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Martensite and nanocrystalline phase formation in rapidly solidified Ni_2MnGa alloy by melt-spinning

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Abstract. Microstructure of rapidly solidified Ni_2MnGa ferromagnetic shape memory alloy has been investigated experimentally by melt-spinning technique. At a constant ribbon width of 3 mm, two speeds of melt spinning 17m/sec and 30m/sec at the extrema of conditions for a good quality of ribbon resulted in two thicknesses of the ribbon, viz., 62 µm and 44 µm, respectively. TEM and AFM analysis reveals the formation of very fine clusters of Ni_2MnGa at lower wheel speeds. However at higher wheel speeds nanocrystalline Ni_2MnGa particles of size about 10-20 nm and martensitic phases were confirmed.

Introduction

Rapid solidification by melt spinning route is a well established technique to process many commercial materials such as ribbons for transformer cores [1]. Properties of the materials processed through this technique are also known to be a strong function of the processing parameters [2]. Wheel speed and thickness of the ribbon are known to be important parameters as they affect the thermal field at the solid/liquid interface strongly and result in significant interface undercooling. Due to a large amount of undercooling achievable during rapid solidification, metastable phases can be synthesized [3].

Ferromagnetic shape memory alloys have attracted the attention of researchers since their discovery in 1996 [4]. Ni_2MnGa alloys show giant magnetic field induced strain of about 9.5% at ambient temperature in a magnetic field. This property finds many commercial applications. These alloys undergoes a typical transformation sequence as follows: P → 5M → 7M → T or P → 7M → T, where P stands for the Parent Phase (Austenite), 5M – five layer modulated (Tetragonal), 7M- seven layer modulated (Orthorhombic) and the T non-modulated (Tetragonal) which is the most stable martensitic phase and, therefore, it exists at low temperatures. These transformation sequences are highly dependent on compositional homogeneity and also for most of the actuator applications, relatively large single crystals or coarse grained, preferentially oriented polycrystalline materials are desirable. Local compositional variations may be expected to influence key parameters such as the transformation strain, twinning flow stress and magneto crystalline anisotropy [5]. The compositional inhomogeneities are usually a consequence of the solidification process adopted and consequently affect the solid state transformations. It is known that the chemical homogeneity much more easily achieved in rapidly solidified materials [6, 7]. Since the length scale of these chemical inhomogeneities depends on the kinetics of the process, a study of microstructure and properties of these materials as a function of processing parameters is important. In this study, we have chosen the Ni_2MnGa system and report the microstructural characterization.

Experiments

Ni_2MnGa alloy is prepared by vacuum arc melting of the 99.99% pure nickel, manganese 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_2MnGa alloy under vacuum. In each case, (for 17 m/sec and 30 m/sec wheel speed) approximately 5 g of alloy was induction melted in a quartz tube having an orifice diameter of 0.8 mm, and ejected with a 16 psi back-pressure of argon gas. The ribbons at different wheel speeds obtained after melt spinning were characterised using transmission electron microscopy[1] and atomic force microscopy[2]. Phase identification was also confirmed using X-ray diffraction[3] studies using Cu-Kα radiation.

Results and Discussion.

As Cast Ni_2MnGa alloy: The optical micrograph of Vacuum arc remelted Ni_2MnGa alloy is shown in Fig. 1a. Grain boundaries are clearly seen and the average grain size is reported as 200 µm to 300 µm. Secondary electron image of as-cast Ni_2MnGa alloy at lower magnification is shown in Fig. 1b. The intensity difference between the grains can be attributed to the electron channeling as the composition has been confirmed to be reasonably uniform. Figure 1c and 1d show the EDS results from the darker and lighter grains. Vacuum arc melting can thus be said to result in a compositionally homogeneous sample.

