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Premartensite transition in Ni_2FeGa Heusler alloy

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ABSTRACT

Martensitic phase transformation of Ni_2FeGa Heusler alloy was studied by differential scanning calorimetry. Atomic ordering induced in the austenite structure by quenching from high temperature plays a significant role on martensitic phase transformation. Higher magnetization and larger magneto-crystalline anisotropy of martensite phase than that of austenite phase are noticed. Tweed contrast regions observed in the transmission electron microscopy were correlated to premartensite phenomena. A shift in premartensitic transition temperature prior to martensitic transformation as measured by differential scanning calorimetry is being reported for the first time in this system.

1. Introduction

In the last decade, many literatures have been published on Ni–Fe–Ga Heusler alloys. They show promising characteristics for magnetic shape memory applications. The presence of γ-phase along with the austenite phase has been reported in Ni_2FeGa Heusler alloys [1–3]. The γ-phase improves ductility and hot deformation behavior in Ni–Fe–Ga Heusler alloys [2]. Qian et al. [3] showed that the traces of γ-phase embedded in the matrix of single crystal Ni_2FeGa generate residual stress and result in anisotropic two way shape memory effect. HRTEM images of typical modulated structures (5 M and 7 M) were reported elsewhere [4,5]. Modulated martensite structures generate large amount of magnetic field induced strain in Heusler alloys. Liu et al. [6] reported microtwins within martensite lamellae which are induced due to high internal stress in the vicinity of grain boundaries. High stacking fault energy coupled with low transformational activation energy leads to the martensite transformation with little irreversibility [7]. Martensite transformation and shape memory properties have been studied by Huang et al. [8]. Complete pseudoelastic recovery of 5% was obtained at 0° intersection angle between loading direction and grain boundary of highly oriented polycrystalline Ni–Fe–Ga Heusler alloys. The homogeneous strain exhibited by low temperature martensite phase was assumed to be linearly coupled with micromodulation of the phase [9]. Thus, Ni–Fe–Ga system is chosen as it has the potential for future shape memory application. This article focuses on martensite transformation and related phenomena in Ni_2FeGa Heusler alloy.

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Though several authors have studied the origin of modulated structures in Ni–Mn–Ga system [9–11], the literatures on the origin of modulated structures in Ni_2FeGa Heusler alloys are limited. The dynamic instability towards low temperature transition generates modulation in the structure due to lattice shuffling and is associated with premartensitic transition [12]. Premartensitic transformation in $Ni_{51.5}Fe_{21.5}Ga_{27}$ single crystal has been analyzed using phonon dispersion, elastic diffusion scattering and TEM [5,12]. Premartensite transition prior to martensite transformation exhibits the lattice dynamic effect in Ni_2FeGa Heusler alloy. The coupling of vibrational and magnetic degrees of freedom is quite essential to generate large magnetic field induced strain. In this paper we discuss the appearance of premartensitic transition in Ni_2FeGa Heusler alloy using differential scanning calorimetry (DSC) and transmission electron microscopy. Both DSC and TEM results have been correlated to explain the premartensitic transition. The effect of multiple thermal cycling on premartensitic transition and martensite transformation has been also studied.

2. Materials and methods

Ni_2FeGa Heusler alloy was prepared from high purity (99.99%) Ni, Fe and Ga elements by choosing the alloy composition close to stoichiometry X_2YZ, but with higher Ni-content. This was done hoping that Ni substituting Ga would increase the transition temperature to near room temperature. The alloy sample preparation is similar to an earlier study [13]. Initially the furnace was evacuated up to 3×10^{-5} mbar and backfilled with argon to maintain inert atmosphere. The alloy was cast into button shape (approximately 4 g) using chilled copper hearth. It was melted four times, each time flipping the sample, to promote compositional homogeneity. The alloy is then annealed at 1273 K for 1 h and quenched in water. Phase identification and microstructural characterization were

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carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM) and TEM. XRD was used as the primary technique for phase identification. The microstructure and compositions of different regions were analyzed using SEM and its energy dispersive spectroscopy attachment. The structure of the phases present in the alloy was confirmed independently using electron diffraction in the TEM studies. Structural phase transition was characterized by DSC at heating/cooling rate of 10 °C/min in the temperature range of −125 °C to +100 °C (148 K–373 K). Magnetic properties were studied by VSM both below and above transition temperature.

