CHAPTER – 2

Materials

and

Experimental Details

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MATERIALS AND EXPERIMENTAL DETAILS

The materials and technique used to prepare the HEAs are discussed in details in this chapter. Mechanical alloying (MA) and concerned parameters have been briefly mentioned. The microstructural and morphological characteristics of HEAs have been characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), as well as X-ray diffraction (XRD) techniques. The chemistry of the phases was analyzed using scanning electron microscope-X-ray energy dispersive spectroscopy (SEM-EDS) and transmission electron microscope-X-ray energy dispersive spectroscopy (TEM-EDS) techniques. Differential scanning calorimetry (DSC) and heat treatment experiments have been carried out to determine the thermal stability. The density and hardness were evaluated. The following sections go into the specifics of the synthesis and the techniques described above.

2.1 Materials and Alloy Synthesis

As the starting material, we used pure (≥99%) elemental powders of Mg, Al, Si, Cr, Fe, Ni, Cu and Zn with particle sizes of ≤ 325 meshes. Table 2.1 lists the fundamental properties of the selected elements. The present study employed three alloy compositions: MgAlSiCrFe, MgAlSiCrFeNi, and MgAlSiCrFeCuZn HEAs. Table 2.2 lists the powder compositions used in this analysis. MA produced these alloys in equiatomic form using a high-energy planetary ball mill. In Table 2.3, the milling parameters adopted have been mentioned. The same milling parameters were used for all of the alloy compositions. Using XRD, the powder samples were collected at regular intervals to monitor the phase evolution with milling time. The detailed results are mentioned in chapters 3, 4 & 5.

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

Element	**Al**	**Fe**	**Cr**	**Mg**	**Si**	**Ni**	**Cu**
Crystal Structure (20 ℃)	FCC	BCC	BCC	HCP	DC	FCC	FCC
Atomic Radius (nm)	0.143	0.124	0.125	0.162	0.118	0.125	0.127
Density ($g.cm^{-3}$)	2.71	7.87	7.19	1.73	2.33	8.90	8.92
Melting Point (℃)	660	1538	1907	650	1410	1455	1083

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

Alloys	Mg	Al	Si	Cr	Fe	Ni	Cu	Zn
MgAlSiCrFe	20	20	20	20	20	-	-	-
MgAlSiCrFeNi	16.66	16.66	16.66	16.66	16.66	16.66	-	-
MgAlSiCrFeCuZn	14.28	14.28	14.28	14.28	14.28	14.28	14.28	14.28

Table 2.3: Parameters for milling utilized in the production of HEA powder

Type of mill	Planetary ball mill (Retsch PM 400 & 400/2)
Type of balls and Vials	Tungsten carbide (WC)
Diameter of ball	10 mm
Ratio of Ball to powder	10:1
Speed of rotation	200 rpm
Process control agent (PCA)	Toluene
Milling Medium	Wet
Running protocol	15 min stop after every 30 min (to prevent the overheating)
Time of milling (max.)	Upto 60 h

2.2 Spark Plasma Sintering of HEA Powder

The milled powders were put in a graphite die with a 20 mm inner diameter and sintered at 800°C for 15 min with a holding pressure of 50 MPa. The heating rate during the Spark Plasma Sintering (SPS) was maintained at 100℃.min^{-1}. The SPS utilizes high-pulsed current through the alloy powder, which is kept inside the graphite die with the arrangement of simultaneous pressure application.The plasma is induced at the particle-particle interfaces in a short duration, causing immediate heating of the powder. Short period of soaking time helps in retaining the nano-structured nature in the alloy powder compaction.

2.3 Density Measurement

The Archimedes theory was used to determine the density of sintered compacts. This was accomplished utilizing an electronic weighing scale equipped with a density measuring kit (Model No. CAH-503, CONTECH Instrument Ltd., Mumbai, INDIA). To determine the theoretical density of alloys, the rule of mixing was followed.

