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Microstructure and Magnetic Properties of Rapidly Solidified $Ni_2(Mn,Fe)Ga$ Heusler Alloys

R.V.S. Prasad[1,a], M. Manivel Raja[2,b] and G. Phanikumar[1,c]
[1]Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras Chennai- 600036, India
[2]Advanced Magnetic Materials Group, Defence Metallurgical Research Laboratory Hyderabad-500058, India
[a]rvsp@smail.iitm.ac.in [b]mraja@dmrl.drdo.in [c]gphani@iitm.ac.in

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Abstract. This study reports detailed microstructural and magnetic characterization of rapidly solidified $Ni_2(Mn,Fe)Ga$ heusler alloys processed using the melt spinning technique. Series of $Ni_{50}Mn_{(25-x)}Fe_{(x= 2, 5, 8, 11)}Ga_{25}$ alloys were prepared by vacuum arc melting and then melt spun at constant wheel speed of 20 m/sec to obtain samples in the form of ribbons. X-ray diffraction analysis of as-cast $Ni_2(Mn,Fe)Ga$ alloy with different 'Fe' concentrations revealed austenite phase with $L2_1$ Heusler atomic order at room temperature. Transmission electron microscopy of melt spun ribbons reveals a precursor tweed structures due to magnetic tweed contrast when the 'Fe' concentrations are 8% and 11%. In case of 11% 'Fe' substituted alloy martensite phase was found to from at the grain boundary triple junctions. Thermo magnetic measurements determine that, as the 'Fe' concentration increases from 2 to 11%; it enhances the magnetic transition temperature from 375 to 403 K.

Introduction. Melt spinning is a well established technique in rapid solidification processing by which one can produce variety of materials with extraordinary properties [1]. Electrical and magnetic materials, ribbons for transformer cores, tool steels and bearing materials are numerous applications for rapidly solidified alloys by melt spinning [2]. Melt spinning results in the microstructures with refined grain sizes, increased solubility of alloying elements, reduced levels of segregation and in some cases formation of metastable crystalline and amorphous phases [3].

The research on Ni_2MnGa Ferromagnetic shape memory alloys is intense during last decade owing to their application as a potential material in the field of sensors and actuators [4, 5]. However these alloys suffer, in the manufacturing of thin plates or wires due to their fragile nature. Earlier researchers studied the addition of "Fe" element enhances the toughness of the Ni–Mn–Ga alloy without sacrificing its magnetic and thermoelastic properties. The structure, shape memory effect, magnetic properties, cycling characteristic and ultrasound-induced martensitic transition of Fe-doped Ni–Mn–Ga alloys have been studied. The addition of a fourth element can be an effective method to change the characteristics of the magnetic and structural transformations of these alloys [6, 7]. The effect of many different elements has been studied in the Ni–Mn–Ga alloys; however, much less information exists in the phase transformations and physical metallurgy aspects of Fe-doped Ni-Mn-Ga alloys.

In our previous studies, we reported phase transformation behaviour of rapidly solidified Ni_2MnGa alloy ribbons [8, 9]. In this study we present microstructural and magnetic characterization of $Ni_2(Mn,Fe)Ga$ alloy ribbons with different "Fe" concentrations prepared by melt spinning.

Experiments. A series of $Ni_{50}Mn_{(25-x)}Fe_{(x= 2, 5, 8, 11)}Ga_{25}$ alloys were prepared by vacuum arc melting of the 99.99% pure nickel, manganese, iron and gallium in an argon atmosphere. Five gram button samples were prepared and melted four times to ensure a highly homogeneous ingot. A conventional copper wheel was used for melt-spinning ribbons of the $Ni_{50}Mn_{(25-x)}Fe_{(x=2,\ 5,\ 8,11)}Ga_{25}$ alloys under vacuum. A constant wheel speed of 20 m/s chosen for each alloy composition after several trails to achieve a good quality of ribbon with uniform thickness (65µm). For each composition (with different "Fe" concentrations) approximately 5 g of alloy was induction melted in a quartz tube having an orifice diameter of 0.8 mm, and ejected with a 1.10 bar back-pressure of argon gas. The ribbons of different alloy composition with constant wheel speed obtained after melt spinning were thinned down further by using Gatan Ion beam mill to characterize structurally by CM20 Transmission Electron Microscope and Phase identification of as-cast and melt spun ribbon samples were also confirmed using by X-Ray diffraction studies using Bruker Discover D8 diffract meter with Cu-Kα radiation. Room temperature Magnetic and Thermo magnetic measurements on melt spun ribbon samples obtained by Vibrating sample magnetometer (VSM).

