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Martensitic transformation and accompanying magnetic changes in Ni–Fe–Ga–Co alloys

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Two series of cobalt substituted Ni–Fe–Ga ferromagnetic shape memory alloys with lower gallium content (<27 at. %) were studied by differential scanning calorimetry, x-ray diffraction, and thermomagnetic measurements. Co substitution for Fe or Ni promotes an increase in the Curie temperatures and a variation in the martensitic transformation (MT) temperatures, in accord with the alloy valence electron concentration change. For alloys with MTs below room temperature, a field dependent thermomagnetic hysteresis was evidenced and discussed in connection with the effect of cobalt substitution, on the magnetic hardness of the martensite phase. A direct interpretation of the evolution of the thermomagnetic hysteresis versus the applied field was provided. © *2010 American Institute of Physics*. [doi:10.1063/1.3429231]

I. INTRODUCTION

Specific to shape memory alloys (SMA) is the so called martensitic transformation (MT), which is a thermoelastic reversible structural phase transition, between high and low symmetry phases. When cooling the alloy, the high temperature austenite phase undergoes a diffusionless transformation in which atoms shift cooperatively reducing the symmetry and forming the low temperature martensite phase. Ferromagnetic SMA (FSMA) are materials in which MT appears at temperatures lower than the magnetic transition temperatures. The large magnetic field induced strain (MFIS), the high frequency response and the shape memory effect evidenced in FSMA recommend them as promising materials for magnetically controlled actuators.

After reporting a huge MFIS (about 10%) in Ni–Mn–Ga single crystals,[1] this alloy was intensively studied and a large amount of knowledge concerning physics related to the effect has been acquired. However, the high fragility of this alloy was the main reason to search for new FSMA. Binary Fe–Pd (Ref. 2) or other Heusler alloys like Co–Ni–Al(Ga) (Refs. 3 and 4) and Ni–Mn–Al (Ref. 5) have been reported in this regard. Recently, a thermoelastic MT in the ferromagnetic state, associated with a shape memory effect, was evidenced in Ni–Fe–Ga Heusler type alloy.[6]

It is generally accepted that MT in Ni–Fe–Ga takes place between austenite with B2 or L21 structure and either a seven-layer modulated or five-layer modulated as well as a non-modulated ($L1_0$ tetragonal structure) martensite structure, depending on composition and thermal history. For the stoichiometric Ni_2FeGa, the MT temperature is around 145 K, the system being ferromagnetic up to 430 K. For the off-stoichiometric compounds, the martensitic transition shifts to higher temperatures with increasing Ni content. The practical advantage of Ni–Fe–Ga alloys over the other mentioned compounds is related to its better ductility which is associated with the presence of a second γ—[face-centered cubic (fcc)] phase.[6]

Several studies have been focused on the influence of thermal history,[7,8] iron concentration,[9] and trace elements[10] on the MT of Ni–Fe–Ga alloy, preponderantly on composition containing 27 at. % Ga. Cobalt is one of the most studied substitution elements in Ni–Fe–Ga alloys. Besides its well known effect in increasing the Curie temperature, cobalt may increase or decrease the MT temperature, depending on the element which is partially substituted. Hence, the MT temperature increases in Ni–Fe–Ga–Co alloys with Co substituting Fe (Ref. 11) or Ga (Ref. 12) and has an opposite evolution for Co substituting Ni.[11] Also the thermal history of the sample influences drastically the MT temperature such as: a slow cooling from moderate temperature promotes a highly ordered $L2_1$ type structure with a lower MT temperature than that of the poorly ordered alloys obtained by fast cooling.[13] A higher Co content and/or a longer thermal treatment promote the precipitation of the γ—fcc—phase, with direct influence on the composition of the main phase and MT temperature. However, in spite of the induced changes, the mechanical properties of the alloy are unexpectedly enhanced.[12,14]

The present work investigates the influence of cobalt substitution on the MT and the way how this is reflected on the magnetic properties of two series of compounds with lower Ga concentration: $Ni_{55}Fe_{20-x}Co_xGa_{25}$ (x=0, 1, 3) and $Ni_{54-y}Co_yFe_{20}Ga_{26}$ (y=1, 2), respectively.

