

## Ball milling effect on structural and magnetic properties of Ni–Mn–Ga ferromagnetic nanoparticles\*

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**Abstract:** The off-stoichiometric Ni<sub>2</sub>MnGa ferromagnetic alloys are one of the active materials that are of great interest when they are ball milled into nanopowder. These powders are prospective materials for nanosystem applications. However, the properties of the nanocrystalline Ni–Mn–Ga alloys depend strongly on their structure and internal stress, which develop during the milling process.

Ni–Mn–Ga nanoparticles were prepared by ball-milling method, and characterized by X-ray diffraction (XRD) and vibrating sample magnetometer (VSM) techniques. The powders are found to be a disordered mixture structure of austenite and martensite. We calculated that an average internal stress is 0.28 to 2.05 MPa stored in the distorted lattice due to milling. Reduction in particle sizes is accompanied by increase of the lattice strain level when the milling time increases. The VSM reveals that magnetic saturation and coercivity decrease with increase of the milling duration. This phenomenon causes deterioration in the hard magnetic properties.

**Keywords:** ferromagnetic alloys; magnetic properties; nanoalloys; nanocrystalline alloys; nanoparticles; Ni–Mn–Ga alloys.

### INTRODUCTION

Ferromagnetic shape-memory alloys (FSMAs) and, in particular, Ni–Mn–Ga alloys are keenly studied materials [1,2]. These materials exhibit the large strain of 6–10 % when being subjected to thermal or mechanical load, which is caused by the change in crystallography associated with a reversible austenite to martensite phase transformation [3,4]. In conventional SMAs, which are paramagnetic, the martensitic transformation underlying the shape memory effect (SME) is induced by changes in temperature, stress, or both [5,6]. In spite of the large strain achieved, the activation of the thermoelastic SME is slow and inefficient because it depends on the transportation of heat, i.e., heating, especially cooling of the sample. On the other hand, FSMA alloys have more recently emerged as an interesting addition to this class of materials. Moreover, in Ni–Mn–Ga the actuation is much faster than in conventional SMA. The martensitic transformation in FSMAs can be triggered not only by changes in temperature and stress, but also by changes in the applied magnetic field. This enables the devices to operate at high frequencies and facilitates their remote control [7]. FSMAs distinguish themselves from the thermoelastic SMAs by the fact that the magnetic field induced shape change occurs fully within the

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low-temperature martensitic phase. This new FSM effect is associated with the motion of twin boundaries between regions in which the magnetization direction differs.

The composition and temperature dependence of magnetic, structural, and thermal properties of the bulk Ni–Mn–Ga alloys have been studied intensively [8–10], as we know, the poly- and single-crystalline bulk alloys having limited application owing to brittleness. To overcome this problem, fine particles are needed to prepare the polymer composite [11,12]. This is a very easy technique to reduce the brittleness and attain the shape we desired. Therefore, it is necessary to study the fabrication, structural, and other properties of Ni–Mn–Ga particles. The magnetic and structural properties of fine particles fabricated by spark erosion were investigated [13,14]. Compared with the spark erosion, ball milling is simple and cost-effective. So far, the research on Ni–Mn–Ga has focused on its bulk, melt spin ribbon, and thin film properties, but for the fabrication of nanocomposites, the material should be in powder form to develop the nanomechanical components. Therefore, high-energy ball milling is an effective technique to prepare nanostructure of various FSMAs. Exploring nanostructured high-surface-area materials for this purpose has recently attracted much interest. Particularly, understanding the underlying structural transformation of off-stoichiometry composition and its connection to the structural and magnetic properties are of most practical interest. In the present work, fine particles are prepared by planetary ball milling (PBM). This work is attempted to investigate the relation between the internal stress and strain on structural transformation.