2.4 Structural Characterization

The structural and microstructural features of powders as well as cast high-entropy alloys (HEAs) were analyzed using the following techniques:

2.4.1 X-ray Diffraction (XRD)

For structural studies, an XRD system 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. XRD patterns were acquired using a 0.02º step size and a scan rate of 10º& 5º/min in the angular (2θ) range of 20º to 100º. Rigaku Smart Lab (45 kV-200mA) used high-temperature XRD with Cu-Kα radiation at a scan rate of 2º/min to examine phase transformations associated with the heating of milled powder. After

removing the instrumental broadening contribution by using a regular silicon sample, the Pseudo-Voigt function was used for the XRD peak profile analysis. For accurate determination of crystallite size and lattice strain after removing the effect due to instrumental broadening is given as:

Gaussian: $\beta^2 = \beta^2_{sample} - \beta^2_{instrumental}$

Lorentzian: $\beta_{total} = \beta_{sample} - \beta_{instrumental}$

Peak broadening (β) is measured by Pseudo-Voigt function fitting of experimentally obtained X-ray data. Voigt function is defined by convolution of Gaussian and Lorentzian distribution which has significance due to its goodness of fit into experimental data. Particle size is described by Lorentzian and the lattice strain by Gaussian function. The Scherer's equation describes the widening of the peaks owing to the tiny crystallite size.

$$\beta = \frac{0.9\,\lambda}{t\cos\theta} \tag{2.1}$$

where, 't' is crystallite size and λ is wavelength of the radiation. The peak broadening due to strain 'ε' is given by

$$\beta = 4\varepsilon\tan\theta \tag{2.2}$$

The dislocation density in MgAlSiCrFeNi milled HEAs was calculated using the expression given below [129]

$$\rho = \frac{3\sqrt{2\pi}(\varepsilon^2)^{1/2}}{tb} \tag{2.3}$$

where't' and 'ε' are the crystallite size and lattice strain, b is the burger vector of BCC metals ($b = \frac{a\sqrt{3}}{2}$; a= lattice parameter (Å)).

The presence of different phases in diffraction patterns was investigated using the International Centre for Diffraction Data (ICDD) PDF2.

2.4.2 Scanning Electron Microscopy (SEM)

SEM (FESEM-Quanta 200 FEG & Zeiss - EVO18) was employed to describe the morphological characteristics, particle size, and microstructure of sintered and as-cast alloy samples at sufficient accelerating voltages. The secondary electron (SE) and back - scattered electrons (BSE) imagery modes of energy - dispersive spectroscopic (EDS) detectors were used to capture the micrographs. The engagement of the beam of electrons with the specimen results in the emission of two distinct types of electrons: (1) Secondary electrons (SE) — electrons released from the surface of specimen by highly-energetic beam electrons. The SE has a kinetic energy that varies from 0 to 50 eV. (2) Backscattered electrons (BSEs) - after scattering and deflection from the samples, electrons escape the specimen with a substantial portion of their incident energy unaltered.

2.4.3 Transmission Electron Microscopy (TEM)

In an FEI Tecnai G^2T20 S-twin microscope fitted with the transmission electron microscopy (TEM) at 200 kV was done using an elevated annulus dark field (HAADF) and an EDS detection device. Powder samples were produced by dispersing a small amount of powder in acetone/ethanol and ultrasonically dissolving it for 10-20 minutes to create an agglomeration-free suspension. A single drop of the solution was sonicated and mounted on the copper grid.

2.5 Thermal Analysis

2.5.1 Differential Scanning Calorimetry (DSC)

In a nitrogen atmosphere, thermal analysis of milled powder and as-cast alloy was performed using a NETZSCH differential scanning calorimetry (DSC) 404 F3 Pegasus apparatus. DSC thermograms were taken at various heating speeds. This method is used to

calculate the thermal changes in a substance that occur when heat is exchanged. As a result, it assists in assessing the transformation temperatures.

2.5.2 Heat Treatments

The muffle furnace was used to heat treat the milled powder. The alloy samples were sealed inside a quartz tube filled with argon. These samples were held in the furnace for a fixed period of time at varying temperatures. The numerous heat-treatment conditions are detailed in the respective chapters.

2.6 Mechanical Testing

2.6.1 Hardness Measurement

The instrumented indentation tester (Make: Anton Paar, MHT^3) was used to evaluate the hardness (H) and modulus (E) of the SPSed samples. The samples were indented at a load of 5000 mN with a dwell time of 20 s. At least ten readings were taken for estimating the hardness of SPSed samples. The yield strength (σ_y) has been estimated by using Tabor's equation as follows [130]:

$$\sigma_y = \frac{H}{3} \tag{2.4}$$

However, the estimated YS computed using empirical relationship merely gives an idea about the YS and may not be exactly same to the tensile YS of the bulk samples

2.7 CALPHAD approaches

In the present work, solid solution database (SSOL-5) have been used for the prediction of phases, volume fraction of phases and phase transformation temperatures of the chosen alloy. The binary phase diagrams of the binary subsystems in the HEA composition was generated to investigate the high and low temperature phases present. The present of such phases were also co-related through the experimental results.