II. EXPERIMENTAL

The polycrystalline samples were prepared by arc melting in argon atmosphere. The alloys were remelted three times to ensure the homogeneity. Subsequently, a thermal treatment in high vacuum for 25 h at 950 °C was performed, followed by a quenching in iced water.

The samples were structurally investigated by X-ray diffraction (XRD) using a Seifert diffractometer (Cu K_α radiation). The phase transformation temperatures were determined by using a differential scanning calorimeter (DSC) model 204 F1 Phoenix (Netzsch) within a scanning rate of 10 K/min. The low temperature magnetic measurements

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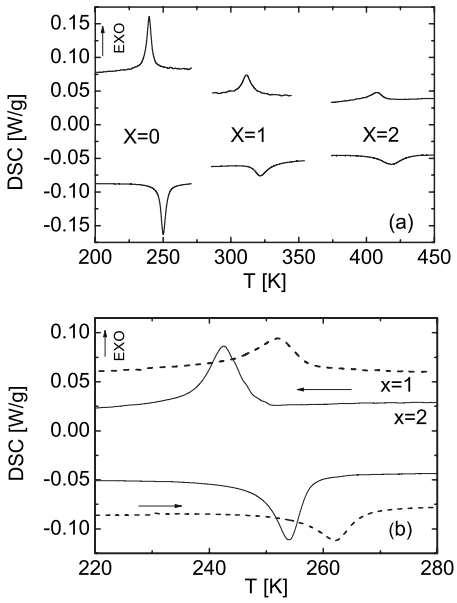

FIG. 1. DSC curves of (a) $Ni_{55}Fe_{20-x}Co_xGa_{25}$ and (b) $Ni_{54-y}Co_yFe_{20}Ga_{26}$ samples annealed for 25 h at 950 °C. The MT shifts to higher temperatures for the alloys with cobalt substituting iron and to lower temperatures for those with cobalt substituting nickel.

were performed with a high field measurement system (Cryogenic Ltd.) working in the vibrating-sample magnetometer (VSM) mode. Above room temperature, the magnetic measurements were done by using a Weiss-type home made balance.

III. RESULTS AND DISCUSSIONS

DSC measurements (Fig. 1) show clearly that all the prepared Ni–Fe–Ga–Co alloys experience reversible MTs. Details on the characteristic parameters of the transformations as well as on the Curie temperatures are listed in Table I.

The thermal hysteresis, i.e., the difference between Austenite finish (Af) and Martensite start (Ms) temperatures is about 10 K (see Table I), in agreement with results reported in literature on NiFeGa alloys of different concentrations.[15]

In order to analyze the effect of iron or nickel substitution by cobalt, it is appropriate to evaluate the thermodynamic MT temperature, $T_o=(Ms+Af)/2$. The data from Table I show that, in iron substituted series, T_o increases dramatically with cobalt concentration (~50 K/Co atom), while in the nickel substituted series, T_o decreases slowly, with only 10 K/Co atom.

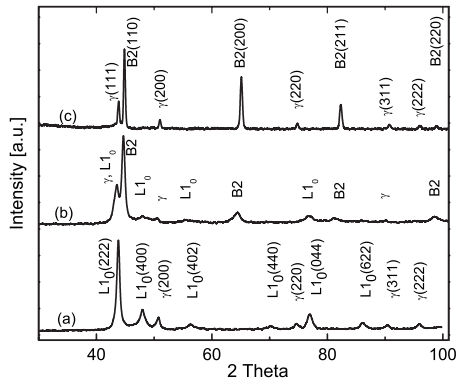

FIG. 2. Room temperature XRD patterns of (a) $Ni_{55}Fe_{17}Co_3Ga_{25}$, (b) $Ni_{55}Fe_{20}Ga_{25}$ and (c) $Ni_{52}Co_2Fe_{20}Ga_{26}$. Apart from the peaks attributed to a secondary, un-transforming, fcc phase, γ, the main peaks are indexed with a non-modulated tetragonal structure ($L1_0$-martensite) or with a B2 (austenite) structure, in concordance with the DSC results

