of a structural material. The factors on which Corrosion resistance/behaviour depends are schematically shown in Fig 5.2. Thermodynamics and electrochemistry are of great importance in understanding and controlling corrosion. Thermodynamic studies indicate the spontaneous direction of reaction. Thermodynamic calculations can determine whether or not corrosion is theoretically possible [17]. Since the rate of corrosion is of primary interest for engineering applications, electrochemical theory and concepts will be considered in greater detail in the later sections.

5.2.1 Corrosion Rate

Corrosion behaviour of a material is quantitatively expressed in terms of corrosion rates. Corrosion rates have been expressed in a variety of ways in the literature, such as percent weight loss, grams per square inch per hour and milligrams per square decimeter per day (mdd) and this is commonly used in English and American literature. A good corrosion rate expression should involve:

(i) Familiar units
(ii) Easy calculation with minimum opportunity for error
(iii) Ready conservation to life in years
(iv) Penetration (rate of penetration or thinning of a structural piece)
(v) Whole numbers without cumbersome decimals

The parameters, which affect the corrosion rate of a material, can be broadly classified as:

(a) Solution chemistry (Environmental): concentration, pH, temperature, velocity, conductivity, presence of foreign ions, aging of the medium, exposure period, type of exposure (alternate, partial, total submersion etc.), bacteria, microbes etc

(b) Metallurgical: microstructure, grain orientation, texture, alloy composition and purity, presence of defects etc

(c) Mechanical: presence of stress (applied, residual and thermal), rate of application, type of stress (tensile, compression or cyclic), strain rate, notches, application of stress before or after exposure to medium etc
Fig 5.1 Factors affecting choice of an engineering material.

Fig 5.2 Factors affecting the corrosion resistance of a metal.
Corrosion rates can be determined by the

- Non-electrochemical method and
- Electrochemical method

These are described in Secs 5.2.1(a) and 5.2.1(b) below

5.2.1 (a) Non-Electrochemical Method

Non-electrochemically, the rate of corrosion is determined by the conventional weight loss/gain technique [17]. Using this technique, the loss of a metal due to corrosion is measured by exposing the metal specimen of known area to the corrosive environment for a particular period and finding the difference in weight before and after exposure.

The expression ‘mils per year’ (mpy) is the most widely used way of expressing the corrosion rate. Corrosion rate is calculated using the formula,

$$\text{Corrosion Rate (mpy)} = \frac{534W}{DAT}$$

where $W$ = weight loss in mg
$D$ = density of the specimen in g/cm$^3$
$A$ = Area of the specimen in sq in
$T$ = exposure time in hr

Corrosion rate in mpy can also be calculated by using the formula

$$\text{mpy} = \frac{0.129 \times a \times i_{corr}}{n \times D}$$

where $a$ = atomic weight
$n$ = valence charge
$i_{corr}$ = corrosion current density in $\mu A/cm^2$
$D$ = density in g/cm$^3$

The weight loss method yields the average rate for the exposure period and is inherently inaccurate when it involves measuring small differences between initial and final weights of corroded specimens.

The criteria for selection of the materials for construction in industries are based on corrosion rates and can be classified as:
**Corrosion rate (mpy)** | **Relative corrosion resistance of material**
--- | ---
Less than 1 | Outstanding
1-5 | Excellent
5-20 | Good
20-50 | Fair
Greater than 50 | Not suitable

### 5.2. 1(b) Electrochemical Theory of Corrosion

The electrochemical theory of corrosion [17] states that corrosion proceeds by electrochemical reactions involving an anodic or oxidation reaction and a cathodic or reduction reaction, which for a given metal $M$ in an acidic medium is given as

$$M \rightarrow M^+ + e^- \quad \text{(Anodic reaction (Oxidation))} \quad (5.1)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad \text{(Cathodic reaction (Reduction))} \quad (5.2)$$

Eqs (5.1) and (5.2) are partial reactions and both of them must occur simultaneously and at the same rate on the metal surface, otherwise the metal would become charged which is impossible. This leads to the most basic principle of corrosion "During corrosion, the rate of oxidation equals the rate of reduction." So any reaction that can be divided into two or more partial reactions of oxidation and reduction is termed electrochemical. During corrosion, more than one oxidation and one reduction may occur. Since these reactions are mutually dependent, it is possible to reduce corrosion by reducing the rates of either of these reactions. The interpretation of corrosion processes by superimposing electrochemical partial processes was developed by Wagner and Traud [18], which is the well known 'Mixed potential theory'. The two hypotheses of this theory are:

1. Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions.
2. There can be no net accumulation of electric charge during the electrochemical reaction.

In general the following are the commonly employed electrochemical techniques to measure corrosion rates.
(a) Polarisation and (b) ac Impedance Spectroscopy

The theoretical background and experimental procedures of the above methods to determine the corrosion rates are described below.

