This chapter deals with the details of the alloy synthesis, synthesis parameters, characterization techniques, physical, mechanical, and surface properties of the alloys. The various high entropy steels and Fe-based HEAs were prepared through mechanical alloying in a high-energy ball mill followed by spark plasma sintering. The alloying behaviour, phase formation and transformation were examined using X-ray diffraction (XRD). The phase formation after the milling was investigated through transmission electron microscopy (TEM). The morphology, microstructural features, and chemical composition of the milled powder and the SPSed samples were discerned using scanning electron microscopy (SEM) equipped with EDS detector. Thermal stability of the milled powder samples was also tested using differential scanning calorimetry (DSC). Various physical, mechanical, and surface properties of the SPSed samples were systematically studied. The deformation and wear mechanism of the fractured and worn surfaces were analysed using SEM. The details of the preparation and the above-mentioned techniques have been discussed in details in the following sections.

2.1 Alloy designations

In the present work, six alloys were synthesized, and it is mentioned in Table 2.1. The reason behind choosing this composition is to form the dual-phase high entropy steels and Fe-based HEAs. That's why firstly, we designed FeMnNiAlSiC high entropy steel, by adding Ni in the FeMnAlSiC high entropy steel to promote a secondary phase (B2). Then adding Ti and Cr, to promote the nano precipitates formation i.e., carbides to further enhance the strength due to precipitation strengthening. This also improve the wear resistance and biocompatibility.

The design rationale to prepare the Fe-based HEAs is to form dual-phase structure with some precipitates, which have good combination of strength and ductility. Therefore, Al and Ti are added to form precipitates, and high Mn (around 20 at. %) should stabilize BCC phase. Then, by

varying the Ni and Cr, it is intended to see the effect on microstructure and mechanical properties on Fe-based HEAs.

Table 2.1: The details of the alloy composition and designations.

S.No.	Alloy composition (at. %)	Alloy designation
1	$(Fe_{40}Al_{15}Si_{10}C_1)$ $(Mn_{19}Ni_{15})$	HES1
2	$(Fe_{40}Al_{15}Si_{10}C_1)$ $(Mn_{14}Ni_{10}Cr_{10})$	HES2
3	$(Fe_{40}Al_{15}Si_{10}C_1)$ $(Mn_{14}Ni_{10}Ti_{10})$	HES3
4	$Fe_{40}Mn_{20}Cr_{20}Ti_{20}Al_{20}$	HEA1
5	$Fe_{40}Mn_{20}Cr_{15}Ni_{05}Ti_{20}Al_{20}$	HEA2
6	$Fe_{40}Mn_{20}Cr_{10}Ni_{10}Ti_{20}Al_{20}$	HEA3

2.2 Alloy synthesis

The powders of the elements Al, Cr, Fe, Mn, Ni, Ti, Si, and C were procured from Alfa Aesar with purity 99.93 % and particle size of 325 mesh, and were used as the starting material for the synthesis, and their composition are mentioned in Table 2.2. The physicochemical properties of the elements used in the present alloy systems are listed in Table 2.3.

Table 2.2: Atomic percentages to weight percentages for the various alloys.

Alloys		Fe	Mn	Ni	Cr	Ti	Al	Si	C
HES1	at. %	40.00	19.00	15.00	---	---	15.00	10.00	1.00
	wt. %	46.00	21.50	18.13	---	---	8.34	5.78	0.25
HES2	at. %	40.00	14.00	10.00	10.00	---	15.00	10.00	1.00
	wt. %	46.47	16.00	12.21	10.82	---	8.42	5.84	0.25
HES3	at. %	40.00	14.00	10.00	---	10.00	15.00	10.00	1.00
	wt. %	46.87	16.14	12.31	---	10.04	8.49	5.89	0.25

HEA1	at. %	40.00	20.00	---	20.00	10.00	10.00	---	---
	wt. %	43.61	21.46	---	20.31	9.35	5.27	---	---
HEA2	at. %	40.00	20.00	5.00	15.00	10.00	10.00	---	---
	wt. %	43.34	21.32	5.69	15.13	9.29	5.27	---	---
HEA3	at. %	40.00	20.00	5.00	15.00	10.00	10.00	---	---
	wt. %	43.06	21.18	11.31	10.02	9.23	5.20	---	---

Table 2.3: Physical and chemical properties of elements used for the synthesis of alloys.

