Chapter 2

Experimental details

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Introduction

This chapter describes the synthesis processes adopted for the materials used for the present study and various structural characterization tools used for their analysis. The pure Mn-Bi alloys and nanocomposites of MnBi alloy with Fe_3C@C,FeNi@C and Co@C were synthesized using both room temperature and cryogenic ball milling techniques. The phase identification and their structural properties were analysed with the help of X-ray diffraction (XRD). Scanning electron microscope (SEM) was used to determine the morphology and size distribution of the nanoparticles. EDX (Energy dispersive x-ray spectroscopy) analysis for compositional understanding of the samples was also done using SEM. Transmission electron microscope (TEM) was further used to corroborate the phases formed, through electron diffraction studies, and also observe their morphologies under bright field and dark field. HAADF (High-angle annular diffraction) mode of TEM was used to understand the elemental distributions in the samples. The oxidation states of the element present in the samples were analysed by X-ray photoelectron spectroscopy (XPS). Further, Raman spectroscopy was carried out to identify the phases, especially the nature of carbon in the soft-phase nanoparticles. The magnetic properties of the samples were investigated using magnetic properties measurement system (MPMS).

2.1. Vacuum arc-melting

The starting materials for Vacuum Arc Melting were Manganese flakes (99.98% pure) and Bismuth metal Ingots (99.99% pure) purchased by CDH Pvt. Ltd. The chosen bulk alloy compositions $Mn_{55+x}Bi_{45-x}$ (x=0, 1, 3, 5 and 8) were prepared in the form of ingots by vacuum arc melting. The melting was carried out with pure elements of targeted alloy

compositions by discharging an electric arc between the two electrodes using a large voltage in a chamber at low pressure. A schematic diagram of high vacuum arc melting furnace (make of M/s Vacuum Techniques Pvt. Ltd, Bangalore) used in this work is shown in Figure 2.1. The arc melting system consisted of a vacuum chamber integrated with anode A and cathode B. The cathode holds a Cu crucible in which the elements to be melted are loaded. It is cooled by continuous water flow to avoid excess heating and melting of the copper cathode. The anode A holds a sharp rod of a refractory material such as tungsten with 2% Thorium so that it withstands very high temperatures without melting.

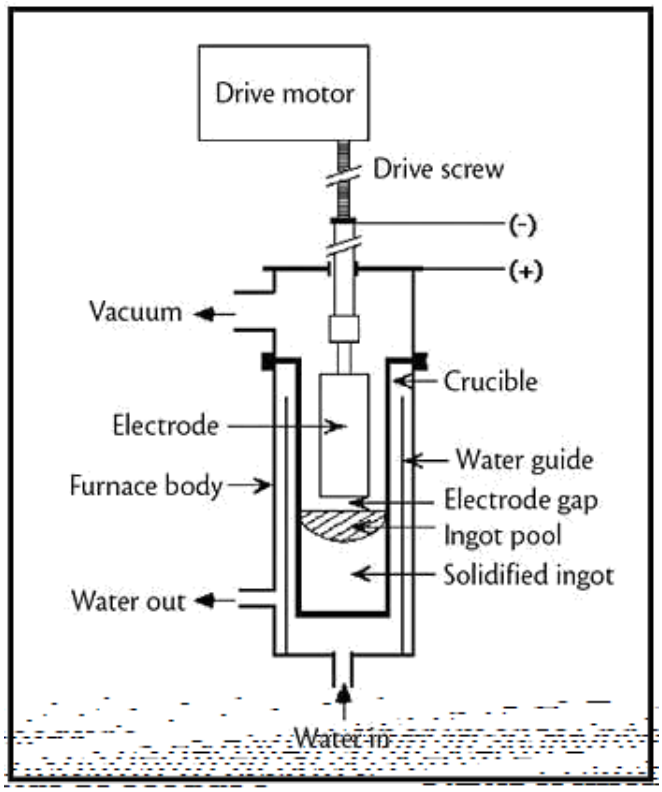

Figure 2.1. Schematic diagram of a vacuum arc-melting furnace used for the preparation of the bulk alloys

A DC power supply with 20-40 V and 200-1500 A current was used during the Arc melting process. The furnace chamber was maintained under high vacuum of about 10^{-6} torr

and then back filled with Ar gas at 200 mm pressure of Hg. In addition, to prevent the oxygen contamination, oxygen getter (Ti, 99.99%, Alfa Aesar) was arc melted prior to the chosen alloys. When the cathode was close enough to the anode, ionized Ar gas in the chamber was allowed to discharge an arc that melted the elements in the crucible. The alloy was re-melted 4-5 times by flipping it back and forth to ensure good homogeneity of the elements. Alloy buttons of 20 g each were melted; however, there might be some material loss during this process. In the present study, alloys were prepared maintaining the vacuum inside the chamber to be 10^{-6} torr, voltage of 13V and current of 100 A.