Results and Discussion

Melt spun alloy Melt spun ribbons of $Ni_{50}Mn_{(25-x)}Fe_{(x=2,\ 5,\ 8,\ 11)}Ga_{25}$ alloy at constant wheel speed of 20 m/s with different "Fe" concentrations of 2%, 5%, 8% and 11% termed as MSP-1, MSP-2, MSP-3 and MSP-4 respectively. These notations are used in further discussion of the paper. Phase analysis was done using X-Ray diffraction of the as-cast alloy samples as well as melt spun ribbons with different "Fe" concentrations. Fig. 1, 2 and 3 show the transmission electron microscopy micrographs of the melt spun ribbon samples. Room temperature magnetic measurements and thermo magnetic measurements of the melt spun samples were performed. The results are discussed as given below.

X- Ray diffraction studies. The XRD spectra (figure not shown here) of as-cast $Ni_{50}Mn_{(25-x)}Fe_{(x=2,\ 5,\ 8,\ 11)}Ga_{25}$ alloy samples with different "Fe" concentrations of (2%, 5%, 8% and 11%) were indexed to the austenite phase (with $L2_1$ Heusler atomic order) of Ni_2(Mn,Fe)Ga Heusler alloy and it can also be confirmed that the peaks were very sharp indicating poly crystalline nature of the sample. The X-Ray diffraction patterns of melt spun ribbon samples were also indexed to austenite phase but the reflections are sharper. The phase content of all ribbons can be said to be crystalline and single phase in nature within the detectable limit of the X-Ray diffraction technique. The alloying element "Fe" has resulted in a solid solution of the austenite phase at all the concentrations attempted in this study. However, as can be seen from the following section, the volume fraction of martensite phase in the MSP-4 sample is too low to be detected by the XRD technique.

Transmission Electron microscopy studies. Detailed transmission electron microscopy of the rapidly solidified Ni_2(Mn,Fe)Ga alloy ribbons are shown in Figures 1 to 3. Fig. 1a, 1b and c shows the TEM images of MSP-2 sample. The Bright field image shown in Fig. 1a and the same image at higher magnification shown in Fig. 1b. The Fig. 1c represents corresponding (SAEDP) selected area electron diffraction pattern taken with $[\bar{1}3\bar{1}]$ zone axis and can be well indexed to $L2_1$ structure with Heusler atomic order and belongs to austenite phase of Ni_2(Mn,Fe)Ga alloy. From the bright field images (Figure 1a and 1c) one can confirm that the microstructure consists of homogeneous equiaxed grains with an average grain size between 0.5 to 1.5µm. Such a microstructure may be attributed due to moderate nucleation rate at the melt-wheel interface where the cooling rate is relatively high. One can rationalize such a homogeneously distributed equiaxed grain morphology seen in the bright field images of TEM in Fig. 1a and Fig. 1b respectively also from a possible rise in the melt temperature due to recalescence during solidification of the melt [10].

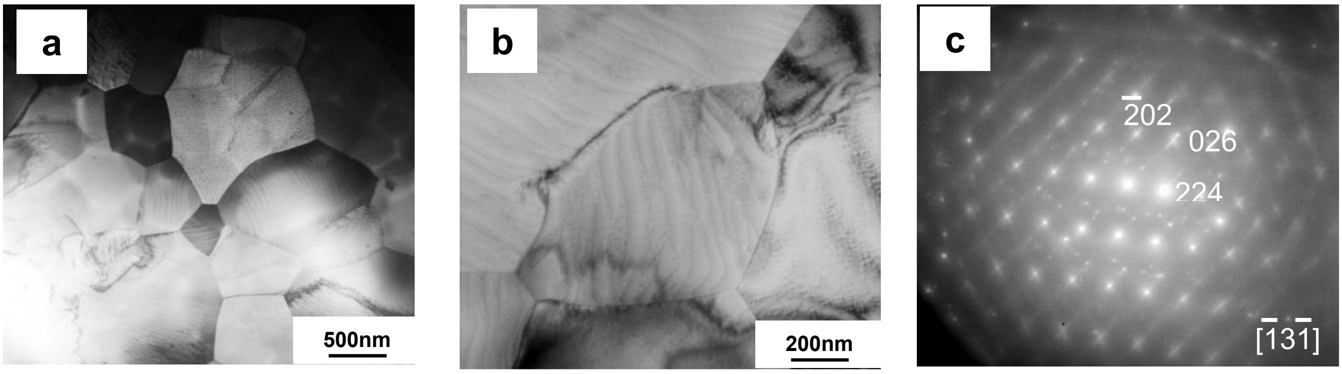

Fig. 1 (a) and (b) Bright field images of (MSP-2) $Ni_{50}Mn_{(25-x)}Fe_{(x=5)}Ga_{25}$ alloy (c) SAED Pattern

