

Characterization of martensitic transformation in some Ni-Fe-Co-Ga ferromagnetic shape memory alloys

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The martensitic transformation characteristics in two series of cobalt substituted Ni-Fe-Ga Ferromagnetic Shape Memory alloys have been studied by differential scanning calorimetry, X-ray diffraction, electrical resistivity and thermomagnetic measurements. Co substitution for Fe or Ni promotes an increase of the Curie temperatures but the changes of the martensitic transformation temperatures are in agreement with the valence electron concentration and unit cell volume variations. A large hysteresis observed between cooling and heating curves as feature of a first order phase transition was evidenced by $r(T)$ and thermomagnetic measurements.

(Received April 20, 2011; accepted May 31, 2011)

Keywords: Ferromagnetic shape memory alloys, Martensitic transformation. Magnetic properties

1. Introduction

The development of more efficient materials for sensors and actuators is attaining increasing interest in the materials science community. Shape Memory Alloys (SMA) is a class of active materials that have been used as key actuator materials with application in biomedical, naval, aerospace, etc. These materials allow their shape to be changed, producing a displacement, during thermal activation of a structural transition. The shape-memory effect (SME) is associated with a thermoelastic reversible structural phase transition between high and low symmetric phases, the so called martensitic transformation (MT). An induced deformation in the martensite phase with lower symmetry can be recovered upon transformation to a higher symmetry, austenite phase, with increasing temperature. For all (until now) known SMA, the parent austenite phase has a cubic crystalline structure (bcc or fcc). Close to the transition, the lattice deformation along one of any 3 directions generates some variants of structural units with the same deformation, the so called twin variants. The martensite microstructure is a characteristic one, composed of variable volume fractions of the twin variants to accommodate the elastic strain. The high mobility of twin boundary is exploited in the temperature driven shape memory effect. The velocity of shape recovering is restricted by the heating and cooling processes which are slow. Therefore a way to drive the shape change with a faster response would be desirable for many applications. This can be achieved by taking the magnetic freedom degree into play.

Ferromagnetic Shape Memory Alloys (FSMA) are materials in which MT lie in the temperature region of magnetic order. The large magnetic field induced strain (MFIS), the high frequency response and the shape memory effect evidenced in FSMA has drawn attention as promising materials for magnetically controlled actuators. The MFIS derives from the large magnetic anisotropy

installed in the low symmetry martensite phase. By applying an external magnetic field it is energetically favorable to move the twin boundaries instead to rotate the twin magnetization direction. The martensite variants that have their easy axis along the applied field direction grow at the expense of other variants giving rise to a large strain. A huge MFIS, of about 10% was observed on Ni₂MnGa, the FSMA prototype [1]. The high fragility of this alloy was the driving force to search for new FSMA as Fe-Pt, Fe-Pd, Fe-Ni-Co-Ti or other Heusler alloy like Co-Ni-Al(Ga), Ni-Mn-Al [2-6]. Recently, a thermoelastic martensitic transformation in the ferromagnetic state, associated with a shape memory effect was evidenced Ni-Fe-Ga off-stoichiometric Heusler type alloy [7]. For the stoichiometric Ni₂FeGa, MT is around 145K being ferromagnetic until 693 K. For the off-stoichiometric compounds, the martensitic transition shifts to higher temperature with increasing Ni content [8]. The advantage, in field of application, of Ni-Fe-Ga alloys is its better ductility which is associated with the presence of a second phase γ – (face –centered cubic A1 structure) [7].

The purpose of this work is to put in evidence the martensitic transformation via different type of physical measurements and to analyse the effect of cobalt substitution of iron or, respectively, of nickel in some Ni-Fe-Ga off-stoichiometric Heusler alloys.

2. Experimental

The polycrystalline samples with nominal composition Ni₅₅Fe_{20-x}Co_xGa₂₅ ($x=0, 1$) and Ni_{54-y}Co_yFe₂₀Ga₂₆ ($y=1, 2$) were prepared by arc melting in argon atmosphere. The alloys were remelted three times to ensure the homogeneity. Subsequently, a thermal treatment was performed in high vacuum for 25h at 950 °C followed by a quenching in iced water.