(a) Polarisation Studies

During electrochemical corrosion the anode and cathode are not at their equilibrium potential at the surface of the metal. This deviation from equilibrium potential is called polarisation. Polarisation can be defined as the extent of potential difference or the displacement of electrode potential caused by net current flow to or from an electrode measured in volts, commonly known as over voltage or over potential represented by \( \eta \). Polarisation is an extremely important corrosion parameter, which enables one to understand the corrosion rate processes.

There are three types of polarisation:

1. Activation polarisation: This refers to an electrochemical process that is controlled by the sequence of reaction taking place at the metal-electrolyte interface. In other words, activation polarisation is caused by a slow electrode reaction because the reaction at the electrode requires activation energy. Both anodic and cathodic reactions can be under activation polarisation.

2. Concentration polarisation: This is observed when the electrochemical reactions occur that are controlled by the diffusion in the electrolyte. This behaviour usually occurs when the concentration of reducible species in the environment is small, e.g., corrosion in aerated salt solutions.

3. Resistance polarisation: This usually includes an ohmic potential drop through either a portion of the electrolyte surrounding the electrode or through a metal-reaction product film on the surface or both. Resistance polarisation may be written as

\[
\eta_k = RI = \gamma i
\]

where \( R \) = film resistance for electrode surface in ohms

\( I \) = current in amperes

\( \gamma \) = film resistance for 1 cm\(^2\) area in ohm/cm\(^2\)

\( i \) = current density in amp/cm

In electrochemical corrosion testing, two different approaches are apparent.
Control of current (i.e., corrosion rate) and control of potential (i.e., the oxidizing power) and measuring the resulting current.

In each case the potential of an electrode in a conducting medium is changed by the flow of current in the electrolytic cell.

The formation of the mixed potential of a corroding metal surface is illustrated in the polarisation diagram sometimes called Evans diagrams [19]. The determination of these polarisation curves and the corrosion rate of a specimen can be done very quickly. A complete curve can be determined in an hour in laboratory setup, whereas the conventional method to determine corrosion rate, i.e., by weight loss measurements takes several days or weeks.

The schematic Fig 5.3 illustrates some of the terminologies in a polarisation diagram, which is plotted potential vs log current density. The solid lines represent the net anodic and cathodic currents for each reaction, while the dashed lines represent the forward and backward parts of each reaction. The intersection of the dashed lines gives the open circuit corrosion potential, $E_{corr}(\phi_{corr})$, (when applied current density, $I_{appr} = 0$) and the corrosion current density $i_{corr}$. The intersection of the dashed lines gives the reversible potential for the reaction and its exchange current density. The anodic polarisation curve is predominant at potentials more $+$ve (noble) than $E_{corr}$ and cathodic polarisation curve is predominant at potentials more $-$ve (active) than $E_{corr}$. $\beta_a$ and $\beta_c$ are the Tafel slopes in anodic and cathodic reactions and the intersection gives corrosion exchange current density. The corrosion rate of the system is proportional to $i_{corr}$, which is determined by the intersection between the total reduction rate and the total oxidation rate. Polarisation measurements have been used to

1. Study the effect of change of material composition or environment on corrosion rate,
2. Develop alloys with improved corrosion resistance,
3. Control quality during manufacture of a specific material of known behaviour,
4. Measure corrosion rate of structure which are not easily accessible like underground pipe line, tanks and large chemical plant components and
Fig. 5.3 Schematic illustration of a polarisation diagram with different terminologies.
Determine corrosion rates lesser than 0.1 mpy, which are important in pharmaceutical and food industries.

The two different techniques in this are Tafel’s extrapolation and Linear Polarisation methods.

**Tafel’s extrapolation method**

This method was used by Wagner and Traud [18J to verify the Mixed potential theory. A Tafel plot for a metal specimen can be obtained by polarising the specimen to about 300 mV anodically and cathodically from the corrosion potential, \( E_{corr} \), as shown in Fig 5.3. Extrapolation of the Tafel region in either cathodic or anodic polarisation curve to the corrosion potential will give corrosion current density \( i_{corr} \), and it can be used to calculate corrosion rate.

The anodic and cathodic Tafel plots are described by the Tafel equations:

\[
\eta = \beta \log(i / i_{corr})
\]

where \( \eta \) = over voltage, the difference between the potential of the specimen and the corrosion potential

\( \beta = \) Tafel constant

\( i_{corr} = \) corrosion current density in \( \mu \text{A/cm}^2 \)

\( i = \) current density at over voltage \( \eta \) in \( \mu \text{A/cm}^2 \) or rate of oxidation or reduction in terms of current density at \( \eta \).

Rearranging Eq (5.3) we get,

\[
\eta = \beta (\log i - \log i_{corr})
\]

So a plot of \( \eta \) vs \( \log i \) is a straight line with a slope \( \beta \). Further, when \( \eta = 0 \) (\( E_{corr} \)), \( \log(i / i_{corr}) = 0 \) or \( i = i_{corr} \).