2.2. Homogenization treatment

The vacuum arc melted samples were subjected to a homogenization heat treatment. The as-cast samples ~20 g were encapsulated in a quartz tube backfilled with Argon gas. These encapsulated samples were annealed at 300 ºC for a duration of 24 h in a muffle furnace with a heating rate of 10 °/min and furnace cooled to room temperature. The phases in annealed samples were confirmed through ex-situ XRD, and these were further co-related to heating events of DSC thermogram.

2.3. Synthesis procedure

2.3.1. Fe_3C@C nanoparticles: For the synthesis of Fe_3C@C nanoparticles, two solutions were prepared. The first solution involved ultra-sonication and stirring of desired quantities of high-purity $FeCl_3$ (99.0% pure, CDH Chemicals) in 30 mL of ethylene glycol (AR grade, CDH chemicals), while the second solution consisted of sodium acetate ((99.0% pure, CDH Chemicals) in 50 mL of ethylene glycol solvent. The $FeCl_3$ solution was then added dropwise to the sodium acetate solution and stirred for 2 h at 40. The resulting solution was transferred to a Teflon-coated autoclave and heated at 200 ºC for 15 h in a vacuum oven. This led to the

formation of a black precipitate, which was washed multiple times with double-distilled water and ethanol using a magnet. The washed precipitate was then dried in a vacuum at 70 ºC for 12 h to obtain Fe_3O_4 powder. This powder was placed inside a tubular furnace in an alumina boat along with Ethylenediamine in an adjacent boat. Under N_2 gas flow, the sample was calcined at 700 ºC for 1.5 h to obtain the desired Fe_3C@C nanoparticles. The schematic representation can be seen in the below Figure 2.2.

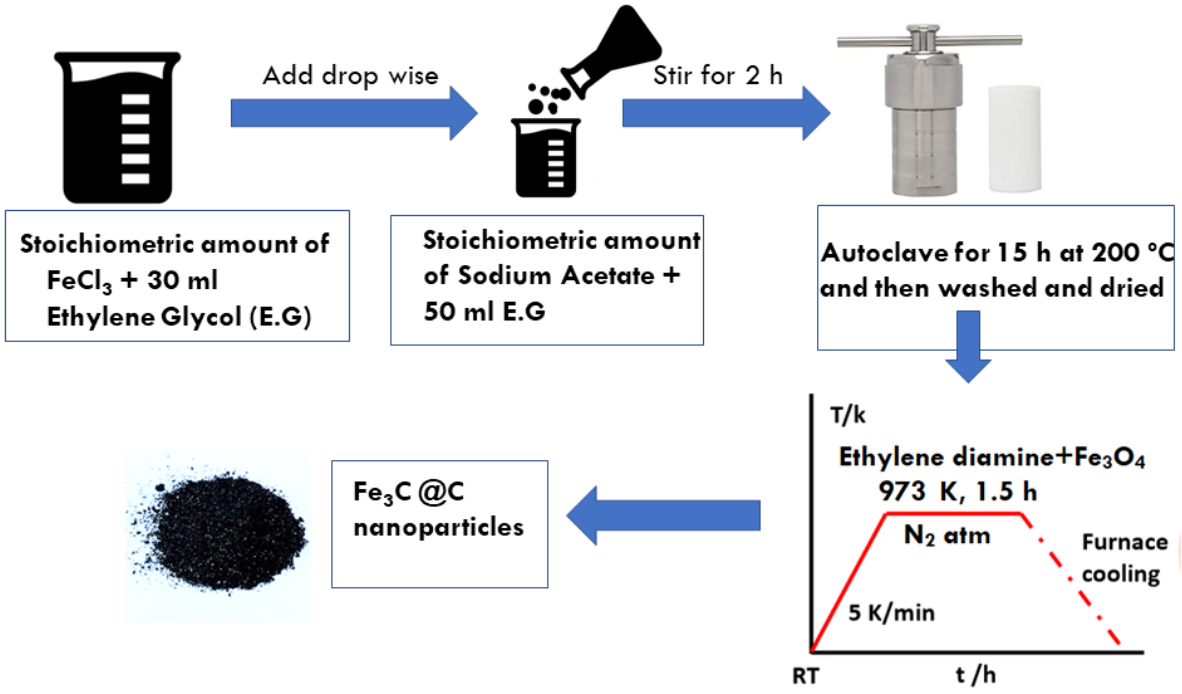

Figure 2.2. Schematic representation of the synthesis method for Fe_3C@C nanoparticles

