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Investigation of Route to Martensitic Transition in Ni-Mn-In Shape Memory Alloys

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Abstract. The temperature dependent x-ray diffraction and magnetization measurements on the off stoichiometric $Ni_2Mn_{1+x}In_{1-x}$ alloys have confirmed the appearance of martensite at critical Mn concentration of x=0.35. The high temperature phase of all the alloys have cubic $L2_1$ structure with the lattice constant steadily decreasing with increase in Mn concentration. Martensitic transition begins to appear in $Ni_2Mn_{1.35}In_{0.65}$ at about 197K and the structure seems to adopt two phases including the major cubic along with the modulated monoclinic phase. This has been explained on the basis of number of Mn-Ni-Mn hybridized pairs that are responsible for inducing martensitic transition.

INTRODUCTION

Materials undergoing a change in shape in the presence of magnetic field (ferromagnetic shape memory alloys) are receiving a great deal of attention due to a potential use as magnetic actuators, refrigerants etc. [1]. The atoms move from high symmetry cubic (austenite) to a lower symmetry martensitic state causing a change in shape. It is a self organizational phenomenon in solids where atoms move without diffusion below transition temperature T_M called the martensitic transformation [2]. The determination of movement of atoms is a crucial step in understanding the underlying physical phenomenon subject to shape change since the atomic movement causes change in the electronic structure of solid along with their physical properties. Generally, the motion of atoms is consistent with the symmetry of crystal structure and is considered as the long range ordering of the elastic strain vector.

Ni_2MnGa is one such alloy with Heusler $L2_1$ structure in its austenitic state that undergoes martensitic transformation below 210K and assumes a 5M modulated structure [3]. Replacement of Ga with In/Sn/Sb results in a non-martensitic alloys. However, by increasing the Mn concentration to obtain $Ni_2Mn_{1+x}Z_{1-x}$ (Z = In/Sn/Sb) concludes in martensitic alloys [4]. Nevertheless, the phase diagram is quite interesting. Firstly, the martensitic phase suddenly appears at a critical Mn concentration [5]. Secondly, the transformation temperature is critically dependent on composition of the alloy as well as method of preparation [6]. EXAFS investigations have revealed presence of local structural distortions even in the austenitic phases [7, 8]. All these observations indicate a possibility of pre-transition phase in these alloys. The present study seeks to investigate the reason for sudden appearance of marternsitic transition at a critical concentration of x = 0.35 and to study the structure of martensitic phase of this alloy.

EXPERIMENTAL

The series $Ni_2Mn_{1+x}In_{1-x}$ (x = 0, 0.3, 0.32, 0.35 and 0.4) was prepared using vacuum arc melting the constituent high purity elements in argon atmosphere. The resulting beads were then cut and some of the pieces were finely ground using agate mortar and pestle. The powder was covered in tantalum foil and along with the remaining pieces were enclosed in evacuated quartz tube, annealed at 750°C for 48 hours and quenched in ice cold water. To study

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the evolution of structure, x-ray diffraction patterns of the powdered samples were recorded using Cu K_α radiation at various temperatures. The dc magnetization measurements were performed using Quantum Design SQUID magnetometer. For this the samples were cooled in zero applied field to 5K and magnetization was recorded while warming (ZFC) in a field of 100 Oe. Subsequent cooling (FCC) and warming (FCW) data in the same value of applied field were also recorded.

RESULTS AND DISCUSSION

Ferromagnetic ordering temperature and martensitic start and finish temperatures for all the alloys along with structural information at room temperature (RT) are listed in Table 1. It can be seen that while the compositions with x = 0, 0.3 and 0.32 exhibit only a Curie temperature (T_C) at around 300K, x = 0.35 has a martensitic transition at about 197K along with a T_C = 305.37K. $Ni_2Mn_{1.4}In_{0.6}$ does not show a clear ferromagnetic transition presumably because it coincides with martensitic transition at about 330K [9]. Rietveld refinement carried out using Jana2006 of the room temperature x-ray diffraction pattern seen in Fig 1 confirms cubic $L2_1$ phase for the alloys $Ni_2Mn_{1+x}In_{1-x}$ (x = 0, 0.3, 0.32, 0.35) while x=0.4 is in its martensitic state with incommensurate monoclinic structure.The structural details are presented in Table 1.