Table 1
Elemental compositions of Ni_2FeGa Heusler alloy and of the respective phases present in the microstructure.

Composition	Ni	Fe	Ga
Ni_2FeGa Heusler alloy	52	25	23
γ-Phase	52	32	16
Austenite	52	21	27

All the elemental compositions are given in at.% taken from SEM–EDX analysis.

3. Results and discussion

The microstructure of Ni_2FeGa Heusler alloy studied by SEM is shown in Fig. 1c. It consists of two phases, the dark contrast gamma phase is dendritic and the light contrast austenite is the interdendritic phase. The composition of the alloy and the corresponding phases are given in Table 1. The phase separation and their evolution were discussed in an earlier study on the same alloy system [1]. The structures are confirmed by XRD (Fig. 1a, b) as fcc (γ-phase) and $L2_1$ (chemically ordered) austenite phases. The γ-phase has disordered fcc structure and its presence in microstructure is known to improve the ductility [2] — a desirable property of Ni_2FeGa Heusler alloys. After annealing and quenching from 1273 K, the high angle peaks of austenite are visible. This confirms the improvement in chemical ordering in $L2_1$ structure. Annealing does not affect the morphologies of the phases present in the microstructure. The as-cast alloy did not undergo martensitic transformation (see Fig. 1a). Martensite transformation in Heusler like ferromagnetic shape memory alloys depends on the ability of high temperature austenite phase to undergo structural transition. The evolution of chemical ordering in $L2_1$ structure after annealing and quenching from 1273 K (Fig. 1b) modifies the electronic and magnetic properties of austenite phase aiding in a martensitic transformation. The increase in martensitic transformation temperature due to evolution of atomic ordering has also been reported elsewhere [14–16].

TEM bright-field image of both the phases along with their phase interface and the corresponding diffraction patterns are shown in Fig. 2. The electron diffraction patterns were taken from the respective phases on either sides of the phase boundary and confirm the phases to be fcc and $L2_1$ ordered structures, respectively. The TEM images captured only from the austenite grain (Figs. 2b and 3) show the presence of localized microtwins as tweed structure. In the magnified view, the pattern of the tweed structures is clearly visible (Fig. 3d) as a grid-like network of strain fields. Tweed patterns observed in TEM (Figs. 2, 3) are regions of distorted lattice due to localized atomic displacement. These tweed regions are inhomogeneous, highly anisotropic and could act as elastic scattering centers [17]. The presence of tweed patterns around dislocations and stacking faults (Figs. 2 and 3) confirms the role of these defect interactions in formation of precursor effect prior to martensitic transformation. The diffuse spots around the main Bragg reflecting spots are quite prominent (Fig. 3b) and are attributed to the tweed.

The structural phase transformation was studied by differential scanning calorimetry (DSC) and shown in Fig. 4. Different cooling and heating cycles were performed (up to 8 in number) to study the reproducibility of the martensitic transformation. DSC curves in each cycle show two reversible peaks, one of them appears while cooling and the other while heating the sample that corresponds to the first order martensitic transition. While cooling it shows exothermic peak corresponding to the release of energy due to the transformation from high temperature austenite phase to low temperature phase martensite. The reversible transformation takes place while heating and the endothermic peak is at a higher temperature indicating transformation hysteresis. The hysteresis is due to the elastic strain energy stored during forward structural transformation. Additionally, two small peaks at $T_{p1} = 273$ K and $T_{p2} = 265$ K prior to martensite transformation were also observed (Fig. 4) while cooling the sample in DSC experiment in the 1st cycle in the temperature range of 148 K–373 K and these disappear during the heating portion of the cycle.

