Magnetocaloric effect in Ni-Fe-Ga Heusler alloys with Co and Al substitutions

F. Tolea a, M. Sofronie, A. D. Crisan, M. Tolea, M. Valeanu

National Institute of Materials Physics, POB MG-7, 77125 Bucharest-Magurele, Romania

Abstract. The functionality of the ferromagnetic shape memory alloys is related to the martensitic and magnetic order-disorder transformations, both of which may be tailored by doping with other elements or by suitable thermal treatments, so that alloys with concomitant (or sequential but close) structural and magnetic phase transitions may be obtained. Concerning the magnetocaloric applications, it is assumed that the thin melt-spun ribbons assure a more efficient heat transfer. In the present work we investigate the influence of Co and Al substitutions on magnetocaloric effect characteristics of NiFeGa in bulk and also in ribbons prepared by melt spinning method and subjected to different thermal treatments. X-ray diffraction, differential scanning calorimetry, magnetocaloric and magnetoresistive characterizations have been performed. The results highlight the differences between the bulk and the ribbons (both as prepared and annealed) and the role of substitutions.

1 Introduction

Ferromagnetic shape memory alloys (FSMAs) are a new class of smart materials which exhibit the well known martensitic transformation (MT) bellow Curie temperature and their functionality is related, besides the magnetic order-disorder transition, also to a first order phase transformation [1]. The huge magnetic field induced strain (MFIS) exhibited by the Ni2MnGa alloy [2] justified the increased interest in FSMAs with Heusler disordered B2 austenite structure. Further developments indicated the off-stoichiometric Ni-Fe-Ga alloys as good candidates to replace the brittle Ni-Mn-Ga [3,4,5] due to improved mechanical durability when experiencing a reversible austenite-martensite transformation.

The martensitic phase in these alloys features structural twinning, responsible for their good magnetoelastic properties. The precipitation of the secondary FCC (γ) phase is inherently found for Ni-Fe-Ga alloys with Ga≤27%at, this composition being located in the β+γ two phase zone; in addition, this phase, located mainly at the grain boundaries, is responsible for the improved ductility of Ni-Fe-Ga based alloys [6]. New families of Heusler type alloys such as Ni-Mn-(Ga, Al, In, Sn) [7,8,9], Co-Ni-(Ga, Al) [10, 11], Ni-Fe-Al [12], that undergo a MT, were intensively studied and besides the magnetic shape memory, magneto-caloric effect (MCE), magneto-resistance effect (MRE), magnetic-field-induced strain (MFIS) have been investigated. All these phenomena appeared in systems undergoing magnetic and structural phase transitions, simultaneously or delayed, but not very likely in the same alloy.

The MCE or adiabatic temperature change represents the effect of heating or cooling of a magnetic material by the application of a magnetic field. This intrinsic magneto-thermodynamic phenomenon is related to the magnetic entropy associated with the spin structure of an alloy and its change under application of an external magnetic field [13]. Several rare earth based systems (Gd5(SiGe)4, DyMn2Ge, Gd RuGe2) exhibiting magnetic and structural phase transitions occurring in the same temperature range, have been reported to show very large MCE [14].

FSMA of the Heusler type materials exhibit simultaneously ferromagnetism and thermoelastic structural MT. As effect of coupling between the structural and magnetic transitions (magnetostructural coupling) a giant MCE is expected, promoting these alloys as potential performing magnetic refrigerant materials. Also, transport properties depending on crystal structure and phase transformations may offer another possibility for practical use of FSMAs: switching devices or actuators, displacement/force sensors, and motion dampers. Because ductility is an important issue in the application of FSMA as magnetocaloric materials, MCE in Ni-Fe-Ga alloys was investigated [13,15,16]. Numerous substitutions have been tested on Ni-Fe-Ga alloys in order to increase the Curie temperature, magneto-crystalline anisotropy or the mechanical properties [6, 17, 18, 19]. Morito et al. [20] found that the addition of Co in Ni-Fe-Ga increases the magnetocrystalline anisotropy energy and the Curie temperature, while the MT is around room temperature. These findings motivated our study of different

a Corresponding author: felicia.tolea@infim.ro
substitutions possibly of fundamental but also applicative interest.