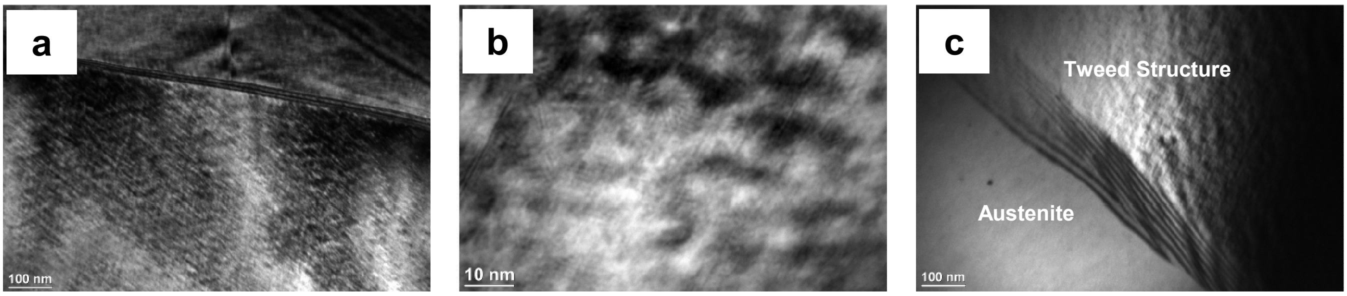

Fig. 2 (a) and (b) Bright field images of (MSP-3) $Ni_{50}Mn_{(25-x)}Fe_{(x=8)}Ga_{25}$ alloy (c) SAED Pattern

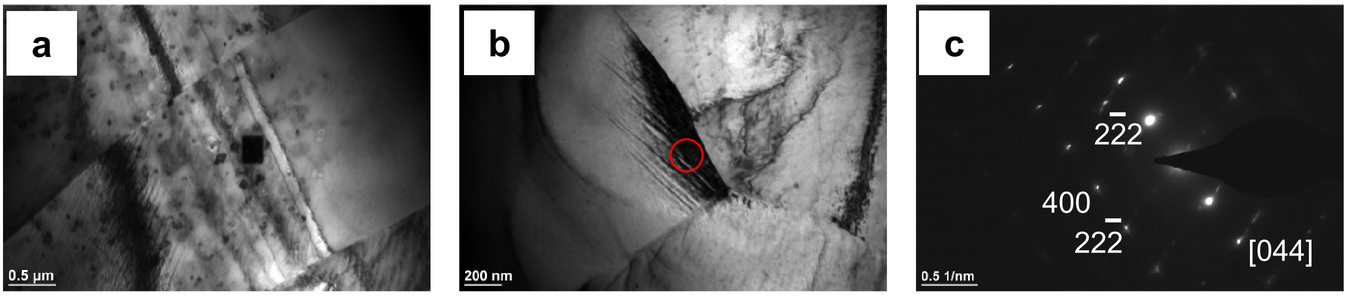

Fig. 3 (a) and (b) Bright field images of (MSP-4) $Ni_{50}Mn_{(25-x)}Fe_{(x=11)}Ga_{25}$ alloy (c) SAED Pattern

Figure 2a, b and c represents the bright field images of MSP-3 sample. Figure 2b shows the typical tweed structure [11, 12]. Figure 2c shows the grain boundry fringes at austenetic and tweed grain boundary interface. Earlier researchers observed "Tweed" structures in electron micrographs above the transition temperature. Generally these structures observed in medium and weak martensites, in shape memory alloys like Fe-Pd and Ni-Al. Bright field images from MSP-4 sample are shown in Figure 3. Figure 3b clearly reveals that the alternate twins of martensite phase evolve from grain boundaries. To corroborate the same, SAED pattern (as shown in Figure 3c) taken with [044] zone axis has been indexed and the corresponding reflections confirm martensite phase with non-modulated tetragonal crystal structure. The high cooling rate and growth rate characteristic of the melt spinning technique usually lead to significant undercooling of the melt during solidification resulting in metastable microstructures. Local compositional fluctuations could be the likely reason for a local mixture of deformed (austenite) and undeformed (martensite) regions as precursor tweed structure in the MSP-3 sample. Such microstructures were not observed in the case of MSP-1 and MSP-2 samples which have lower alloying content of iron. The higher "Fe" concentration as solid solution in the austenite phase in case of MSP-3 could result in larger lattice strain and higher compositional inhomogeneity leading to the formation of "Tweed" structures [11, 12]. In case of MSP-4 sample, martensite phase can be noticed at the grain boundary triple junction [13] as shown in TEM Bright field images and corresponding SAED pattern in figure 3. Thus, the phase evolution sequence indicates that as the concentration of "Fe" is increased, the microstructure changes from a single phase austenite phase to a mixture with tweed contrast and martensite.