Tafel Constants, designated by \( \beta_a \) and \( \beta_c \) can be calculated for both the anodic and cathodic portion of the Tafel plot. The unit of Tafel constant is either mV/decade or V/decade. The disadvantages of Tafel plots are:

- The polarisation of test specimen by several hundred mV from the corrosion potential can disturb the system enough to distort further periodic measurements which might be made using the same specimen.
- Concentration polarisation and the IR drops can combine to reduce the linear
region to a point where extrapolation to $i_{\text{corr}}$ is difficult

- It can sometimes happen that extrapolation of the anodic and cathodic linear Tafel region do not intersect at $E_{\text{corr}}$
- Though faster than weight loss methods, still several hours are required to obtain data for each polarisation curve. This may not be convenient in many cases, especially in plant application

**Linear polarisation method**

The disadvantages of the Tafel extrapolation method can be largely overcome by using the linear polarisation method, which is also known as polarisation resistance method. This method was developed during mid 1960s and has developed considerably [19]. The principle of this method is that within 10 mV more noble or more active than the corrosion potential, the applied current is a linear function of the electrode potential. This is shown in Fig 5.4. In this figure, the corrosion potential is used as an over voltage reference point and a plot of over voltage vs applied anodic and cathodic current, ($i_{\text{appl}}$) is shown on a linear scale. This plot represents the first 20 mV polarisation of the curve shown in Fig 5.3. The slope of the linear polarisation curve is related to the kinetic parameters of the system according to the following equation derived by Stern and Geary [20]

$$\frac{\Delta E}{\Delta i_{\text{appl}}} = \frac{1}{2.303i_{\text{corr}}} \left[ \frac{\beta_a\beta_c}{\beta_a + \beta_c} \right]$$  \hspace{1cm} (55)

where $\Delta E$ is the potential shift from the corrosion potential $E_{\text{corr}}$, $\Delta i_{\text{appl}}$ is the measured external current flowing due to this potential shift $\Delta E$ and $\beta_a$ and $\beta_c$ are the Tafel slopes of the anodic and cathodic reactions respectively. $\frac{\Delta E}{\Delta i_{\text{appl}}}$ is the slope of the linear polarisation plot and $i_{\text{corr}}$ is the corrosion current density. If the $i$ values are known, $i_{\text{corr}}$ corrosion current density can be calculated using Eq. (5.5) which is a measure of the corrosion rate of the systems.

The slope of the linear polarisation curve $\frac{\Delta E}{\Delta i_{\text{appl}}}$, is mainly controlled by $i_{\text{corr}}$ and is relatively insensitive to changes in $\beta$ values as shown in Eq. (5.5). Therefore, it
Fig. 5.4 Schematic representation of a linear polarisation diagram.
is possible to formulate reasonably accurate approximation of Eq (5.5), assuming that anodic and cathodic values of 0.12 V represent the average of all corrosion systems. Eq (5.5) may reduce to:

$$\frac{\Delta E}{\Delta i_{\text{app}}} = \frac{0.026}{i_{\text{corr}}}$$  \hspace{1cm} (5.6)

Eq (5.6) can be used to calculate the corrosion resistance of a system without knowledge of its electrode kinetic parameters. Though the accuracy of this method may not be sufficient, Eq (5.6) provides a unique basis for the determination of relative corrosion rates rapidly.

(b) ac Impedance Spectroscopy method

Polarisation resistance method often gives erroneous results for systems in which the electrolyte resistance is very high. Impedance technique has been proved to be effective in these cases. ac impedance measurements, when applied to the study of electrochemical systems can provide a wealth of kinetic and mechanistic information. For this reason, the technique is becoming very popular for the study of corrosion. The ac impedance approach offers some distinct advantages over dc techniques:

1) ac impedance technique uses very small excitation amplitudes, generally in the range of 5 to 10 mV peak to peak. Excitation amplitudes of this magnitude cause only minimal perturbation of the electrochemical test system, thus reducing errors caused by the measurement technique itself.

2) Since ac impedance experiments can provide data on both electrode capacitance and charge transfer kinetics, the technique offers valuable mechanistic information.

3) Because the method does not involve a potential scan, measurements can be made in low conductivity solutions where dc techniques are subject to serious potential-control errors. In fact, ac impedance method can be used to determine the uncompensated resistance of an electrochemical cell.

Electrochemical systems can be examined with respect to their equivalent electrical circuits. A simple system could be represented by the circuit shown in Fig 5.5. \( R_{\text{cell}} \) is the uncompensated resistance between the working electrode and the reference electrode. \( R_p \) is the polarization resistance at the electrode/solution interface.
Fig 5.5 Equivalent electronic circuit for a simple electrochemical cell.
Knowledge of $R_p$ permits the calculation of electrochemical reaction rates [21]. Capacitance measurements can provide information about film formation processes at the electrode.