2.3.2. FeNi@C nanoparticles : For the preparation of FeNi@C nanoparticles, calculated amounts of $FeCl_3$ and $NiCl_2$ (each one 99.0% pure, CDH Chemicals) were dissolved and stirred for 30 min in 60 mL DI water. Another solution with desired amounts of KOH in 30 mL DI water was also prepared by magnetic stirring. Subsequently, the solution with dissolved salts is added drop wise into the KOH solution and stirred for 2 h. This solution was shifted to a Teflon coated autoclave, which is further, heated in a vacuum oven to 200

ºC for 15 h. The resultant precipitate was washed several times using DI water followed by ethanol with the help of a permanent magnet. Further, it was dried to obtain $NiFe_2O_4$ powder, which in turn was calcined at 700 ºC for 1.5 h in an inert N_2 atmosphere along with ethylenediamine to obtain the aimed FeNi@C nanoparticles as shown in Figure 2.3.

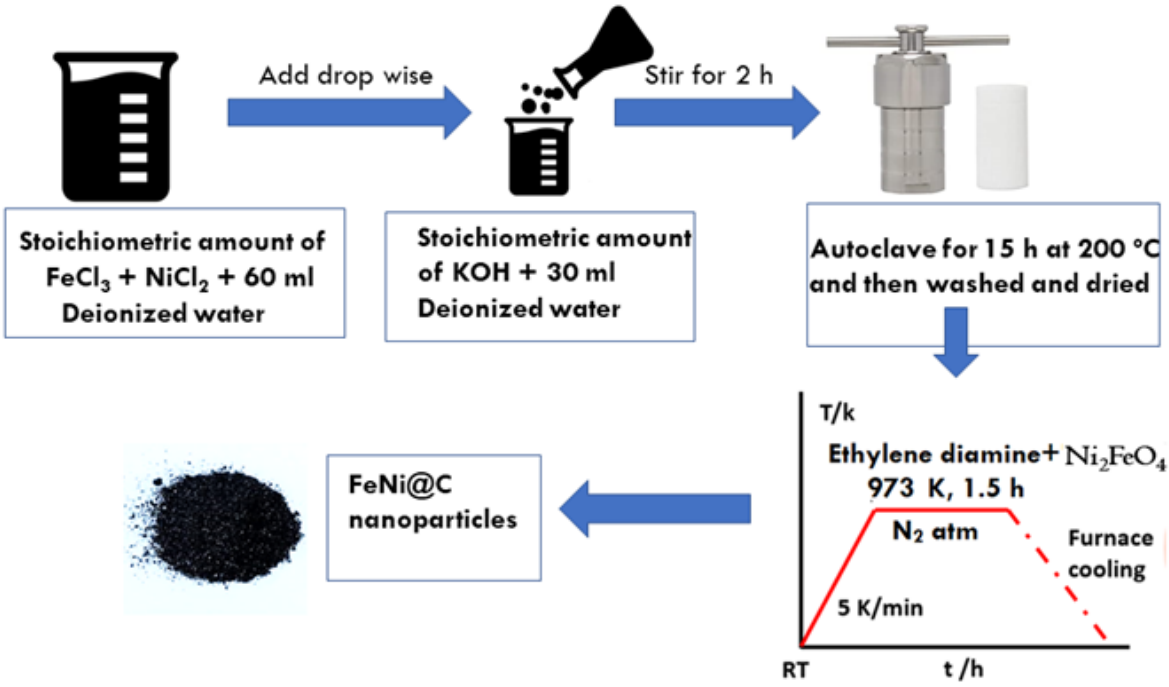

Figure 2.3. Preparation method of FeNi@C nanoparticles.

2.3.3. Co@C nanoparticles: It was successfully synthesized through the sol-gel, wet chemical method. To prepare the product, cobalt chloride ($CoCl_2.6H_2O$) powder, urea precursor, ethanol, and cetyltrimethyl ammonium bromide (CTAB) as a surfactant were used. For the synthesis of carbon-coated cobalt, a liquid medium was prepared by mixing 40 mL DI water with 40 mL of ethanol. The mixture was then heated to 80°C using a hot plate. Then 7 M of urea is added to the liquid solution and stirred until a clear mixture was obtained. 1 M of cobalt chloride and CTAB was mixed with the above solution one by one, respectively.