TABLE 1

Composition	**Phase**	**Space group**	**Lattice parameters** (Å)	**T_C(K)**	**M_S(K)**	**M_F(K)**
Ni_2MnIn	Cubic	F m -3 m	6.070755(72)	309.23		
$Ni_2Mn_{1.3}In_{0.7}$	Cubic	F m -3 m	6.013390(97)	302.96		
$Ni_2Mn_{1.32}In_{0.68}$	Cubic	F m -3 m	6.012965(98)	311.13		
$Ni_2Mn_{1.35}In_{0.65}$	Cubic	F m -3 m	6.007012(103)	305.37	197.84	72.17
$Ni_2Mn_{1.4}In_{0.6}$	Cubic	F m -3 m	5.988852(204)	305.48	330.61	299.49
	Monoclinic	I2/m(a0g)00	a = 4.388768(253)			
			b = 5.560048(365)			
			c = 4.332141(187)			
			β = 92.93878(567)			
			Modulation Vector			
			q = 0.338014(774)			

The refined martensitic structure obtained for x = 0.4 is in fair agreement with that reported in literature [10]. Ni2Mn1.35In0.65 also undergoes martensitic transformation but its martensitic structure is hitherto not known. This is of further importance because the alloy with x = 0.32 is austenitic down to 5K and so x = 0.35 is the first composition in Ni2Mn1+xIn1-x series to exhibit martensitic transformation. Therefore, is the martensitic structure of x = 0.35 similar to that of x = 0.4? To explore this aspect, x-ray diffraction patterns recorded at different temperatures above and below their respective martensitic transition temperature for x = 0.35 and x= 0.4 are displayed in Fig 2. For clarity the patterns are displayed in limited 2 theta range around the most intense austenitic reflection (220). The reflections corresponding to modulated structure also appear in this range.

Figure 2 (a) depicts x-ray diffraction plots for Ni2Mn1.4In0.6 at 363K, 333K, 123K and 93K. The diffraction pattern at 363K is cubic austenitic. As the temperature is lowered to 333K new peaks appear just below the major cubic 220 peak indicating martensitic transformation of the sample. Appearance of martensitic peaks at 333K coincides well with the martensitic start transformation temperature determined from magnetization measurements. Further lowering of temperature results in decrease of cubic reflections and growth of martensitic reflections. The diffraction patterns below 300K are purely martensitic as indicated by refined pattern at room temperature in Figure 1 and patterns at 123K and 93K displayed in Fig 2(a).

Figure 2 (b) depicts x-ray diffraction plots for Ni2Mn1.35In0.65 at 233K, 213K, 123K and 83K. The diffraction pattern at 233K is cubic austenitic just as that at room temperature (Fig. 1). As the temperature is lowered to 213K new peaks appear just below the major cubic 220 peak indicating the presence of two phases at low temperature. The two phase pattern can also be seen at 123K and 83K. Refinement of these patterns (not shown here) exhibits

presence of two phases – cubic austenite and modulated martensite in the 80:20 ratio. A similar ratio is also obtained from refinement of neutron diffraction pattern recorded at 10K.

