Microstructures and Magnetic Properties of Rapidly Solidified $Ni_{54}Fe_{27-2x}Ga_{19+2x}$ Ferromagnetic Heusler Alloys

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Rapidly solidified $Ni_{54}Fe_{27-2x}Ga_{19+2x}$ (x=0, 1, 2, 3, and 4) ferromagnetic shape memory alloys were made by melt-spinning with variation of Fe and Ga contents to report on the martensitic phase transformation, microstructures, and magnetic properties. Rapid solidification produced pure $L2_1$ phase by preventing the formation of γ-phase. To study the effect of heat treatment on the phase transitions, microstructures, and the magnetic properties, the melt-spun ribbons were partly heat treated at different temperatures of 800, 900, 1000, 1100, and 1200 K with holding times of 5, 10, and 15 min followed by either water quenching or air cooling. The microstructures of the as-spun ribbons as revealed by electron microscopy studies exhibited a gradual transition from cellular to dendritic structure with increasing Ga concentration and with the presence of some internal martensitic twin bands at higher Ga content. The ribbons exhibited very low coercivity with high saturation magnetization, as high as ~87 emu/g (decreasing with Ga concentration). The above-ambient Curie temperature (T_C) and the subambient martensitic transition temperature (T_m) were observed to be ~320 and ~195 K, respectively. At higher heat treatment temperatures formation of ductile γ phases was observed.
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I. INTRODUCTION

Ferromagnetic Heusler alloys are attracting much more attention as promising magnetic smart materials because of their large magnetic field induced strain (MFIS) and high frequency response, especially for sensing and microactuation in the thin-film industry.[1] After achieving high MFIS (~10%) in Ni–Mn–Ga single crystal,[2] this alloy is the mostly studied alloy system among all other important ferromagnetic Heusler alloy systems,[3–5] such as NiMnAl,[6] CoNiGa,[7] and CoNiAl.[8] However, the inherent brittleness of NiMnGa (Ref. 9) and a constant driving force to search for a new magnetic shape memory alloy to improve the quality of application eventually resulted in the discovery of new Ni–Fe–Ga ferromagnetic shape memory alloys (FMSMAs), a good replacement of the relatively brittle Ni-Mn-Ga FMSMAs, which have been attracting a great deal of attention as a new member of FMSMAs for potential applications.[1,10] Rapid solidification (melt-spinning) technique helps to suppress the formation of γ-phase [which degrades the martensitic transformation (MT) and thus results in poor transformation temperature] by enforcing a rapid cooling of the liquid state directly into the pure $L2_1$ phase. Although several observations have been recorded for Ni–Fe–Ga alloys, the nature of the phase transitions has not been extensively studied. Specifically, the interest here is on the microstructures and magnetic properties of rapidly solidified Ni–Fe–Ga alloys with varying Fe/Ga ratio (1.4, 1.2, 1.0, 0.84, and 0.70). This study reports on the martensitic phase transformation, microstructures, and magnetic properties of a series of rapidly solidified $Ni_{54}Fe_{27-2x}Ga_{19+2x}$ (x=0, 1, 2, 3, and 4) alloys.

II. EXPERIMENTAL PROCEDURES

A series of alloy ingots of $Ni_{54}Fe_{27-2x}Ga_{19+2x}$ (x=0, 1, 2, 3, and 4) were produced by arc-melting in a tungsten inert-gas electrode arc furnace and later they were melt-spun in quartz tubes onto a copper wheel with a linear velocity of 20 m/s. The resulting ribbons were ductile, ~50 μm thick, ~5–6 mm wide, and with a metallic shiny surface luster. The melt-spun ribbons were heat treated at different temperatures of 800, 900, 1000, 1100, and 1200 K with holding times of 5, 10, and 15 min followed by either water quenching or air cooling. The microstructural studies were performed by field emission scanning electron microscopy (CAMSCAN-2 JEOL) as well as high-resolution transmission electron microscopy (JEOL 2100 at 200 kV), and com-