At last, the solution was constantly stirred at 80 ºC for 4 h to obtain the final product, which is a violet-colored gel. Then the gel was kept in a drying furnace to obtain dried powder samples. The powder sample is then heat-treated at 700 ºC for 2 h using a horizontal tube furnace to get Co@C.

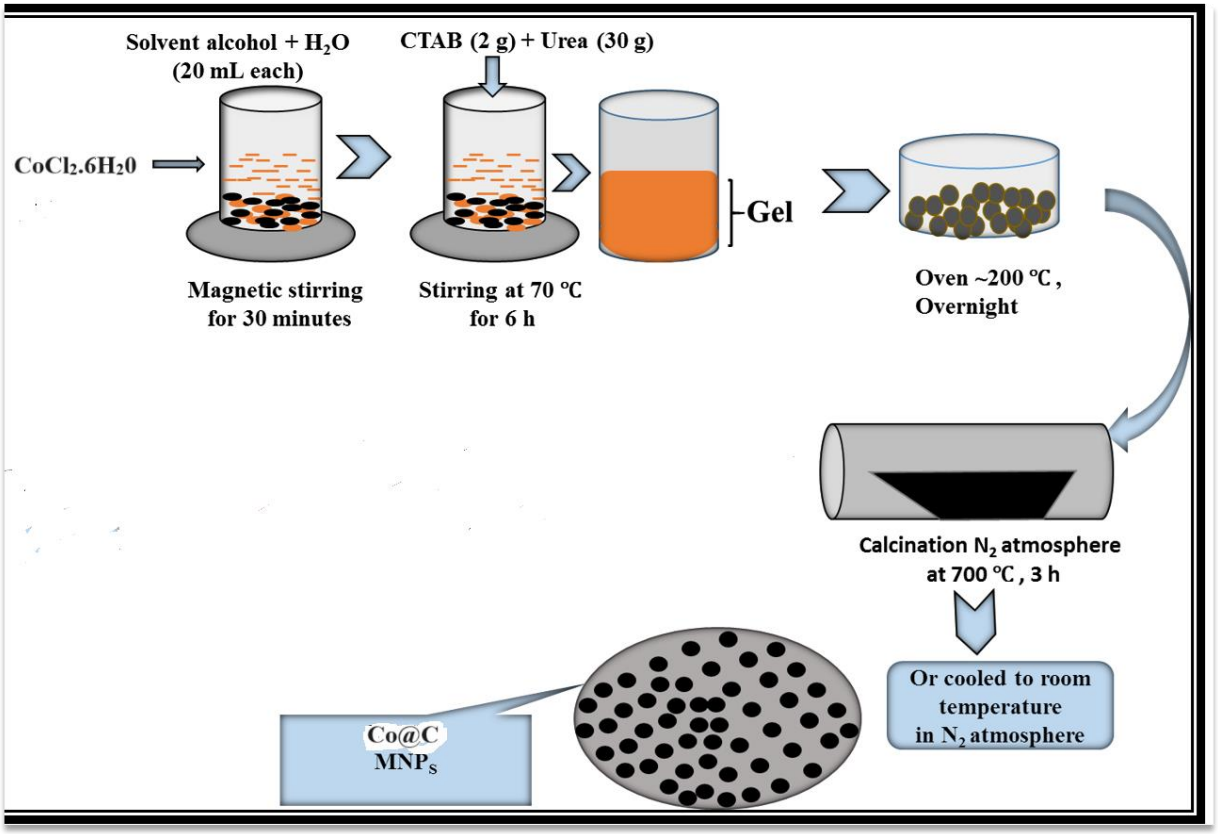

Figure 2.4. Synthesis protocol of Co@C nanoparticles using sol-gel route.

2.4. Ball milling

Room temperature and cryogenic high-energy ball milling techniques were utilized for crushing and reducing the particle size of as-cast and homogenised Mn-Bi alloys. For initial room temperature ball milling of Mn_{55+x} $Bi_{45—x}$ (x = 0, 1, 3, 5, 8) alloys, the annealed alloy ingots were initially manually crushed. The crushed alloy powders were then subjected to mechanical milling in a high-energy planetary ball mill (Retsch PM 400) in wet condition

using Toluene. Tungsten carbide (WC) vials and balls of 10 mm diameter with a ball to powder weight ratio of 15:1 and milling speed of 150 rpm were utilized up to 8 h. Toluene as a milling media was used to avert oxidation and cold welding during the process. The milled powders for different samples were also collected after 4 h of milling.

