ABSTRACT

This research work presents experimental studies on the phase formation, magnetostructural and magnetocaloric (MC), thermal conductivity and magnetostriction properties of a novel series of ferromagnetic shape memory materials of non-stoichiometric Heusler alloys Ni_2MnSn in the form of cylindrical discs. The objective of this investigation is two-fold; one, from fundamental aspects and the other from an applied point of view. In the fundamental part, it is to develop a basic understanding of coupled magnetostructural, thermomagnetic, magneto-transport and MC properties in relation to the microstructure, whereas in the other part, it is to develop a magnetic refrigerant with large MC properties near room temperature in low magnetic fields. The Mn-rich and Ni-rich alloys in the Ni-Mn-Sn system are chosen in view of tuning the martensite transition with optimal MC properties near room temperature. A partial Ni → Ag substitution in the Mn-rich $Ni_{41-x}Ag_xMn_{50}Sn_9$ ($x \leq 2$) series promotes the martensite phase stabilization near room temperature. In the other series $Ni_{50}Mn_{37-y}Cr_ySn_{13}$ ($y \leq 2$), a small Mn → Cr substitution triggers a single magnetostructural transition with functional MC properties. An advantage with the $Ni_{41-x}Ag_xMn_{50}Sn_9$ ($x \leq 2$) alloy series is that it yields inverse MC properties near room temperature.

The results of the structural, thermal, mechanical, electrical, MC, and magnetoresistance (MR), magnetostriction and thermal conductivity studies on these two-alloy series under selective experimental conditions are presented in four chapters (Chapters 3-6). Chapter-1 gives a general introduction to the subject of ferromagnetic Heusler alloys, with the statement of the problem, review of the literature along with the drive behind selecting this specific class of materials, and typical physical properties and applications of such alloys. Chapter 2 describes experimental details of the alloy formation and sample preparation for the measurements and analysis of the different properties. Chapters 3 and 4 deals with the structural transformation, microstructure, and magnetic properties the $Ni_{41-x}Ag_xMn_{50}Sn_9$ ($x \leq 2$) and $Ni_{50}Mn_{37-y}Cr_ySn_{13}$ ($y \leq 2$) alloys, respectively. X-ray diffraction (XRD) patterns reveal a single martensite phase formed as Ni → Ag increases from 0.5% to 2.0%, and content so as to exist at room temperature in a $L1_0$ tetragonal crystal structure. The FESEM/ HRTEM images reveal the growth along the (222) plane. The thermomagnetic curves clarify the suppression of both magnetic saturation value and magnetic transition temperature as the percentage of Ag increases. The $Ni_{41-x}Ag_xMn_{50}Sn_9$ ($x \leq 2$) alloy exhibits exchange bias phenomenon. In $Ni_{50}Mn_{37-y}Cr_ySn_{13}$ ($y \leq 2.0$), the XRD shows a twin along (131) plane and the FESEM describes a second level hierarchal structure. Chapter 5 describes the relationship of hardness and strain with variation in Ag/Cr content in the alloy compositions. Both the Vickers hardness and Young's modulus soften in a parabolic curve over the Ag-doping whereas, Cr-doping increases the Vickers hardness, Young's modulus, as well as microstrain through a broad maximum observed around y → 1.0. Chapter 6 describes MC, MR and MS properties in both $Ni_{41-x}Ag_xMn_{50}Sn_9$ ($x \leq 2$) and the $Ni_{50}Mn_{37-y}Cr_ySn_{13}$ ($y \leq 2$) alloys of thin microscopic layers of small crystallites. A maximum MR ≅ (-) 55% (at ΔH = 8 kOe field) is observed in a critical x → 1.5 at% Ag-doping in the first alloy series at T_M of 256 K, while it dropped to (-) 36% in y → 2.0 at% Cr doping in the other alloy series of a tailored T_M → 320 K in the martensite ← austenite transitions. The Ag-doping has tuned T_M from 380 K to 243 K as x → 2.0, while the ΔS progressively decreased to 7.91 J-kg^{-1}-K^{-1}, with an intermediate value ΔS = 9.73 J-kg^{-1} found at near room temperature, T_M ~ 324 K as x → 0.5, in the DSC thermograms. A summary of the work with important implications achieved in this work is described in Chapter 7 along with the future scope of the work in this series.

Keywords: Heusler alloy; Martensite transition; Magnetocaloric, magnetostriction and magnetoresistance properties; Magnetic entropy