PREFACE

The conventional alloy design concept is based upon one major solvent element in which small amount of solute elements are added for achieving specific properties of the resultant alloy. In 2004, the novel alloy design concept known as high entropy alloy (HEAs) was advocated. These classes of alloys contain at least five principal elements, which may be equiatomic or non-equiatomic, ranging from 5 to 35 at. % concentration. The HEAs are grouped in to several distinct classes such as 3d-transition elements, refractory HEAs, and low density HEAs. Further advancement in the field of HEAs are sub categorized into eutectic HEAs, precipitation HEAs, high entropy intermetallics, Fe-based and high entropy steels, etc. The class of non-equiatomic high entropy alloys have practically infinite composition space, which can give unexpected structural and functional properties. High entropy steel is one such novel class of high entropy material, which gives a new concept to design the advanced structural steel, by varying or adding the elements to get the desired structural and microstructural features and excellent mechanical properties.

The most common and widely synthesis routes to prepare the HEAs are vacuum arc melting (VAM), vacuum induction melting (VIM), mechanical alloying followed by spark plasma sintering, additive manufacturing, and sputtering. The alloys prepared using VAM and VIM have some disadvantages, namely, evaporation of low-vapour pressure elements during the melting, formation of heterogenous microstructure with phase segregation, coarsening of grains, and evolution of dendritic and inter-dendritic microstructure, resulting in inferior mechanical properties. Further, secondary treatment is required like annealing, hot and cold rolling, and aging to refine the grains size, for better mechanical properties. These inadequacies of the liquid metallurgical route can be easily overcome by the solid-state processing route, which provides

more homogeneous and finer microstructures favourable for superior properties. The powder materials consolidated by spark plasma sintering (SPS) can effectively retain the nanocrystalline nature. That's why powder metallurgy route is preferred to prepare the high entropy steel and Fe-based HEAs.

The present work deals with the synthesis of high entropy steels and Fe-based HEAs using mechanical alloying and consolidation by SPS. It aims at understanding the alloying behaviour, and phase transformation of the milled powder of the alloys. The structural and microstructural evolution, and mechanical as well as surface properties of the SPSed samples are studied in detail. Phase prediction using calculation of phase diagram (CALPHAD) are correlated with the experimental data after the mechanical alloying, annealing, and SPS. The mechanical properties of these spark plasma sintered (SPSed) samples are understood with the help of various theoretical strengthening mechanisms.

The thesis contains seven chapters. **Chapter 1** deals with the introduction and literature review on the subject related to the present work. This chapter describes the timeline for the design and development of various engineering materials i.e., steels, Al- and Ti-alloys, superalloys, amorphous, and HEAs. The basic design concept of Fe-based HEAs and high entropy steels is addressed. The various methodologies to prepare the HEAs and high entropy steels are described. The various theoretical strengthening mechanisms of the HEAs system are mentioned. The motivation and objectives of the present work are highlighted at the end of this chapter.

Chapter 2 deals with the details of the material and experimental procedures used for the present work. The details of the equipment and its parameters used for processing, characterization, heat treatment, and testing of the alloys are described. The high entropy steel and Fe-based HEAs are prepared using mechanical alloying (MA) and densification by spark plasma

sintering (SPS). The phase analysis at different milling times, annealing and SPSed samples are done using the X-ray diffraction (XRD) technique. The microstructure features and chemical analysis of milled powder, SPSed, fractured, and worn samples have been done by scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) detector. The thermal stability of mechanically alloyed powder samples was examined using differential scanning calorimetry (DSC). The mechanical properties of these SPSed samples are calculated with the help of microindentator and universal testing machine (UTM). The wear properties of the SPSed samples were investigated using the multifunctional universal tribometer. Further, the biocompatibility (quantitively assessment) of these SPSed samples and control (316L) was done in the MG-63 cell line.

Chapter 3 presents the detailed analysis of the synthesis, characterization, and properties of Fe_{40} $Mn_{15}Ni_{14}Al_{15}Si_{10}C_1$ high entropy steel by MA and followed by SPS. The alloying behaviour of the milled powder samples with milling time through XRD was done. After 35 h of milling, the formation of multiphase structures i.e., BCC phase (a = 0.286 nm; cI2), γ-brass type (a = 0.872 nm; cI52), and partially ordered B2-type (a = 0.290 nm; cP2) phases with trace amount of Si was observed. The milled powder was found to be thermally stable up to ∼500 °C, however, the formation of the Fe_5Si_3-type phase was evident at ∼520 °C. The spark plasma sintered (SPSed) sample was able to retain the BCC phase, B2, and γ-brass type along with the formation of Fe_5Si_3 type silicide phase (a = b = 0.667 nm, c = 0.468 nm; hP16). The SPSed sample of HES was found to have low density (∼6.49 ± 0.3 gcm^{-3}), high microhardness (∼7.8 ± 0.3 GPa), and good compressive strength (∼2046 ± 160 MPa) with an appreciable amount of ductility of ∼19 %. The enhanced mechanical properties of the SPSed sample can be attributed to dual-phase microstructure i.e., BCC and B2 along with finer nano-sized silicide precipitates, as well as grain-