For consequent studies and for the preparation of exchange spring composites, the heat-treated $Mn_{55}Bi_{45}$ alloy button was manually crushed, and the crushed alloy powder was mixed with soft phase (Fe_3C@C/FeNi@C/Co@C) powder in varying proportions (5, 10, 15, and 20 %). The mixing was performed using a Retsch MM500 mixer mill. The composites of alloy powder and soft phase (e.g. Fe_3C@C or FeNi@C or Co@C) powder were placed in a stainless steel vial along with stainless steel balls, maintaining a ball-to-powder ratio of 10:1. The stainless steel vial was cooled with liquid nitrogen for 10 minutes, and cryo-milling was conducted at 1200 rpm (20 Hz) for 10 minutes, followed by dipping in liquid nitrogen. This cycle was repeated until a cryo-milling period of 2 h was achieved. For comparison, room-temperature wet milling was also performed using similar stainless steel vials and balls, with toluene as the milling medium, and the milling duration and rpm were kept identical to cryo-milling.

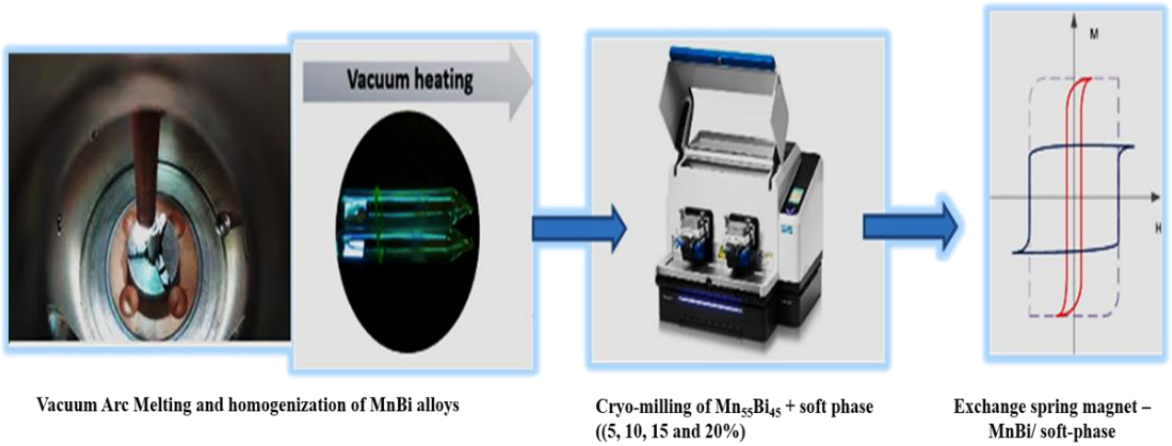

Figure 2.5. Schematic representation of preparation method of MnBi based composites.

2.5. Materials Characterization

2.5.1. X-Ray diffraction

The x-ray diffraction patterns of the powder samples were collected using Rigaku Miniflex 600 diffractometer. The Cu K_α radiation with 1.5406 Å wavelength was used for performing the diffraction studies under an applied voltage of 40 kV and a current of 200 mA. Majority of the samples were scanned in the 2θ range of 20-60º with a scanning rate of 5 º/min and a step size of 0.02. The obtained diffraction peaks were indexed and relevant phases were identified using the International Centre for Diffraction Data (ICDD) database. Further, crystallite size calculations of as-cast and homogenized samples were done after peak fitting using the Scherrer's equation as given below:

$$\text{Crystallite size} = 0.9\,\lambda / \beta_L \cos\theta$$

where, λ is the wavelength of incident radiation, θ refers to the Bragg angle and β_L is the full width half maxima (FWHM) (radians). It is obtained from the difference of FWHM experimental (β_{exp}) and instrumental broadening (β_I) i.e., $\beta_L = \beta_{exp} - \beta_I$. The β_I was estimated from the calibration with standard Si sample. In the case of ball-milled and cryo-milled samples the simultaneous determination of crystallite size (t) and lattice strain (ε) was done using the Williamson-Hall plot, based on the following formula as shown in the figure . The slope of the plot gives the lattice strain and the y-intercept is used to determine the crystallite size.