Magnetic Characterization studies. Table.1 represents the summary of Crystal structure and Magnetic properties of $Ni_2(Mn,Fe)Ga$ Heusler alloy melt spun ribbons with different "Fe" concentrations.

Table . 1 Summary of Crystal structure and Magnetic properties of $Ni_2(Mn,Fe)Ga$ Heusler alloy melt spun ribbons

Fe- content (x)	Crystal structure at Room Temp	Magnetic structure at Room Temp	Magnetisation M (emu/g)	Coercivity HC(Oe)	Curie temperature Tc (K)
2 at.%	Austenite	Ferro	65.4	58.0	375 K
5 at.%	Austenite	Ferro	63.0	62.0	387 K
8 at.%	Austenite	Ferro	64.2	54.0	400 K
11at.%	Austenite + Martensite	Ferro	62.0	63.0	403 K

Summary

$Ni_2(Mn,Fe)Ga$ alloy with different 'Fe' concentrations (2, 5, 8 and 11) results in a single austenite phase with $L2_1$ Heusler atomic order at room temperature. However, after melt spinning $Ni_2(Mn,Fe)Ga$ alloy with 2 and 5% Fe remains as austenite phase, where as 8 and 11% Fe doped alloys exhibits a tweed structures. The 11% Fe doped alloy after melt spinning reveals the evolution of matensite phase from the grain boundary triple junctions. Thermo magnetic measurements realize increase in magnetic transition temperature from 375 to 403 K as the 'Fe' concentration increases from 2 to 11%, which would provide a superior opportunity to these materials for above room temperature applications. The increase in the magnetic transition temperature could have significant impact on above room temperature applications in the field of sensors and actuators.

References

[1]D.M. Herlach, Mater. Sci. Eng. **R12** 177 (1994).
[2] Carl H.Smith, *Rapidly solidified alloys* (Process, structure, properties and applications) edited by H. Liebermann, Marcel Decker, New York, ISBN: 0-8247-8951-2, (1993).
[3] H. Jones, *et al*., Materials Science and Engineering A, **11–19** 304 (2001).
[4] Ullakko. K, *et al*., Applied Physics Letters, **69,** 1966 (1996).
[5] M. L. Richard, *et al*., Philosophical Magazine, **87**, 3437 (2007).
[6] H.B. Wang, *et al.,* Materials Science and Engineering A 438–440 (2006)
[7] Daniel Soto, *et al.,* Physical Review B **77**, 184103, 2008
[8] R.V.S. Prasad and G. Phanikumar, Material Science forum (to be published)
[9] R.V.S. Prasad and G. Phanikumar, Journal of Material Science **44**, 2553 (2009)
[10] Li.Changping, Solidification Process in melt spun Nd-Fe-B type Magnets, M.S thesis.
[11] Sivan Kartha, *et al*., Physical Review Letters, **67** 3630 (1991).
[12] S.M. Shapiro, *et al*., Physical Review Letters, **57** 3199 (1986).
[13] K. Tsuzaki, *et al*., Journal De Physique-IV **5**, (1995).

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References

[1]D.M. Herlach, Mater. Sci. Eng. R12 177 (1994).

[2] Carl H.Smith, Rapidly solidified alloys (Process, structure, properties and applications) edited by H. Liebermann, Marcel Decker, New York, ISBN: 0-8247-8951-2, (1993).

[3] H. Jones, et al., Materials Science and Engineering A, 11–19 304 (2001).

[4] Ullakko. K, et al., Applied Physics Letters, 69, 1966 (1996).

[5] M. L. Richard, et al., Philosophical Magazine, 87, 3437 (2007).
doi:10.1080/14786430701297582

[6] H.B. Wang, et al., Materials Science and Engineering A 438–440 (2006)

[7] Daniel Soto, et al., Physical Review B 77, 184103, 2008
doi:10.1103/PhysRevB.77.184103

[8] R.V.S. Prasad and G. Phanikumar, Material Science forum (to be published)

[9] R.V.S. Prasad and G. Phanikumar, Journal of Material Science 44, 2553 (2009)[10] Li.Changping, Solidification Process in melt spun Nd-Fe-B type Magnets, M.S thesis.

[11] Sivan Kartha, et al., Physical Review Letters, 67 3630 (1991).
doi:10.1103/PhysRevLett.67.3630
PMid:10044784

[12] S.M. Shapiro, et al., Physical Review Letters, 57 3199 (1986).
doi:10.1103/PhysRevLett.57.3199
PMid:10033982

[13] K. Tsuzaki, et al., Journal De Physique-IV 5, (1995).