2.1 Introduction

“Thermal Analysis” refers to the analysis of properties of a materials that change with temperature. These properties include mass, dimensions, dielectric permittivity, thermal diffusivity, mechanical stiffness, optical properties, etc. In other words, thermal analysis involves various techniques that are used to study the changes in physical or chemical properties of materials when they are subjected to heat, i.e., heated, cooled or kept at constant temperature. Along with providing some basic information about the properties of materials, these techniques are also a prominent engineering tool required for the development of new functional materials. A wide variety of materials, including polymers, ceramics, metallic glasses, composites, thin films, etc., can be studied by thermal analysis techniques. Different properties are studied by different techniques. Table 2.1 reports different techniques and various properties associated with them.

Table 2.1 Different thermal analysis techniques [2.1]

Techniques	Properties measured
Dielectric thermal analysis (DEA)	Dielectric permittivity and loss factor
Differential thermal analysis (DTA)	Temperature difference
Differential scanning calorimetry (DSC)	**Heat difference**
Dilatometry (DIL)	Volume
Dynamic mechanical analysis (DMA)	Mechanical stiffness and damping
Evolved gas analysis (EGA)	Gaseous decomposition products
Laser flash analysis (LFA)	Thermal diffusivity and thermal conductivity
Thermogravimetric analysis (TGA)	Mass
Thermomechanical analysis (TMA)	Dimension
Thermo-optical analysis (TOA)	Optical properties
Derivatography	A complex method in thermal analysis

The general instrumentation for the thermal analysis primarily includes (shown in fig. 2.1):

i. A sample holder, where the sample is kept

ii. Sensors for detecting the required properties with respect to temperature

iii. A closed chamber where the sample and sensors can be placed and the experimental parameters can be controlled according to the requirements.

iv. A computer for adjusting the experimental parameters, collecting data and performing further calculations.

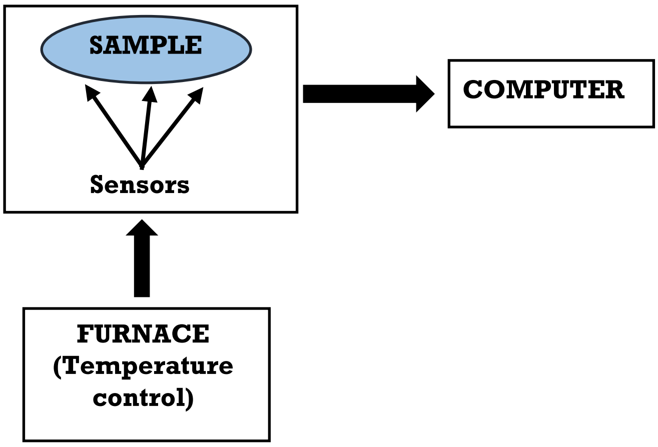

Fig. 2.1: General instrumentation of thermal analysis techniques

Sometimes, TGA and DSC are used simultaneously, since they require same experimental conditions for their operation. This concurrent use of two instruments is known as simultaneous thermal analysis (STA) [2.1].

Apart from controlling temperature profile, it is very important to control other parameters such as atmosphere inside the chamber. Some reactions need inert atmosphere, whereas others can be done in air also. Depending upon the reaction; air, nitrogen, or helium atmospheres can be used in the instruments.

2.2 Differential Scanning Calorimetry (DSC)

One of the most common thermo-analytical technique is “**Differential Scanning Calorimetry**” (**DSC**). E.S. Watson and M.J. O'Neill developed this technique in 1962 and commercialized it in 1963 at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy [2.2]. The transitions associated with the change in temperature are referred to as *thermal transitions*. DSC provides useful information about the thermal transitions occurring in a sample. It is a very informative tool for studying the phase changes taking place in an amorphous material as a function of temperature.

Basic phase changes occurring in an amorphous material when it is heated are:

a) **Glass transition**: It is a reversible phase change that involves change in the structure of an amorphous material form a relatively hard state to a rubbery state. Knowledge of the temperature at which glass transition occurs (known as “glass transition temperature”) is of great significance as it gives information about the stability of the glassy or amorphous state.

b) **Crystallization**: It is an irreversible phase change that involves the ordering of the disordered structure through nucleation and growth processes, thereby forming crystalline structure.

c) **Melting**: It is a phase change in which the crystalline lattice breaks into a disordered state (solid to liquid transition → “fusion”). It is single step endothermic process, unlike crystallization which is a two-step, exothermic process (nucleation and growth).

