Chapter 2 : Materials and Methods

This chapter covers the details of materials and methodology used to prepare the alloys of NiMn, semi-Heusler NiMnSb, and vanadium added semi-Heusler NiMnSbV through induction melting route and mechanical alloying. The parameters of the processing techniques, i.e. induction melting and mechanical alloying (MA) have been discussed briefly. The microstructural and structural characterizations of as-solidified alloys and mechanically alloyed powders were carried out by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM). The chemistry of the microstructures has been determined through scanning electron microscope X-ray energy dispersive spectroscopy (SEM-XEDS) and TEM-EDS techniques. The details of the synthesis and above-mentioned techniques have been described in the following sections.

2.1 Materials and alloy synthesis

The metallic shots of Ni, Mn, Sb and V (purity ≥ 99 %; Alfa Aesar India) were used for the synthesis of equi-atomic NiMn, semi-Heusler NiMnSb, and NiMnSbV alloys. The elemental powders of Ni, Mn, Sb and V of ~325 mesh having a purity ≥ 99.5 %; Alfa Aesar was used for the synthesis of medium entropy NiMnSb and NiMnSbV mechanically alloyed powders. The physical properties of metallic shots and elemental powder used in the present investigation are briefly mentioned in Table 2.1.

Table 2.1: Physical properties of the elements for the synthesis of alloys [85]

Element	Ni	Mn	Sb	V
Crystal Structure	CCP	Complex cubic	Rhombohedral	BCC
Atomic radius (nm)	0.197	0.205	0.206	0.207
Density (g/cm^3)	8.9	7.3	6.6	6.0
Melting Point (°C)	1455	1246	630	1910

Boiling Point (°C)	2913	2061	1587	3205

2.1.1 Vacuum induction melting

The binary NiMn, semi-Heusler NiMnSb and V added semi-Heusler NiMnSbV equi-atomic alloys were synthesized by vacuum induction melting (VIM). The metal shots of Ni and Mn for binary NiMn, Ni, Mn and Sb for semi-Heusler and Ni, Mn,Sb and V for NiMnSbV alloys in stoichiometric proportions weighing 30g was placed in a recrystallized alumina crucible inside the chamber of vacuum induction melting furnace. The recrystallized alumina crucible containing the metal shots were surrounded inside a large graphite crucible. The chamber was backfilled with Argon gas to avoid the vaporization of metals due to the difference in relative partial vapour pressures of the constituent elements. The copper coil which is surrounding large graphite crucible is connected with the solid-state RF generator for supplying AC current. The metal shots placed inside the alumina crucible experiences a varying magnetic field as well as eddy current. The flow of the eddy current inside the metal leads to its resistive heating and may be varied as a function of RF power. The melting was carried out at ~ 1100 °C and the melt was allowed to homogenize for 15 minutes. The melting process was repeated for three times in order to ascertain the compositional homogenization. The thermocouple was attached above the crucible for measuring the temperature local temperature.

2.1.2 Differential Scanning Calorimetry

The DSC systems function based on the heat flux principle. Using this approach, both a sample and a reference undergo a controlled temperature regimen (heating, cooling, or isothermal testing at constant temperature). The primary measurements taken are the sample temperature and the temperature variance compared to the reference. By analysing the raw data signals, the heat flow disparity between the sample and reference can be calculated. A DSC measuring cell comprises a furnace and a built-in heat-flux sensor that includes specific locations for the sample and reference pans. The sensor surfaces are linked to thermocouples or can be integrated into them, enabling the measurement of both the temperature differential between the sample and reference sides (DSC signal) and the absolute temperature of either the sample or reference side.

Depending on whether the reference temperature was subtracted from the sample temperature or vice versa during this calculation, the peak in the graphs may point upwards or downwards. The area under the peak correlates with the heat content of the transition (enthalpy in J/g).

2.1.3 High energy ball milling

The powder particles of Ni, Mn and Sb and Ni, Mn, Sb and V were taken in the stoichiometric proportion, as mentioned in Table 2.1. This was fed (~20-25g) as a starting material for synthesizing NiMnSb and NiMnSbV medium entropy alloys through mechanical alloying. The mechanical milling was carried out in a high-energy planetary ball mill (PM 400 & PM 400/2; Make: Restsch, Germany) at 200 r.p.m with a BPR (Ball to Powder ratio) of 10:1. The elemental powders were milled in 250 ml tungsten carbide (WC) vials with WC balls of 10 mm diameter. In the present work, toluene was used as a process control reagent to avoid oxidation during milling. The process parameters for milling are mentioned in Table 2.2. Mechanical alloying process was interrupted in regular intervals of one hour to control the rise in temperature during alloying. In addition, small amount of milled powder was extracted at regular interval of 10 h, 40 h, 70 h, 100 h for phase analysis.