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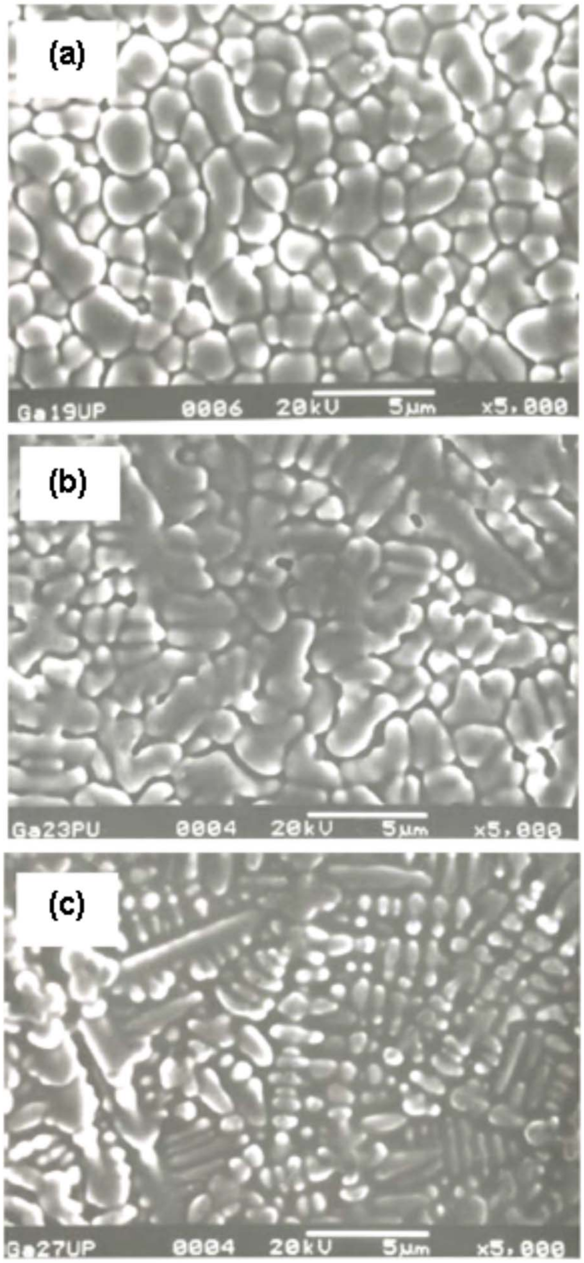

FIG. 1. (Color online) Scanning electron micrographs of $Ni_{54}Fe_{27-2x}Ga_{19+2x}$ as-spun ribbons with (a) $x=0$, (b) $x=2$, and (c) $x=4$.

positions were analyzed using energy dispersive x-ray spectroscopy (EDS-OXFORD). The MTs were monitored by differential scanning calorimetry. The magnetic properties were measured with superconducting quantum interference device magnetometry.