In the present work, we have investigated the influence of Co and Al addition on the magnetic properties and MT characteristics of NiFeGa as bulk and also in ribbons prepared by melt spinning method and subjected to different thermal treatments. We chose Ni$_{52}$Co$_2$Fe$_{20}$Ga$_{26}$ and Ni$_{52}$Fe$_{20}$Co$_2$Ga$_{23}$Al$_3$ alloys, prepared as bulk or ribbons, with the same valence electrons concentration (e/a=7.76). It is known that the valence electrons concentration has a direct effect on the MT temperature [21], making it insightful to compare alloys in which the same e/a value is obtained by different substitutions, in particular in regarding the MCE and MR effects.

Reversible thermo-elastic transformation was highlighted in all samples. The Curie temperatures slightly decrease with Al addition. All investigated alloys have MT temperatures below $T_C$, so qualify as FSMAs.

From the studied samples, the most appropriate material for magnetic refrigeration turned out to be the Ni$_{52}$Co$_2$Fe$_{20}$Ga$_{26}$ alloy, prepared as ribbons and annealed at 400°C, which shows relatively close magnetic and structural transitions near room temperature.

2 Experimental

Ingots of nominal composition of Ni$_{52}$Co$_2$Fe$_{20}$Ga$_{26}$ and Ni$_{52}$Fe$_{20}$Co$_2$Ga$_{23}$Al$_3$, denoted Co2 and respectively Co2Al3, were prepared from high purity elements, by arc melting under argon protective atmosphere. Small pieces of each ingot were preserved as bulk reference and subjected to a thermal treatment in high vacuum for 25 h at 1223 K, followed by a quenching in iced water. The remaining ingots were inductively melted in quartz tubes under argon atmosphere and rapidly quenched by melt spinning technique (Buhler Melt Spinning Device). The melt spun ribbons were subjected to thermal annealing: 10 minutes at 400°C (TT1) and 2 minutes at 900°C (TT2) followed by rapid cooling. Each samples have been tested for the MT by thermal analyses using the differential scanning calorimeter (Netzsch DSC 204 F1 with the Proteus Software) in the temperatures range 80-400K with different scanning rate under He protective atmosphere and the MT enthalpy and characteristic temperatures were evaluated. The identification of the phases and the structural study was performed by X-ray diffraction using a Bruker D8 Advantage diffractometer in the Bragg–Brentano geometry, with Cu Ka radiation, at room temperature (RT).

The MT temperatures and enthalpies have been correlated with crystalline structure and microstructure on “as quenched” and after different thermal treatments to outline the special features of the MT in textured polycrystalline ribbons obtained by melt spinning. Magnetic characterization [M(T) in low and high fields; M(H)] was done with the SQUID magnetometer in RSO mode (for T<350K); the resistivity and magnetoresistance of the samples were measured by standard four-probe method using QD-PPMS-14.

3 Results and discussions

3.1. Structure

The room temperature XRD diffractogram performed on Co2_AQ ribbons is highlighting the coexistence of the martensitic phase with modulated tetragonal structure with disordered B2 austenite structure. For Co2Al3_AQ ribbons, the room temperature XRD pattern shows only peaks belonging to disordered austenite B2 structure proving the martensite transformation below room temperature. Heat treatment at relatively low temperatures, 400°C, has the effect of relaxation of frozen tensions during rapid cooling process in ribbons, which is manifested by the decrease in martensitic transformation temperatures. Thus, Co2_400 alloy has at room temperature the ordered L2$_1$ cubic structure of Heusler alloys type specified in austenite. The thermal treatment at 900°C has a much more dramatic effect on the MT temperature and the explanation is given by XRD patterns showing the characteristic lines of the cubic structure of austenite but in addition there is a secondary phase - γ - face-centered cubic phase.