Room temperature X-ray diffractions were performed using a Seifert diffractometer (Cu K α radiation). The phase transformation measurements were performed by differential scanning calorimeter (DSC- 204 F1 Phoenix, Netzsch) with a scanning rate of 10K/min. Informations about microstructure was obtained by transmission electron microscopy (TEM) using a JEOL 200CX microscope operated at 200 kV. The TEM specimen has been prepared by mechanical polishing followed by ion milling on a Gatan Duo Mill installation.

The temperature dependences of the electrical resistivity were carried out by standard four-probe measurements in a measuring platform from Cryogenic Ltd. The low temperature magnetic measurements were performed with a High Field measurement system (Cryogenic Ltd.) in the VSM mode. Above room temperature, the magnetic measurements were done using a Weiss-type home made balance.

3. Results and discussion

The most accessible method to check the existence of a first order transition is via calorimetric measurements. The DSC results presented in Fig. 1 evidence the reversible martensite transformation for all reported samples. By cooling, at a temperature M_s (martensite start), the free energy of the martensite state become lower than the free energy of the austenite state and the transformation is initiated. The transformation continues to evolve as the temperature is lowered until the structural transformation is completed at a temperature denoted by M_f (martensite finish). The reverse transformation takes place by heating; it begins at a temperature A_s (austenite start) and continues until the entire material reaches the austenite phase at a temperature denoted by A_f (austenite finish). Throughout the transformation a latent heat is release (exothermic process) during the A-M transformation and absorbed (endothermic process) during the reverse M-A transformation.

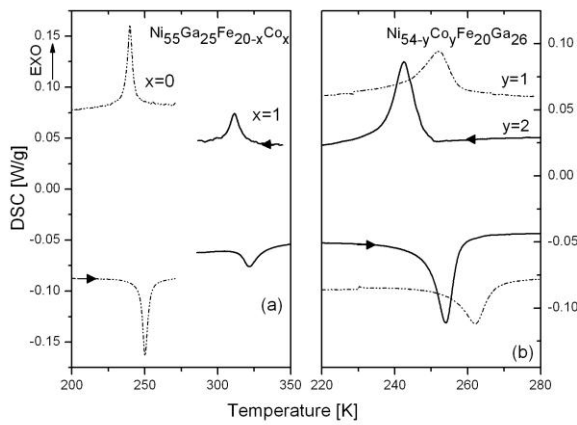


Fig. 1. DSC curves of $Ni_{55}Fe_{20-x}Co_xGa_{25}$ (a) and $Ni_{54-y}Co_yFe_{20}Ga_{26}$ (b) alloys. The MT shifts to higher temperatures for the alloys with cobalt substituting iron and to lower temperatures for those with cobalt substituting nickel.

The characteristic transformation temperatures (M_s , M_f , A_s , A_f), enthalpies (ΔH_M and ΔH_A) together with the valence electron concentrations (e/a) and the Curie temperatures for the studied alloys are presented in Table 1.

Table 1. Composition, characteristic temperatures - Martensite start (M_s) and finish (M_f), Austenite start (A_s) and finish, (A_f), transformation enthalpies (ΔH_M and ΔH_A), valence electron concentrations (e/a) and Curie temperatures (T_c) 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)	e/a	T_c [K]
$Ni_{55}Fe_{20}Ga_{25}$	244.5	235	2.055	246	254.5	-2.06	7.85	305
$Ni_{55}Fe_{19}Co_1Ga_{25}$	322	302	1.21	307	333	-1.39	7.86	329
$Ni_{53}Co_1Fe_{20}Ga_{26}$	257	244	2.53	255	267	-2.77	7.77	324
$Ni_{52}Co_2Fe_{20}Ga_{26}$	248	237	2.69	249	257	-2.61	7.76	345

