JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 4, April 2010, p. 854 - 857

Some physical properties of Ni_2MnGa Heusler shape memory alloys with substitutions

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Ni_2MnGa Heusler alloy is well known as potential smart material, is ferromagnetic and have a $L2_1$ type structure at RT. Our aim is to find structural and magnetic transitions in $(Ni_{2-x}Co_x)(Mn_{1-y}Co_y)(Ga_{1-z}Al_z)$ alloys. Some $(Ni_{2-x}Co_x)(Mn_{1-y}Co_y)(Ga_{1-z}Al_z)$ alloys were melted in a furnace in Ar atmosphere, homogenized at 1273 K and aged at 1073 K 48 hours. Phase composition and structural parameters (lattice constants, microstrains, average size of coherent blocks etc) were determined by XRD at room temperature. Magnetic measurements were performed by using a Foner type magnetometer at H = 4 kOe, between 77 and 673 K. Substituted alloys contain orthorhombic and cubic phases. The presence of Co leads to an increase of Curie temperature, but no martensite-austenite transition was observed in investigated range of temperatures for alloys substituted with Co.

(Received April 7, 2010; accepted April 26, 2010)

Keywords: Shape memory alloy, Heusler alloy, Martensite, Curie temperature

1. Introduction

Some Heusler alloys, as Co_2MnGa, Ni_2MnGa, Ni_2MnAl, Co_2MnAl etc exhibit a shape memory effect (SME), that are characterized by a martensitic transition (MT) from a high temperature phase (β) to close-packed low-temperature phases (*M* phases) [1-3]. Heusler alloys are possible candidates for magnetic shape memory (MSM) alloys, due its high Curie and martensitic/austenitic transformation temperature. The B2 crystallographic state has been reported as antiferromagnetic or spin-glass, while the $L2_1$ phase is associated with the ferromagnetic state. The SME of the Ni_2MnGa and Ni_2MnAl alloys can be controlled by an applied magnetic field. Giant magnetic-field-induced strain (MFIS) caused by the rearrangement of martensite variants in ferro-magnetic state, has attained considerable attention during last years, the Ni_2MnGa and Ni_2MnAl alloys are under investigation now as promising candidates for practical applications [4-6].

There is a large difference between the magnetic properties of a quenched B2 phase (antiferromagnetic and/or spin glass state) and the $L2_1$ phase, which is ferromagnetic and exhibts a martensitic transformation at low temperatures. The temperature of the martensitic transformation and the Curie temperature are very sensitive to the chemical composition, the ferromagnetic state being observed only in a very limited area of composition.

Our aim is to determine the influence of Co and Al substitution on structure and magnetic properties of some as cast/sintered and treated $(Ni_{2-x}Co_x)(Mn_{1-y}Co_y)(Ga_{1-z}Al_z)$ stoichiometric Heusler alloys.

2. Experimental

The $(Ni_{50-x}Co_x)(Mn_{25-y}Co_y)(Ga_{25-z}Al_z)$ alloys ($Ni_{50}Mn_{25}Ga_{25}$ – symbol NMG; $Ni_{25}Co_{25}Mn_{25}Ga_{25}$ – NCMG; $Ni_{50}Mn_{12.5}Co_{12.5}Ga_{25}$ – NMCG; $Ni_{50}Mn_{25}Al_{12.5}Ga_{12.5}$ – NMAG), were obtained by arc melting the constituent elements in an inert Ar atmosphere and then suction chill casting into copper moulds to produce a sample in the shape of bands or rods. Remelting the alloys several times ensured homogeneity. These alloys were betatized and homogenized at 950ºC for 48 h. The specimen was cooled in air at room temperature (20ºC). A part of the alloys were prepared from corresponding mixtures of Ni, Mn, Co, Ga and/or Al metallic powder, presintered at 600°C/3h + 750°C/4h, sintered at 1200°C/3h in vacuum and treated 24h at 850°C in Ar.

The phase composition, the lattice type and the unit cell constants were also determined, using the literature data, the CheckCell and Rietveld type programs. The intensities and the corresponding Bragg angle were achieved from a DRON 2,0 diffractometer, with a data acquisition system and CoK_α filtered radiation. The data were corrected for the goniometer zero and the offset of the sample reported to the goniometer axis.