This behavior is in qualitative agreement with the general accepted dependence of T_o in a series of FSMAs, on the valence electron concentration (e/a), and on the volume of the unit cell. Accordingly, the MT temperature increases with the increase in e/a and with the reduction in the unit cell volume. This feature was evidenced on different single phase semi-Heusler alloys.[9,13,16–18] The valence electron concentration, given in Table I, is calculated for each nominal alloy composition taking for the number of valence electrons 10, 9, 8, and 3 for nickel, cobalt, iron, and gallium, respectively. Even the samples discussed in this paper are two-phase alloys (see Fig. 2) the results show still the correct trend. It is worth mentioning that in the analyzed cases was not possible an appropriate evaluation of the relative phase content, either from the XRD patterns or from the thermomagnetic curves. On the other hand, based on the same single phase hypothesis, an increase in T_o is expected in alloys where Fe is substituted by Co, which is an atom with a relatively smaller atomic radii but with more valence electrons. On the contrary, an decrease in T_o is expected if Ni is substituted by Co, with its relatively higher atomic radii and less valence electrons.

Room temperature XRD measurements of the alloys treated at 950 °C reveal a multiphase structure (Fig. 2). Common for all the compounds, is the presence of a γ fcc

TABLE I. Composition, characteristic temperatures—Martensite start (Ms) and Martensite finish (Mf), Austenite start (As), and Austenite finish, (Af)—transformation enthalpies (ΔH_M and ΔH_A), the thermodynamic MT temperature (T_o), valence electron concentrations (e/a) and Curie temperatures (Tc) for all the studied alloys.

Sample	M_s (K)	M_f (K)	ΔH_M (J/g)	A_s (K)	A_f (K)	ΔH_A (J/g)	T_o (K)	e/a[a]	Tc (K)
$Ni_{55}Fe_{20}Ga_{25}$	244.5	235.1	2.055	246	254.5	−2.066	249.5	7.85	305
$Ni_{55}Fe_{19}Co_1Ga_{25}$	322	302	1.21	307	333	−1.39	327	7.86	329
$Ni_{55}Fe_{17}Co_3Ga_{25}$	408	400	0.71	411.7	422.8	−0.977	415.4	7.88	341
$Ni_{53}Co_1Fe_{20}Ga_{26}$	257.	244	2.53	255	267	−2.77	262	7.77	324
$Ni_{52}Co_2Fe_{20}Ga_{26}$	248	237	2.69	249	257	−2.61	252.5	7.76	345

[a]Calculated for nominal alloy composition.

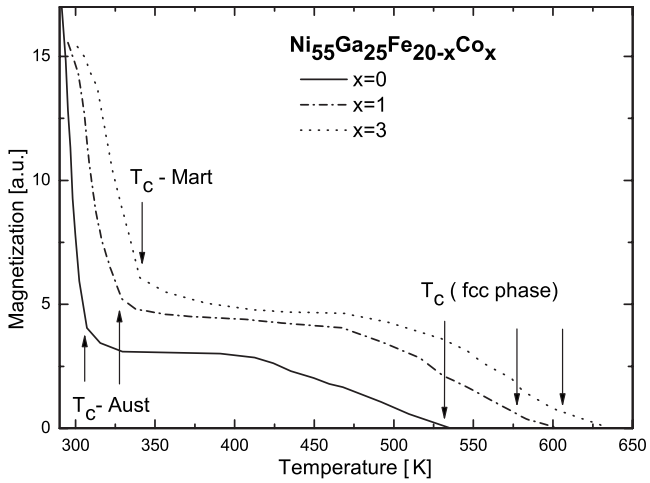

FIG. 3. High temperature thermomagnetic measurements on $Ni_{55}Fe_{20-x}Co_xGa_{25}$ alloys evidence two magnetic phases. The Curie temperatures of the majority phase, in the range from 300 to 350 °C, were attributed to either austenite or martensite, in accord with the DSC results on the MT temperatures