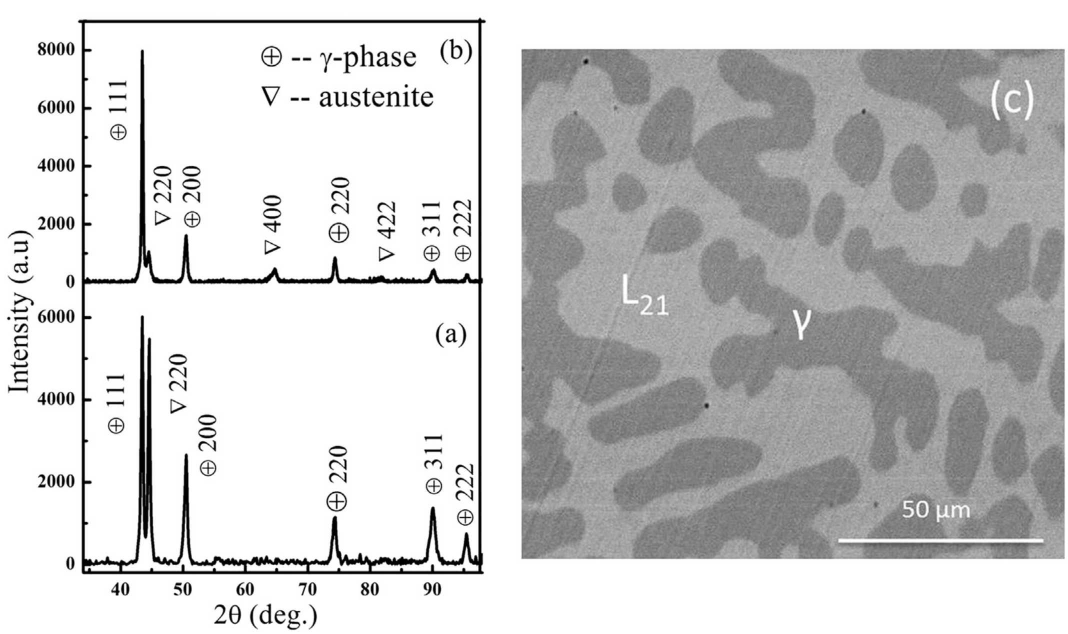

Fig. 1. X-ray diffraction pattern of Ni_2FeGa Heusler alloy (a) as cast, (b) after heat treatment at 1273 K, (c) SEM back scattered electron image shows the morphologies of both γ-phase and austenite (marked as $L2_1$).

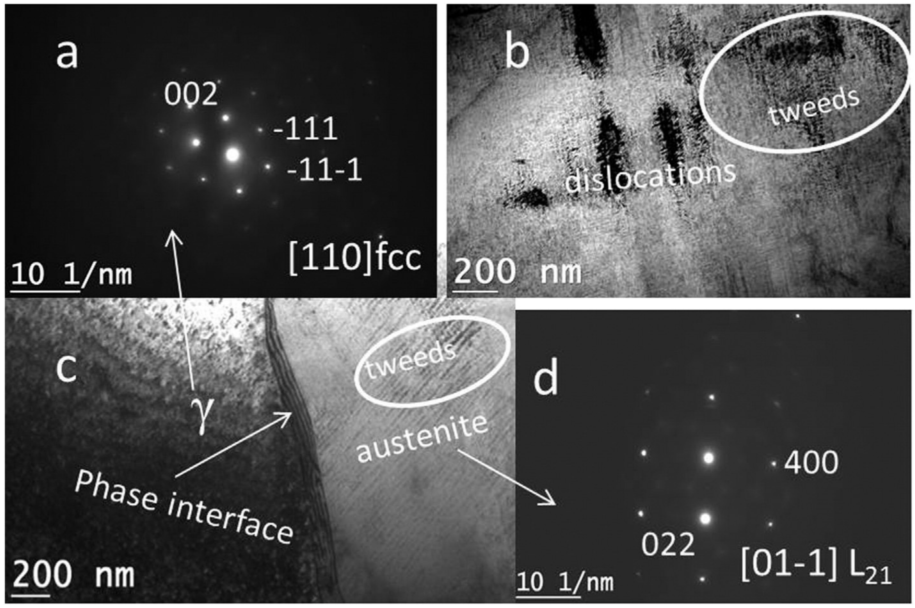

Fig. 2. TEM bf-images of Ni_2FeGa Heusler alloy (a) diffraction of γ-phase, (b) magnified view of austenite phase shows the generation of tweeds around dislocations, (c) both γ-phase and austenite, (d) diffraction of $L2_1$ ordered austenite phase.

