CHAPTER-III

INSTRUMENTATIONS

3.1 Introduction:

This chapter deals with the various experimental techniques employed for the synthesis, characterization of metals and alloys. Various characterization techniques were used for the characterizations. They are as follows: Energy Dispersive X-ray-Fluorescence (EDXRF), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Evolved Gas Analysis (EGA) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Electrochemical techniques like cyclic voltammetry and square wave voltammetry were also used in the study.

3.2 X-Ray Fluorescence Spectrometry

The X-ray fluorescence spectrometry is generally used for qualitative and quantitative determination of elemental composition. It is based on the principle of measurement of the energies or wavelengths of the X-ray spectral lines emitted from the sample, which are the characteristic or signature of the elements present in the sample. H.G.J. Mosley in 1913 discovered the relationship of photon energy and element [113] and laid down the basis of XRF. X-rays are proportional to the atomic number (Z). X-ray spectra originate from the inner orbitals, which are not affected substantially by the valency of the atom; normally the emitted X-ray lines are independent of the chemical state of the atom. However, in the case of low and medium atomic number elements, the energy of the characteristic X-rays depends on oxidation state.
In XRF, the primary beam from an X-ray source (or electrons or charged particles) irradiates the specimen thereby exciting each chemical element. These elements in turn emit secondary X-ray spectral lines having their characteristic energies or wavelengths in the X-ray region of the electromagnetic spectrum. The intensities of these emitted characteristic X-rays are proportional to the corresponding elemental concentrations. Since the X-rays penetrate to about 100 μm depth of the surface of the sample, XRF is near surface characterization technique. This method of elemental analysis is fast and has applications in a variety of fields. This technique has also got sample versatility as sample in the form of solid, liquids, slurry, powder, etc. can be analyzed with little or no sample preparation. In most cases, XRF is a non-destructive/non-consumptive technique. All elements having atomic number Z > 11 (Na) can be detected and analyzed in conventional XRF. But, nowadays, with the advances in the XRF instrumentation, like use of very thin or windowless tubes and detectors, multilayer analyzer crystals, reduction in the path length of X-rays (tube – to sample and sample – to- detector) and application of vacuum or helium atmosphere, elements up to B (Z=6) can be detected and quantified [114]. Further, with the development of synchrotron radiation technology, a vast improvement in terms of detection limits has been obtained by tuning of the excitation energies [115]. XRF method has a large dynamic range, sensitive up to microgram per gram level and is considerably precise and accurate. For these reasons, XRF has become a well established method of analysis. It has got a variety of applications in industries of material production, quality control laboratories, scientific research centers, environmental monitoring, medical, geological and forensic laboratories [116-119]. There are two major modes of analysis in X-ray spectrometry: Wavelength Dispersive X-Ray Fluorescence (WDXRF) and Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometry. The difference in these two modes of analysis lies in the detection component. In EDXRF, the detectors directly measures the energy of the X-rays with the help of multichannel analyzer, whereas in WDXRF, the X-rays emitted from the samples are dispersed spatially using a dispersion crystal and wavelength of the each emitted X-rays is
determined by the detector sequentially. Here, we will only discuss about the ED-XRF technique which was used in the present investigation.

### 3.2.1 Energy Dispersive X-Ray Fluorescence (EDXRF)

In Energy dispersive X-Ray fluorescence (EDXRF), the wavelengths of all the elements emitted by the specimen are not dispersed spatially prior to detection, but the detector receives the undispersed beam. The detector itself separates the different energies of the beam on the basis of their average pulse heights. Energy dispersive spectrometer consists of three basic units:

1. (a) Excitation source,
2. (b) Sample holder unit and
3. (c) Detection system

In XRF spectrometers, X-ray beam emitted from X-ray tube or radioisotope sources. In tube excited XRF systems, the energy distribution of the spectrum arriving from the sample depends on the tube target element, voltage and current applied. Standard commercial EDXRF spectrometer comprise of the following components: an X-ray tube, sample holder with auto sampler unit, solid state semiconductor detector Si (Li) with liquid nitrogen cooled detectors and the spectrometer electronics. Unfiltered direct excitation leads to a combination of both continuum and characteristic peak to fall on the sample. The spectrum shape can be altered by use of various filters and secondary targets present in the filter changer unit. Optimum selection of target, current, voltage and primary beam filter / secondary target are important in obtaining the best data from an EDXRF system. In XRF, primary beam filters are used to eliminate the scattered background drastically and improve the signal to noise ratio at the region of interest (ROI). Apart from this, it also reduces the dead time of the detector significantly \([120]\). All these features ultimately improve the detection limits. Schematic of EDXRF equipment is shown in Fig.3.1.
the present investigation, EDXRF was carried out using EX-3600 M spectrometer from Xenemetrix.

![Diagram of ED-XRF equipment]

**Fig.3.1 Schematic of ED-XRF equipment.**

### 3.3 X-ray diffraction (XRD):

X-ray diffraction (XRD) is the most extensively used technique to identify the crystalline phases and to determine the crystal structures of condensed matter. It is the most commonly used technique for fingerprint characterization of the crystalline materials, as well as for determination of their unit cell, lattice parameters, phase and probable crystal structure. In our present study we have used the technique to identify the phase rare earth metals and alloys synthesized in the study.

The German physicist Max von Laue recognized that the wavelength of X-ray are comparable to the spacing between adjacent atoms in crystal and thus proposed that a crystal could be used as a diffraction grating in three dimensions. X-rays are electromagnetic radiation with typical photon
energies in the range of 100 eV - 100 keV. For the diffraction applications, only short wavelength X-rays (hard X-rays) in the range of a few angstroms to 0.1 angstrom (1 keV - 120 keV) are used. As the wavelength of X-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays can penetrate deep into the materials and provide information about the bulk structure.

The theory of diffraction is based on the Bragg’s law, which describes how the electromagnetic waves of a certain wavelength $\lambda$ interfere with a regular lattice. At a certain angle of incidence, also called as Bragg’s angle ($\theta$), with regard to a set of parallel crystal planes, which are, therefore, called reflectors, constructive interference take place according to the equation (3.1) where $n$ is a positive integer, $d_{hkl}$ represents the inter planer spacing between the crystal planes that cause constructive interference, and $\lambda$ is the wavelength of the incident X-ray beam.

$$n\lambda = 2d \sin\theta$$  \hspace{1cm} (3.1)

In XRD, the sample is irradiated by a monochromatic X-ray beam, which are generated by a cathode ray tube, by heating a filament to produce electrons, accelerating the electrons toward a target, by applying a voltage, and bombarding the target material (Cu, Fe, Mo, Cr) with the electrons. When the electrons have sufficient energy, to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. The typical X-ray spectrum of elemental Cu is given in Fig. 3.2.
Fig. 3.2 Typical X-ray of Cu target

Though the X-rays are produced in all the directions, it is allowed to escape from a particular direction (commonly using a beryllium window) for experiments. The background and radiations are filtered using β-filters. The beam of X-rays is passed through the divergence slits and then allowed to fall on the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray), when conditions satisfy the Bragg’s law. These diffracted X-rays are then detected, processed and counted. For the detection of X-ray, the gas filled tube or scintillation counters are commonly used. These tubes can either be the proportional counter or Geiger-Muller counter. This particular tube is usually filled with a gas, which gets ionized by the impact of the radiation. Applying a potential difference between the two electrodes, the ions are collected. The typical current obtained is proportional to the number of photons reaching to the detector. The diffracted rays are scanned by sweeping the detector
from one angle to another. By scanning the sample through a range of 20 angles, all the possible diffraction directions of the lattice can be attained due to the random orientation of the powdered material. The conversion of the diffraction peaks to d-spacing allows identification of the material, because each material has a set of unique d-spacing. Typically, this is achieved by comparison of the d-spacing with the standard reference patterns. The intensity distribution of the peaks is governed by the nature and the kind of distribution of the atoms/ions in the unit cell. The absolute intensities of the peaks depend on the source intensity and counting time, in addition to the nature and the kind of distribution of the atoms/ions in the unit cell. A schematic diagram of XRD equipment is shown in Fig.3.3.