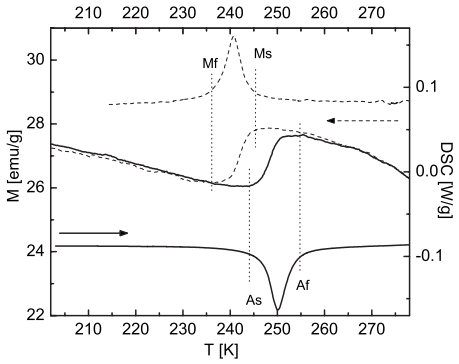

FIG. 4. DSC curves and VSM thermomagnetic scans (at constant magnetic field of 40 mT) for $Ni_{55}Fe_{20}Ga_{25}$ alloy (dashed line at cooling and solid line at heating). A good correspondence between all the involved transition temperatures in the DSC curves and the thermomagnetic scans can be observed.

phase which contribution is increasing with the cobalt content. Beside this phase, the x-ray patterns point out the B2 structure of the austeniticlike phase (disordered Heusler-type structure) for the alloys with MT below room temperature ($Ni_{54-y}Co_yFe_{20}Ga_{26}$ with y=1, 2 and $Ni_{55}Fe_{20}Ga_{25}$). In the case of $Ni_{55}Fe_{20-x}Co_xGa_{25}$ with x=1 and 3, for which DSC results indicate the MT above room temperature, XRD patterns show the characteristic peaks of the martensite nonlayered tetragonal phase ($L1_0$).

Low field thermomagnetic measurements performed on $Ni_{55}Fe_{20-x}Co_xGa_{25}$ alloys evidenced two magnetic phases (Fig. 3). The majority phase shows an order–disorder magnetic transition temperature above room temperature which slightly rises with cobalt content, in good agreement with other reported results.[7]

The secondary phase, with higher Curie temperature, was assigned to the γ-fcc phase appearing in XRD patterns. The thermomagnetic experimental data suggest an increase in the volume fraction of this secondary phase, with the cobalt content. This aspect can be further correlated with the reduction in the transformation enthalpies for the direct and reverse transformations, namely ΔH_M and ΔH_A (Table I) of $Ni_{55}Fe_{20-x}Co_xGa_{25}$ alloys. It is worth to notice that, in the first order phase transformations, the enthalpy variation (ΔH) is produced by the lattice distortion[17] and is related to the amount of transforming active phase; an increased amount of residual fcc phase means a decreased amount of active phase and consequently, a smaller variation in the enthalpy.

When comparing the Curie temperatures of the majority phase with the values obtained for T_o, it is concluded that for x=0 and 1, the austenite phase supports the magnetic transition, whereas for x=3, the martensite phase is the one which supports the magnetic transition. From this point of view $Ni_{55}Fe_{17}Co_3Ga_{25}$ is definitely a SMA and not a FSMA.

Figure 4 exhibits the thermomagnetic scans for $Ni_{55}Fe_{20}Ga_{25}$ measured in a field of 40 mT during heating and cooling processes together with the DSC curves of the same alloy. The locations of the peaks, in the temperature dependence of the DSC results correspond well with the steps in the thermal variations in the magnetization and reveal all the involved transition temperatures between the high temperature austenite phase and the low temperature martensite phase. Therefore, the thermomagnetic measurements represent a powerful tool to study the influence of the magnetic field on phase transitions in FSMA.

The thermal variation in magnetization under different applied fields (in range of 0–1500 mT) was performed in order to get more information concerning how the MT is reflected in the variation in magnetization. The measurements were done by cooling down the samples in constant magnetic field, from room temperature to a temperature well below the transformation temperature and warming them up again, back to room temperature. Only samples with MT below room temperature were considered. The corresponding plots collected, at increasing fields, on the FSMA with Ni substituted by Co are shown in Fig. 5. It is worth to notice