An interesting observation with regard to these additional peaks is the following. When the DSC runs were repeated with identical conditions on the same after 24 h, the two intermediate peaks did not appear (Fig. 4, 2nd cycle). However, an intermediate peak was seen to reappear when the sample was tested after 168 h. This was at a temperature of 278 K (Fig. 4, 3rd cycle) which is 5 K (ΔT_p) higher than the observation in the 1st cycle. The peaks corresponding to martensite transition were reproducible in all the runs. The intermediate peak was absent in the second and subsequent cycles of a multi-cycle DSC run as verified several times. We believe that the appearance of an intermediate peak in the DSC run after a long holding time at room temperature in the first heating cycle and its disappearance in subsequent cycles indicate the role of local chemical ordering on the premartensite phenomena.

The observation of premartensitic phenomena in DSC is likely to be due to the energy involved in localized atomic movement in the vicinity of lattice defects to form an unstable transitional state which later transforms to martensitic state upon subsequent cooling. This peak does not appear while heating as it acts as a precursor to martensitic transformation [10], not involved in reverse phase transformation. The disappearance of these peaks in subsequent DSC cycle could be attributed to the loss of inhomogeneity in the microstructure (As the energy involved becomes insensitive for its appearance in DSC). Similar observation of premartensitic transition has been reported elsewhere using highly sensitive calorimetry [18]. The interaction of defects in Ni_2FeGa Heusler alloy leads to premartensite transition. This transition is irreversible in nature. Thus the defects in microstructure are annihilated. This

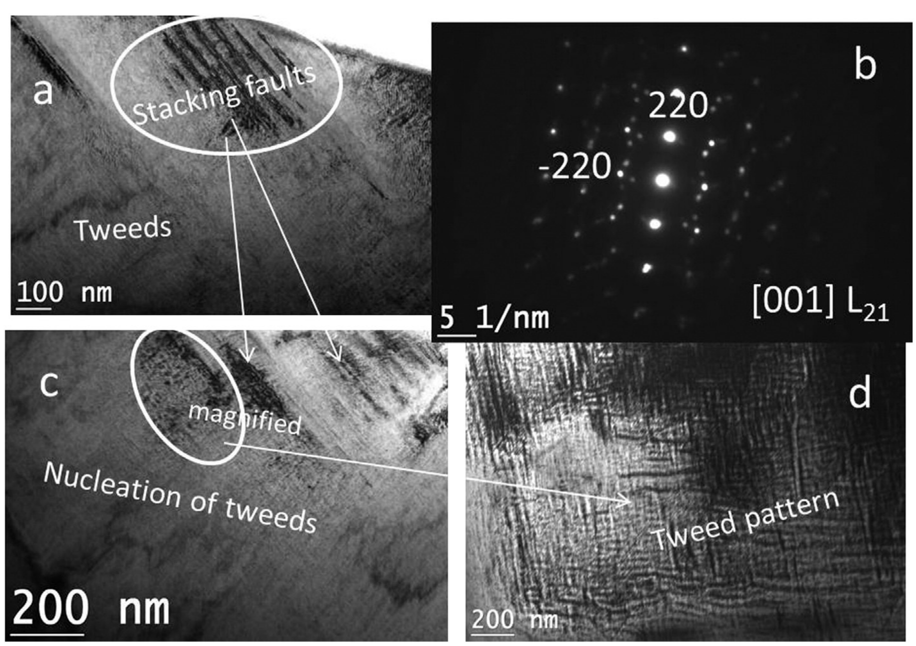

Fig. 3. TEM bf-images of Ni2FeGa Heusler alloy shows (a, c) the nucleation of tweeds around stacking faults, (b) weak diffuse spots around the main reflections representing the tweed diffraction pattern, (d) magnified image of network like pattern of tweeds.