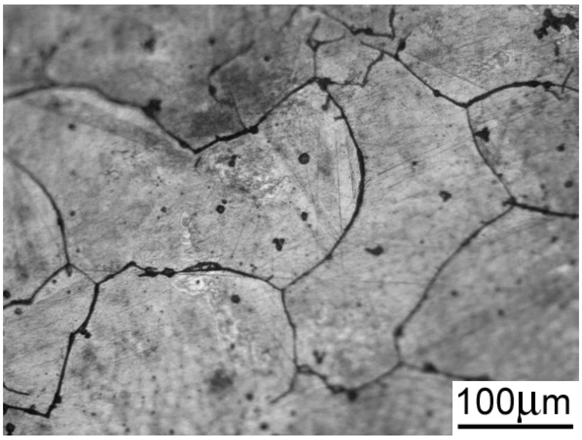


Fig. 1 (a) As cast Ni_2MnGa alloy

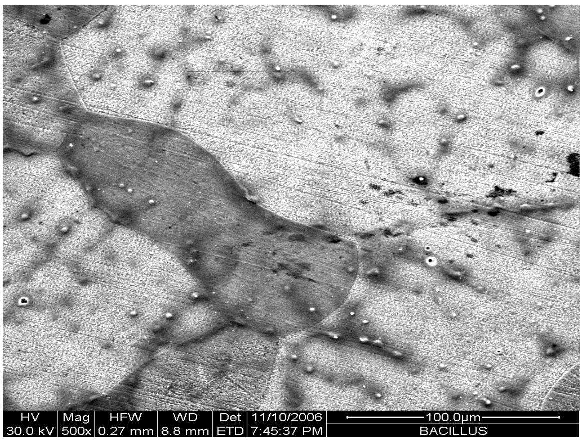
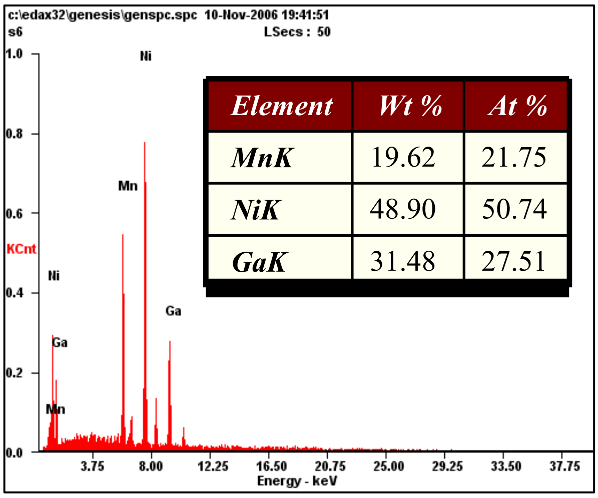
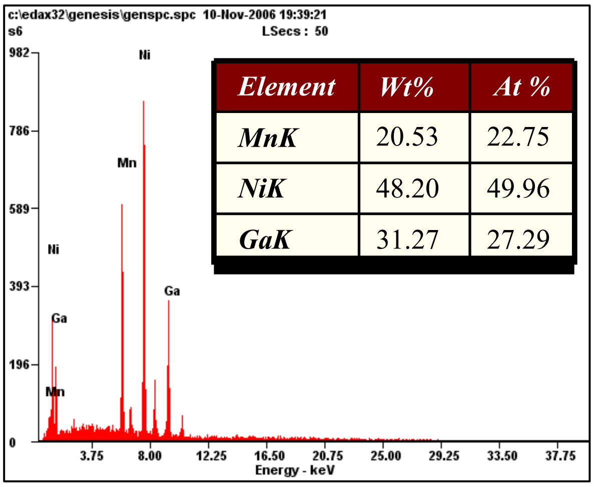


Fig. 1 (b) SE Image of as cast Ni_2MnGa alloy



Element	Wt %	At %
MnK	19.62	21.75
NiK	48.90	50.74
GaK	31.48	27.51

Fig. 1 (c) EDX spectrum of as cast Ni_2MnGa alloy (reflection from darker grains)