Table 2.2 Protocol for mechanical alloying of powders

Type of mill	High energy planetary ball mill (Retsch PM 400 & 400/2)
Vials and Balls	Tungsten carbide (WC)
Ball Diameter	10 mm
Ball to powder ratio (BPR)	10:1
Rotational Speed	200 r.p.m
Process control agent (PCA)	Toluene

Milling Medium	Wet

2.2 Crystal Structure and Microstructural characterization

In order to investigate the structural transformation of induction melted as-solidifed alloys and mechanical alloyed powders, to ascertain the size, shape and distribution of phases, microstructural features, and phase composition, several analytical methods were used. The microstructure evolution and phase stability of the as-solidified (NiMn, semi-Heusler NiMnSb, NiMnSbV) and mechanically alloyed (NiMnSb and NiMnSbV) medium entropy alloys were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The microstructure of these alloys was discerned though scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For evaluating the elemental composition of alloys, analytical techniques like SEM-XEDS (X-ray energy dispersive spectroscopy) and TEM-EDS were used.

2.2.1 X-ray diffraction (XRD)

X-ray diffraction analysis was performed with Cu-Kα radiation (λ= 0.154 nm) on a Rigaku Mini flex-600 operated at 40 kV-15 mA. The patterns were acquired using a slow scan rate at 5°/minute with a step size 0.02°. Some XRD characterization were performed with Co-Kα (λ= 0.178 nm) on a Panalytical Empyrean High-Resolution X-ray Diffractometer operated at 40 kV- 40 mA. In this case, the scan rate was kept low at 2°/minute with a smaller step size of 0.01° to acquire more data points with higher sensitivity. The phase transformation in as-solidified semi-Heusler NiMnSb and NiMnSbV alloys as a function of temperature were investigated through in-situ XRD (Rigaku Smart Lab 9kW) having Cu-Kα radiation (λ=0.154 nm). This high-resolution data was used as input for multiphase Rietveld refinement performed on Fullprof software platform.

2.2.2 Scanning electron microscopy (SEM)

The scanning electron microscopy is a useful instrument for characterizing the microstructural details from a length scale ranging from micrometers to nanometres. In general, SEM operates in two types of modes i.e., secondary electron (SE) mode and backscattered electron (BSE) mode. The BSE mode is used for topographical information of samples and is also used for detecting the contrast between the areas of different chemical composition.

In the present work, characterization of the as-solidified alloys was studied through EVO 18 (Carl Zeiss) SEM and high-resolution FESEM (Quanta 200F & NOVA NanoSEM 450) with FEG source operating at 20kV. For elemental analysis, the SEM is equipped with an X-ray energy dispersive spectroscopy (EDS) detector.

2.2.3 Transmission electron microscopy (TEM)

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 G^2 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) was drop cast onto a 3 mm copper grid (200 mesh size) and was dried with the help of an infrared lamp for 30 min. The bulk samples of NiMn samples were prepared by sectioning through low speed diamond saw (Chennai Metco) 500 μm thick foil. This foil was mechanically polished using SiC papers of 400 – 2500 μm grit size for reducing its thickness to ~70 μm. The 70 μm thick foil was punched to 3 mm diameter foil with disk puncher (from GATAN) followed by electrolytic thinning for preparing electron transparent samples for TEM. The electrolytic thinning was done using twin-jet electro-polisher (Model I20, FISCHIONE) with the electrolyte of 20% HNO_3 and 80% CH_3OH (volume fraction) at the cryogenic temperature of -20 °C (253 K) for preparing the electron transparent samples for TEM investigations.

The correlation between the diffraction patterns and corresponding bright/dark field images articulates the crystallographic relationship between various phases in the microstructure. Their mutual orientation can be established through nano-beam diffraction patterns taken from individual features. For this study, rotation calibration was done with the help of ZnO nanowire. Since ZnO nanowire always grows along

[0001] direction, an angular correlation has been made with various camera lengths at various magnifications.