$$\beta.\cos\theta = (0.9\,\lambda/t) + 4\varepsilon.\sin\theta$$

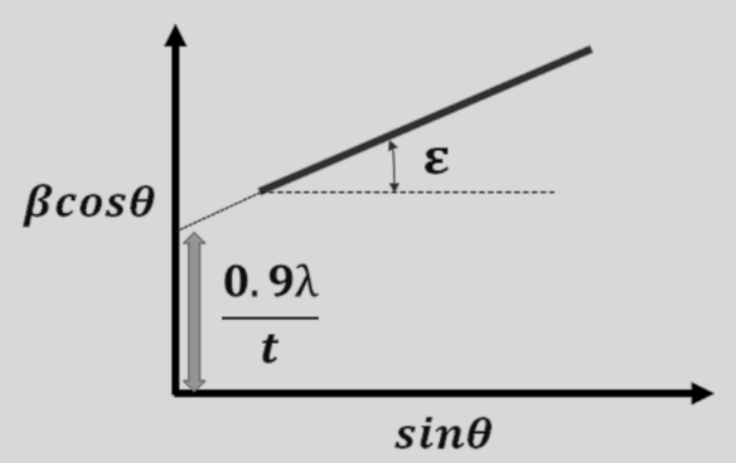

Figure 2.6. Williamson – Hall plot for calculating the crystallite size and the lattice strain values of milled powders.

2.5.2. Scanning electron microscopy

For the present work, the particle size estimation and morphology of milled powders was evaluated using the high-resolution scanning electron microscope (HRSEM), Nova Nano SEM 450, FEI. The secondary electron mode was used for imaging purpose and for compositional analysis of the samples; the EDX attachment (Team Pegasus Integrated EDS-EBSD with Octane Plus and Hikari Pro) was utilized. The powder sample preparation before examination under SEM consisted of sprinkling them over a carbon tape stuck to the SEM stub. This was followed by Au coating on the samples using sputtering technique to avoid any charging artefacts arising from the sample during imaging.

2.5.3. Transmission electron microscopy

To confirm the structure obtained by XRD experiments and to investigate fine microstructural features, transmission electron microscopy (TEM) was used. TEM studies

were performed using a FEI Tecnai G2 T20 S-twin microscope equipped with the high-angle annular dark-field (HAADF) and EDS detectors operating at 200 kV.

The powder samples were dispersed in methanol/ethanol, followed by ultrasonication (for 15 – 20 min) for avoiding the accumulation of powder particles. These suspended powder particles in methanol/ethanol (1 – 2 drop) were dropped cast onto a 3 mm copper grid (200 mesh size) and dried with the help of an infrared lamp for 30 min.

2.5.4. Differential scanning calorimetry

The thermal analysis of as-cast sample was done using a differential scanning calorimeter (DSC-60 Plus, Shimadzu) under a continuous flow of nitrogen gas. The alumina crucible was used as a reference and a sample holder crucible. They were charged with ~2 to 3 g of sample. The calibration of DSC instrument was done using indium, silver, and nickel with temperature error well within the permissible range. The DSC of samples was performed at 10 °C/min heating rate to confirm the phase transformation events and compute activation energy associated with those events.

2.5.5. X-ray photoelectron spectroscopy

The surface of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) of PHI5000 Versaprobe II photoelectron spectrometer (ULVAC-PHI) to determine the elements present and their respective oxidation states. Al K_α X-ray beam (1486.61 eV) having dual anode was used as the source. Shirley background function was used for baseline correction.

2.5.6. Magnetic measurements

The field-dependent magnetic properties of the powder samples were measured at a temperature of 300 K in ±60 kOe range using a SQUID (superconducting quantum

interference device) magnetometer (MPMS®5, Quantum design). For the measurement few mg of samples were loaded in an instrument specific Teflon tubes and magnetic data were collected up to the applied field of ± 60 kOe. The zero field cooled, field cooled (applied field=400 Oe) and AC susceptibility measurements (10 Oe field and 100 Hz frequency) were taken from room temperature to 5 K.

2.5.7. Raman Spectroscopy

The nature of carbon coating on the soft phases was understood using Raman spectroscopy, in this study. For this purpose, Raman spectroscope (alpha 300 R, Oxford Instruments) with a 532 nm diode laser was employed as the excitation source. This measurement utilized a laser power of 0.71 mW and an exposure time of 5 s on the powder samples.