	Fe	**α-Mn**	**Ni**	**Cr**	**Ti**	**Al**	**Si**	**C**
Atomic radius (Å)	1.27	1.40	1.24	1.24	1.47	1.40	1.11	0.91
Density (g/cc)	7.87	7.43	8.91	7.15	4.50	2.70	2.33	2.10
Melting point (°C)	1536	1244	1455	1907	1668	660	1414	3550
Crystal structure (20 °C)	BCC	Cubic	FCC	BCC	HCP	FCC	Diamond cubic	HCP
Self-diffusion coefficient (m^2/s)	10^{-31}	10^{-36}	10^{-36}	10^{-36}	10^{-7}	10^{-15}	10^{-62}	---

2.2.1 High energy ball milling

The elemental powders in their respective proportions for each designated alloys were mixed as per the Table 2.2. The amount was taken as ~65-70 g as a starting material for the preparation of each alloy viz. HES1, HES2, HES3, HEA1, HEA2, and HEA3 powders by mechanical milling. The milling was done in a planetary ball mill (Retsch PM 400/2, Germany, and Fritsch Pulverisette, Germany) at 200 r.p.m. The ball-to-powder ratio was taken as 10:1. Toluene was used as the

process control agent (PCA) to avoid oxidation of milled powders during milling. Various milling parameters are listed in Table 2.4. Milling was interrupted for 20 min in every1 h to avoid any overheating. To understand the phase evolution during milling, 2-3 g of milled powder was taken after every 5 h and 10 h of milling for high entropy steels and Fe-based HEAs, respectively.

Table 2.4: Parameters for milling of various HEAs powder.

<table>
<tr><th colspan="7">Retsch PM 400/2 & 400, Germany</th></tr>
<tr><th rowspan="2">Alloys designation</th><th rowspan="2">Milling time</th><th rowspan="2">Sample extraction time</th><th colspan="2">Running procedure</th><th rowspan="2">Vials and balls material</th><th rowspan="2">Milling condition</th></tr>
<tr><th>Run time</th><th>Break time</th></tr>
<tr><td>HES1</td><td>35 h</td><td>5 h, 10 h, 15 h, 20 h, 25 h, 30 h, 35 h</td><td rowspan="3">60 min</td><td rowspan="3">20 min</td><td rowspan="3">WC</td><td rowspan="3">Wet</td></tr>
<tr><td>HES2</td><td>40 h</td><td>5 h, 10 h, 15 h, 20 h, 25 h, 30 h, 35 h, 40 h</td></tr>
<tr><td>HES3</td><td>30 h</td><td>5 h, 10 h, 15 h, 20 h, 25 h, 30 h</td></tr>
<tr><th colspan="7">Fritsch Pulverisette 5/4, Germany</th></tr>
<tr><td>HEA1, HEA2, and HEA3</td><td>40 h</td><td>10 h, 20 h, 30 h, 40 h</td><td>60 min</td><td>20 min</td><td>Stainless steel vials and WC balls</td><td>Wet</td></tr>
</table>

2.2.2 Spark plasma sintering

The milled powder samples were consolidated using the spark plasma sintering (Dr. Sinter SCM 1050, Japan, and FCT System GmbH, HPD 10-GB, Germany). The sintering parameters for

the consolidation of the milled powder samples of high entropy steels and Fe-based HEAs are mentioned in Table 2.5.

Table 2.5: Sintering (SPS) parameters of various HEAs.