By analyzing the DSC measurements can be concluded that the MT temperatures increase dramatically ($\sim 80^\circ$) for the alloy in which iron is substituted by cobalt, the effect being opposite and less pronounced ($\sim 10^\circ$) in those alloys where nickel is replaced by Co. It is generally accepted that MT temperatures increase with the augment of valence electron concentration per system and with the reducing of the volume of the unit cell [9, 10]. The observed changes in the MT temperatures are in qualitative agreement with the valence electron concentration variation for both series of alloys. It is worth mentioning that the valence electron concentrations given in Table 1, were estimated based on the atomic concentration per formula unit and considering for the number of valence electrons 10, 9, 8 and 3 for nickel, cobalt, iron and gallium, respectively. To understand the more pronounced M_s increase in the alloys with Co substitution for Fe, the atomic size factor had to be taken into account; the atomic radii are 0.1246 nm for Ni, 0.1252 nm for Co and 0.1274 nm for Fe [11]. Thus, substitution of Fe atoms by Co would cause a larger unit-cell volume reduction than the volume increase created by replacing Ni atoms by Co, which can stand for the higher change of MT temperatures in $Ni_{55}Fe_{20-x}Co_xGa_{25}$ alloys.

Previous studies [12] concluded that the crystalline structure for Ni-Fe-Ga changes from austenite with B2 (disordered Heusler -type) or L2₁ (Heusler -type) structure to different martensitic structure, depending on composition. There are two basic martensitic symmetries: tetragonal and orthorhombic named non-layered martensite. In addition, the basic structure may be modulated by shuffling atomic planes; the (110) plane undergoes a periodic shuffling in the [1, -1,0] direction, while every 5th (or 7th) (110) plane remains in its original position giving rise to the so called 5 (or 7)- modulated structure. The abbreviations 5M (or 7M) or 10M (14M) seen in literature stand for monoclinic unit cell, considering the B2 and respectively L2₁ atomic ordering of the cubic austenite phase [13]. The problem of martensite nomenclature arises from the fact that

martensite has a long ordering period structure and in the interest of describing more precisely the crystal structure, the stacking order must be specified too.

Room temperature X-ray diffraction measurements of the alloys treated at 950 °C reveal a bi-phase structure (Fig. 2). Common for all the compounds, is the presence of a γ face centered cubic (fcc) phase. Besides this secondary fcc phase, the main phase is in agreement with the DSC results. For the alloy with MT above room temperature (RT), the main phase show the characteristic peaks of the martensite tetragonal phase ($L1_0$). When the austenite is the stable phase at room temperature (Ms being lower than RT), the XRD patterns point out to a B2 structure.

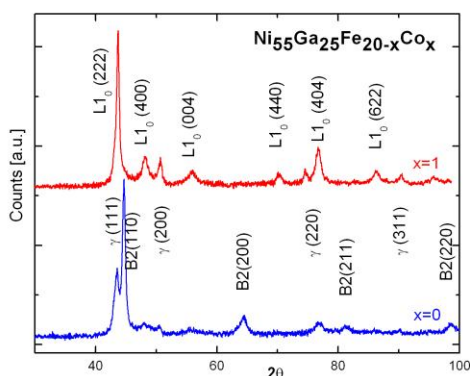


Fig. 2. Room temperature XRD patterns of $Ni_{55}Fe_{20-x}Co_xGa_{25}$ ($x=0$ and $x=1$). Apart from the peaks attributed to a secondary, un-transforming, face centered cubic phase, γ , the main peaks are indexed with a non-modulated tetragonal structure ($L1_0$ martensite) or with a B2 (austenite) structure, in concordance with the DSC results.

Two specimens of samples $Ni_{55}Fe_{20-x}Co_xGa_{25}$ ($x=0, 1$), prepared by mechanical polishing followed by ion milling on a Gatan Duo Mill installation, have been examined by transmission electron microscopy (TEM) using a JEOL 200CX microscope operated at 200 kV.

The images on the sample $Ni_{55}Fe_{20}Ga_{25}$ (Fig. 3) reveal a micron grain size and each grain has a tweed structure characteristic for a premartensite phase.