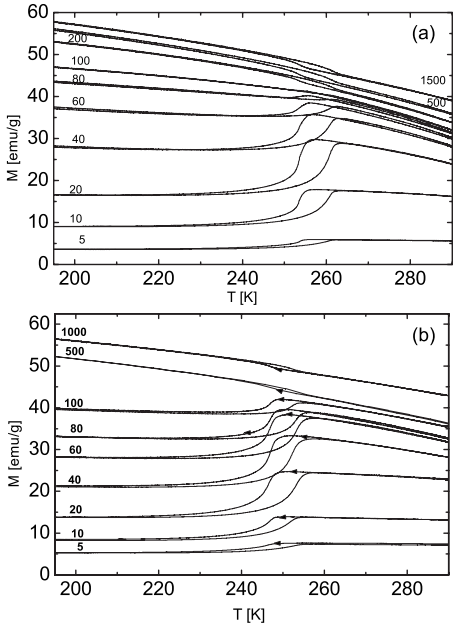

FIG. 5. The thermal variation in magnetization, on cooling and heating, under different magnetic fields (the magnetic field values, given on each curve, are in mT) for $Ni_{53}Co_1Fe_{20}Ga_{26}$ (a) and $Ni_{52}Co_2Fe_{20}Ga_{26}$ (b) alloys. The hysteresis area shows always a maxim at a given field.

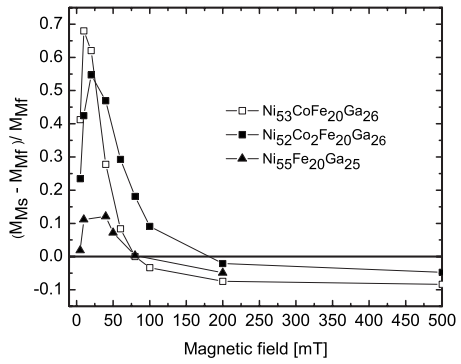

FIG. 6. The relative variation in the magnetization, $\Delta M_{rel}=(M_{Ms}-M_{Mf})/M_{Mf}$, versus the induction of the applied field, for $Ni_{54-y}Co_yFe_{20}Ga_{26}$ (y=1, 2) and $Ni_{55}Fe_{20}Ga_{25}$ alloys.

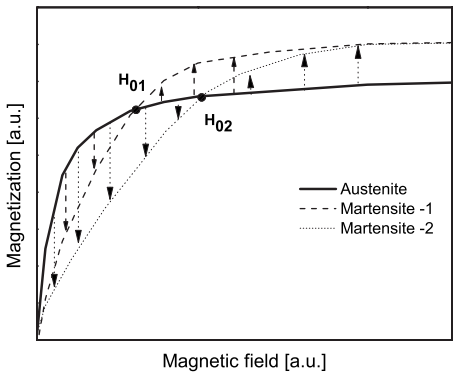

FIG. 7. Magnetization curves for a pure austenite phase (physically, it is stabilized at $T \geq Ms$) of low anisotropy and for two martensite phases (physically the martensite phase is stabilized at $T \leq Mf$), of higher anisotropies. Martensite 1 has a lower anisotropy than martensite 2. By cooling and passing from austenite to martensite, the magnetization variation is field dependent. At low fields, the magnetization of austenite is higher than that of martensite and their difference, counted by ΔM_{rel}, is positive. The difference reaches a maxim around the field value which saturates the austenite phase. At a certain field value, H_0, the two phases have the same magnetization and the difference becomes zero. For $H > H_0$ the magnetization of austenite remains lower than of the martensite and their difference become negative.

that the magnitude of the magnetic field only slightly affected the characteristic transformation temperatures while the area of thermomagnetic hysteresis provides strong evidence on field dependency.

For the clearness of discussion it is useful to define a sign for the hysteresis area; let us consider a positive hysteresis area with a counterclockwise evolution when start with cooling and then heating the sample. With increasing the field, the hysteresis area reaches a maximum and then decreases passing through zero and finally witness a sign change. This behavior certainly proves a change in magnetocrystalline anisotropy during the MT. At low fields, due to its smaller magnetocrystalline anisotropy, the austenite phase is easier magnetized than the martensite ones, giving rise to a higher magnetization. By cooling the sample and passing through the Ms temperature, magnetization shows a reduction, due to the lower magnetization of the martensite. (Similarly, by heating the sample through As, the magnetization shows an augmentation.)