DSC measures the amount of heat required to raise the temperature of sample, with respect to reference, as a function of temperature. In other words, it provides information about the exo- and endo-thermic processes occurring in sample by measuring the amount of heat absorbed or released during heating or cooling of the sample. It provides information about the characteristic temperatures of a sample like the glass transition temperature, crystallization and melting temperatures, heat of phase changes such as fusion and melting, heat capacity, etc.

There are two types of DSC:

1. Power compensated DSC
2. Heat flux DSC

They differ in their construction and working. The furnace of a power compensated DSC uses two separate blocks for sample and reference, whereas a heat flux DSC has a single block for heating both sample and reference. Power compensated DSC works on the principle of keeping the temperature difference between sample and reference constant. The amount of heat flow to be supplied to the sample and reference is determined by the differential thermal power between them. Heat flux DSC, on the other hand, allows the temperature difference between the sample and reference to vary and this temperature difference is used to get required heat flow. Power compensated DSC have better resolution of thermal events occurring during heating of a sample, whereas heat flux DSC is more sensitive towards the thermal events.

The schematic diagram of DSC is shown in fig. 2.2 [2.3]. The sample and reference both are kept adjacent to each other and a common heating profile is applied to both of them. Both of them are sealed in aluminium pans (or copper). Reference is commonly an inert material like alumina, or an empty pan with lid. The crucibles used are made up of platinum, aluminium, copper, gold, etc., in order to withstand with the high temperatures applied to them and to avoid any reaction with them. Different atmospheres, such as air, nitrogen, argon, vacuum, etc, can be maintained in order to achieve desired outcome. Both (sample and reference) are connected to a temperature sensor and a heater coil. Heater coil heats them at a constant rate and temperature sensor senses the temperature difference between the sample and reference. Same Linear heating rate is applied to both of them, i.e., temperature is increased at a constant rate. Both the sample and reference are maintained at same temperature.