From the Selected Area Electron Diffraction (SAED) pattern of specimen area oriented along the $[110]$ zone axis presented in the inset of Fig. 3 the single crystal austenitic structure with $\langle 1, -1, 0 \rangle$ orientation is observed.

As one can notice on the TEM image for the $Ni_{55}Fe_{19}Co_1Ga_{25}$ (Fig. 4) corresponding to the analyzed SAED pattern, the twin stripes have widths in the 5-15 nm range. Two families of fine fringes may be observed, one set along an almost vertical direction and another set along an oblique direction. The vertical fringes are well defined and separated at 2 nm. The other fringes are more or less diffuse and show a variable period around 1.8 nm, as revealed by the SAED pattern. This is an expected result, since the sample is in martensitic phase at room temperature.

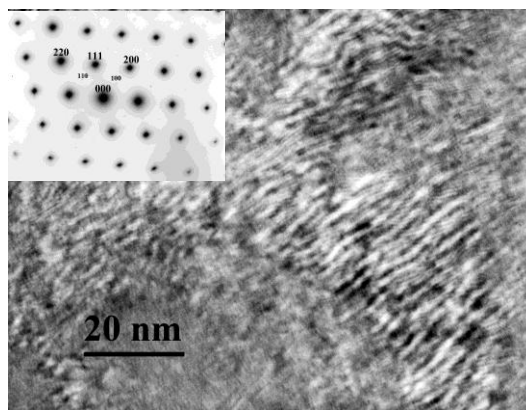


Fig. 3. A highly magnified detail. Notice the fine modulation with periodicity 1.1 nm and moiré type fringes of approx 2.5 nm (inset: SAED image of one of the grains from the main image in Fig. 3; one can notice the single-crystal austenitic phase $\langle 1, -1, 0 \rangle$ oriented).

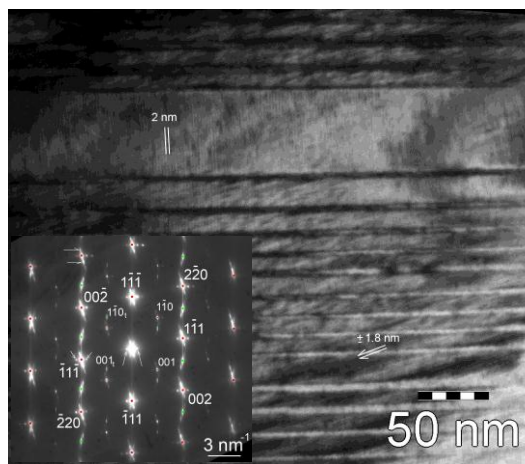


Fig. 4. TEM image of the twinned region corresponding to the SAED pattern (inset: SAED pattern of a specimen region oriented along $B = [110]$; tetragonal system: $a = b = 3.78 \text{ \AA}$, $c = 3.29 \text{ \AA}$, $c/a = 0.87$; twinning plane (-111)).

The SAED pattern shows that the matrix and twin diffraction spots are surrounded by satellite spots. The separation distance between the satellites is independent of the diffraction spot order (hkl indices), which means that they are not caused by a Moiré effect, but by a periodic structural modulation. The relation between the period of fringes and the lattice parameters of tetragonal system suggests 5M modulation for the martensitic structure.

A first order phase transition may strongly influences the transport properties. Particularly, in the temperature range of MT, the experimentally observed $\rho(T)$ data shows anomalies for the FSMAs [14] but also for the nonmagnetic SMA like NiTi [15]. In Fig. 5 the temperature dependence of resistivity for $Ni_{52}Co_2Fe_{20}Ga_{26}$ alloy is presented. A large hysteresis effect observed between the cooling and heating curves is a characteristic of a first order phase transition. The DSC measurements,

presented for comparison on the same graph, validate the fact that hysteresis is located in the temperature region where the two phases coexist.