Alloys designation	Machine	Sintering temperature (°C)	Sintering Pressure (MPa)	Heating rate (°C/min)	Holding time (min)
HES1	Dr. Sinter SCM 1050, Japan	900	50	100	15
HES2		1000	50	100	15
HES3		900	50	100	15
HEA1	FCT System GmbH, HPD 10-GB, Germany	900	50	100	15
HEA2		900	50	100	15
HEA3		900	50	100	15

The milled powder sample of HES1, HES2, HES3, HEA1, HEA2, and HEA3 was put in the hollow cylindrical graphite die after wrapping a 0.2 mm thick graphite foil at the inner surface of the die and in between the punch and powder samples. Graphite foil is used for easy withdrawal of the samples from the die after consolidation. The K-type thermocouple was used to determine the temperature during the SPS. To minimize the temperature error between the sample and the die, the thermocouple was placed near (0.002 mm) to the inner surface of the graphite die. The dimensions of the die were as follows: outer diameter = 50 mm, inner diameter = 30 mm, and thickness = 50 mm. The dimensions of the punch were, height (h) = 30 mm and a 30 mm diameter (d). The sintering was done under a vacuum of 6 Pa.

2.3 Structural and microstructural characterization

The following techniques were used to ascertain the alloying behaviour, phase evolution, microstructural feature, morphology and particle size of the powder, annealed and SPSed samples.

2.3.1 X-ray diffraction

The structural analysis of the powder and SPSed samples was done using the X-ray diffractometer. The details of instrument and 2θ range for the powder, annealed (details are mentioned in the 2.4.2 section in the below), and SPSed samples, are mentioned in Table 2.6. The step size used is 0.02º with a scan rate of 5º/min. The diffraction patterns of the powder, annealed, and SPSed samples of the alloys were analysed with help of "International Centre for Diffraction Data (ICDD)" PDF2 database.

The XRD patterns were also analysed by Rietveld refinement method using the General Structural Analysis System (GSAS-II) software [222]. The lattice parameter, phase fraction, crystallite size, and microstrain were calculated using the Rietveld refinement. The background was fitted with the Chebyschev-I background function with 10 coefficients. The profile fitting was done by the pseudo-Voigt profile function. The phase fraction was determined using the histogram scale factor. The average crystallite size and isotropic microstrain were based on the uniaxial model [223]. The least-square method was used in order to minimize the difference between the experimental and observed data to achieve the acceptable goodness of fit (GOF) factor [223].

Table 2.6: Parameters using during the structural characterization of the powder, annealed and SPSed samples of the alloys.

Alloys designation	Synthesis route	X-ray diffractometer	2θ range
HES1	Powder	HR-XRD (EMPYREAN, PANalytical) ($\lambda_{k\alpha}$ = 0.178 nm)	20º - 100º
	Annealed	XRD (Miniflex-600, Rigaku) ($\lambda_{k\alpha}$ = 0.154 nm)	20º - 100º
	SPSed	HR-XRD (EMPYREAN, PANalytical) ($\lambda_{k\alpha}$ = 0.178 nm)	30º - 100º
HES2	Powder	XRD (Miniflex-600, Rigaku) ($\lambda_{k\alpha}$ = 0.154 nm)	20º - 100º
	Annealed	HR-XRD (EMPYREAN, PANalytical) ($\lambda_{k\alpha}$ = 0.178 nm)	20º - 110º
	SPSed	HR-XRD (EMPYREAN, PANalytical) ($\lambda_{k\alpha}$ = 0.178 nm)	30º - 100º
HES3	Powder	HR-XRD (EMPYREAN, PANalytical) ($\lambda_{k\alpha}$ = 0.178 nm)	30º - 110º
	Annealed	XRD (Miniflex-600, Rigaku) ($\lambda_{k\alpha}$ = 0.154 nm)	20º - 100º
	SPSed	HR-XRD (EMPYREAN, PANalytical) ($\lambda_{k\alpha}$ = 0.178 nm)	30º - 110º
HEA1	Powder	XRD (Miniflex-600, Rigaku) ($\lambda_{k\alpha}$ = 0.154 nm)	20º - 100º
	Annealed	XRD (Miniflex-600, Rigaku) ($\lambda_{k\alpha}$ = 0.154 nm)	20º - 100º
	SPSed	HR-XRD (SmartLab, Rigaku) ($\lambda_{k\alpha}$ = 0.154 nm)	20º - 100º
HEA2	Powder	XRD (Miniflex-600, Rigaku) ($\lambda_{k\alpha}$ = 0.154 nm)	20º - 100º
	Annealed	XRD (Miniflex-600, Rigaku) ($\lambda_{k\alpha}$ = 0.154 nm)	20º - 100º
	SPSed	HR-XRD (SmartLab, Rigaku) ($\lambda_{k\alpha}$ = 0.154 nm)	20º - 100º
HEA3	Powder	XRD (Miniflex-600, Rigaku) ($\lambda_{k\alpha}$ = 0.154 nm)	20º - 100º
	Annealed	XRD (Miniflex-600, Rigaku) ($\lambda_{k\alpha}$ = 0.154 nm)	20º - 100º
	SPSed	HR-XRD (EMPYREAN, PANalytical) ($\lambda_{k\alpha}$ = 0.178 nm)	20º - 120º