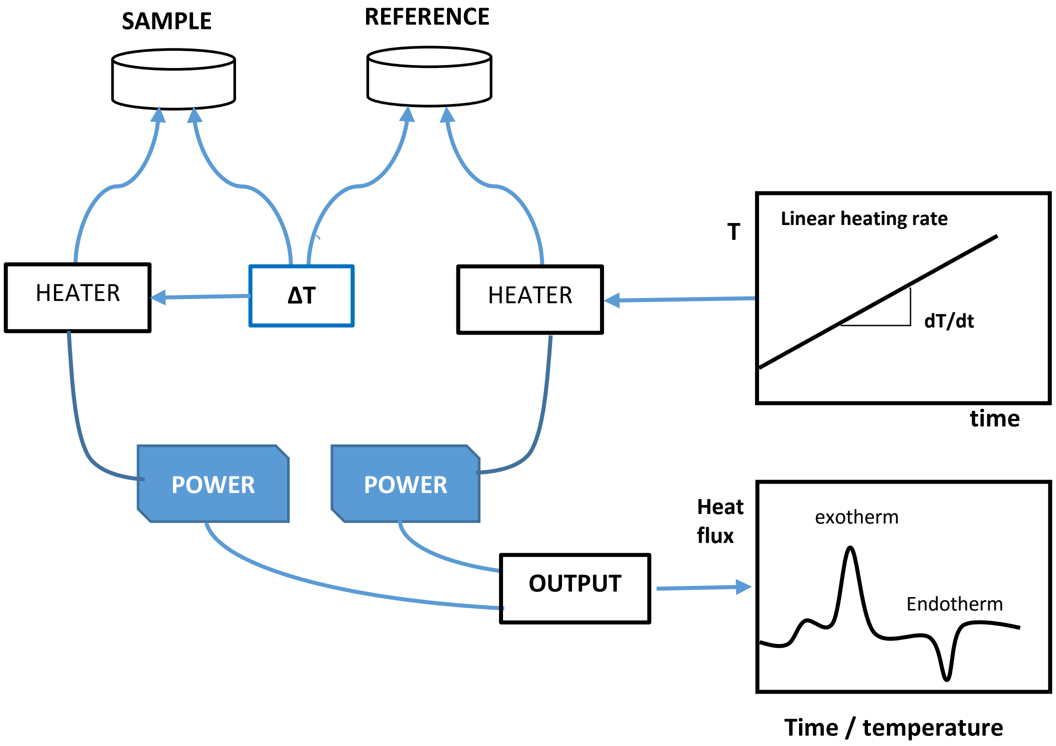

Fig. 2.2: Schematic diagram of a Differential Scanning Calorimetry (DSC)

When the heating is carried out, the sample tends to release or absorb heat as a result of phase changes occurring in it. In order to maintain same temperature for both sample and reference, more or less heat is needed to be supplied to the sample undergoing phase transitions. This amount of heat supplied or taken out determines the exo- or endo-thermic processes occurring in the sample. The amount of heat transferred to the sample is monitored using a PC and the output is received in form of a thermo-gram showing different exothermic and endothermic peaks. Two different conventions are used to represent the exo- and endo thermic processes. Exothermic and endothermic reactions are shown in positive and negative directions respectively, or vice-versa depending upon the kind of conventions used in the instrument. A typical DSC plot is shown in fig 2.3. The thermogram can be used to understand many important properties of a material, such as heat capacity, temperature and enthalpy of phase changes such as glass transition, crystallization, and melting.

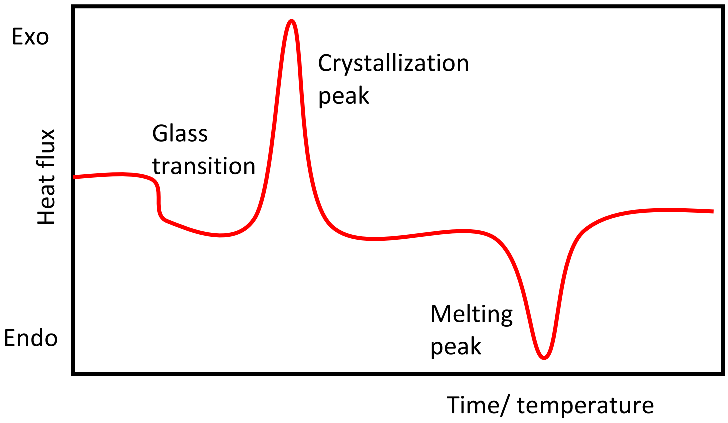

Fig. 2.3: Typical DSC thermogram

Heat capacity: Heat capacity (C_p) is defined as the amount of heat required to raise the temperature of a material by 1^0C. It can be calculated by the ratio of amount of heat flow and the heating rate [2.4]. The amount of heat flow is the heat flowing per unit time, i.e., $Heatflow = \frac{Heat}{Time} = \frac{q}{t}$, and heating rate is the time rate of change temperature, i.e., $\frac{\Delta T}{t}$, where, *t* and *T* are time and temperature respectively.

Hence, heat capacity can be written as,

$$C_p = \frac{q/t}{\Delta T/t} = \frac{q}{\Delta T} \tag{2.1}$$

Thus, the slope of heat supplied versus increase in temperature gives the value of heat capacity of that sample.

Glass Transition: Glass transition is a downward shift in the baseline (fig. 2.4) with increase in temperature (or time). This shift in baseline does not occur instantly, rather it takes place over a temperature range. Due to this the determination of the glass transition temperature (T_g) becomes difficult and generally it is taken out to be in the middle of the transition. It is an endothermic transition, i.e., it absorbs heat. Hence the heat capacity of the material increases during glass transition.