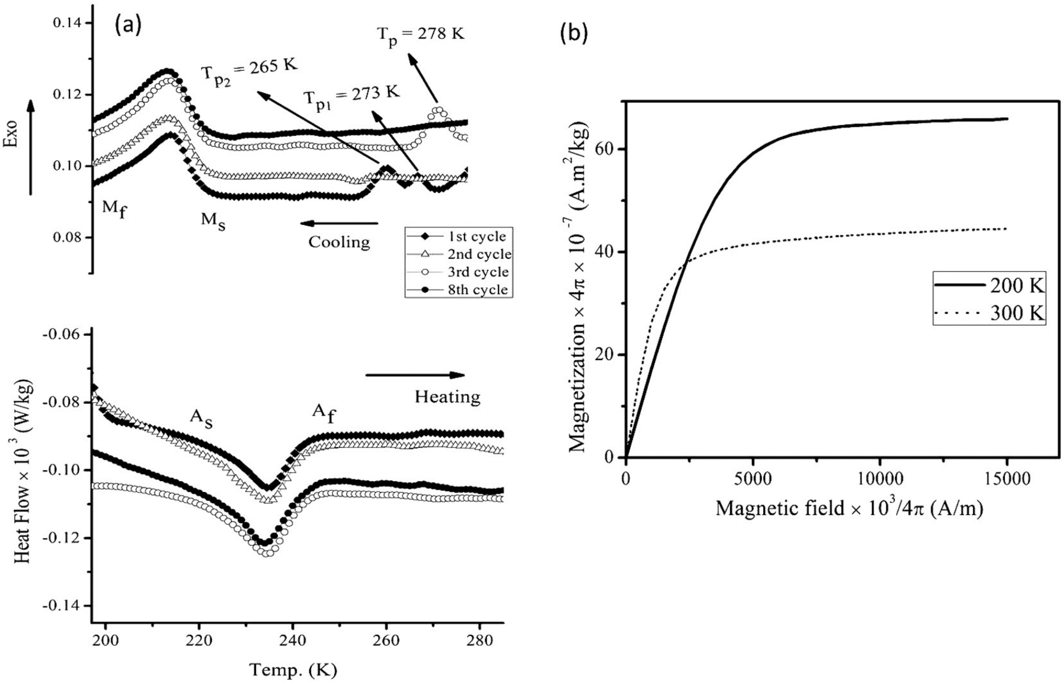

Fig. 4. (a) DSC thermal cycles of martensitic transformation in Ni2FeGa Heusler alloy and premartensitic transition, (b) magnetic properties of Ni2FeGa Heusler alloy studied at 200 K and 300 K.

inhomogeneity loss leads to the modification of electronic structure of material.

While cooling the sample after a long interval of time, the coupled effect of electronic and vibrational properties of material becomes sensitive for the reappearance of these premartensitic peaks in DSC. The appearance of premartensitic peak in DSC could be correlated with the observation of central peak in elastic scattering experiment [11]. As temperature decreases, premartensite peak appears prior to martensitic transformation due to phonon instability. The shifting in T_p was also reported elsewhere [19] when subjected to external magnetic field. This was explained due to magneto-elastic coupling in Ni–Mn–Ga alloys whose origin lies in strong electron–phonon coupling [10]. Thus, the shift in premartensite transition temperature reported here is being attributed to strong electron–phonon coupling in Ni_2FeGa Heusler alloys.