The dislocation density [224] was calculated using the formulae, given as,

$$\rho_{dd} = \frac{(3\sqrt{2\pi}<\varepsilon^2>^{\frac{1}{2}})}{tb} \quad (2.1)$$

where, ρ_{dd} is dislocation density, t is crystallite size in nm, b is Burger's vector = $\frac{\sqrt{3}}{2}$ a for BCC, B2-type = $\frac{1}{2}$ a, and for FCC = $\frac{1}{\sqrt{2}}$ a, a = lattice parameter in nm, ε = microstrain. The microstrain [225,226] was calculated using equation,

$$\beta = 4\varepsilon\tan\theta \quad (2.2)$$

where, θ = Bragg angle, and β = Full width at half maximum (FWHM).

2.3.2 Scanning electron microscopy and electron probe micro analyzer

In SEM, two types imaging signals were detected such as secondary electron (SE) and back-scattered electron (BSE). The interaction between the electron beam and the samples is inelastic in nature and comes directly from the sample (surface regions) are the secondary electrons. The secondary electron mode is generally used for the topological information of the samples. The electron interaction (between the electron beam and the samples) is elastic in nature and comes from deeper regions of the samples are termed as BSE, and is used to examine the different phase contrast areas of having different chemical compositions.

The microstructural feature, morphology, and particle size of the milled powder and SPSed samples were studied using the field emission SEM (FEI model no. Nova Nano SEM 450, Gemini 500, and Quanta 200F) and Evo 18 Carl Zeiss SEM. The chemical analysis of the milled powder and SPSed samples were examined by X-ray energy dispersive spectroscopy (EDS) method. The fractured (compression test) and worn (wear test) pellets were examined using the Evo 18 Carl

Zeiss SEM. Electron Probe Micro Analyzer (EPMA) (CAMECA SXFive) was used for BSE imaging, quantitative point analysis, and X-ray elemental mapping of the SPSed sample of the HES1. The SPSed samples were carbon coated with a 20 nm layer using the LEICA-EM ACE200 instrument. The acquisition, data processing, and routine calibration were carried out using SxSAB version 6.1 and SX-Results software of CAMECA.

The samples prepared for the SEM were first cut from the SPSed samples into cylindrical pieces of diameter of 5 mm and 6 mm height and then ground using a belt grinder with 60 grit size silicon carbide paper. Then, the sample was manually polished using the emery papers of different sizes from 400 to 2000 grit size. The mirror like finish samples were obtained by the cloth polishing using the diamond suspension and colloidal silica (0.02 μm). For microstructural features, the SPSed samples of high entropy steel and Fe-based HEAs were chemically etched with the Nital acid solution consisting of 5% nitric acid and 95 % methanol solution, and Aqua regia solution (75 % of hydrochloric acid and 25 % of nitric acid), respectively. The Aqua regia solution was diluted before etching the Fe-based HEAs with distilled water in the 1:4 ratio (Aqua regia: distilled water). The powder (after green compaction) and SPSed sample were hot mounted using Cu-filled epoxy thermosetting (Maker: METATECH Industries). The hot mounting of the powder and SPSed samples was done using the hydraulic mounting press (Bainmount-1, Bain Metgraphy, India) at a temperature of 180 ℃ and holding pressure of 190 MPa for 10 mins and then cooled down to room temperature to take out the samples from the die.