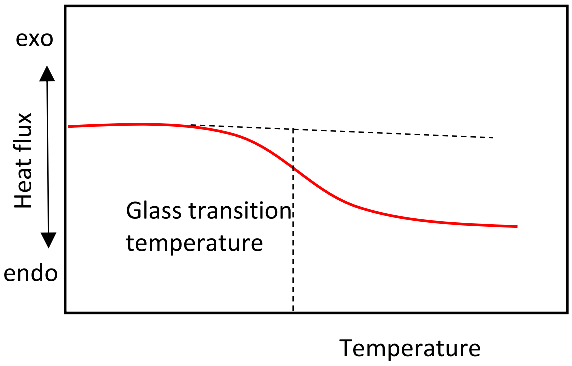

Fig. 2.4: Glass Transition

Crystallization: It is an exothermic event, in which the material releases heat and forms a low energy (stable) ordered structure. The enthalpy of crystallization can be obtained by calculating the area under the peak, and dividing it by the heating rate. Further the percentage crystallinity at a particular degree of conversion can also be calculated. Along with the enthalpy of crystallization and the crystallization temperature, DSC can also be used to determine whether the amorphous material crystallizes in a single step or it takes multiple steps to crystallize.

Melting: As heating of a material is continued beyond crystallization, eventually it melts. Melting is an endothermic process that transforms a solid material into liquid.

Crystallization and melting are first order phase transitions since they involve latent heat. Whereas, no latent heat is associated with glass transition, rather it involves an increase in heat capacity. Hence, it is considered to be a second order phase transition.

The advantages of DSC technique can be summarized as [2.5]:

i. It is a fast technique, i.e., it takes a small time to perform one run.

ii. Different kind of samples such as solid, liquid, powders, thin films can be tested in a variety of environments (air, vacuum, inert gas, etc.)

iii. A wide range of temperature can be used to analyse the phase transitions in a material, and quantitative analysis of these transitions can be done easily using softwares.

iv. The applicability of DSC can be extended to a wide variety of materials that includes the pharmaceutical and drug industry, polymers, liquid crystals, and food science. DSC can also be used to determine the oxidative stability of a material.

Though DSC has many advantages, still its accuracy and precision are limited by some factors that are listed below:

i. In case of overlapping processes, it measures only the average value of heat flow. The difficulty to separate multiple events make further analysis complicated.

ii. The sensitivity and resolution of DSC cannot be improved simultaneously. In case of processes like transitions having low energy, sensitivity can be increased by increasing sample size or heating rate. But this, in turn decreases the resolution.

iii. Further, the sensitivity of the measurements also depend upon the laboratory conditions (temperature, humidity, etc) and the cooling process. Due to this small transitions like glass transition are difficult to detect.

2.3 Modulated Differential Scanning Calorimetry (MDSC)

Modulated DSC (MDSC) is basically an extension of DSC, in a way that it has all the advantages of traditional DSC, but has a capability to overcome its limitations. It operates on the same principle on which DSC operates, has the same heat flux chamber and the sample preparation is also done in the same way as it is done in DSC. But the point of difference of MDSC from DSC is that it uses modulated heating profile, which comprises of the traditional linear ramp overlaid by a sinusoidally varying heating rate. The modulated heating rate, as shown in fig. 2.5, depends upon the amplitude and frequency of sinusoidal heating rate along with the linear heating rate [2.4]. Higher resolution can be achieved by decreasing heating rate and period of oscillation, and increasing amplitude.

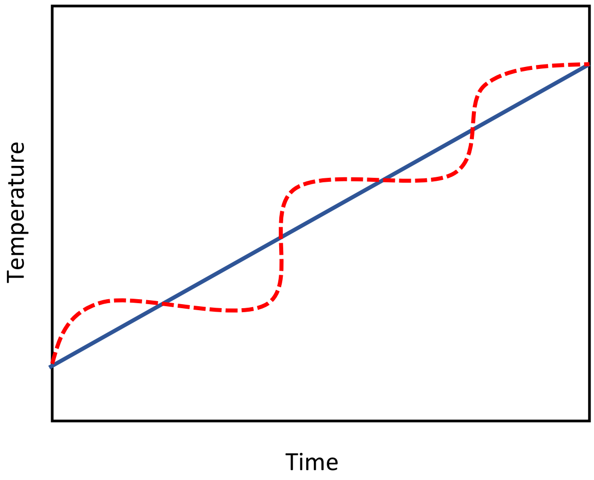

Fig. 2.5: Typical modulated heating rate

MDSC can detect weak transitions due to its higher sensitivity than DSC. Moreover, its resolution does not decrease with increase in sensitivity. It is a combination of high sensitivity and high resolution. Further, MDSC can easily separate different overlapping processes, which are difficult for DSC. Hence, complex transitions can easily be interpreted by MDSC.