The object of an ac impedance experiment may be to determine the values of the various elements in the equivalent circuit or simply to confirm that a given electrochemical system fits a particular equivalent-circuit model. This is done experimentally by studying the response of the electrochemical system to an ac excitation over a wide range of frequencies. The excitation can be applied as an ac voltage or an ac current. The measured response will be, respectively, an ac current or an ac voltage, from which the system impedance can be calculated. A full description of the electrochemical system's behaviour requires both in-phase and quadrature components of impedance at a number of frequencies over the desired range. These can be calculated from the real and imaginary components of the excitation and response waveforms using the following equation

$$Z_{TOTAL} = Z' + Z''j$$

(5.7)

where $Z_{TOTAL}$ is the resultant ac impedance vector, $Z'$ and $Z''$ are the real and imaginary parts of the impedance vector. Most electrochemical systems can be characterized by impedance data over a range of $0.001$ to $10^4$ Hz.

A variety of formats can be used to plot the impedance data. Each format offers specific advantages for revealing certain characteristics of a given test system. Fig. 5.6 shows ac impedance profile for a simple electrochemical system in Nyquist form and that in the form of a Bode plot is shown in Fig. 5.7 which is explained below.

**The Nyquist plot**

This form of the plot is also known as Cole-Cole plot or a complex impedance plane diagram. The imaginary component of impedance ($Z''$) is plotted against the real component of impedance ($Z'$) at each excitation frequency. This plot could be used to compute the values of the uncompensated resistance between the working electrode and the reference electrode, $R_{DL}$, the polarisation resistance at the electrode/solution interface, $R_p$, and double layer capacitance at this interface, $C_{dl}$.
Fig. 5.6 Impedance profile for a simple electrochemical system in the form of Nyquist plot.
Fig. 5.7 Impedance profile for a simple electro-chemical system in the form of Bode plot.
Knowledge of $R_p$ permits the calculation of electrochemical corrosion reaction rates.

From the Fig 5.6 it is clear that at high frequencies only the uncompensated resistance contributes to the real portion of impedance, while at very low frequencies the polarization resistance also contributes to this measurement. Once the excitation waveform becomes much faster than the charge-transfer rate, the polarization resistance ($R_p$) becomes transparent to the technique. An ohmic resistance ($R_{\Omega}$) on the other hand will represent a constant impedance at all frequencies. This is consistent with the fact that $R_p$ can also be measured by the dc technique while $R_{\Omega}$ cannot.

The Bode plot

The Bode plot is a useful alternative to the Nyquist plot to avoid longer measurement times associated with low frequency $R_p$ determinations as this is a plot of log $|Z|$ vs log $\omega$. It allows a more effective extrapolation of data from higher frequencies. This form of the plot permits examination of the absolute impedance $|Z|$ and the phase shift $\theta$ as calculated by the following equation

$$|Z| = \sqrt{(Z')^2 + (Z'')^2} \quad \text{and} \quad \tan \theta = \frac{Z''}{Z'} \quad (58)$$

of the resultant waveform, each as a function of frequency. The log $|Z|$ vs log $\omega$ curve can yield values of $R_p$ and $R_{\Omega}$. At intermediate frequencies, the "break-point" of this curve should be a straight line with a slope of 1 3. Extrapolating this line to the log $|Z|$ axis at $\omega = 1$ (log $\omega = 0$) yields the value of $C_{dl}$ from the relationship

$$Z = \frac{1}{C_{dl}} \quad (5.9)$$

5.3 Materials and Specimen Preparation

The samples in thin ribbon form of about 5 mm width prepared by single roller melt spinning technique and as received from Allied Signals, USA, were used in the present study. The two surfaces of the ribbons were not quite the same. One of these was shiny and another was not so shiny and is referred to as dull surface. X-ray diffraction patterns on both sides of these samples confirmed their amorphous nature as described earlier.

Specimen working electrodes were prepared in the following manner to study
selectively either the dull or the bright surface 10x5 mm sample strips were taken, cleaned thoroughly with acetone and polished with alumina to remove surface oxides present, if any. These strips were soldered to a copper wire at one end to provide an electrical contact and subsequently the rough surface was fixed to a 20x5 mm Perspex disc using an epoxy resin. The bright side of the samples were thus exposed to the corrosive medium. In addition barring an area (in the range 0.25-0.5 cm²), the remaining sample was insulated with the epoxy resin. Samples were washed in acetone, etched in HCl, rinsed in double distilled water and immersed in the corrosive medium, within 5 min of preparation.

Fig 5.8 shows the schematic diagram of a conventional electrochemical cell commonly used for corrosion measurements by electrochemical methods. It is a glass vessel similar to ASTM G5 specification. The cell consists of a 500 ml flat glass beaker with an acrylic lid on the top. Holes were suitably drilled to position Platinum counter electrode, specimen working electrode and a Saturated Calomel reference electrode (SCE). During the experiment the cell was maintained at room temperature.