2.3.3 Transmission electron microscopy

The structural analysis of milled powder samples of various alloys was done using selected area diffraction mode in the transmission electron microscope (TEM) (TECNAI G^2T20), operated at 200 kV. The as-milled powder was dispersed in ethanol solution followed by ultrasonication in

the digital ultrasonic instrument (Model no. LMUC-3, Labman scientific instruments) at 40 kHz frequency for 20-30 mins to have agglomeration free suspension. Then suspension (1-2 drops) was drop cast in to the copper grid (Carbon Subset B 300M CU, Maker: TED PELLA INC), then dried for 25-30 mins using the infrared lamp.

2.4 Thermal stability

The thermal stability of the 40 h milled sample was done using differential scanning calorimeter (DSC) (Netzsch, DSC404 Pegasus). To substantiate the thermal events occurred in the DSC, the ex-situ XRD of the annealed samples were done.

2.4.1 Differential scanning calorimetry

The thermal analysis of the milled powder sample was done by the differential scanning calorimeter (DSC) (Netzsch, DSC404 Pegasus, Germany). The DSC was done under the nitrogen (N2) atmosphere up to 1000℃ with a heating rate of 20 K/min. 50-60 mg of as milled powder was taken in the alumina crucible. The alumina crucible was also used as the reference sample.

2.4.2 Annealing treatment

To correlate the DSC findings, the milled powder sample was annealed at different temperatures, and then water quenched so that the high temperature phase is arrested to room temperature. Before annealing, the powder samples were sealed in a quartz tube, backfilled with argon gas. The different quartz tubes carrying ~15-20 g of milled powder samples was separately heated at different temperatures i.e., 400 ℃, 500 ℃, 600 ℃, 700 ℃, 900 ℃, and 1100 ℃ in a muffle furnace and held for 1 h, and then water quenched. The ex-situ XRD analysis of the annealed samples was done to ascertain the phases formed at that temperature and compared with DSC results.

2.5 Physical and mechanical properties

2.5.1 Density calculation

The relative densities of the consolidated pellets of the alloys were calculated using the equation, given as

$$\rho_{RD} = \frac{\rho_{exp}}{\rho_{the}} \times 100 \quad (2.3)$$

where, ρ_{RD} is relative density (%), ρ_{the} (g/cc) is theoretical density computed by the rule of mixture. ρ_{exp} (g/cc) is average experimental density calculated by the Archimedes principle, is given by

$$\rho_{exp} = \frac{m_{air}(\rho_{liquid} - \rho_{air})}{m_{air} - m_{liquid}} \quad (2.4)$$

where, ρ_{liquid} = density of the liquid medium, ρ_{air} = density of the air, m_{liquid} = sample weight in liquid medium and m_{air} = sample weight in atmosphere (air). The density measurement module was put in the electronic weighing instrument (model no. AUX220, Shimadzu, Japan) to measure the sample weight in atmosphere (air) and liquid medium. This experiment was repeated for six times to calculate the experimental density.

2.5.2 Microhardness

The microhardness and elastic modulus of the SPSed samples was computed using instrumented indentation tester (MHT^3, Anton Paar). The microhardness was measured at applied load of 5000 mN with dwell time of 20 s. The Vickers diamond indenter was used and ten measurements were taken to measure the average microhardness. The microhardness and elastic modulus of the SPSed pellets was determined using Oliver-Pharr method [227]. The detailed procedure of the sample preparation is mentioned in the section 2.3.2.

2.5.3 Compression test

The compression test of the SPSed samples was done using the 100 kN Universal Testing Machine (Model No. 5982; Instron) at room temperature. The cylindrical samples were prepared as per the ASTM E9-89a specification. The wire EDM machine (Model no. EXPRESSCUT EX-2530, Medha enterprises, India) was used to prepare the three cylindrical samples of each composition (sample dimensions: diameter = 4 mm and height = 8 mm) for the compression test.