By cooling, and hence, passing from austenite to martensite phase, at M_s , the resistivity shows an increase of about 20%. (In variance, by heating the sample through A_s , the resistivity decreases). The abrupt variation of the electrical conductivity in the MT vicinity had to be assigned to an important change in the processes that influences the transport properties: electron–phonon and electron–magnon scattering cross-sections or the residual resistivity. According to the Bloch–Grüneisen function, the electron–phonon contribution is mainly controlled by the Debye temperature, θ_D . From specific heat measurements [16] one can deduce that θ_D is larger for the martensite than for the austenite state, consequently giving rise to an opposite resistivity variation at MT. The electron–magnon scattering depends on both the magnetic moment and the Curie temperature: in the martensite state [17]. For the martensite state the magnetic moment is only slightly higher than in the austenite state however the Curie temperature is difficult to evaluate. Since the mentioned effects are small, the residual resistivity must play an important role. The crystalline disorder appearing once nucleation of the martensite (phase) begins and the low symmetry of the new established phase are valuable reasons to justify the sudden resistivity increase at M_s and its hysteretic behavior.

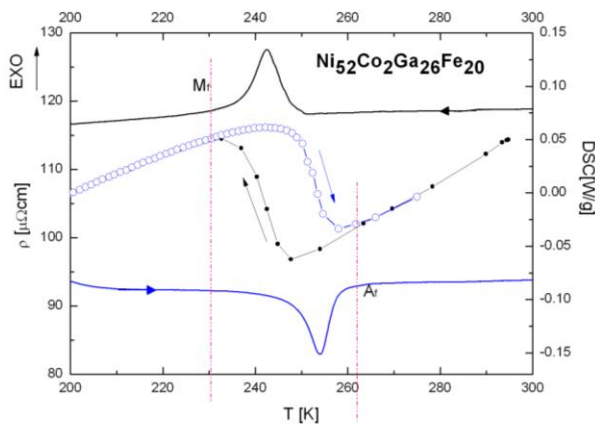


Fig. 5. Thermal variation of the electrical resistivity and DSC curves for $Ni_{52}Co_2Fe_{20}Ga_{26}$ alloy. A good correspondence between all the involved transition temperatures in the DSC curves and the $\rho(T)$ scans can be observed.

Low field thermo-magnetic measurements were performed by cooling down the samples, in a constant magnetic field of 0.04 T, from room temperature to a temperature well below the transformation temperature and warming them up again, until the magnetization is vanishing. Measurements performed on the alloys with MT below room (Fig. 6) evidenced two magnetic phases. The majority austenite phase shows an order–disorder magnetic transition temperature above room temperature which slightly rises with cobalt content, in good agreement

with other reported results [18]. There is also a secondary phase, with higher Curie temperature, that was assigned to the γ -fcc phase appearing in X ray diffraction patterns. The thermo-magnetic experimental data suggest an increase with increasing cobalt content of the volume fraction of this secondary phase.

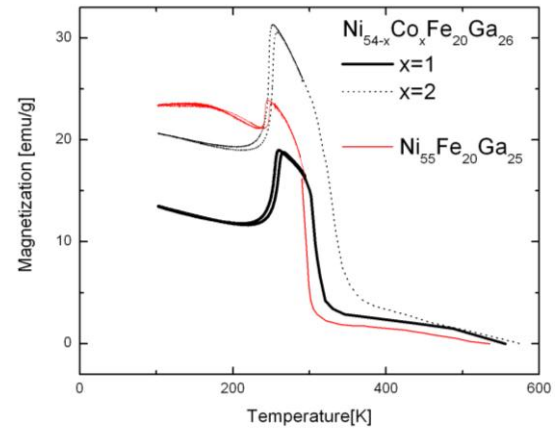


Fig. 6. Low field VSM thermo-magnetic scans for $Ni_{55}Fe_{20}Ga_{25}$ and $Ni_{55}Fe_{20-x}Co_xGa_{25}$ alloys evidence two magnetic phases. The Curie temperatures of both the majority austenite phase and the fcc secondary phase increase with cobalt content.