1N H₂SO₄ and 1N HCl acids which were the two corrosive media used, were prepared from their respective analytical reagent (AR grades) using distilled water. The corrosive medium was freely exposed to atmosphere.

5.4 Experimental Techniques

The measurements are usually made employing a potentiostat. This instrument automatically maintains the desired potential between the working and reference electrodes by passing an appropriate current between the working and counter electrodes. A basic circuit for a potentiostat is schematically shown in Fig. 5.9. A potentiostat is a controller circuit that maintains the potential between the working and the reference electrodes equal to the value $E_{in}$ shown in Fig. 5.9. If there is a small difference $E$ volts, this is sensed, amplified and a current $I$ flows. This process continues till the difference $AE$ becomes zero. The direction of the current flow depends upon the sign of $\Delta E$. Since the input impedance is very high, very low current flows through, and the reference electrode is not polarised. Using the potentiostat, polarisation may be accomplished either potentiostatically (in steps) or potentiodynamically (continuously).
Fig. 5.8 Schematic diagram of a conventional electrochemical cell used.
Fig. 5.9 Schematic of a basic circuit for a potentiostat.
Different models of Potentiostats are commercially available and in the present study, potentiodynamic polarisation measurements were carried out using an EG & G PARC potentiostat model 273 driven by m352 software, to calculate different corrosion kinetic parameters. The electrode was cathodically polarised at 2V (SCE) for half a minute, thus facilitating the removal of surface oxides (air formed films) present, if any. The electrode was allowed to reach a stable corrosion potential, before potentiodynamic polarisation was carried out. Potentiodynamic scans were initiated in the cathodic region and then proceeded in the anodic direction at a scan rate of 1 mV/s. All the potentials were measured with respect to SCE. Polarisation data was plotted in the form of Evans plot i.e., potential (E) vs log current density.

Impedance spectra were taken by Electrochemical Impedance Spectroscopy (EIS) using a Solatron 1255 frequency response analyser, interfaced with EG & G PARC model 273 potentiostat and driven by m388 software. Measurements were made in the frequency range 10¹ to 10⁶ Hz with an ac excitation potential of 5 mV. Impedance spectra were analyzed using EQUIVCRT commercial software package supplied by Boukamp. Impedance spectra were plotted in the form of Nyquist plots.

5.5 Results and Discussion

Figs 5.10 and 5.11 show the polarisation behaviour of the metallic glasses under investigation, in 1N HCl and 1N H₂SO₄ solutions respectively. Notably the anodic curves in 1N HCl show a weak tendency for passivation, indicated by limits of passive regions a and b as shown in Fig.5.10, although the passive current densities exhibited by these alloys are high lying between 2.5×10⁻⁶ and 2.7×10⁻³ A/cm². On the contrary these alloys show an active dissolution without any revelation of passivity in H₂SO₄. Various kinetic parameters namely, corrosion potential (E_corr), corrosion current density (i_corr), anodic (βₐ) and cathodic (β_c) Tafel slopes derived from these polarisation curves as explained earlier from Fig.5.3 are summarized in Tables (5.1) and (5.2). Polarisation resistance, R_p, calculated from Stern-Geary Eq. (5.5) using the above parameters is also shown in the Tables (5.1) and (5.2) for both the corrosive media.

From the values of i_corr or R_p in Tables (5.1) and (5.2), it is clearly indicated
Fig. 5.10 Typical polarisation curves of Fe_{0.8}Ni_{1.4-x}Mo_xSi_2B_{16} (x=0, 1, 2, 3 and 4) alloys in 1N HCl.
Fig. 5.11 Typical polarisation curves of Fe$_{68}$Ni$_{14-x}$Mo$_x$Si$_2$B$_{16}$ ($x=0,1,2,3$ and $4$) alloys in 1N H$_2$SO$_4$. 

$$E(V) \text{ vs. SCE}$$

$$\log(I/\text{area})(\text{amp/cm}^2)$$
Table 5.1 Kinetic parameters obtained from the polarisation curves in 1N HCl.

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>$E_{corr}$ mV(SCE)</th>
<th>$i_{corr}$ μA/cm$^2$</th>
<th>$\alpha$ mV/decade</th>
<th>$\beta$ mV/decade</th>
<th>$R_p$ Ohm cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-571</td>
<td>153</td>
<td>109</td>
<td>203</td>
<td>201</td>
</tr>
<tr>
<td>1</td>
<td>-540</td>
<td>226</td>
<td>71</td>
<td>223</td>
<td>103</td>
</tr>
<tr>
<td>2</td>
<td>-567</td>
<td>153</td>
<td>79</td>
<td>237</td>
<td>167</td>
</tr>
<tr>
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<td>-506</td>
<td>271</td>
<td>31</td>
<td>154</td>
<td>41</td>
</tr>
<tr>
<td>4</td>
<td>-554</td>
<td>141</td>
<td>70</td>
<td>134</td>
<td>142</td>
</tr>
</tbody>
</table>