III. RESULTS AND DISCUSSION

The phase formations were analyzed from the x-ray diffraction patterns obtained throughout the experiments. Rapid solidification produced mostly pure $L2_1$ phase, especially at higher Ga concentration, by preventing the formation of γ-phase including a small fraction of γ-phase present at lower Ga concentration. The microstructures of the as-spun ribbons exhibited a gradual transition from cellular to dendritic structure with increasing Ga concentration or decreasing Fe/Ga ratio (Fig. 1). The origin of this morphological change from cellular to dendritic in the Ni–Fe–Ga system is attributed to the Ga-induced structural instability during magnetic transition in the system. Some internal martensitic twin bands were also observed at higher Ga content with modulated as well as nonmodulated martensite [Fig. 2(a)]. Figure 2(a) shows martensite band structures (each ~200 nm wide) oriented in two different directions 90° apart. The domain structure of $Ni_{54}Fe_{21}Ga_{25}$ martensite is clearly visible in the bottom-right corner inset in Fig. 2(a), which is a magnified view of the bottom-right area of Fig. 2(a) marked with a white dotted circle. The dark and bright bands inside the inset represent the domain structure in twin orientations with respect to each other. The domain periodicity can be defined as the total width of a dark and a bright band, which is ~30–40 nm. The top-right inset of Fig. 2(a) shows the selected area diffraction (SAD) pattern of the martensite bands. The streaks in the SAD pattern indicate the presence of modulated martensite bands. After annealing (heat treated at 1000 K AC) the matrix of the annealed ribbons exhibited the presence of small black patches of precipitates (~10–20 nm) at lower Ga content. At higher Ga concentration, the ribbons annealed at the same conditions showed very large micron-sized grain (1–2 μm) with the presence of some micron-sized gray grains at highest %Ga ($x=4$) sample [Fig. 2(b)], which are known as the γ-phase. The morphology of the γ-phase is consistent with previous results mentioned elsewhere.[11] Larger sized grains were observed at higher heat-treatment temperature with reduced martensitic domain size. The magnetization curves exhibited the typical characteristics of ferromagnetic materials. The ribbons exhibited very low coercivity (~10 Oe) with high saturation magnetization (M_s), as high as ~87 emu/g (at 5 K). Figure 3 shows the hysteresis loops of $Ni_{54}Fe_{27-2x}Ga_{19+2x}$ as-spun ribbons measured at 300 K. The maximum M_s value observed at this temperature was ~73 emu/g (decreasing with Fe/Ga ratio). As a nonmagnetic element, Ga dilutes the magnetization of the alloy and, at higher Ga content, the alloy shows reduction in the overall expected saturation magnetization just from the dilution standpoint (i.e., fewer magnetic atoms per unit mass of material). The top-left inset of Fig. 3 represents the normalized magnetization data, where the vertical axis of the graph has been normalized (M/M_s) to remove the dilution effect of nonmagnetic Ga from the data. The bottom-right inset of Fig. 3 shows the nature of the initial magnetization curves, which shows higher M_s value at a temperature of 4 K, which is below the

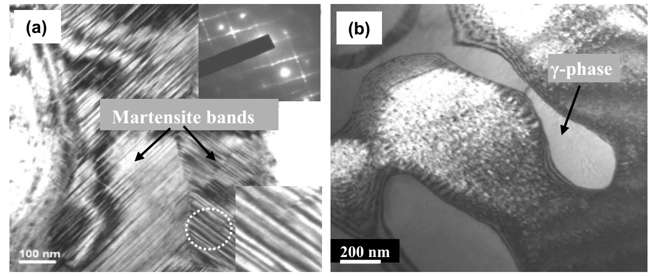

FIG. 2. Transmission electron micrographs of $Ni_{54}Fe_{27-2x}Ga_{19+2x}$ alloys: (a) as-spun ribbon ($x=3$) and (b) after heat treatment (1000 K AC) ($x=4$).

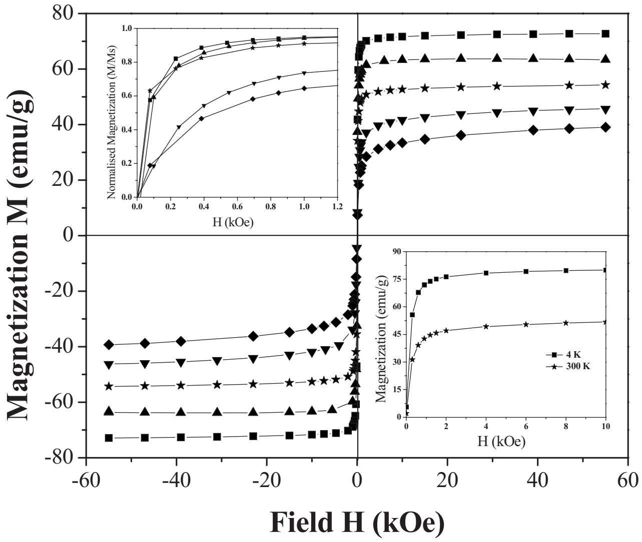

FIG. 3. Magnetic hysteresis loops of $Ni_{54}Fe_{27-2x}Ga_{19+2x}$ as-spun ribbons, where $x=0$ (■), $x=1$ (▲), $x=2$ (*), $x=3$ (▼), and $x=4$ (◆). Inset (top-left): normalized magnetization curves of $Ni_{54}Fe_{27-2x}Ga_{19+2x}$ as-spun ribbons. Inset (bottom-right): initial magnetization curves of $Ni_{54}Fe_{27-2x}Ga_{19+2x}$ alloy ($x=3$, Fe/Ga=0.84) at 4 and 300 K.