The specific magnetization and the Curie temperatures were obtained with a vibrating sample magnetometer (VSM) and a corresponding data acquisition system. A Ni sphere (Erba, Italy) was used as etalon. In agreement with the data used in references we considered that the magnetic moments of Mn, Ni and Co are 3.35, 0.59 and 1.0 μ_B; the Al and Ga magnetic moments are too small to be considered. The atomic radii of Mn, Ni, Co, Ga and Al are 0.137, 0.125, 0.125, 0.153 and, respectively, 0.143 nm.

3. Results and discussion

Brown et al. shown that Ni_2MnGa have a $L2_1$ structure at T > 400 K and orders ferromagnetically at T_C ≈ 365 K [7]. A superstructure appears at T < 260 K, known as premartensitic transformation. This phase, known as the premartensitic phase, persists down to the structural phase transition at T_M ≈ 200 K. Below 200 K, the structure is characterized by an orthorhombic unit cell with lattice parameters $a_{ortho} = a_{cubic}/\sqrt{2}$, $b_{ortho} = 3a_{cubic}/\sqrt{2}$, $c_{ortho} = a_{cubic}$ (Pnnm) [7]. At $T < T_M$ Ni_2MnGa has a related orthorhombic super-cell with $b_{ortho} \approx 7a_{cubic}/\sqrt{2}$.

Zuo et al. reported a correlation between the change in the magnetization change with temperature, M(T), and the premartensitic transition, T_p, for the stoichiometric Ni_2MnGa alloy [8]. The variation of magnetization with temperature at various applied field shown an evidence of a premartensitic transition (a peak in M(T) at T_p) well above the T_M temperature. Zuo et al. observed a dependence of premartensitic temperature of the magnetic field intensity [8]. The substitution of Ni with Co should lead also to a disorder of the atoms on (4b) position, but the level of lattice strains should remains unchanged, because the atomic radii of Ni (125 pm) is the same as those corresponding Co (125 pm). On other hand, the substitution of Mn with Co or Ga with Al, should increase the distortion level of the lattice. For an increase with a small amount of Ni (or a small decrease of Al/Mn) content and a chaotic distribution of the Mn and Ni atoms on (4b) sites, the $L2_1$ constant lattice should decreases with the increase of Ni concentration in the samples. We have used large substitution, which can modify substantially the phase composition and/or the structure of major phase. For illustration, the NMG alloy homogenized at 950ºC for 48 h, at room temperature (RT) show a β solid solution monophasic structure (Fig. 1). By substitution of half of Mn quantity in this alloy with Co (NMCG alloy) in the same heat treatment conditions, at RT the structure become biphasic (needle-shaped martensite – light color and residual β phase – dark color) (Fig. 2), this meaning an unfinished martensitic tranformation. Simultaneously presence of these two phases at RT indicates an increase of martensitic transition temperature from about 200 K for Ni_2MnGa alloy until nearly 295 K.

Fig. 1. The β solid solution structure of homogenized Ni_2MnGa alloy at RT. x200.

Fig. 2. Needle-shaped martensite and residual β phase in homogenized NMCG alloy at RT. x200

Some casted samples are formed by a single phase (Fig. 3), with a $L2_1$ structure, while the treated samples seem to contain usually two phases: an orthorhombic phase and a cubic phase (Fig. 4 - 7). Because the number of observed lines is relatively small, we could, by using the CeckCell program, only to obtain the best estimated space groups. For treated $Ni_{50}Mn_{25}Ga_{25}$ alloy, the best group is $Pca2_1$; $Ni_{25}Co_{25}Mn_{25}Ga_{25}$ – C222, Cmm2 and Cmmm, but the majority of the maxima of the observed pattern can be indexed also as $Pca2_1$; $Ni_{50}Mn_{12.5}Co_{12.5}Ga_{25}$ – Pnna and $Pca2_1$; $Ni_{50}Mn_{25}Al_{12.5}Ga_{12.5}$ – Imma and $Pca2_1$.

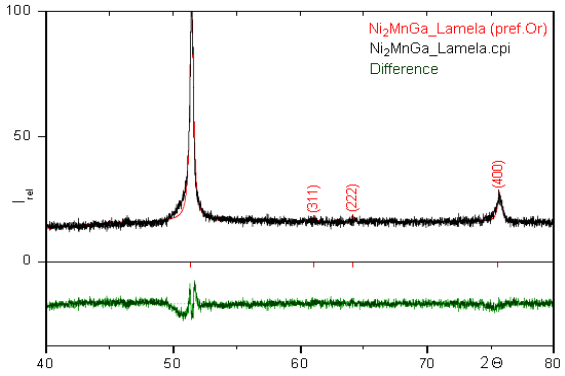

Fig. 3. Diffractogram of as cast Ni_2MnGa. Bottom: difference between calculated and observed diffractogram (Rietveld method)