Table S.2 Kinetic parameters obtained from the polarisation curves in 1N H$_2$SO$_4$

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>$E_{corr}$ mV(SCE)</th>
<th>$i_{corr}$ μA/cm$^2$</th>
<th>$\alpha$ mV/decade</th>
<th>$\beta$ mV/decade</th>
<th>$R_p$ Ohm cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-357</td>
<td>13</td>
<td>125</td>
<td>176</td>
<td>2774</td>
</tr>
<tr>
<td>1</td>
<td>-290</td>
<td>50</td>
<td>25</td>
<td>103</td>
<td>154</td>
</tr>
<tr>
<td>2</td>
<td>-310</td>
<td>400</td>
<td>137</td>
<td>137</td>
<td>148</td>
</tr>
<tr>
<td>3</td>
<td>-317</td>
<td>200</td>
<td>169</td>
<td>169</td>
<td>264</td>
</tr>
<tr>
<td>4</td>
<td>-331</td>
<td>125</td>
<td>109</td>
<td>109</td>
<td>116</td>
</tr>
</tbody>
</table>
that these alloys exhibit very high corrosion rates in HCl as well as $\text{H}_2\text{SO}_4$. The cathodic Tafel slope, $\beta_c$, does not show any systematic variation though a few Mo containing alloys exhibit lower values than the base alloy without Mo. However, examination of the cathodic curves of Figs 5 10 and 5 11 reveal that the cathodic reaction most likely the $\text{H}_2$ evolution has higher reaction rate with Mo addition than without Mo. This is inferred from the fact that most of the cathodic curves are shifted towards right side. Such a tendency is possible only when the exchange current density for the $\text{H}^+/$H equilibrium ($i_{\text{eq}}$ H) increases with Mo addition. In contrast to $\beta_c$, there is a significant reduction in $\beta_a$ due to Mo addition both in HCl and H$_2$SO$_4$. These observations emphasize the fact that mere amorphous nature of the alloy is inadequate to provide resistance towards corrosion. The addition of Mo follows the Cr effect for improvement of corrosion resistance of Fe-P-C type of alloys. It is also noted that addition of Mo ($\approx$5 at%) in HCl leads to a greater decrease in corrosion rate and anodic current density than the addition of an equal amount of Cr in HCl and leads to anodic passivation in 1N HCl [22,23]. The passivating capabilities of glassy metals arise when both Cr and Mo are present and addition of P increases this effect remarkably. Much of the work by Hashimoto, Naka, Masumoto et al. [6-12,22,24] confirms these results. Also, it is known that addition of Ni is considered to promote passivation only in the presence of Cr, providing good corrosion resistance [10]. Presence of one or more passivating elements like Cr and P in the alloys is a necessary condition to extend the benefit of amorphous structure of alloys. Thus Fe-Cr-Mo-B in 6N HCl [24] Fe$_{40-x}$Mo$_x$P$_{11}$C$_7$ in 1N HCl [11] and Fe$_{42-x}$Mo$_x$C$_{18}$ [22] in 1N HCl have been reported to exhibit excellent corrosion resistance.

The present alloys fail to exhibit large corrosion resistance on two accounts. Firstly, the metalloids B and Si are inferior to P [61] in offering corrosion resistance. Secondly, unlike Fe$_{40}$Ni$_{18}$Mo$_{18}$B$_{18}$ and Fe$_{40}$Ni$_{18}$Mo$_{18}$Si$_{18}$B$_{12}$ [25] glasses, which possess good resistance to corrosion, the present alloys do not contain high Ni, which is relatively a nobler element than Fe. From the Table (5 1) there appears to be no systematic change in $i_{\text{corr}}$ in HCl medium with the variation in x. A possible improvement in corrosion resistance due to the raise in Mo is off-set by the simultaneous reduction in Ni content of the alloy. With respect to $\text{H}_2\text{SO}_4$ solution a
gradual decrease in corrosion resistance occurs as $x$ is increased from 0 to 2, which can be seen from the values of $R_p$ given in Table (5.2). On further increasing $x$ a steady raise in corrosion resistance is noticed. This indicates that at higher $x$ values Mo has higher beneficial effect than Ni. Indeed, in a systematic study of Fe-Mo crystalline alloys, Ambrose [26] has shown that if the Mo content of Fe-Mo alloy exceeds 5 wt%, it offers good corrosion resistance, while at lower amounts Mo tends to be detrimental, agreeing with the present trend. Nevertheless, the effective role of Mo is decided by the complementary role played by other alloying elements. This becomes clear from the fact that in austenitic stainless steels even 2 wt% Mo brings out a significant improvement in corrosion resistance and passivity as has been shown by AISI 304 and 316 ss while even 5 wt% Mo brings out only a marginal change.

