Synopsis

The aim of the present thesis work was to synthesize and explore the phase transformation behavior of a binary Heusler alloy based on AlMn system. The intermetallic phase with the stoichiometry AlMn, which is usually termed as τ phase, is metastable and the only phase in the system that exhibits ferromagnetic behavior. Thus, good magnetic properties are directly related to the amount of τ phase present in the alloy. Due to its metastability, synthesis of τ phase in bulk form has always been a challenging task for the materials scientists. In this work, we have demonstrated a possible route for synthesizing complete τ phase (i.e., without any other nonmagnetic phases) in bulk form. This has been achieved without any addition of τ phase stabilizers such as C, B etc. We have carried out several heating and cooling (including isothermal) experiments to understand the exact nature of phase transitions that can yield hundred percent τ phase. The thesis is divided into 6 chapters.

Chapter 1 deals with a brief introduction on magnetism and types of magnetic behavior with several examples. Following this, we have given a brief review on Heusler alloys based on Mn with a special emphasis on AlMn binary alloy.

Chapter 2 discusses the experimental techniques employed during the present investigation. Vacuum arc melting/casting unit was used to make the alloys. Microstructural features were studied using scanning electron microscopy (SEM) while the phase identification was carried out using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The thermal analysis of the samples was carried out using differential scanning calorimetry (DSC) while a vibrating sample magnetometer (VSM) used for magnetic measurements.

Chapter 3 outlines the detailed procedure for synthesis of complete τ phase in bulk form without any addition of stabilizers. This was achieved through a controlled solidification of a

$Al_{45}Mn_{55}$ at.% alloy composition and subsequent heat treatment. To obtain the domain for the formation of the τ phase from high temperature ε phase, isothermal transformation experiments were carried out, that helps to generate a complete TTT diagram. The τ phase start and end times were obtained through magnetic and X-ray measurements. Subsequently, the obtained TTT curve was converted to CCT curve by using standard Avrami method. The τ phase formation is a process of solid - solid phase transformation that depends on the cooling rate (*i.e.* heat extraction rate during cooling). Hence, thermal modeling was carried out to predict the heat extraction rate for different diameter copper mold (2 to 12 mm) containing hot solids and the obtained cooling rate curves were overlapped with the calculated CCT diagram. Hence we can approximately estimate the diameter of the mould to be used for obtaining τ phase directly during casting. We found that 10 mm diameter casting is suitable to get complete τ phase. This has been further experimentally verified. A saturation magnetization of 128 emu/gm at room temperature was measured for this 10 mm sample containing only τ phase. This represents the highest value reported till now in this system. The Curie point for this phase was found to be 395 ^{o}C. Additionally, the cast rod exhibits compressive strength of 1170 MPa with > 10% compressive ductility that is higher than other existing permanent magnets.

Chapter 4 discusses the nature of phase transformation behavior of ferromagnetic $Al_{45}Mn_{55}$ at.% alloy (τ phase) during heating to high temperature. Experiments were carried out non-isothermally using differential scanning calorimetry (DSC) to evaluate the structural changes during heating. The progressive structural (or phase) changes with temperature and time were recorded and analyzed. The DSC heating and cooling curves exhibit endothermic and exothermic peaks, which reflect the phase or structural changes and have been discussed in detail. To identify the phases responsible for the transformation peaks, the samples were heated in a muffle furnace at a rate of 10 °C/min upto the temperatures just below and above the peaks followed by rapid quenching in water to arrest the phase. In situ X-ray diffraction was also performed to correlate and confirm the phase transitions that are seen during heating in DSC. The present study confirms transformation of $\tau \rightarrow \beta + \gamma_2 \rightarrow \beta + \gamma_{bcc} \rightarrow \varepsilon$ and $\varepsilon \rightarrow \tau \rightarrow \beta + \gamma_2 \rightarrow \beta + \gamma_{bcc} \rightarrow \varepsilon$. We found that the γ_{bcc} phase (high temperature phase) cannot be retained during quenching experiments and hence was not detected by earlier investigators. Therefore, this study provides a more complete understanding of the τ phase decomposition.

Chapter 5 demonstrates the effect of mechanical ball milling on the evolution of phases with starting materials having τ phase (10 mm cast rod) as well as ε phase. A planetary ball mill P7 was used for milling and the samples were collected at regular intervals of time. We observed no effect of milling on the magnetic properties of ε phase since it is a nonmagnetic phase. But subsequent annealing at 350 °C for 30 min after milling results in structural change and exhibits magnetic response. The phase transitions were found to depend on prior milling history. The saturation magnetization and coercivity for 4 h milled (and annealed to 350 ^{o}C for 30 min) was measured to be 23 emu/gm and 5 kOe respectively. In the case of τ phase as a starting material, we found no decomposition upto 9 h of milling even though the particle size reduction was observed with increasing milling time. Additionally we found that after 3 hours of milling, the saturation magnetization value reduces to 23 emu/gm and coercivity increases to 5.2 kOe. Further milling causes decrease in both the values. Annealing of the 3 h milled powder at 350 °C for 30 min, resulted in slight decrement in coercivity (Hc = 5 kOe) but significant increase in saturation magnetization (32 emu/g) value. Experimental results suggest that magnetization reversal is domain nucleation controlled and that the nonmagnetic phases present can act as the pinning sites.

The final chapter summarizes the major conclusions of the present work.