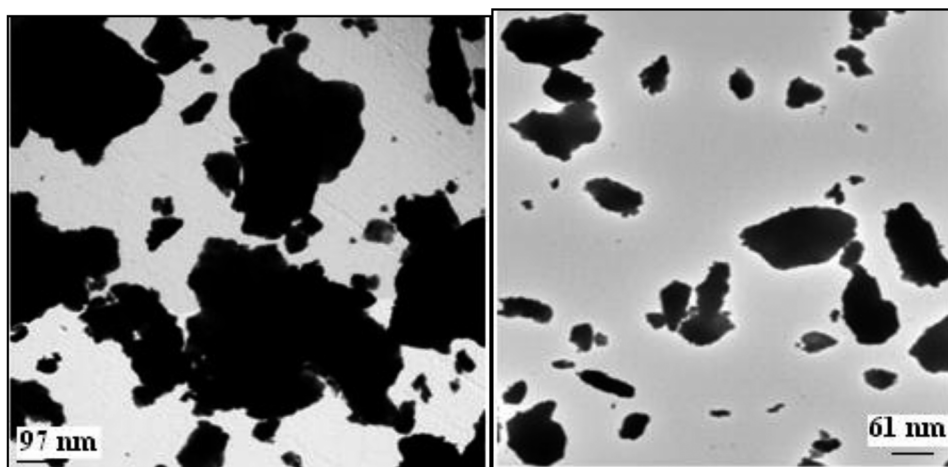
## EXPERIMENTAL PROCEDURE

Polycrystalline of Ni–Mn–Ga alloy has been prepared using conventional arc-melting technique in an argon atmosphere. High-purity raw elements nickel (99.99 %), manganese (99.8 %), and gallium (99.99 %) were used and melted. The samples were inverted and melted again, the arc-melting process being repeated four times. The resultant alloy has been annealed at 973 K for 24 h to ensure better homogeneity. The composition of the resultant powder was found to be  $\text{Ni}_{48.2}\text{Mn}_{26.8}\text{Ga}_{25.1}$  using X-ray energy dispersion analysis (EDAX). The ingot was mechanically crushed and followed by tungsten carbide ball milling for different periods (1, 2, 3, and 4 h) to achieve the nanosize particles. Ball mass-to-powder mass ratio of 15:1 was chosen to produce the alloyed powders. The wet ball milling was performed with a rotation speed of 600 r/min and mixed with toluene. The powder X-ray diffraction (XRD) measurement has been carried out to study the crystal structures using Cu *K* $\alpha$  radiation at room temperature. The magnetization measurements were performed in a vibrating sample magnetometer (VSM) at room temperature. The nanostructure of the alloy was observed by using transmission electron microscopy (TEM).

## RESULTS AND DISCUSSION

### TEM images

In order to perform TEM observations, the particles of the ball-milled powder are spread over a copper grid with 400  $\mu\text{m}$  mesh size with the carbon film. The samples placed in an FEI single tilt holder were investigated in a FEI Tecnai T20 microscope, which has a LaB6 gun and super twin lens and was operated at 200 kV. For imaging, the standard bright field and dark field techniques were used. X-ray energy-dispersive spectrometry (EDS) was used to identify the chemical composition of the disordered and nanoparticles with an Oxford Instrument Si (Li) detector. Figure 1 shows the TEM micrographs for two different samples. Figure 1a depicts the 1 h milled sample, and Fig. 1b depicts the 4 h milled sample. It is clear that with increase in the milling time, particle size decreases. Figure 1a shows a shape distribution of agglomerated particles. The irregular nature of the particles is evident in the 1 h milling; however, in 4 h milling the particles have some uniformity and the shape of particles is close to each other. It is clear that particle size decreases from 100 to 60 nm with increasing milling duration from



**Fig. 1** TEM images of Ni<sub>48.2</sub>Mn<sub>26.8</sub>Ga<sub>25.7</sub> alloy milled at (a) 1 h, and (b) h.

1 to 4 h. The particle sizes measured by using the Debye–Scherer formula are comparable to those measured through TEM.

### Structural transition

The XRD pattern is shown in Fig. 2 for ball-milled samples with different hours. It is reported [15,16] that the bulk alloy can be indexed as coexistence of distorted martensitic and austenite such as (002), (112), (220), (044), (220), and (204). A similar mixture phase has also been reported elsewhere [17,18]. After ball milling for 1, 2, 3, and 4 h by PBM, the diffraction peak (220) of the disordered mixture structure became weak and the rest of the peaks disappeared. Only one main peak appears at (220) plane position with a wide diffusion diffraction feature, indicating a disordered state for this ball-milled sample. This disordered crystal structure is due to the high-speed collision during ball milling [19]. It clearly reveals that when the ball-milling duration increases, the intensity of the prominent peak gets suppressed with increase of full width at half-maximum (FWHM). It indicates the particle size is reduced up to 65 nm. For ball-milled Ni<sub>2</sub>MnGa particles, the diffraction peaks can be indexed as a distorted phase structure, which has also been found by Wang et al. [15,19].

In Fig. 2, the ball-milled Ni<sub>48.2</sub>Mn<sub>26.8</sub>Ga<sub>25.1</sub> alloy particles do not undergo a phase transformation when the ball-milling duration extends from 1 to 4 h. However, according to the earlier studies, the thermoelastic martensitic transformation can be observed with an increase of annealing for ball-milled particles. The particle sizes of the sample have been calculated using the Debye–Scherer formula [20].