![Schematic of XRD equipment](image)

**Fig.3.3 Schematic of a XRD equipment**
The peaks (also called as reflections) in the plot correspond to a set of parallel planes with inter-planar spacing $d_{hkl}$. The d-values are calculated from the position of the peaks. Thus, for a particular sample a set of d-values giving constructive interference is observed. The peak positions (d values) are related with the unit cell parameters of the lattice. Hence they can be used for identification of the materials and they generally act as the finger print for the crystalline materials. The intensity distribution of the reflections is governed by the nature and kind of distribution of atoms in the unit cell.

The data collection protocols often depend on the specific purpose of the data collections. In general a short time scan in the two-theta ($2\theta$) range of 10 to 80° is sufficient for the identification of a well crystalline inorganic material. However, low symmetry samples and samples with not good X-ray scattering power may need a slow scan. The scan time was optimized for getting good intensity peaks. After the data collection, the observed d-values were fitted to standard patterns and the unit cell parameters were refined with respect to the standard values. By comparing the observed diffraction pattern with JCPDS (Joint Committee on Powder Diffraction Standards, 1974) files available for reported crystalline samples, fingerprinting of sample materials is normally done. The unit cell parameters are made free to adjusting the best way to fit the observed experimental data. The use and interpretation of the powder diffraction patterns are explained in several books [121-123]. In our study, XRD characterizations were carried out using Philips (Panalytical X-pert-pro) equipment.

3.4 Electron Microscopy:

Micro-structural characterization has become important for all types of materials as it give substantial information about the structure-property correlation. Micro-structural characterization broadly means ascertaining the morphology, identification of crystallographic defects and
composition of phases, estimating the particle size, etc. Electron microscopic techniques are extensively used for this purpose. Electron microscopy is based on the interaction between electrons (matter wave) and the sample. In the present study, Scanning Electron Microscopy (SEM) has been used to characterize the alloy powders. The principle and experimental details of the SEM technique is given below.

### 3.4.1 Scanning Electron Microscopy (SEM):

In a typical scanning electron microscope, a well-focused electron beam is incident and scanned over the sample surface by two pairs of electro-magnetic deflection coils. The signals generated from the surface by secondary electrons are detected and fed to a synchronously scanned cathode ray tube (CRT) as intensity modulating signals [124-125]. Thus, the specimen image is displayed on the CRT screen. Changes in the brightness represent changes of a particular property within the scanned area of the specimen. Schematic representation of SEM is shown in Fig.3.4.
For carrying out SEM analysis, the sample must be vacuum compatible (~ 10^-10 Torr or more) and electrically conducting. The surfaces of non-conductive materials are made conductive by coating with a thin film of gold or platinum or carbon. In this study, the SEM technique was used to study the microstructure evolution of rare earth metal and alloys. EDS (energy dispersive X-ray spectroscopy) was used for the compositional analysis.

In the present study, SEM instrument used was from Seron Inc. (Model AIS 2100) having standard tungsten filament. An accelerating voltage of 20 kV and magnification of 10kx was used for recording the micrographs.
3.5 Thermal analysis:

Thermal analysis methods are essential for understanding the compositional and heat changes involved during reaction. They are useful for investigating phase changes, decomposition, and loss of water or oxygen and for constructing phase diagrams.

3.5.1 Thermo gravimetric analysis (TGA):

In thermo gravimetric analysis the sample is heated at a constant heating rate and the sample weight is measured as function of temperature [126]. In this technique the heating can be done under air (oxidative) or nitrogen/argon (inert) atmosphere. Loss of water of crystallization or volatiles (such as oxygen, CO₂, etc.) is revealed by a weight loss. Oxidation or adsorption of gas shows up as a weight gain.