The heating rate in a MDSC can be expressed as [2.6]:

$$dT/dt = \beta + A_T \omega \cos \omega t \tag{2.2}$$

Where: dT/dt = instantaneous heating rate (^{o}C/minute)

β = underlying heating rate (^{o}C/minute)

A_T = modulation amplitude (^{o}C)

ω= angular frequency = 2π/modulation period (min^{-1})

t = time (minutes)

The linear heating rate applied in MDSC is slower than the conventional DSC in order to allow sufficient modulations during the heating event. The amplitude of instantaneous heating rate should be high since greater amplitude implies a higher heat flow. Larger amplitudes increase the sensitivity of the measurement. But the amplitude must not be very large as it hampers the modulation process. Also, large period of oscillation allows the material to respond to the modulated temperature. Hence, the modulated signal needs to be maintained in terms of linear heating rate, and amplitude and period of modulation.

The heat flow in any DSC or MDSC can be expressed as the sum of heat flow component and kinetic component [2.5],

$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T,t) \qquad (2.3)$$

Where:

dH/dt is the Total Heat Flow due to the underlying or linear heating rate.

C_p dT/dt is the Reversing Heat Flow Component of the Total Heat Flow

C_p is the Heat Capacity

dT/dt is the heating rate, which has both a linear and sinusoidal (modulated) component

f (T,t) is the Kinetic Component of the Total heat flow

DSC provides the total heat flow dH/dt at an average heating rate. It can be observed from equation (2.3) that the total heat flow (dH/dt) actually comprises of two components; heat capacity related and kinetic component. The kinetic component is the function of temperature and time. It is also known as non-reversible heat flow component as it is a time dependent component. Whereas the heat capacity related component (reversing heat flow component) depends upon the heat capacity and the heating rate. MDSC measures the total heat flow along with its two components. The linear heating rate of MDSC allows it to calculate the total heat flow and the sinusoidal heating rate helps it in calculating the heat capacity related information. The kinetic component can be calculated by subtracting the reversing heat flow component from the total heat flow. Its ability to separate total heat flow into different components reduce the errors and improves the data interpretation. Hence, complex reactions involving overlapping events can be easily studied by MDSC. Its high sensitivity also helps in studying small transitions like glass transition. Its advantages, further include the increased resolution without loss of sensitivity, and determination of total heat flow and heat capacity in a single experiment.

In present thesis, thermal analysis of amorphous ribbons of $Ti_{20}Zr_{20}Cu_{60}$ metallic glass has been carried out using DSC 2910 (TA Instruments Inc., USA) system in modulated DSC mode. Fig. 2.6 shows the picture of DSC 2910 (TA Instruments Inc., USA). Heating experiments were performed at four heating rates, 1, 2, 4, and 8^0Cmin^{-1}, in order to study the non-isothermal crystallization kinetics of $Ti_{20}Zr_{20}Cu_{60}$ metallic glass. Mass of the sample was kept in between 2-6 mg. The detailed analysis of crystallization kinetics of $Ti_{20}Zr_{20}Cu_{60}$ metallic glass by iso-conversional is explained later in this thesis in chapter 3. Single roller melt spinning technique was employed to prepare amorphous ribbons of $Ti_{20}Zr_{20}Cu_{60}$ metallic glass at the Institute of Material Research, Tohoku University, Sendai, Japan. Argon atmosphere was used for the preparation of sample. XRD and TEM analysis were done to confirm the amorphous nature of $Ti_{20}Zr_{20}Cu_{60}$ metallic glass.