Element	Wt%	At %
MnK	20.53	22.75
NiK	48.20	49.96
GaK	31.27	27.29

Fig. 1 (d) EDX spectrum of as cast Ni_2MnGa alloy (reflection from lighter grains)

1 Philips CM12
2 Dimension 3100 atomic force microscope, Nanoscope IV (Digital Instruments, USA)
3 Bruker Discover D8 diffractometer

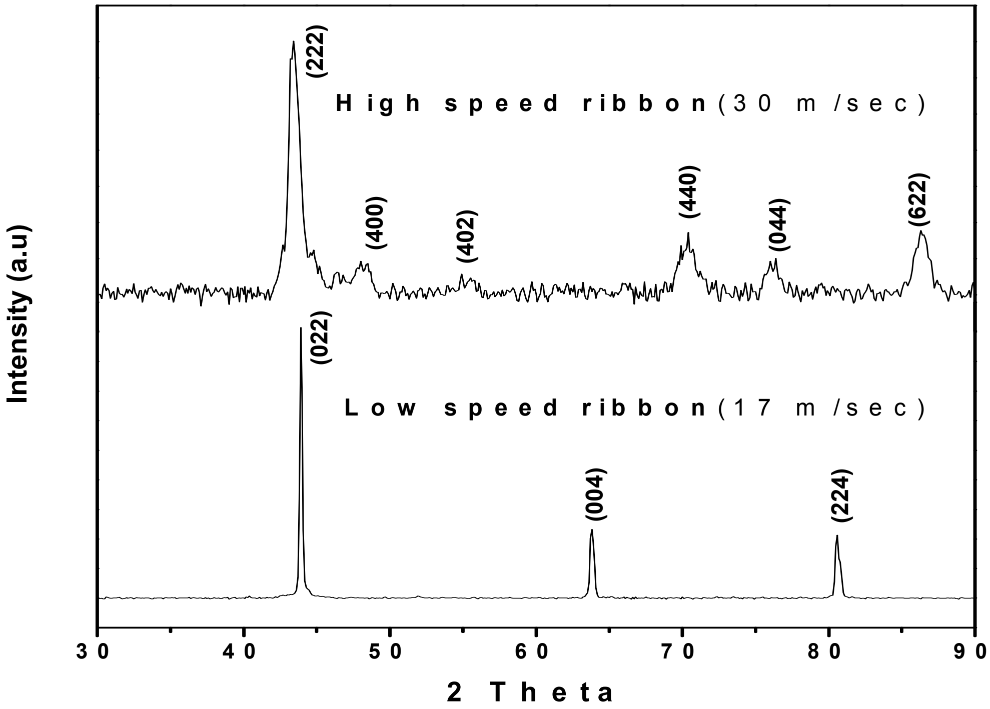


Fig. 2 XRD Pattern of Low Wheel Speed and High Wheel Speed Ribbon

Melt spun alloy:
The XRD patterns of the melt-spun Ni_2MnGa alloys are shown in Fig. 2, the lower of the two patterns corresponding to the lower wheel speed. Figures 3-5 show the transmission electron microscopy of the melt spun samples. Atomic force microscopy is shown in figure 6-7. The observations from the characterization studies of the two conditions of ribbons are as follows.

Low wheel speed (17 m/sec):
The XRD pattern of the ribbon melt-spun at lower speed shows sharp peaks. All the peaks could be indexed to the austenite phase of Ni_2MnGa. Transmission electron micrographs of this ribbon are shown in Figs.3a,b. In the bright field image (Fig 3a) the g-vector corresponding to [004] direction is shown. Selected area diffraction (SAD) pattern of this region (Fig 3b) taken using [110] zone axis shows faint streaks apart from the spots. Bright field image confirms that the grains are of fine size. The AFM image of this sample is shown in Fig. 6. The surface morphology of the sample shows fine and equiaxed crystals with a grain size of around 250 nm. The formation of very fine micro crystals of Ni_2MnGa either because of dendrite disintegration or by partial remelting and breakage of grains. Also at lower wheel speed the excess free energy available due to under cooling can be used and then the possibility of getting very fine micro crystals[8].

