Preface

The work of serendipity of Pol Duez and co-workers marks the beginning of a paradigm shift in alloy design and technology that gave way to the genesis of multicomponent nature of alloys and heuristic thinking became an integral part of the design strategy. Next few decades saw a rapid upsurge in developing alloys through different processing routes which led to the discovery of quasicrystals and almost at the same time bulk metallic glasses, which shattered the dogma of crystallography borne and protected in the custody of science for about 150 years. Essential difference between the quasicrystal forming and bulk metallic glass forming alloys with the conventional alloys are that they are often ternary or higher order in terms of alloying elements and in the absence of enough thermodynamic data and phase diagram information, their phase stability and microstructural evolution are explained through different empirical rules developed over a period of time. These alloys can no longer be treated as dilute alloys. Another milestone in this continuously developing saga is the discovery of high entropy alloys (HEA).

Initially, the high entropy alloys were defined as multicomponent alloys with almost equi-atomic composition that forms single phase solid solution. Without making any reference to the stability of solid solution phase, it was assumed that the phase was configurational entropy stabilized. As more and more number of such alloys came into existence, it was observed that only few alloys formed single phase solid solutions which essentially paved the way of naming these alloys in a different way. Nowadays, the terms multiple principal element alloys or complex concentrated alloy are used equivocally for these alloys. A critical look into the alloy design strategy indicates that the criteria of bulk metallic glass formation are essentially opposite to the Hume-Rothery rules of solid solution formation and the criteria for HEA formation is a mix of both the criteria. The motivation of the current research work is to find out the role of configurational entropy in forming Heusler based high entropy alloys and to understand its stability.

The thesis is organized into six chapters. **Chapter 1** provides a brief introduction and an overview of the current understanding on the subject of study. This chapter describes the distinction between polymorphic and allotropic transformation, how the alloy design principles of high- entropy alloys (HEAs) are different from the conventional alloys and contested the major core effects of HEAs, which is believed to make these alloys to form simple solid solution phases. It also provides information regarding different processing routes along with the major ones for synthesizing HEAs.

Chapter 2 deals with the details of the materials and experimental procedures used for the present work. It briefly introduces the equipment used for processing and characterization of the materials. Mechanical alloying (MA) and induction melting (IM) techniques are used to prepare the HEAs. The phase identification at different milling hour has been done by X-ray diffraction (XRD) technique. The microstructures have been characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) equipped with energy dispersive spectroscopy (EDX). The thermal stability of the alloys is investigated by in-situ x-ray diffraction.

Chapter 3 presents a detailed study of as-solidified Ni-Mn alloy at the equiatomic proportion. The impetus for chosing this system was the phase diagram which is ambiguous at the lower temperatures. Melting of the alloy was done in a vacuum induction melting furnace with Ar filled atmosphere. The characterization was carried out with the help of XRD and TEM. It has been found that there is a self-assembled chessboard-like microstructure which we are reporting for the first time in the metallic system between disordered tI2 NiMn (tetragonal) and ordered mP8 NiMn (monoclinic) phases. The ordered structure has been generated by taking the tI2 as a base structure and implying the directions of ordering only along [110] and [112] as superlattice reflections was observed in the diffraction pattern along these directions only. Mostly the chessboard microstructure is observed between cubic and cubic or cubic and tetragonal phases unlike the present case. The crystal structure of the new phase has been found to be polymorphically related mP8 phase with space group P 2/m (a=5.02 Å, b=5.16 Å, c=3.61 Å). The phase has not been reported so far in Ni-Mn system. The chessboard like morphology between a tetragonal and monoclinic phase is being reported for the first time.

Chapter 4 presents the phase and microstructure evolution in semi-Heusler NiMnSb and vanadium added quaternary equi-atomic NiMnSbV alloys in the as solidified state. In the as solidified NiMnSb alloy, cubic semi-Heusler phase and in the as solidified

NiMnSbV alloy, Frank-Kasper type cubic SbV_3 phase along with the cubic semi-Heusler NiMnSb phase are observed. Nucleation and growth of SbV_3 phase takes place in the alloy through solute rejection mechanism, and at the interface of SbV_3 and NiMnSb semi-Heusler phase, lamellar structure is observed. While SbV_3 phase is stable upto 700ºC, the semi-Heusler NiMnSb phase is not stable beyond 400ºC and it transforms to hexagonal (Ni/Mn)Sb phase. Line defects are observed in the NiMnSb semi-Heusler phase. However, extensive twin like defects are observed in the cubic SbV_3 phase. In the SbV_3 phase edge sharing 12-fold coordinated icosahedral clusters and 14-fold coordinated clusters are present. Atomic size difference of Sb and V indicates that the clusters are distorted, which might be the viable cause behind the formation of such kind of compound deformation twins. The phase formation and stability in these two alloys has been studied through Miedema's model. It is observed that apart from atomic size difference, enthalpy of mixing; the ternary and higher order self-interactions, electronic contribution to enthalpy also play an important role. Systematic substitution in the lattice of semi-Heusler NiMnSb phase based on enthalpy of mixing and atomic radius may not be the ideal design strategy for the development of semi-Heusler NiMnSb based single phase multicomponent/high entropy alloys.

Chapter 5 describes the synthesis and characterization of configurational entropy stabilized NiMnSb and NiMnSbV medium-entropy alloys (MEAs) prepared by mechanical alloying. The 10 h milled MEAs powder were found to have ordered hexagonal (Ni/Mn)Sb phase (Pearson symbol: hP4, SG: $P6_3/mmc$ and a = b = 4.149Å, c = 5.771 Å). On continuing the milling after 10 h, it results in the destabilization of the ordered hexagonal (Ni/Mn)Sb phase to a disordered hexagonal solid-solution phase (SG: $P6_3/mmc$ and a = b = 3.97Å, c = 5.12 Å, c/a=1.28).Amorphous phase is also observed after complete conversion of the ordered hexagonal (Ni/Mn)Sb phase to the disordered hexagonal solid-solution phase. Kinetics of conversion of the (Ni/Mn)Sb phase to the disordered hexagonal phase is slower in case of NiMnSbV medium-entropy alloy than the NiMnSb alloy, due to the involvement of one extra diffusion event of V associated with the NiMnSbV alloy. Upon solidification, NiMnSb semi-Heusler phase is observed in NiMnSb alloy, whereas along with the NiMnSb semi-Heusler phase, Frank-Kasper type SbV_3 phase is also observed in the NiMnSbV alloy. The lamellar structure at the interface of the semi-Heusler phase (NiMnSb) and the SbV_3 phase indicates the formation of the semi-Heusler phase and the SbV_3 phase through solute rejection mechanism. It is discerned that the systematic substitution in the lattice of an intermetallics phase, based on atomic size mismatch and enthalpy of mixing may not be the viable method for design and synthesis of high or medium entropy alloys. The phase formation of various phases in these MEAswas found to be dependent on the synthesis method. The strain induced during mechanical alloying leads to the formation of the solid solution phase with high configurational entropy along with minor fraction of amorphous phase.

Chapter 6 presents an overall summary of the work from the present investigation along with suggestions for future work.