CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

This chapter covers the details of materials and methodology used to prepare the HEAs. The parameters of the processing techniques, i.e. mechanical alloying (MA) as well as of induction melting have been discussed briefly. The microstructural and structural characterizations of HEAs were carried out by optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) respectively. The chemistry of the microstructures has been determined through scanning electron microscope-X-ray energy dispersive spectroscopy (SEM-EDS) and TEM-EDS techniques. The differential scanning calorimetry (DSC) was employed to study the thermal stability. The density and hardness were measured for both MAed and melted sample. Additionally, room temperature compression test was performed for the as-cast alloy. The details of the synthesis and above-mentioned techniques have been described in the following sections.

2.1 Materials and alloy synthesis

The elemental powders of Al, Co, Cr, Fe, Ni, Mn and Ti of purity (≥ 99 %) with particle size ≤ 325 meshes were used as the starting material. The basic properties of the selected elements are listed in Table 2.1. Three alloy systems of AlCoCrFeNi, AlCoCrFeNiMn and AlCoCrFeNiTi HEAs were chosen for the present study. The compositions of powder used in this study are given in Table 2.2. These alloy compositions in equiatomic form were synthesized by MA in a high energy planetary ball mill. The parameters of the milling have been given in Table 2.3. All the alloy compositions were milled by adopting the same milling parameters. The powder samples

were extracted at a definite interval to follow the phase evolution with milling time using XRD.

Table 2.1: Basic properties of the selected elements for the study [134]

Element	Al	Co	Cr	Fe	Mn	Ni	Ti
Crystal Structure (20°C)	FCC	HCP	BCC	BCC	Cubic	FCC	HCP
Atomic Radius (nm)	0.143	0.123	0.125	0.124	0.112	0.125	0.145
Density (g/cm^3)	2.71	8.9	7.19	7.87	7.44	8.90	4.51
Melting Point (°C)	660.4	1495	1875	1538	1244	1455	1668

Table 2.2: Nominal (atomic %) compositions of milled alloys

Alloys	**Al**	**Co**	**Cr**	**Fr**	**Ni**	**Mn**	**Ti**
AlCoCrFeNi	20	20	20	20	20	-	-
AlCoCrFeNiMn	16.66	16.66	16.66	16.66	16.66	16.66	-
AlCoCrFeNiTi	16.66	16.66	16.66	16.66	16.66	-	16.66

Table 2.3: Milling parameters used during the synthesis of HEA powder

Type of mill	High energy planetary ball mill (Retsch PM 400& 400/2)
Vials & balls	Tungsten carbide (WC)
Ball diameter	10 mm
Ball to powder ratio (BPR)	10:1
Rotational speed	200 rpm
Process control agent (PCA)	Toluene
Milling Medium	Wet
Running protocol	½ h stop after every 1 h (to prevent the overheating)

2.2 Consolidation of milled powder

After successful synthesis of nanocrystalline equiatomic HEAs, milled powders were consolidated by cold pressing and compacts were sintered in a microwave furnace (Model-1200 MF-15, OMICRON SCIENTIFIC EQUIPMENT Co., NEW DELHI-INDIA). Green pellets were compacted using steel die of 10 mm diameter with a suitable application of loads at room temperature using a hydraulic press (ALFRED J. AMSLER & Co. Switzerland) of 30-tonne capacity. These green pellets were kept at regular interval of temperature 200 ºC (100-1000 ºC) for 10 min in a microwave heating furnace (with frequency 2.45GHz and power 3kW). These steps were followed to release the internal strain and to avoid crack formation in the alloys. The alloys were kept for 30 min at a suitable final temperature and were allowed to be furnace cooled.

Microwave heating [65] is a new approach to sinter the high-entropy metallic powder samples. This approach utilizes the direct transfer of energy to material through the electromagnetic field. Microwave field and dielectric response of the material leads to heating of the material through wave energy. Direct absorption of microwave takes place by the powder compact and indirect heating by an auxiliary SiC absorber. This volumetric heating ability of the microwave results in short processing time and saving energy.

2.3 Induction melting

Elemental metals of Fe, Cr, Ni, Al, and Co with purity ≥ 99.99% were used as the starting materials in the atomic composition of $Fe_{40}Cr_{25}Ni_{15}Al_{15}Co_5$ for vacuum induction melting (VIM). The melting was carried out in INDUCTOTHERM Co. Ltd, INDIA. The process description of VIM furnace includes a melting crucible inside a steel shell that is connected to the high vacuum system. The crucible of the furnace is attached with the

heating and cooling coils along with refractory lining. The copper coils with a cooling arrangement is heated when the current passes through these coils. During the passage of the current through coils, a magnetic field is generated, which induces the current in the charge inside the refractory line. When heating of the charge materials is enough to melt it, the magnetic field causes the stirring of the molten charge. The presently investigated $Fe_{40}Cr_{25}Ni_{15}Al_{15}Co_5$alloy composition was melted in the magnesium oxide (MgO) crucible at ~1700ºC in open atmosphere and was kept at this temperature for a few minutes to get the better chemical homogeneity through stirring. After that, the molten alloy was poured into the copper mould and got solidified.