In the temperature region of MT a hysteretic anomaly is evidenced in the thermal variations of the magnetization between the cooling and the heating curves. Fig. 7 is a detailed view of the thermo magnetic data points in the vicinity of MT. By cooling at a certain temperature, magnetization shows a distinct drop and then by warming up at a slightly higher temperature shows an increase. The location of the critical points of this thermo-magnetic hysteresis correspond well with all the involved transition temperatures between the high temperature austenite phase and the low temperature martensite phase revealed by DSC measurements. Therefore, the thermo-magnetic measurements represent a powerful tool to study the influence of the magnetic field on phase transitions FSMA.

This evident change of the magnetization value when passing from austenite to martensite state certainly proves a change of magnetocrystalline anisotropy during the transformation. At low fields, due to its smaller magnetocrystalline anisotropy, the austenite phase is easier to be magnetized than the martensite phase, giving rise to a higher magnetization. By cooling the sample and back to the martensite state with higher anisotropy, the low magnetic field does not succeed to rotate the magnetic moments in the field direction, or to produce enough driving force to move the twin boundary of the variant whose easy axis is aligned with the field. Therefore, the measured martensite magnetization is small. The higher difference between the austenite and martensite magnetization, the stronger martensite magnetocrystalline anisotropy is.

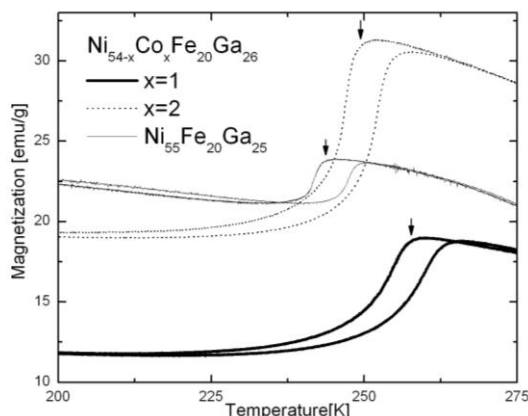


Fig. 7. Detailed view of the thermo-magnetic measurements (at constant magnetic field of 40mT) on cooling and heating for $\text{Ni}_{54-x}\text{Co}_x\text{Fe}_{20}\text{Ga}_{26}$ and $\text{Ni}_{55}\text{Fe}_{20}\text{Ga}_{25}$ alloys. The magnitude of magnetization drop by passing from austenite to martensite is a measure of the difference in magnetic hardening between the two phases. The arrows mark M_s temperatures obtained by DSC measurements.

The results presented in Fig. 7 suggest that martensite magnetocrystalline anisotropy is increasing by increasing the cobalt content. This assumption is also supported by the results obtained by Morito et al [19, 20] on $\text{Ni}_{51}\text{Fe}_{18}\text{Ga}_{27}\text{Co}_3$ and $\text{Ni}_{49}\text{Fe}_{18}\text{Ga}_{27}\text{Co}_6$ alloys. They found that the magneto-crystalline constants, evaluated on monocrystals in single-variant martensite phase near the transition temperature, increase from $4.7 \times 10^5 \text{ erg/cm}^3$ to $1.2 \times 10^6 \text{ erg/cm}^3$ with the cobalt content.

4. Conclusions

Ni-Fe-Ga intermetallic compounds with Co substitutions at Ni and Fe sites were prepared and characterized with respect to their structural, resistivity and magnetic behavior during the martensitic transformation.

The opposite variation of the phase transition temperatures, in the alloys with cobalt substitution for nickel or iron, is found in agreement with valence electron concentration and unit cell volume change. A hysteretic behavior on the $\rho(T)$ data and on the thermo-magnetic measurements in the temperature region of martensite transformation has been evidenced. The increased resistivity in the martensite phase was ascribed to the rise of the residual resistivity due to the decrease of carriers' mobility, as the carriers are scattered at martensite twin boundaries. The magnetization jumps in the temperature region of martensitic transition have been discussed with respect to the magnetic anisotropies of the austenite and martensite phases.

Acknowledgements

This work has been carried out with the financial support of the Romanian Ministry of Education (Projects PN09-450103 and PN72-188/ 2008).

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