XRD pattern for both bulk compositions evidence, apart from the main peaks corresponding to the B2 austenite structure, some fcc γ peaks but there are also several peaks belonging to the non modulated martensite (L1$_0$). This martensite peaks are probably stress induced during sample preparation by polishing. Co2_Bulk sample evidence the austenitic B2 structure and secondary γ FCC phase at RT.
3.2 Calorimetry data

DSC measurements were performed over a temperature range between 100 K and 400 K. The thermoeelastic transformation was evidenced on all samples. The as prepared ribbons exhibit the highest transformation enthalpy (Q). The MT characteristics, namely the forward (TM) and reverse peak (TA) temperatures and the mean value of the transformation heat (calculated as the average between the forward and reverse transformations) for the discussed alloys are given in Table 1. From the analysis of structural and DSC data results that characteristic temperatures of martensitic transformation are strongly influenced by the substitutions. Both samples show the same 7.76 value for e/a (Fig.2a), but replacing 3 Ga atoms with Al, a significant decrease of the MT temperatures occurs. This is probably an atomic size effect; although the Al atomic radii is lower than for Ga the lattice constant for the B2 structure calculated from the XRD patterns remain unchanged for both compositions suggesting a decrease of the system energy due to a lattice relaxation and the stabilization of the austenite phase. The influence of the thermal treatments on the MT temperatures of the both compositions is illustrated in Fig.2b and Table 1.

Table 1. DSC peak transformation temperatures (TM and TA for the direct and reverse MT respectively), the Curie temperature Tc and the average transformation heat Q (calculated as average between the direct and reverse transformation) for studied samples as bulk (Bk) or as quenched (AQ) and thermal treated ribbons (at the indicated temperature). Entropy variation ΔS was evaluated only for the three samples presented in Fig.4b.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TM/TA (°C)</th>
<th>Q (J/g)</th>
<th>ΔS (J/KgK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co2_Bk</td>
<td>243/255</td>
<td>345</td>
<td>2.6</td>
</tr>
<tr>
<td>Co2_AQ</td>
<td>294/308</td>
<td>360</td>
<td>3.6</td>
</tr>
<tr>
<td>Co2 2m400C</td>
<td>269/284</td>
<td>370</td>
<td>2.6</td>
</tr>
<tr>
<td>(TT1)</td>
<td></td>
<td></td>
<td>-2.2</td>
</tr>
<tr>
<td>Co2 2m900C</td>
<td>226/250</td>
<td>340</td>
<td>2.14</td>
</tr>
<tr>
<td>(TT2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co2Al3_Bk</td>
<td>220/230</td>
<td>3</td>
<td>1.3</td>
</tr>
<tr>
<td>Co2Al3_AQ</td>
<td>248/262</td>
<td>350</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-1.6</td>
</tr>
<tr>
<td>Co2Al3_20m</td>
<td>244/259</td>
<td>365</td>
<td>2.74</td>
</tr>
<tr>
<td>400 (TT1)</td>
<td></td>
<td></td>
<td>-0.86</td>
</tr>
<tr>
<td>Co2Al3_20m</td>
<td>181/150</td>
<td>340</td>
<td>0.15</td>
</tr>
<tr>
<td>900 (TT2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3 Thermomagnetic data

With respect to the magnetic behavior of Co2 alloy, AQ and thermal treated ribbons, Fig.3a shows the temperature dependence of magnetization, measured in low magnetic field. Comparatively to the AQ alloys, the Curie temperature for annealed at 400 C ribbons is slightly higher reflecting a higher atomic order and the relaxation of the quench-in strains induced by the processing route.

Interestingly however, for both compositions, the thermal treatment at 900 C does not produce a further increase of the magnetic ordering temperature (Tc). The effect of further structural refinement and lattice relaxation is counteracted, as much as to a decrease, by the precipitation of the secondary γ phase, which depletes the matrix in 3d elements, inducing also a decrease of Tc [22].
3.4 Magnetocaloric effect evaluation

To highlight the magnetocaloric effect, we choose the Co2 sample annealed for 10 min at 400°C, with MT temperatures presented in Fig.3a in a range of temperature (<380K) that allowed full characterization of magnetic alloy with SQUID device.