The Debye–Scherer formula ( $t$ ) is  $= \left[ \frac{0.98\lambda}{\beta \cos \theta} \right]$  where  $\lambda$  is the wavelength of Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ),  $\beta$

is FWHM,  $\theta$  is Bragg's angle. It reveals that the particle sizes are strongly dependent on the stress produced by ball milling [21].

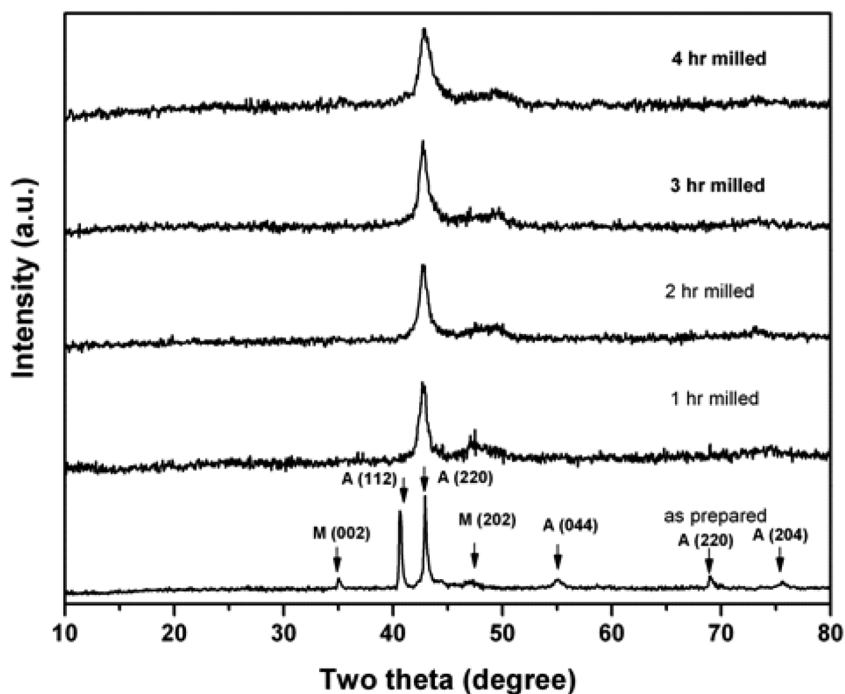


Fig. 2 XRD patterns of  $\text{Ni}_{48.2}\text{Mn}_{26.8}\text{Ga}_{25.1}$  bulk and ball-milled samples for different durations.

It is well known that the X-ray peak broadening increases with large value of FWHM of XRD reflect higher strain as a result of decrease in particle sizes. It can be related to a decrease in crystallite size and increase in residual stress. The calculated values of stress and strain for ball-milled samples with particle sizes are listed in Table 1. Based on the Scherer formula, the identical values of  $\varepsilon$  (strain) are obtained for ball-milled powders from different Bragg's peak. The strain can be calculated by using the equation  $(\varepsilon) = \frac{\beta}{4 \cdot \tan \theta}$ . By measuring the strain, stress can be calculated  $\rho = C \varepsilon$ , where  $C = 1.46 \times 10^{10} \text{ N/m}^2$  is the bulk Young's modulus [22]. The calculated value of internal stress is 0.28–2.05 MPa. This is stored in the distorted lattice as a strain. This strain can be removed completely by the annealing process to get good crystallinity in the ball-milled alloys, but it is in progress.

**Table 1** The average nano strain  $\varepsilon$  related to the particle size ( $D$ ) with stress in the powdered alloy.

Milling duration	Stress (MPa)	Particle size (nm)	Strain (%)
1 h milled	0.280	93	0.276
2 h milled	0.405	87	0.588
3 h milled	1.874	76	2.376
4 h milled	2.052	65	3.082

### Magnetic studies

The magnetic properties of  $\text{Ni}_{48.2}\text{Mn}_{26.8}\text{Ga}_{25.1}$  nanoparticles during milling process were measured at a magnetic field of about 1000 Oe at room temperature by means of vibrating sample magnetometer

(VSM-5, TOEI industries). Typical magnetization curves of the ball-milled samples for different hours are shown in Fig. 3. The magnetization is mainly due to domain wall motion and spin rotation, the comparative contribution of each being a function of the spin directions and the angle between the applied field. The contribution of spin rotation to the magnetization is large when the applied field direction is vertical to the spin direction [23]. For the milled Ni–Mn–Ga alloy, the magnetization is determined mainly by the spin rotation because the average grain size is small enough to be a single domain. In this case, the potential well produced by obstacles hindering the spin rotation is an important factor. The obstacles include internal stress and defects such as dislocation, grain boundaries, and vacancies. The internal stress results from the lattice strain caused by the milling process.