2.4 Density measurement

The density of sintered compacts and cast samples were measured by using Archimedes principle. The electronic weighing balance (Model No- CAH-503, CONTECH Instrument Ltd., Mumbai- INDIA) equipped with a density measurement kit was used for this purpose. The theoretical density ($\rho_{t)}$ of alloys was estimated by using the following relation-

$$\rho_t = C_1 \text{ x } \rho_1 + C_2 \text{ x } \rho_2 + C_3 \text{ x } \rho_3 + C_4 \text{ x } \rho_4 + C_5 \text{ x } \rho_5 + \ldots.$$

where, C_i= Atomic concentration of i^{th} element, ρ_i = density of the i^{th} element.

2.5 Characterization tools

The following techniques were used to study the structural and microstructural features of a powder and cast high-entropy alloys (HEAs) :-

2.5.1 Optical microscopy

Sintered samples were prepared for optical metallographic examination. These samples were mechanically polished on emery papers from 1/0 to 4/0. Final polishing

was done on cloth, mounted on a smooth rotating polishing wheel, using diamond suspension and finally with colloidal silica (0.05 μm, ~ 8.5 pH). The polished samples were etched by reagent at room temperature, and microstructures were seen and recorded through an optical microscope (Metalux-3) at different magnification.

2.5.2 X-ray diffraction (XRD)

The XRD machine equipped with Cu-Kα radiation (λ = 0.154 nm) (Rigaku Mini flex-600 (40kV-15mA)) and Co-Kα radiation (0.179 nm) (PANalytical EMPYREAN (40 kV-40 mA)) were used for structural studies. XRD patterns were acquired in the angular (2θ) range of 20º to 100º using 0.02º step size with the scan rate of 10º & 5º/min respectively. Phase transformation associated with the heating of the milled powder was analyzed through high-temperature XRD by Rigaku Smart Lab (45 kV-200mA) with Cu-Kα radiation with the scan rate of 2º/min. The Pseudo-Voigt function was used for fitting XRD peak profile analysis after eliminating the instrumental broadening contribution by using standard silicon sample. The Crystallite size was calculated by applying the following Scherrer's equation [135] :

$$t = \frac{k\lambda}{\beta \cos\theta} \qquad \text{.....2.1}$$

where t is the crystallite size and θ is the Bragg angle. The peak broadening (β) has been taken after making the suitable correction for instrumental broadening and k is a constant (k=0.9-1.0). Gaussian contribution of the sample subtracted from the Si standard was applied into the Williamson-Hall equation to measure the lattice strain. The International Centre for Diffraction Data (ICDD) PDF2 was used to analyze the presence of various phases in diffraction patterns.

2.5.3 Scanning electron microscopy (SEM)

The morphology, particle size and microstructural characterizations of sintered as well of as-cast alloy samples were made using SEM (FESEM-Quanta 200 FEG & Zeiss - EVO18) operating at suitable accelerating voltages. The secondary electron (SE) & backscattered electron (BSE) imaging mode equipped with energy dispersive spectroscopy (EDS) detector were used to obtain the micrographs. The interaction of the electron beam with the specimen produces two types of outgoing electrons- (1) Secondary electrons (SE) – electrons that are coming from the surface of the specimen produced by high energy beam electron. The kinetic energy of the SE is varying in the range of 0-50 eV. (2) Backscattered electrons (BSEs) - electrons that are emerging from the specimen with a large fraction of their incident energy intact after experiencing scattering and deflection from the samples.

2.5.4 Transmission electron microscopy (TEM)

The transmission electron microscopy (TEM) was carried out at 200 kV in a FEI Tecnai G2 T20 S-twin microscope equipped with the high-angle annular dark field (HAADF) and EDS detectors. Powder samples were prepared by dispersing the little amount of powder in acetone/ ethanol followed by 10-20 mins of ultrasonication for producing agglomeration free suspension. After sonicating the solution, single drop was taken and put it on the copper grid. For bulk HEAs, the conventional route of sample preparation was used. Thin slices were sectioned using the slow speed precision cutter. These slices were thinned down up to a thickness of ~70 microns and further punched out the discs of 3mm diameter for electrolytic thinning. The twin-jet electro-polisher (Model I20, FISCHIONE) with the electrolyte of 90% CH_3OH and 10% $HClO_4$ (volume fraction) at the cryogenic temperature of 253K was used to prepare the samples.

2.6 Thermal analysis

2.6.1 Differential scanning calorimetry (DSC)

Thermal analysis of milled powder and as-cast alloy was performed by using NETZSCH differential scanning calorimetry (DSC) 404 F3 Pegasus apparatus in a nitrogen atmosphere. DSC thermograms at different heating rates were recorded. This technique is used to determine the thermal changes in a material accompanied with an exchange of heat. Hence it helps in finding the transformation temperatures of the material.

2.6.2 Heat treatments

The heat treatments of the milled powder and melted alloy were carried out in the muffle furnace. The alloy samples were encapsulated in quartz tube that is backfilled with argon. The induction melted samples were cut into the desired shapes for heat-treatments. These samples were kept in the furnace at different temperatures for definite holding time followed by water quenching. The different conditions of the heat-treatment are stated in respective chapters.

2.7 Mechanical testing

2.7.1 Hardness measurement

The Vickers microhardness (Shimadzu) tester was used to measure the hardness of the as-cast and heat-treated samples at different loads. At least ten measurements were taken for each sample to verify the results.

2.7.2 Compression testing

The cylindrical specimens of dimension Φ 6×10 mm were used for compression testing. The test was performed in the INSTRON universal testing machine (Model- 4207,

Rating-100kN Static) at room temperature. The strain rate of 1.67×10^{-3} s^{-1} was used with the crosshead speed of 1.036 mm/min during compression testing.