3.5.2 Differential thermal analysis (DTA):

Differential Thermal Analysis measures the temperature difference between a sample and a reference material as a function of temperature, when they are heated or cooled at a constant heating rate. A phase change is generally associated with either absorption or evolution of heat. In DTA experiments, the sample is placed in one cup, and a standard sample (like Al₂O₃) in the other cup. Both cups are heated at a controlled uniform rate in a furnace, and the difference in temperature (ΔT) between the two is monitored and recorded against time or temperature. Any reaction involving heat change in the sample will be represented as a peak in the plot of ΔT vs. T. Exothermic reactions give an increase in temperature, and endothermic reaction leads to a decrease in temperature and the corresponding peaks appear in opposite directions.

3.5.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetric technique is quite similar to DTA, except that, it is an isothermal measurement. It means that, during the measurement the sample and reference
material are simultaneously heated or cooled at a constant rate just like DTA [127]. But here the amount of heat absorbed or released by a sample, to keep both the sample and reference at the same temperature is measured. In case of any exothermic/endothermic transition, the amount of heat flow from the system varies in order to keep both the sample and the reference at same temperature. The difference in temperature between them is proportional to the difference in heat flow (from the heating source i.e. furnace), between the two materials. This technique is applied to most of the polymers in evaluating the curing process of the thermoset materials as well as in determining the heat of melting and melting point of thermoplastic polymers, glass transition temperature (Tg), endothermic & exothermic behaviour. As desorption of hydrogen occurs with absorption of heat, so it can detected for the endothermic peak of DSC. The instrumentation of DSC [Fig. 3.5] is exactly similar to that of DTA, except for the difference in obtaining the result.

![Fig.3.5 Schematic diagram of DTA/DSC](image)

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In the present study, thermo-gravimetric-differential thermal analysis (TG-DTA) of samples was carried out in platinum crucibles using a Setaram, 92-16.18 make TG-DTA instrument.

3.5.4 Evolved Gas Analysis

Evolved gas analysis (EGA) is a method used to study the gas evolved from a heated sample that undergoes decomposition. The identification of the compound is performed by mass spectrometry, Fourier transform spectroscopy, gas chromatography, or Optical In-Situ Evolved Gas Analysis. Here, the gas analyzer used was a quadrupole mass spectrometer to identify the emitted vapors at different temperatures and understand the underlying mechanism. In quadrupole spectrometer, an electrical field is formed in the system. Ions of varying mass are shot axially into the system at approximately equal energy and move through the system at uniform velocity. The applied quadruple field deflects the ions in the X and Y directions, causing them to describe helical trajectories through the mass filter. Ions are separated by the m/e ration in the rod system and then detected at the detector. Here EGA study was carried out using QMS coupled to a TG-DTA, (model-SETSYS Evolution-1750, SETARAM).

3.6 Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

ICP-AES is a spectral method used to determine very precisely the presence of metal analyte and the elemental concentration. There are numerous reports on utilization of this technique for analysis of rare earth elements [128-130]. ICP-AES analysis requires a sample to be in solution. It works by the emission of photons from analytes that are brought to an excited state by the use of high-energy plasma. The plasma source is induced when passing argon gas through an alternating electric field that is created by an inductively couple coil. A peristaltic pump delivers the sample into a nebulizer where it is atomized and introduced directly inside the plasma
flame. When the analyte is excited, the electrons try to dissipate the induced energy by moving to a ground state of lower energy and in doing this they emit the excess energy in the form of light. The wavelength of light emitted depends on the energy gap between the excited energy level and the ground state and is thus specific to the element. In this way, the wavelength of light can be used to determine what elements are present by detection of the light at specific wavelengths. In order to determine the concentration of elements present, a calibration curve is developed using analyte solutions of known concentrations, whereby the intensity of the signal changes as a function of the concentration of the material that is present. When measuring the intensity from a sample of unknown concentration, the intensity from this sample can be compared with the calibration curve to determine the concentration of the analytes within the sample. An ICP-AES system can be divided up into two basic parts; the inductively coupled plasma source and the atomic emission spectrometry detector. Here ICP-AES analyses were carried out using high Ultima 2, Horiba Jobinyvon, France make high resolution ICP-AES. Figure 3-5 shows the common components of an ICP-AES system.
Figure 3.6. Schematic of an ICP-AES equipment
3.7 Background of Voltammetric studies