The electrochemical investigation of the present glassy alloys further enables an understanding of the role Mo plays in ferrous alloys towards passivity when Cr is not present. This has become possible now since homogeneous single phase nature is retained in spite of high Mo content, which would be difficult if crystalline Fe-based alloys are chosen. This is because in crystalline Fe-based alloys the solubility of Mo is low. As a consequence additional phases would be formed which by itself will be a factor influencing corrosion behaviour over the intended compositional variation brought by Mo.

The passivation behaviour of these glasses is further examined using ac impedance spectroscopy. Impedance diagrams in the form of Nyquist plots obtained at $E_{corr}$ in 1N HCl and 1N $H_2SO_4$ solutions are shown in Fig 5.12 and Fig 5.13 respectively and these exhibit two semicircles. As these alloys exhibit an apparent tendency to passivate in HCl their impedance behaviour were also studied at -456 mV and 200 mV (SCE) which are the limits of the passive region which are indicated by points a and b as shown in Fig 5.10. The corresponding impedance profiles in the form of Nyquist plots respectively are brought out in Fig 5.14 and Fig 5.15. In HCl barring a few cases existence of two overlapping capacitive loops are discernible in Nyquist plots obtained at $E_{corr}$. -456 mV and -200 mV (SCE). Nyquist plots for the glassy alloys obtained in $H_2SO_4$ differ from those obtained in HCl by displaying a capacitive loop followed by an inductive loop. The resistance values corresponding to first and second semicircles namely $R_1$ and $R_2$ are summarized in Tables (5.3) and
Fig. 5.12 Nyquist representation of impedance data at $E_{corr}$ in 1N HCl.
Fig. 5.13 Nyquist representation of impedance data at $E_{corr}$ in 1N H$_2$SO$_4$. 
Fig. 5.14 Nyquist representation of impedance data at $-456 \text{ mV (SCE)}$ in 1N HCl.
Fig. 5.15 Nyquist representation of impedance data at -200 mV (SCE) in 1N HCl.
Table 5.3 Variations in $R_1$ and $R_2$ values obtained from the impedance curves in 1N HCl medium.

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>$R_1$ Ohm. cm$^2$</th>
<th>$R_2$ Ohm. cm$^2$</th>
<th>$R_p = R_1 + R_2$ Ohm cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>101</td>
<td>41</td>
<td>141</td>
</tr>
<tr>
<td>1</td>
<td>325</td>
<td>95</td>
<td>420</td>
</tr>
<tr>
<td>2</td>
<td>195</td>
<td>33</td>
<td>228</td>
</tr>
<tr>
<td>3</td>
<td>485</td>
<td>-</td>
<td>485</td>
</tr>
<tr>
<td>4</td>
<td>184</td>
<td>105</td>
<td>289</td>
</tr>
</tbody>
</table>

Table 5.4 Variations in $R_1$ and $R_2$ values obtained from the impedance curves in 1N H$_2$SO$_4$ medium.

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>$R_1$ Ohm. cm$^2$</th>
<th>$R_2$ Ohm. cm$^2$</th>
<th>$R_p = R_1 + R_2$ Ohm cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2060</td>
<td>-</td>
<td>2060</td>
</tr>
<tr>
<td>1</td>
<td>145</td>
<td>-</td>
<td>145</td>
</tr>
<tr>
<td>2</td>
<td>148</td>
<td>49</td>
<td>197</td>
</tr>
<tr>
<td>3</td>
<td>212</td>
<td>59</td>
<td>271</td>
</tr>
<tr>
<td>4</td>
<td>92</td>
<td>48</td>
<td>140</td>
</tr>
</tbody>
</table>
Tables (5.5) and (5.6) show the variations in $R_1$ and $R_2$ values obtained from the impedance spectra taken at fixed potentials of -4.56 mV and 200 mV in 1N HCl medium respectively. The appearance of high and low frequency capacitive loops has been attributed to dielectric relaxation of films and Faradaic processes, respectively, occurring on the electrode surface [27]. With regards to inductive loops no definite processes can be assigned. Literature, however, indicates that inductive loop in Nyquist representation occurs as a result of either of the following reasons namely, pitting [28] and increase in anionic defects over cationic defects [29].

The fact that the glassy alloys exhibit a high frequency capacitive loop in addition to a low frequency capacitive loop suggests that some sort of film exists on these alloys in HCl, further supporting polarisation studies. Therefore it seems that Cl- ions promote formation of corrosion/passive film while SO$_4^{2-}$ ions do not favour such film formation. In this context it is worthwhile to mention the well established fact that the presence of Mo in the film formed on several Mo containing stainless steels passivated in H$_2$SO$_4$ medium only if Cl$^-$ are added to the solution [30]. This suggests that Cl$^-$ differ from SO$_4^{2-}$ with respect to film formation. Further more Ambrose [26] also proposed that Mo minimizes localized corrosion by the formation of salt film on Fe-Mo alloys. This happens when the MoO$_4^{2-}$ concentration in the vicinity of the electrode surface is high. The possibility of salt film formation seems to gain credence from the fact that the metallic glasses in HCl do not show any systematic variation in $R_p$ value with variation in x value [Table (5 1)]. Even for a single composition, the values differ from one specimen to another to some extent. This is because the nature and adherence of salt film formed on the alloy surface will depend more on local chemistry and surface nature than on alloy chemistry. It is also to be noted that the resistance offered by these films at the passive potential ( 200 mV) is much lower than that obtained at $E_{corr}$.