Zhang et al. analyzed the phase transformation in Ni_2FeGa Heusler alloy using *in-situ* transmission electron microscopy and electron energy loss spectroscopy [5]. Micromodulated domains and the corresponding diffuse spots were observed, are temperature dependent and related to the precursor phenomena prior to martensitic transformation. These *in-situ* TEM results showed that micromodulated domains disappear upon either heating to high temperature or cooling below martensitic transformation temperature. Thus the appearance of these intermediate small peaks in DSC experiment is being attributed to premartensite transition due to the formation precursor effect prior to martensitic transformation and the same has been observed in TEM as tweed structure (Figs. 2, 3). The observation of micromodulated domains and associated satellite spots in TEM belongs to an intermediate state which guides the martensitic transformation process. It is not clear if lattice modulation of martensite phase observed in other shape memory alloys was guided by the premartensitic transformation. However, there are several reports [5–12] that suggest that formation of modulated martensite with a c/a ratio <1 is always associated with a premartensitic transition.

Four representative thermal analysis data of martensite transformation in Ni_2FeGa Heusler alloy drawn from DSC experiment are given in Table 2. Both forward and reverse martensitic transformations take place in the same temperature intervals and the heat energy involved in those transitions is nearly equal. Though there is a trend that heat energy released during martensitic transformation decreases and energy absorbed during austenitic transformation increases as experiment cycles are repeated, the increase or decrease is not so significant (Table 2). The spread of transformation temperatures and the hysteresis associated are also identical in all the above cases. The martensitic transformation around equilibrium temperature at 234 K is quite reproducible and reversible having transformation hysteresis of 20 K, is an essential feature for shape memory applications.

The isothermal magnetic properties were studied at 200 K and 300 K to probe the effect of structural transition on the magnetization behavior of the Ni_2FeGa Heusler alloy (Fig. 4b). The saturation magnetization at 200 K (below martensite transition) is 65.9 emu/g where it is 44.54 emu/g at 300 K (above the martensite transition) suggesting that the magnetization of martensite phase is higher than that of austenite phase. The magnetization curve drawn at 200 K has larger critical field to saturation (0.7 T) as compared to the one at 300 K (0.35 T). Higher value of magnetization can be attributed to the modulated structure of martensite which modifies the interatomic distances and affects the exchange interaction. The increase in critical field to saturation

Table 2
Thermal analysis data of martensite phase transformation in Ni_2FeGa Heusler alloy drawn from DSC experiment.

Ni_2FeGa Heusler alloy	M_s	M_f	A_s	A_f	T_o	ΔH	ΔT
	(K)	(K)	(K)	(K)	(K)	(×10^3 W/kg)	(K)
1st cycle	224	203	223	243	233.5	+1.918 −1.622	19
2nd cycle	224	203	223	243	233.5	+1.892 −1.665	19
3rd cycle	224	202	223	244	234	+1.875 −1.69	20
8th cycle	224	203	224	244	234	+1.787 −1.712	20

Heat energy released (+ sign) and absorbed (− sign), martensite start temperature M_s, martensite finish temperature M_f, austenite start temperature A_s, austenite finish temperature A_f, equilibrium transformation temperature $T_0 = (M_s + A_f) / 2$, transformation enthalpy ΔH, transformation hysteresis $ΔT = (A_f − M_s)$

could be attributed to the high magnetocrystalline anisotropy of martensite than that of austenite and similar observation has been reported by V.K. Sharma et al. [20] in Ni–Fe–Ga Heusler alloys. Modulation in the crystal lattice and the arrangement of various twin variants modify the magnetic energies of martensite differently in various possible crystallographic orientations, thus resulting in high magneto-crystalline anisotropic property. In Ni–Mn–Ga Heusler alloys, high magneto-crystalline anisotropy of martensite phase was observed, an essential property required for generating large MFIS. The observation of high magnetization value and high magnetocrystalline anisotropic property below the transition temperature along with the appearance of premartensitic phenomena both in TEM and DSC suggests a modulated martensite structure in the Ni_2FeGa Heusler alloy and makes a case for detailed low temperature transmission electron diffraction study.

4. Conclusions

1. Atomic ordering was induced by quenching from high temperature. Ordering has significant influence on martensitic phase transformation.
2. The observation of tweed contrast in TEM and appearance of intermediate peaks in DSC were correlated to premartensite phenomena.
3. The shift in premartensite peak observed in DSC was attributed to the role played by electron–phonon coupling in Ni_2FeGa Heusler alloy.

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