Fig. 2.6: A picture of DSC 2910 (TA Instrument Inc. USA) system

2.4 Potentiostat

Apart from thermal analysis, this thesis also focusses on the corrosion studies of Co- and Fe-based amorphous alloys. The corrosion studies were performed using potentiodynamic polarization technique. The electrochemical polarization experiments were carried by using an instrument named “Potentiostat”. A potentiostat is an electronic device that controls the potential between electrodes by monitoring the current flow between them. It can be a bi-potentiostat (two electrodes) or a poly-potentiostat (more than two electrodes) [2.7]. A bi-potentiostat comprises of a working and a reference electrode. The limitation associated with bi-potentiostat is that the measurements depend upon the electrode area and the distance between the two electrodes. As the difference between the electrodes is increased, the current decreases due to the increase in resistance. This limits the reproducibility of the results. Generally, the term *potentiostat* refers to a three electrode system that consists of a working, counter and reference electrode. All the three electrodes are placed inside an electrochemical cell that is filled with an electrolyte solution. In a three electrode potentiostat, the voltage between working and reference is controlled by supplying current through the counter electrode. The current flowing between working and reference electrodes is measured. In this way the controlled variable is voltage and the measured variable is current and the parameter that manages these two variables in accordance with the Ohm's law is resistance. First three electrode potentiostat was first built in 1942 by Hickling [2.8]. Fig. 2.7 shows a schematic diagram of a potentiostat [2.9].

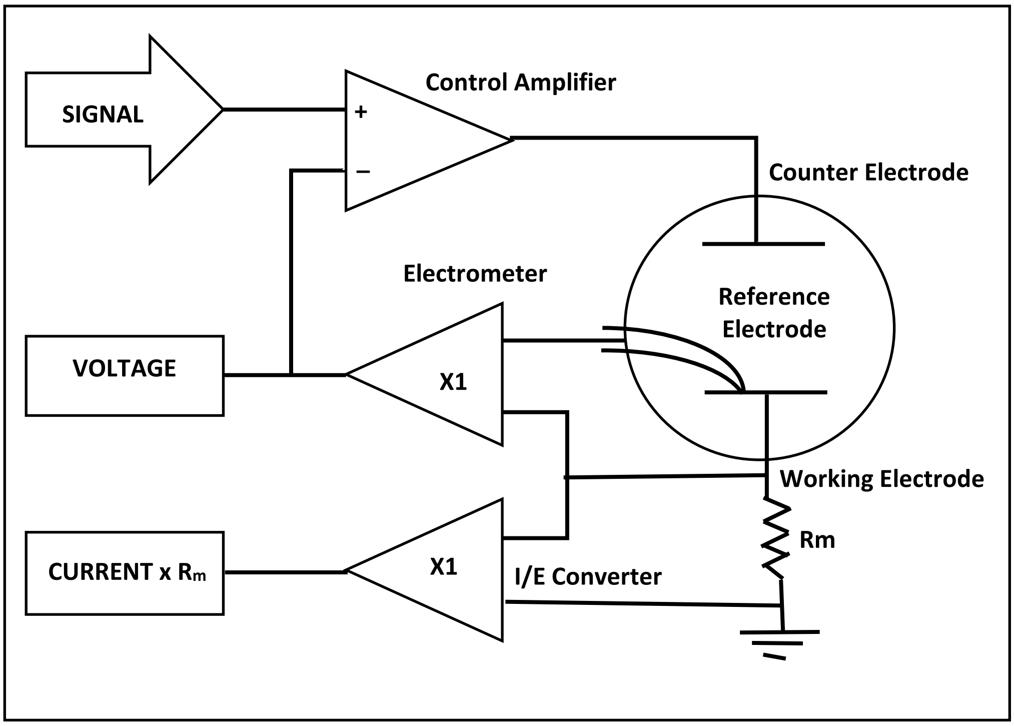

Fig. 2.7: Schematic diagram of a Potentiostat

The components of a potentiostat are discussed below [2.9-2.10]:

Working Electrode: It is the electrode where the current is measured while controlling voltage between it and reference electrode. Generally, gold, platinum or some inert material is used as the working electrode. But in case of corrosion testing, the material whose corrosive ability is to be tested is used as working electrode.

Reference Electrode: This electrode is used to measure the voltage at the working electrode. Its potential must remain unchanged when there is no current flowing through it. Mostly, Calomel electrode is used as reference electrode in laboratory experiments.