During voltammetric studies involving a three electrode assembly, the electrochemical response is dependent on the mode of mass transport. These mass transport phenomena are diffusion, migration and convection [131]. Convection is eliminated by carrying out the experiment under quiescent conditions. Migration is eliminated by adding large excess of inert supporting electrolyte. In voltammetric studies the species that responds to the applied potential or current are known as electro active species. Thus, the essential mode of mass transfer occurs only by diffusion of electroactive species. Such electrode reactions are known as diffusion controlled processes.

3.7.1 Potentiostat

A potentiostat is an electronic amplifier which controls the potential drop between the working electrode and the electrolyte [132]. All the three electrodes as mentioned earlier are controlled by a potentiostat which acts in the manner shown in Fig. 3.7.
Fig.3.7 A schematic of a potentiostat connected to a three electrode assembly. $R_0$ is variable resistance, CE is counter electrode, WE is working electrode and REF is reference electrode.

The potentiostat imposes a fixed potential, $E$, between the working (WE) and the reference (REF) electrode and draws negligible current through the latter electrode.

$$E = (\Phi_M - \Phi_S)_{working} - (\Phi_M - \Phi_S)_{reference}$$  \hspace{1cm} (3.2)

Where $\Phi_M$ is the electrical potential and $\Phi_S$ is the solution potential. Since the reference electrode serves to provide a constant value of $(\Phi_M - \Phi_S)_{reference}$, any changes in $E$ are reflected as changes in $(\Phi_M - \Phi_S)_{working}$. The imposition of the potential drop $(\Phi_M - \Phi_S)_{working}$ on the working electrode-solution interface will typically cause a current to flow. The counter electrode (CE) serves to pass the same current as that induced to flow through the working electrode. Accordingly, the potentiostat drives the counter electrode to whatever voltage is required to pass
this current. The introduction of the third electrode is the only reason why a controlled potential can be applied to the working electrode as expressed by the Eqn. 3.2.

All the electrochemical measurements were carried out using IM6 electrochemical workstation (ZahnerCo.Ltd. Germany). The voltammograms were recorded and analyzed using THALES 2.10 software package.

3.7.2 Cyclic voltammetry (CV)

**Principle:** Cyclic voltammetry involves applying a potential to the working electrode which changes with time as shown in Fig. 3.8.

![Diagram](image)

**Fig. 3.8** Potential simulation (a) and resulting current response (b) in a cyclic voltammetry experiment.

The current flowing through the working electrode as a function of the applied potential and a plot of current versus potential is recorded which is known as the voltammogram. The initial voltage is selected such that the chemical species under investigation are not initially oxidized or reduced. The potential is swept in a linear manner to a certain value and then the direction of scan is reversed usually to its original value. The potential range is usually selected such that the
range contains an oxidation or reduction process of interest. The observed voltammogram depends on the parameters such as the electron transfer coefficient, standard electrochemical rate constant (Ks), formal potential of the redox couple, diffusion coefficient (D) of the redox species and the voltage scan rate (v).

**Procedure:** In the present study, voltammetric studies were carried out over the temperature range 963 – 1053 K. The electrochemical cell was operated under argon during the measurement. The experiments were conducted using a three-electrode assembly, where the alumina crucible served as the container for the electrolyte.

The working electrode consists of 1mm (diameter) molybdenum or tungsten wires. Other Tungsten wires of 2mm and 1 mm diameter were employed as the counter and quasi reference electrode respectively. The surface of each electrode were polished with emery paper of 1200 grit and then cleaned with acetone.