High wheel speed (30 m/sec):
The XRD pattern (Fig 2, upper) of the ribbon melt-spun at higher wheel speed shows significant peak broadening. Such a broadening is usually a signature of the crystalline phase being nanometric in size or presence of amorphous phase in the sample. The refelections could be indexed to the martensite phase of Ni_2MnGa. Figures 4a,b show the bright field image and the corresponding selected area diffraction pattern of the sample. The bright field image shows the g-vector corresponding to [022] direction and the SAD pattern is taken using $[\bar{1}\ \bar{1}\ 1]$ zone axis. The martensite twins, twin boundaries and the variants are clearly seen in the bright field image. Corresponding SAD pattern shows sharp spots indexed for the martensite phase. These reflections clearly indicate that are fine {2 2 0} twins of the martensite and it confirms that the planes belong to

martensite phase of Ni_2MnGa alloy[9]. From the AFM image shown in Fig. 7, the martensite grains with the twin variants within as well as regions devoid of such patterns could be seen. The image confirms the martensitic twin formation of size around 100 – 170 nm .

The Figs. 5a,b show the bright field image of clusters of Ni_2MnGa, corresponding dark field and the SAD pattern in the inset. These nano particles could be second phase particles in the martensite matrix and the volume fraction would be less than 10-15% which could not be detected by XRD analysis (Fig. 2). However, the peak broadening in the XRD pattern of this sample could thus be attributed to these regions of fine clusters in a matrix that is likely to be amorphous. The detailed analysis by TEM confirms that, the reflections from the SAD pattern are the nanometric clusters formed correspond to Ni_2MnGa phase. The rings correspond to the reflections [022], [004]. [124]. The size of the nano crystalline particles formed in the ribbon were calculated from darkfield image and the size comes to be about 10-20 nm. These nano crystalline particles were represented by triangular markers in the corresponding bright field and dark field images. Since the wheel speed is high (30 m/sec) the resultant high cooling rates could be said to have led to the formation of martensite and nanocrystals of Ni_2MnGa [10].