boundary and dislocation strengthening mechanisms. Further, wear properties and biocompatibility of the SPSed samples were systematically investigated, and the alloy showed a low specific wear rate of 1.79 x 10^{-5} mm^3/mN and better biocompatibility as compared with 316L. The experimental findings on phase evolution, thermal stability, and mechanical properties of non-equiatomic HES are correlated with the various thermodynamic parameters, CALPHAD modelling, and strengthening mechanisms.

Chapter 4 deals with the $Fe_{40}Mn_{14}Cr_{10}Ni_{10}Al_{15}Si_{10}C_1$ high entropy steel. They formed dual-phase structure under 40 h of milling, which consisting of a BCC (a = 0.286 nm) and a χ-type (close to gamma brass structure) phase with undissolved Si. The milled powder sample showed the thermal stability up to 400 °C, then phase transformation at elevated temperatures was observed. The FCC (a = 0.362 nm) and B2 (a = 0.290 nm) phases, along with Cr_3Si (a = 0.455 nm) and $Cr_{23}C_6$ (a =1.062 nm) precipitates formed after spark plasma sintering. The SPSed sample showed a density of 6.8 g/cc. Microhardness, compressive strength, and wear properties of the SPSed sample were evaluated and its values are found to be 7.4 ± 0.2 GPa, 1900 ±100 MPa, and 1.99 x 10^{-5} mm^3/mN, respectively. Further, this alloy exhibits better biocompatibility as compared to 316L.

Chapter 5 describes the phase evolution, microstructural, thermal stability, mechanical and surface properties of the $Fe_{40}Mn_{14}Ti_{10}Ni_{10}Al_{15}Si_{10}C_1$ high entropy steel. 30 h milled powder sample was found to have a mixture of BCC (a = 0.287 nm; cI2) and γ-brass type (a = 0.889 nm; cI52) phase. DSC thermogram showed four exothermic heating events at 530 °C, 690 °C, 860 °C and 1000 °C. The phase transformation corresponding to the heating events was correlated with the ex-situ XRD of the as-milled powder. The phases that evolved are ordering/texturing of γ-brass type, FCC, Fe_5Si_3 type, and TiC phases at elevated temperatures. The SPSed sample of HES were

found to have a dual-phase structure containing FCC (a = 0.362 nm; cF4) and B2-type phase along with Fe_5Si_3 type (a = b = 0.678 nm, c = 0.475 nm; hP16) and TiC (a = 0.431 nm; cF8) intermetallic. The mechanical properties of the SPSed samples were discerned through instrumented microindentator and UTM. The microhardness, elastic modulus, ultimate compressive strength and strain were found to be ~10.4 GPa, ~209 GPa ~2300 MPa and ~15%, respectively. The SPSed sample of HES showed excellent room temperature microhardness and strength due to the co-existence of FCC and B2-type phase along with the intermetallics. The strengthening mechanism suggested that the grain boundary, dislocation, and precipitate strengthening have major contribution. Further, the wear and biocompatibility behaviour of the SPSed samples were tested, and the specific wear rate was found to be 1.62 x 10^{-5} mm^3/mN and better biocompatibility as compared with 316L.

Chapter 6 addresses the synthesis, structural and microstructural analysis, and mechanical and surface properties of $Fe_{40}Mn_{20}Cr_{20-x}Ni_xTi_{10}Al_{10}$ (x = 0, 5, 10 at. %) HEAs. After 40 h of MA, phases formed were BCC and χ-phase type structure. The milled powder alloys showed thermal stability up to 500 ℃ and then formed FCC solid solution in all three alloy systems. The BCC (major) phase transformed to a dual-phase i.e., FCC + BCC, and further to the FCC (major) phase as the Ni content increases from x = 0, 5, and 10 at. % after spark plasma sintering. The microhardness and yield strength values of the SPSed sample decreased from 6.4 GPa to 4.2 GPa, and 1961 MPa to 1300 MPa, respectively as the Ni content increased from x = 0 to 10 at. %. Further, these alloys showed better wear resistance and biocompatibility as compared to 316L.

Chapter 7 summarizes the significant findings of the overall work and suggestions for future work.