### 3.7.3 Electron transfer coefficient

The electron transfer coefficient (α) gives the ratio of the change of the height of the energy barrier the electron has to surmount during charge transfer with respect to the change of electrode potential ΔE [132]. A value of α = 0 implies no influence of the electrode potential change on the barrier height. α =1 implies that the change of electrode potential causes an exactly equal change of barrier height. The value of αn (αn is the number of electrons transferred for the reduction process in the rate determining step) can be determined from the equation given by Matsuda and Ayabe (Eqn. 2.2) [133-134].

\[
E_{P/2}^c - E_P^c = \frac{1.857RT}{an_\alpha F}
\]  

(3.3)
\( E_P^C \) is cathodic peak potential, \( E_{P/2}^C \) is cathodic half potential, R is the molar gas constant, T is absolute temperature and F is Faraday constant.

The \( an_\alpha \) also can be evaluated from the following equation

\[
\frac{\Delta E_P^C}{\Delta \log v} = \frac{2.3 RT}{2an_\alpha F}
\]  \( (3.4) \)

\( \frac{\Delta E_P^C}{\Delta \log v} \) is determined from the slope of \( E_P^C \) vs log \( v \) plots.

The current function \( (i_P^C/v^{1/2}) \) i.e. the ratio of cathodic peak current to the square root of scan rate can be measured to determine the mechanism of electrochemical reaction. If the current and peak potential are independent of scan rate, then the electrode process is said to be reversible. In case of quasi reversible process, the current function is virtually independent of scan rate but the peak potential shift with scan rate. The difference between anodic and cathodic peak potential is useful criterion for Nerstian behavior. The electrochemical behavior is said to Nerstian if \( \Delta E_P \) is very close to 2.3RT/nF and the ratio of anodic to cathodic peak current is approximately 1 regardless of scan rate and switching potential.

3.7.4 Square wave voltammetry (SWV):

Square wave voltammetry is one of the recent technique used by electrochemist for analytical, kinetics and mechanistic work. The form of SWV most electrochemists use today, called Osteryoung square wave which is based on work done by Ramaley and Krause in 1969 [135-136].
Fig. 2.10 shows the excitation waveform used in Osteryoung SWV. With this waveform, current response to the potential excitation once on each forward pulse and once on each reverse pulse can be recorded. Using this technique, three possible current potential plots can be generated– forward current versus potential, reverse current versus potential or difference current versus potential. The resulting combination plot has been suggested as the most useful form for investigating kinetics and mechanisms.

\[ I_{\text{meas}} = i_1 - i_2 \]

Fig. 3.9: Excitation waveform and current sampling points for Osteryoung square wave.
Advantages

One of the drawbacks of rapid scanning in CV is that it introduces a large capacitive background current. This background current (or noise) makes it hard to detect the faradic current, which is the signal of interest, and severely affects the signal to noise ratio. Since SWV is a pulsed technique, it can discriminate against the charging current and eliminate this drawback.

3.7.5 Exchange current density:

When a metal in solution is at equilibrium, it implies rates of dissolution and deposition reactions are equal. When the above two reactions (anodic and cathodic) are in equilibrium, the rates (equal and opposite) of each of the two reactions are referred to as exchange current density.

Expressing reaction rates in terms of current density, \( r_{\text{oxid}} = r_{\text{red}} = \frac{i_0}{nF} \) \hspace{1cm} (3.5)

\( r_{\text{oxid}} \) and \( r_{\text{red}} \) are equilibrium oxidation and reduction rates. \( i_0 \) is termed exchange current density which is the rate of oxidation and reduction at equilibrium. There is no net current under the above conditions even through the concept is a useful method of representing rates at equilibrium.

\[
\text{at equilibrium: } \quad i_c = i_a = i_0 \\
\text{net} = i_a - i_c = 0
\]

A Kinetic expression for \( i_0 \) is given as

\[
i_0 = nFAK_s(C_{oxd})^{1-a}(C_{red})^a \hspace{1cm} (3.6)
\]

\( K_s \) is rate constant for the redox reaction, \( a \) = transfer coefficient and \( A = \text{Area of electrode.} \)

Exchange current density (io) is dependent on a) Nature of the redox reaction b) Electrode composition / surface c) Concentration ratio of oxidized and reduced species and d) Temperature.