Mo seems to operate through a different mechanism to enhance passivity in H$_2$SO$_4$. The ESCA work [30] shows that Mo enriches an alloy surface with high Ni or Cr when passivated in H$_2$SO$_4$. The high Ni and or Cr on the surface in turn lower passive current and Mo per se do not contribute to passivity. Viewed in this
Table 5.5 Variations in $R_1$ and $R_2$ values obtained from the impedance curves at a fixed potential of $-456$ mV in 1N HCl medium.

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>$R_1$ (Ohm cm$^2$)</th>
<th>$R_2$ (Ohm cm$^2$)</th>
<th>$R_p = R_1 + R_2$ (Ohm cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>77</td>
<td>40</td>
<td>117</td>
</tr>
<tr>
<td>1</td>
<td>452</td>
<td>-</td>
<td>452</td>
</tr>
<tr>
<td>2</td>
<td>190</td>
<td>37</td>
<td>227</td>
</tr>
<tr>
<td>3</td>
<td>170</td>
<td>-</td>
<td>170</td>
</tr>
<tr>
<td>4</td>
<td>185</td>
<td>83</td>
<td>268</td>
</tr>
</tbody>
</table>

Table 5.6 Variations in $R_1$ and $R_2$ values obtained from the impedance curves at a fixed potential of -200 mV in 1N HCl medium.

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>$R_1$ (Ohm cm$^2$)</th>
<th>$R_2$ (Ohm cm$^2$)</th>
<th>$R_p = R_1 + R_2$ (Ohm cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>73</td>
<td>17</td>
<td>90</td>
</tr>
<tr>
<td>1</td>
<td>76</td>
<td>20</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>85</td>
<td>20</td>
<td>105</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>62</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>83</td>
<td>24</td>
<td>107</td>
</tr>
</tbody>
</table>
Table 5.7 Comparison of Polarisation 

resistance, $R_p$, values obtained from polarisation experiments and impedance experiments at $E_{corr}$ in both the media.

<table>
<thead>
<tr>
<th>Sample (x)</th>
<th>Polarisation</th>
<th>Impedance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1N HCl</td>
<td>1N $\text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td></td>
<td>1N HCl</td>
<td>1N $\text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>0</td>
<td>201</td>
<td>2774</td>
</tr>
<tr>
<td>1</td>
<td>103</td>
<td>154</td>
</tr>
<tr>
<td>2</td>
<td>67</td>
<td>148</td>
</tr>
<tr>
<td>3</td>
<td>41</td>
<td>264</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>116</td>
</tr>
</tbody>
</table>
perspective the present glasses fail to show high passivity because they do not have either high Ni content as in Fe_{50}Ni_{10}Mo_{4}Si_{6}B_{12} [25], Cr [24], or P [11]. On the other hand, absence of these elements results in a gradual increase in corrosion rate. This is clear from the increase in $i_{\text{corr}}$ values listed in Table (5.2) and the decrease in $R_p$ values listed in Table (5.4) though not regularly.

In the present study, an attempt has been made to find out to what extent polarisation data correlate with that of impedance data using $R_p$ as a parameter which is a measure of corrosion resistance. Table (5.7) compares the $R_p$ values obtained through Stern-Geary relationship with those obtained from impedance spectroscopy in both the media respectively at $E_{\text{corr}}$. A good correlation seems to exist between the two data when the alloys undergo active dissolution (H2SO4) and not when they possess passivity. As far as the comparison with respect to passivity is concerned, the values of $R_p$ obtained from impedance curves correspond to the total contribution from the film and the charge transfer resistance. The weak passivation noticed in the polarisation curve has been attributed to salt film formation as opposed to thin passive film obtained in Mo containing alloys. Thus it brings out a fact that $R_p$ cannot be considered to be a factor indicating corrosion resistance of the alloy if the alloy passivates and more so if it forms salt film.

5.6 Conclusions

1. The present glassy alloys exhibit poor corrosion resistance both in 1N HCl and 1N H2SO4 solutions.
2. With increase in Mo content, the passivity of the alloy increases in HCl, though the passive current is quite high, while no such passivity is seen in H2SO4.
3. The mechanism of alloys' dissolution in presence of Mo in HCl seems to be different from that of H2SO4.
4. A good correlation seems to exist between the polarisation resistance values obtained by impedance and polarisation techniques when the alloys undergo active dissolution and not when they possess passivity.
5.7 References


18 C Wagner and W Traud, *Elektrochem.*, 44(1938) 391


26 J R. Ambrose, *Corrosion, 34* (1978) 27