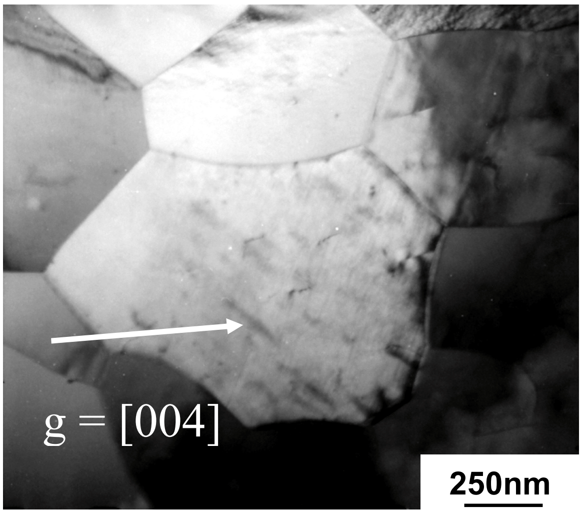


Fig. 3 (a) Bright Field Image of Low Wheel Speed Ribbon

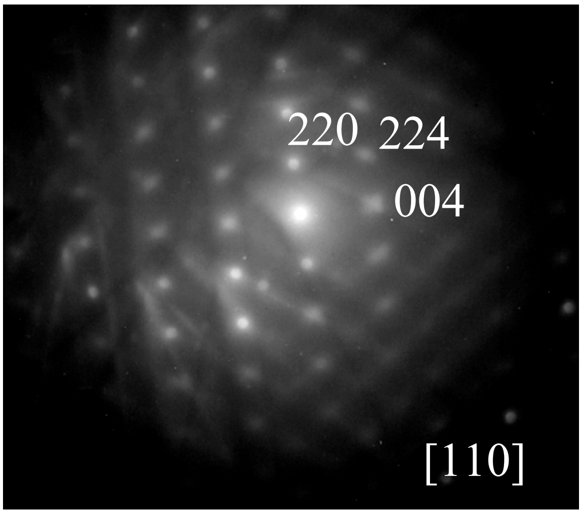


Fig. 3 (b) SAD Pattern of Low Speed Wheel Ribbon

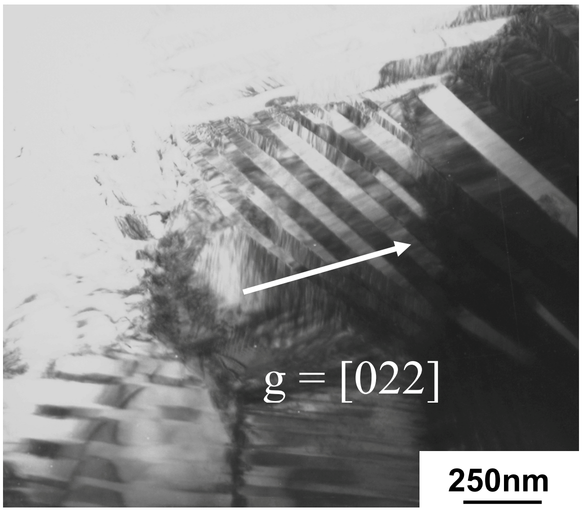


Fig. 4 (a) Bright Field Image of High Wheel Speed Ribbon

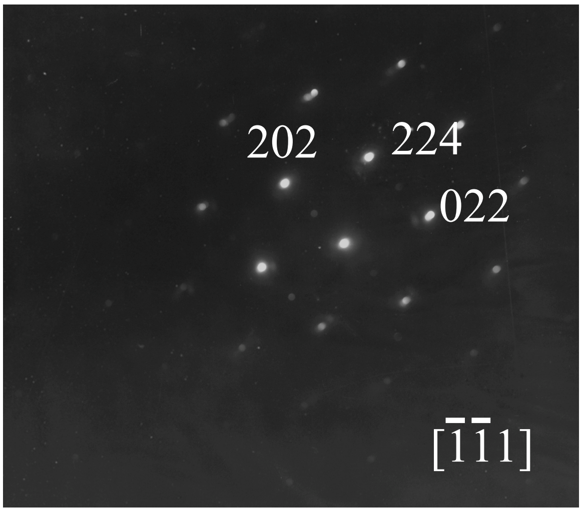


Fig. 4 (b) SAD Pattern of High Wheel Speed Ribbon

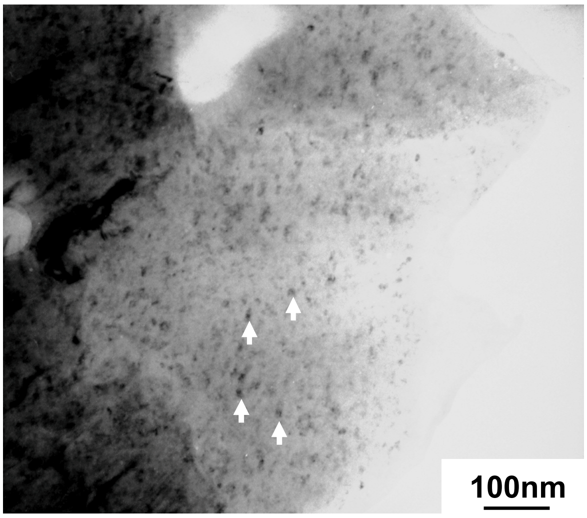


Fig. 5 (a) Bright Field Image of High Wheel Speed Ribbon

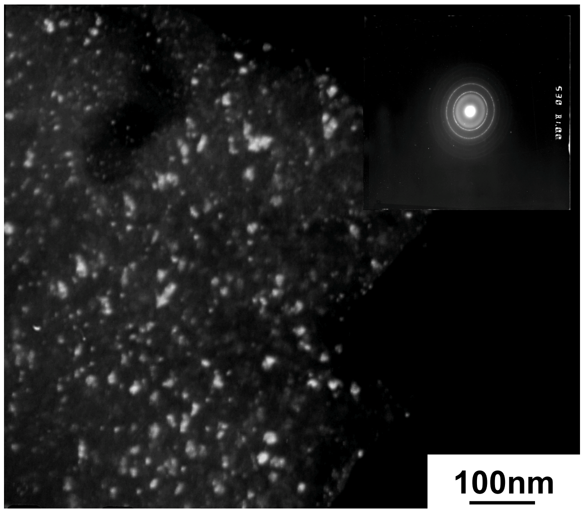


Fig. 5 (b) Dark Field Image and SAD Pattern of High Wheel Speed Ribbon

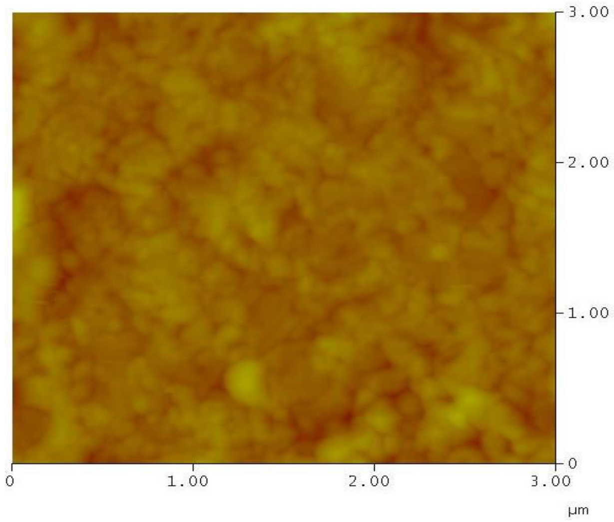


Fig. 6 AFM Image of Low Wheel Speed Ribbon