In order to quantitatively characterize the MCE, an indirect technique to evaluate the \( \Delta Sm \) was used. According to Maxwell relation, \( \Delta Sm \) can be calculated by means of magnetic measurements:

\[
\Delta Sm(T, H) = \frac{H}{0} \left( \frac{\partial M}{\partial T} \right)_{H} dH,
\]

whose discrete version (for isotherms measured at certain field only) reads:

\[
\Delta Sm = \sum_{n} \frac{(M_{n+1} - M_{n})}{(T_{n+1} - T_{n})} \Delta H_{n}
\]

Magnetization isotherms in 4T maximum applied field (measured with 5K temperature increment) (inset Fig.4a) and also isofield magnetization curves at different magnetic fields (Fig. 4a) were used to evaluate the magnetocaloric effect. Entropy variations versus temperature are shown in Figure 4b.

For annealed (at 400°C) Co2 sample, note the occurrence of two maximum magnetic contributions to entropy, the left one in the area of martensitic transformation and the second in the order-disorder magnetic transition temperature ranges. The change in entropy is higher in the MT area whereas the refrigerator capacity (related to the peak area) is higher in Tc area. We have obtained a value of 2.2 J/KgK for the entropy change in Co2 alloy, but estimate that by further tailoring the alloy composition and using proper thermal treatments to tune the magnetic and structural transition temperatures closer (or even concomitant) this value may be improved.

3.5 Magnetorezistive effect

To characterize the magnetorestance in the martensitic transformation range, we actually measured the temperature variation of the resistivity in zero and 5T
magnetic fields (inset Fig 5a) and also the continuous variation of the resistivity with magnetic field at two fixed temperatures, first in the martensite and the second in the austenitic phase for the as prepared and annealed Co2Al3 samples (Fig5b).

An interesting effect of non-monotonous resistance variation (with high amplitude oscillations as the magnetic field is varied) can be seen in Fig.5b for the martensite phases of Co2AI3, both AQ and annealed at 400 C. We attribute this effect to the magnetic field effectively influencing the orientation of the martensite variants which in turn reflects in the total resistance. Changes in domains orientation (and/or domains walls) can in principle both decrease or increase the resistance leading to the observed oscillations, which are also found to be: (i) more pronounced for the AQ martensite sample (ii) starting at lower magnetic fields for the annealed sample in martensite phase and (iii) absent for the austenite samples. Results for the Co2 composition are similar (with less pronounced oscillations in the martensite phase, and are not given here).

4 Conclusions

We have studied the effect of Co and Al substitutions on the magnetocaloric and magnetoresistive properties of NiFeGa ferromagnetic shape memory alloys. The substitutions labeled Co2 and Co2AI3 (see description in text) have been chosen to assure the same e/a valence electrons concentration. The alloys were prepared as bulk and also as melt-spun ribbons - an unconventional preparation route that also allows subsequent tuning of the stress release and crystallites growth by thermal treatment.

All samples presented reversible thermo-elastic transformations. As a general rule, the martensitic transformations temperatures and enthalpies decrease with increasing the temperature of the thermal treatments (on the melt-spun ribbons).

Importantly however, such tuning presents an optimum in respect to the magnetocaloric effect. The highest magnetic field induced entropy variation was found for the Co2 alloy annealed for 10 minutes at 400°C ($\Delta S_m = 2.2$ J/KgK). This can be associated with the fact that the magnetic and structural transitions are in close vicinity (although we did not obtain a coincidence on it).

The magnetoresistive measurements showed a non-monotonic variation of the martensite samples resistivity with the magnetic field, possibly due to realignment of the martensite variants. Also, the MR effect is higher for the austenite than the martensite for all samples.

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References