With increasing the applied field, at a certain value of the magnetic induction, $\mu_0 H_0$, the thermomagnetic hysteresis vanishes. For enough high fields (higher than $\mu_0 H_0$), by passing from austenite to martensite phase, at Ms, the magnetization shows an augmentation, demonstrating that martensite phase has a higher magnetization at saturation. The same behavior was evidenced on Ni_2MnGa single crystal[19] and Ni–Fe–Ga alloy[20,21] but without any mention or comment on the hysteresis area behavior.

Having in mind that the magnetic field practically does not affect the characteristic transformation temperatures, the hysteresis area has to be proportional to the difference between the magnetization values of martensite and austenite phases in the vicinity of transformation. Let us count this difference by the relative variation in the magnetization, $\Delta M_{rel}=(M_{Ms}-M_{Mf})/M_{Mf}$, with M_{Ms} the magnetization at Ms temperature (only austenite contributes to the magnetization) and M_{Mf} the magnetization at martensite finish temperature (only martensite contributes to the magnetization). Figure 6 presents the field dependency of the ΔM_{rel} values during the cooling process, for $Ni_{54-y}Co_yFe_{20}Ga_{26}$ (y=1, 2) and $Ni_{55}Fe_{20}Ga_{25}$ alloys. The relative variation in magnetization during the martensitic transition reaches a maximum value of 68% in a field of 10 mT for y=1 and of 54% in a field of 20 mT for y=2 in the cobalt containing alloys and of only 12%, in a field of 25 mT for $Ni_{55}Fe_{20}Ga_{25}$. The critical field, for which the relative variation in magnetization vanishes, increases with cobalt content, from 75 to 180 mT.

The direct interpretation of this behavior can be emphasized by taking into account the magnetization curves assigned to a pure austenite phase with low anisotropy and to a pure martensite phase with high anisotropy, respectively (Fig. 7). The above analyzed temperature induced structural transitions, from one phase to the other one, can be seen as switching between the two corresponding curves at constant field. It is clearly now why the magnetization steps, presented in Fig. 5 via the relative variation in the magnetization, ΔM_{rel}, depend on the applied field intensity. The magnetization step reaches the maximum value for a field which approaches the saturation of the austenite phase and becomes zero at the field H_0, where the two magnetization curves, of austenite and martensite, respectively (Fig. 7), are crossing over. Above H_0, the magnetization of the martensite phase becomes higher than that of the austenite phase and the magnetization step, defined via ΔM_{rel} becomes negative. At fields much higher than H_0, the magnetization step counts for the difference between the magnetization at saturation for the two phases. One the other side, it is worth to mention that H_0 may be also considered as an indication for the martensite magnetic hardness. Higher H_0 is, stronger is the magnetocrystalline anisotropy of martensite.

The field H_0, for which the thermomagnetic hysteresis vanishes, increases with cobalt content, suggesting that cobalt enhances the magnetic hardness in the martensite phase. This assumption is also supported by the results obtained by Morito *et al.*[22,23] on $Ni_{51}Fe_{18}Ga_{27}Co_3$ and $Ni_{49}Fe_{18}Ga_{27}Co_6$ alloys. They found that the magnetocrystalline constants, evaluated on monocrystals in single-variant martensite phase near the transition temperature, increase from 4.7×10^5 to 1.2×10^6 erg/cm^3 with the cobalt content.

IV. CONCLUSIONS

Ni–Fe–Ga intermetallic compounds with Co substitutions at Ni and Fe sites were prepared and characterized with respect to their magnetic behavior during the MT. It was evidenced that cobalt substitution for iron in $Ni_{55}Fe_{20-x}Co_xGa_{25}$ alloys promotes the increase in both Ms and Curie temperatures. Due to the more pronounced increase in the Ms temperature, the $Ni_{55}Fe_{19}Co_1Ga_{25}$ alloy is at the limit between SMA and FSMA. Cobalt substitution for Ni promotes a decrease in the martensitic transition temperature. It was proved that the thermomagnetic measurements appear as a powerful tool for studying most of the characteristics of the martensitic transition. The field dependency of the thermomagnetic hysteresis and the magnetization jumps in the temperature region of martensitic transition were discussed with respect to the magnetic parameters of the austenite and martensite phases. These features are connected with the interplay of the magnetocrystalline anisotropies of the two phases during the transformation.

ACKNOWLEDGMENTS

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