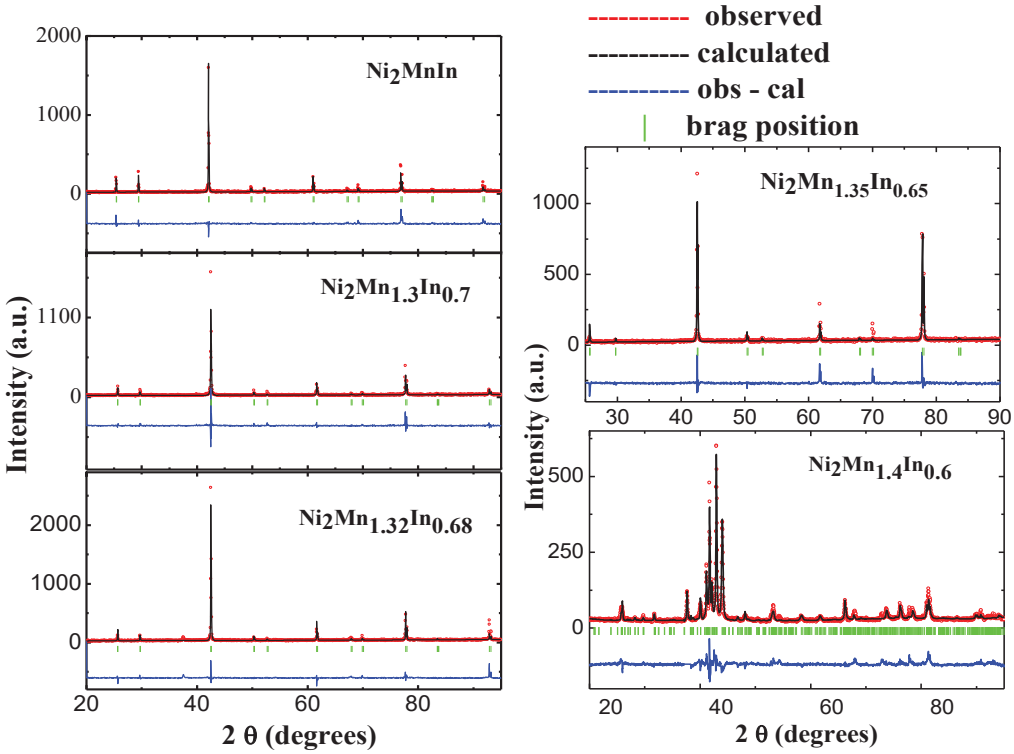

FIGURE 1. The Rietveld refined X-ray diffraction patterns at room temperature.

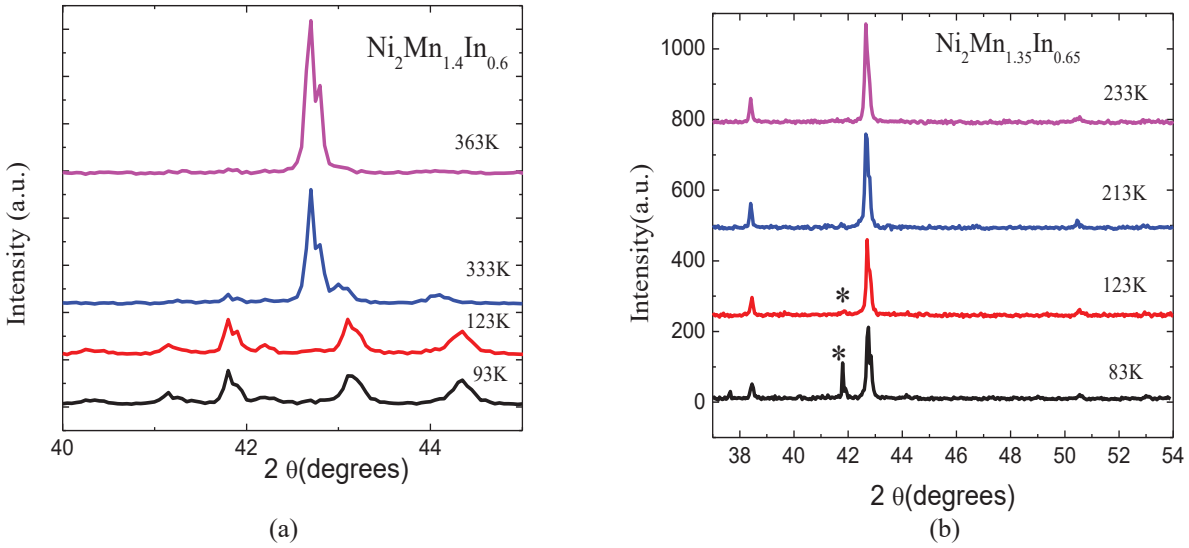

FIGURE 2. X-ray diffraction patterns of the two alloys (a) $Ni_2Mn_{1.4}In_{0.6}$ in the 2θ range of 40°-45° and (b) $Ni_2Mn_{1.35}In_{0.65}$in the 2θ range of 38°-54° at different temperatures. The peak marked with * disappears with increasing temperature.

The presence of austenitic phase well below the martensitic transition temperature in Ni2Mn1.35In0.65 indicates the sample to be transforming only partially. Such a scenario could be understood in light of already reported EXAFS study [8] according to which martensitic transition occurs due to a local structural distortion. This distortion leads to shorter Ni-Mn bond distance and a stronger hybridization between Ni 3d and Mn 3d bands. In Ni2Mn1.35In0.65 only just enough such hybridized pairs are created for it to undergo a partial martensitic transformation. This observation gains importance in light of recent observation of phase separation leading to shell ferromagnetism in Ni50Mn45In5 [11].

CONCLUSIONS

In conclusion, structural transformation from austenitic to martensitic state in Ni2Mn1+xIn1-x has been investigated. Martensitic transformation appears in all alloys with $x \geq 0.35$. However, in $x = 0.35$, cubic austenitic phase persists well below martensitic transformation temperature and is the major phase leading to co-existence of austenitic and martensitic phases well below martensitic finish temperature of the alloy.

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