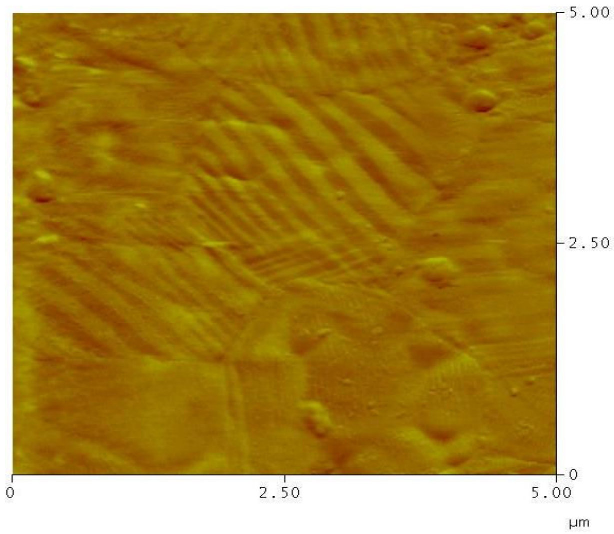


Fig. 7 AFM Image of High Wheel Speed Ribbon

Summary

Ni_2MnGa alloy upon rapid solidification by melt spinning transforms into very fine micro crystals at lower wheel speed (17 m/s). At higher wheel speed (30 m/s) it transforms into martensite with twins of 120 to 125° included angle and size about 100 – 170 nm and regions that contain uniformly distributed Ni_2MnGa nano particles of size 10 – 20 nm. The ease of forming the nanometric crystallites in the Ni_2MnGa alloy by melt spinning technique could have interesting implications on its ferromagnetic properties.

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