Counter Electrode: The purpose of this electrode is to complete the circuit, in which the current flows from the working electrode to the counter electrode. Generally the counter electrode is an inert metal like platinum or graphite rod for lab experiments.

Control Amplifier (CA): The function of CA is to maintain the potential between the reference and working electrodes according to the input signal. It tries to control the cell voltage identical to the signal source voltage. It also controls the current in the electrochemical cell so as to maintain the equilibrium condition.

Electrometer: It measures the voltage difference between the reference and the working electrodes. It serves two main functions: firstly its output is the feedback to the CA and secondly it acts as signal whenever cell voltage is required. Ideally, it should have zero input impedance and infinite output impedance. But practically, it has very small but non-zero input impedance.

I/E Converter (Current-to-Voltage): It measures the cell current by forcing it to move through the current x R_m signal. R_m is used to measure current in the cell by calculating the voltage drop across it. For corrosion experiments, where the current varies in 7-9 orders of magnitude, single resistor R_m is switched to many different resistors in the I/E converter in order to measure a wide range of current.

Finally, the signal is a voltage source that is controlled by computer, and X1 is the differential amplifier that has unit gain.

In present thesis, the electrochemical polarization experiments on $Co_{66}Si_{12}B_{16}Fe_4Mo_2$ and two Fe- based ($Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ and $Fe_{67}Co_{18}B_{14}Si_1$) metallic glasses were performed using Gammry reference 600 potentiostat, using a typical three electrode system. The tests were performed using calomel electrode as reference, graphite electrode as counter electrode and test sample as working electrode. Table 2.2 reports the operating parameters of potentiodynamic test.

Table 2.2 Operating parameters of potentiodynamic test

Parameters	**Values**
Initial voltage	-0.5 V w.r.t. ref. Electrode
Final voltage	1.5 V w.r.t. ref. Electrode
Scan rate	5 mV/sec
Conditioning time	60 sec
Initial delay	60 sec
Sample exposure area	5mm x 5mm = 0.25 cm^2

In chapter 5, the bio-corrosion resistance of $Co_{66}Si_{12}B_{16}Fe_4Mo_2$ and two Fe-based ($Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ and $Fe_{67}Co_{18}B_{14}Si_1$) metallic glasses have been discussed in detail. Four artificially synthesized body fluids, viz artificial saliva solution (ASS, pH 6.2), phosphate-buffered saline solution (PBS, pH 7.4), artificial blood plasma solution (ABP, pH 7.4), and Hank’s balanced saline solution (HBSS, pH 7.4), were prepared using analytical reagent based chemicals using distilled water, maintained at constant room temperature. The compositions of these electrolytes are reported in table 2.3 [2.11]. SEM was used to study the surface morphology of corroded sample.

Table 2.3 Compositions (g/L) of Artificial Saliva Solution (ASS), Phosphate-Buffered Saline (PBS) Solution, Artificial Blood Plasma (ABP) Solution and Hank's Balanced Saline Solution (HBSS)[2.11]

Composition (g/L)	**Solutions**			
	Artificial Saliva Solution (ASS, pH 6.2)	**Phosphate-Buffered Saline Solution (PBS, pH 7.4)**	**Artificial Blood Plasma Solution (ABP, pH 7.4)**	**Hank's Balanced Saline Solution (HBSS, pH 7.4)**
$NaCl$	1.5	8.0	8.036	8.0
$NaHCO_3$	1.5	-	0.352	0.35
NaH_2PO_4	0.5	1.15	-	-
KCl	-	0.2	0.225	0.4
$KSCN$	0.5	-	-	-
KH_2PO_4	-	0.2	-	0.06
Lactic Acid	0.9	-	-	-
$Na_2HPO_4.3H_2O$	-	-	0.238	-
$MgCl_2.6H_2O$	-	-	0.311	-
$CaCl_2$	-	-	0.293	-
Na_2SO_4	-	-	0.072	-
$CaCl_2.2H_2O$	-	-	-	0.19
$MgSO_4.7H_2O$	-	-	-	0.2
$Na_2HPO_4.7H_2O$	-	-	-	0.09
Glucose	-	-	-	1.0

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