In Mn-based Heusler alloys ( $X_2MnY$ ), the magnetic moment is mainly localized on Mn and ferromagnetism is originated by their strong interaction with the X-atom. The magnetic behaviors of the Ni–Mn–Ga alloys are dependent on the Mn–Mn interaction [24,25]. The Mn atoms ( $3.45 \mu\text{B}$ ) give rise to a major contribution to the total magnetic moment ( $4.13 \mu\text{B}$ ) of the  $\text{Ni}_2\text{MnGa}$  alloy, whereas contributions from Ni and Ga atoms are small (i.e.,  $0.74$  and  $-0.04 \mu\text{B}$ , respectively) [24]. Since the Mn–Mn distance is  $\geq 4 \text{ \AA}$ , there is no significant direct interaction between the Mn atoms. RKKY-type indirect exchange interaction gives rise to magnetism in this material [25]. Hence, a decrease in both magnetic saturation and coercivity is thought to be suppression of Mn–Mn exchange compared with Ni–Mn [26]. For the milled powder, the destruction of Mn–Mn ferromagnetic exchange is induced by ball milling [27]. This is why the ferromagnetic order is suppressed owing to the high-speed collision during ball milling. Generally, some magnetic properties can be enhanced when the grain size is reduced to nanoscale and the stresses introduced by ball milling will impair the magnetic property. Therefore, coercivity, and magnetization of the bulk sample is  $62 \text{ Oe}$  and  $8.74 \text{ emu}$ , respectively, which is decreased to  $7 \text{ Oe}$  and  $6.12 \text{ emu}$  for  $3 \text{ h}$  milled sample. This phenomenon causes deterioration in the hard magnetic properties.

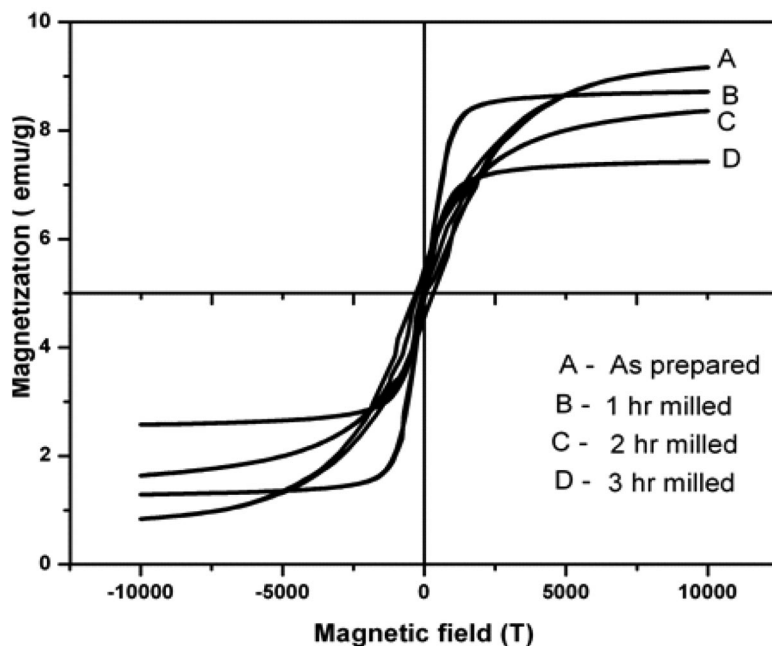


Fig. 3 Magnetization plots of  $\text{Ni}_{48.2}\text{Mn}_{26.8}\text{Ga}_{25.1}$  bulk and ball-milled samples at different durations.

## CONCLUSIONS

Ball milling is found to alter the ordered crystal structure of the  $\text{Ni}_{48.2}\text{Mn}_{26.8}\text{Ga}_{25.1}$  alloy into a disordered structure, apparently via atomic displacement. For ball-milled particles, the XRD indicates that change of particle size results in widening characteristic peak with large value of FWHM. Ball milling also severely weakens the magnetization of the alloy, which is apparently caused by the destruction of Mn–Mn ferromagnetic exchange induced. The TEM image confirms the nanoparticle. Further post-annealing for the milled samples would be needed to elucidate the degree of atomic ordering and particularly improve the ferromagnetic nature.

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