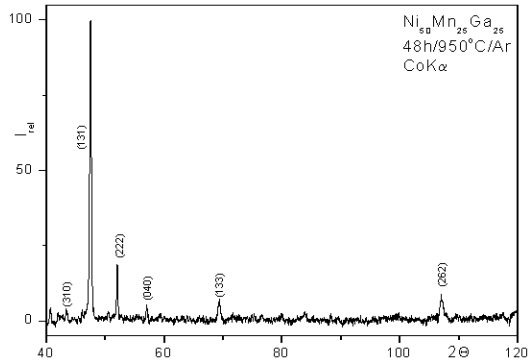

Fig. 4. Diffractogram of NMG treated alloy.

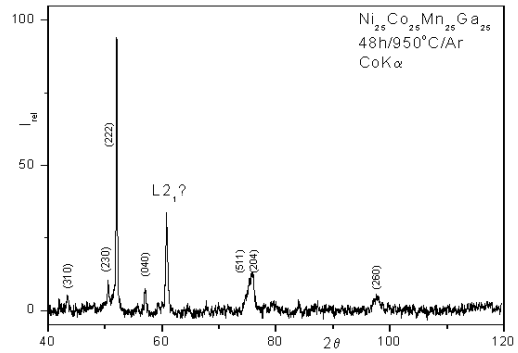

Fig. 5. Diffractogram of NCMG treated alloy.

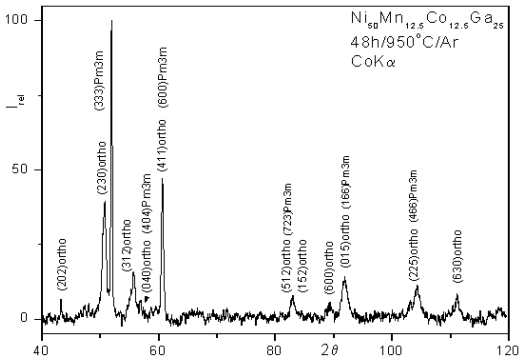

Fig. 6. Diffractogram of NMCG treated alloy.

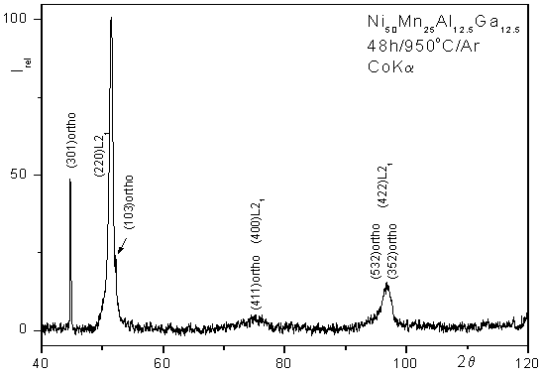

Fig. 7. Diffractogram of NMAG treated alloy.

In the treated alloys was observed a cubic phase, which was indexed as $L2_1$ (Fm3m) phase, except $Ni_{50}Mn_{12.5}Co_{12.5}Ga_{25}$, where the pattern of the majority phase was attributed to a Pm3m unit cell. The substitution of Ni or Mn with Co and of Ga with Al had little influence on the unit cell volume of orthorhombic phase, but leads to an increase of the unit cell volume and concentration of the cubic phase (Tab. 1 and Tab. 2).

On some alloys (NMG and NMAG) was possible to perform a Rietveld analyze (Fig. 3), which confirm the data obtained with CeckCell programme. We observed for treated alloys that despite the metallic radius of Al is smaller that thus of Ga, the unit cell volume of the orthorhombic phase remains constant, while the lattice constant of cubic phase of NMAG alloys is higher as thus of NMG (as cast) alloy (Tab. 1 and 2). A change of the chemical composition in cubic and orthorhombic phases seems possible due to the thermal treatment.

Table 1. Lattice constants and unit cell volume of the orthorhombic phase in the treated samples.

Code	a_o (Å)	b_o (Å)	c_o (Å)	V (Å^3)
NMG	7.6814	7.5040	6.2982	363.04
NCMG	7.6783	7.5045	6.2963	362.80
NMCG	7.6360	7.5146	6.3214	362.73
NMAG	7.6250	7.5128	6.3375	363.04

Table 2. Lattice constant of cubic phases in the treated samples.