2.6 Surface properties

2.6.1 Wear properties

The coefficient of friction and specific wear rate of the SPSed samples was evaluated using the reciprocating wear tester (RTEC multi-functional tribometer) at room temperature under dry conditions. The dimension of the sample used for the wear test was 12 mm in length, 4 mm in height, and 6 mm in width. The rectangular samples were prepared using the wire EDM machine. The sample polishing procedure was mentioned in the section 2.3.3. An alumina (Al_2O_3) ball of diameter (6 mm) was used as the material (counter) for the reciprocating wear test. The wear test parameters for the SPSed sample of the HES1, HES2, and HES3 were carried out at a constant frequency of 10 Hz with stroke length of 2 mm and acceleration of 1000 mm/s^2 for 600 seconds. The wear test parameters for the SPSed sample of HEA1, HEA2, and HEA3 were done at the same above-mentioned conditions other than the test duration of 300 seconds. The wear test was done in the three different load conditions of 5 N, 10 N, and 20 N for all the alloys in the present work. The wear tests were repeated three times to evaluate the average coefficient of friction for all the alloys. The specific wear rate was calculated using the Archard equation [228], which can be expressed as:

$$W.R. = \frac{\Delta V}{P.S} \tag{2.5}$$

where, W.R. = wear rate in mm^3/mN, ΔV = Volume loss (mm^3) which was calculated using the 3D profilometer connected to the universal tribometer, P = applied normal load (N) and S = sliding distance (m).

2.6.2 Biocompatibility

The biocompatibility of the SPSed sample of all the alloys in the present work was done to see the cell growth using the MTT (3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyl-tetrazolium- bromide). MG-63 was used for the cell proliferation study for the time period of 3, 5, and 7 days of culture on the SPSed sample of all the alloys in the present work and control (316L; as-received from Madani steel). The MG-63 cell was taken from the National Centre for Cell Sciences (NCCS), Pune, India. The growth media was cleaned after the completion of the incubation period. The samples were cleaned with the help of phosphate buffer saline. The modified MTT (MTT: PBS in the ratio of 1:10) was added to each sample and again incubated for 6 h at 37 °C to permit the formation of formazan crystals. Finally, the suspension of formazan crystals was done by dissolving into the dimethyl sulfoxide (DMSO). The optical density of the formazan crystals (concentration) was calculated using the ELISA microplate (iMark Bio-red) reader, at the wavelength of 595 nm. The mean optical density [186] was calculated from the equation given as,

$$\% \text{ Viability} = \frac{\text{Mean absorbance of the samples}}{\text{Mean absorbance of the control (316L)}} * 100 \tag{2.6}$$

SPSS (IBM) software was used to statistically examine the MTT result for the alloys of the present work and control. The substantial differences between the analysed samples were studied by means of the ANOVA method ($p < 0.05$).

2.7 CALPHAD

The property diagram of the HES1, HES2, HES3, HEA1, HEA2, and HEA3 was predicted using the steel database (TCFE8) in the Thermo-Calc software, respectively. The phase formed, phase fraction, phase transformation, and melting point of the alloys were predicted using the CALPHAD approach. The elemental composition in all the phases for the various alloy systems and their stability with respect to temperature were also predicted. The predicted results were correlated with the experimental findings after the milling, annealing, and SPS for the various alloy systems in the present work.

2.8 Melting point prediction

In the present work systems, the prediction of the melting point is done to the compute the sintering temperature. HEA melting temperature (T_m) is stated as the weighted average of binary liquidus temperatures (machine learning approach), and it is calculated using the binary phase diagram. From the binary phase diagram, the liquidus temperatures are taken for all the possible binary pairs in the HEAs at the composition where the i and j element relative ratio is C_i: C_j. C_i and C_j are the atomic percentages of the i^{th} and j^{th} elements. The melting point of the whole system is calculated using the equation [229],

$$T_m = \frac{\sum_{i \neq j} T_{i-j} \times C_i \times C_j}{\sum_{i \neq j} C_i \times C_j} \quad (2.7)$$

where, T_{i-j} = binary liquidus temperature (°C) at the element relative ratio (C_i: Cj), C_i and C_j are the molar percentages of the i^{th} and j^{th} elements, respectively.

Melting point estimation is also done using rule of mixture as to compared with computed using machine learning approach, and CALPHAD modelling. The melting point by the rule of mixture is calculated using following equation,

$$T_{rom} = \sum_{i=1}^{N} C_i T_i \quad (2.8)$$

where, T_{rom} is the melting point through rule of mixture, C_i is atomic concentration of i^{th} element, and T_i is the melting point of the i^{th} element.