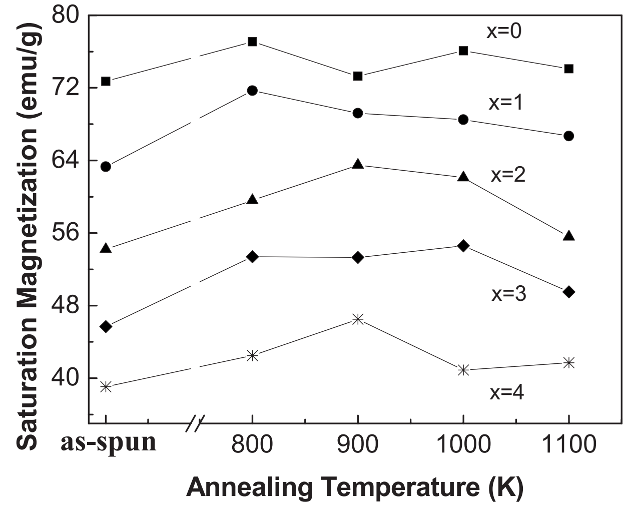

FIG. 4. Variation of saturation magnetization with annealing temperature of $Ni_{54}Fe_{27-2x}Ga_{19+2x}$ alloys with $x=0$, 1, 2, 3, and 4.

MT temperature (T_m), and lower M_s value at 300 K, which is above T_m. The linear tendency of the *M-H* curve after the saturation field indicates the nature of a fairly homogeneous ferromagnet. However, the alloys did not show any significant remanence value ($M_r < 10$ emu/g) throughout the hysteresis loops, which indicates that the grown materials did not have any significant built in orientation to them due to the shear imparted by the wheel during the cooling process. The MT temperature (T_m) and the Curie temperature (T_C) were observed in the range of 190–200 K and 310–330 K, respectively, which are good enough in the practical field from an application point of view in the case of a FMSMA. At higher annealing temperature enhanced values were observed for the martensitic transition temperature (T_m) as well as for the saturation magnetization (M_s), whereas an increase in annealing temperature resulted in a decrease in the Curie temperature (T_C). Figure 4 shows how saturation magnetization depends on annealing temperature with different %Ga content. For all the as-spun ribbons annealing helped to enhance the saturation magnetization value to some extent. But at higher heat treatment temperatures, the formation of ductile γ-phases was observed and, due to the presence of these γ-phases, the M_s value decreases. Deviations were observed for this trend in a couple of cases, significantly at $x=0$ (Fig. 4). At $x=0$, the M_s value decreased at 900 K followed by a sudden increase at 1000 K, which may be due to experimental error. However, variation in annealing time in such a short interval (5, 10, and 15 min) did not affect the experimental results significantly.

IV. CONCLUSIONS

Ferromagnetic Heusler alloys of NiFeGa with varying Fe/Ga ratio were synthesized successfully by using the rapid solidification (melt-spinning) technique. The melt-spun ribbon exhibited mostly pure cubic $L2_1$ structure with a thermoelastic MT from cubic to orthorhombic structure at ~195 K. The rapidly solidified ribbon exhibited some interesting magnetic properties—a very high saturation magnetization ~87 emu/g (at 5 K for the parent alloy) with a low saturation field ~0.6 T, which is half of that of NiMnGa,[12] narrow hysteresis loop with small coercive force (~10 Oe), and an average Curie temperature of ~315 K, which is above room temperature. All of these interesting and attractive properties made this Ni–Fe–Ga alloy a promising magnetic Heusler alloy for important applications.

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