Code	a_c (Å)	Structure	$C_{cubic\ phase}$* (%)
NMG**	5.8332	Fm3m	100
NCMG	5.8582	Fm3m	30
NMCG	10.6392	Pm3m	60
NMAG	5.8801	Fm3m	80

*) estimated values; **) as cast

The as casted alloys are characterized by very small size of coherent blocks and a low level of the lattice microstrains. The substitution of Ga with Al leads to a decrease of both microstrains and of the average size of the crystalline blocks. The appearance of a martensitic (orthorhombic) phase at room temperature in $Ni_{50}Mn_{25}Ga_{25}$ alloy was attributed to a small deviation from the chemical composition [9]. The substitution of Ni with Co in $Ni_{50}Mn_{25}Ga_{25}$ alloy resulting $Ni_{25}Co_{25}Mn_{25}Ga_{25}$ alloy increases the magnetic moment of the alloys and the Curie temperature (Fig. 8 and Tab. 3). Substitution of Ga with Al decreases the magnetic moment and the Curie temperature, indicating a decrease of the exchange interaction (Tab. 3).

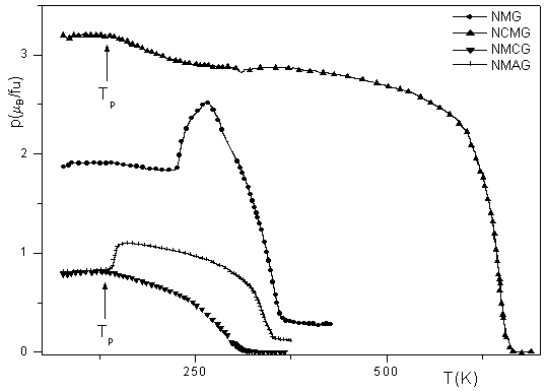

Fig. 8. Variation of molecular magnetization with the Co/Al concentration and temperature.

Table 3. Curie temperature (T_C) and observed ($p_{max, obs}$) and calculated ($p_{max, calc}$) molecular magnetizations of the treated samples.

Code	T_C (°C)	$p_{max, obs}$ (μ_B/fu)	$p_{max, calc}$ (μ_B/fu)
NMG	86.9	2.515	4.08
NCMG	386.0	3.195	4.08
NMCG	43.0	0.810	2.94
NMAG	77.6	1.099	4.08

Premartensitic transition can be observed at low temperatures at the Co substituted alloys: the premartensitic transition temperature is not depended on Co substitution. On other hand, the presence of Co moves the martensitic transition, at temperatures lower than 77 K (Fig. 8). A sudden decrease of the specific magnetization takes place at low temperature in $Ni_{50}Mn_{25}Ga_{25}$ and $Ni_{50}Mn_{25}Al_{12.5}Ga_{12.5}$ alloys, attributed to the transition from the austenitic ($L2_1$) to martensitic (orthorhombic) state. Substitution of Ga with Al leads to a decrease of the transition temperature and of the magnetic moment of the low temperature martensitic phase (Fig. 8). It is known that the Mn-based Heusler alloys have a B2 disordered structure (paramagnetic) at high temperature and a $L2_1$ ordered structure (ferromagnetic) in equilibrium at low temperatures [9]. These structures are very close one to other; a mixture between them can not be excluded and can partially explain the difference between the calculated and observed specific magnetization values of the investigated alloys. The magnetic properties are conditioned by the Mn magnetic moment ($4.17\mu_B$), the magnetic moments corresponding to Ni (~ $0.3\mu_B$) and Co (~ $0.7\mu_B$) having smaller contribution to the magnetization of the samples. We consider that the calculated values of the molar magnetization are different of those observed (Tab. 3), because: 1) the disorder induced by the presence of two or more different atoms on the same place, implicitly, to the presence of B2 disordered phase and 2) the presence of orthorhombic phase, which have a molecular magnetization smaller than that due to the $L2_1$ austenitic phase.

4. Conclusions

We have obtained $(Ni_{50-x}Co_x)(Mn_{25-y}Co_y)$ $(Ga_{25-z}Al_z)$ alloys with $L2_1$ structure, as cast. The high temperature treatment leads to the segregation of two phases: an orthorhombic phase and a cubic phase, with different chemical compositions. A secondary cubic disordered phase is present. When the Co substitutes Ni, it participates to the exchange interaction, contributing to the increase of the Curie temperature and the magnetic moment and to the appearance of the premartensitic transformation. Substitution of Ga with Al leads to a decrease of the exchange interaction and of the martensitic transformation temperature.

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