Martensite-austenite and Ferromagnetic-paramagnetic Transformations in $Ni_{2-x}A_xMn_{1-y}B_yGa_{1-z}C_z$ (A, B=Co; C=Al) Heusler Alloys

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Ni_2MnGa Heusler alloy is known as a potential smart material. At room temperature it has a $L2_1$ type structure, undergoing a martensitic transition (T_M) at low temperatures. Some authors have classified Ni-Mn-Ga Heusler alloys on the values of martensitic transformation and Curie temperatures: first group formed by alloys with T_M below room temperature and T_C, second group with T_M around room temperature and third group with $T_M > T_C$. The partial substitution of Ni with Mn leads to an increase of the transition temperature and a decrease of the Curie temperature. The $Ni_{2-x}Mn_{1+x}Ga$ alloys have a complex tetragonal structure at room temperature. The substitution of Ga with Al can change the crystalline and magnetic structure of Heusler alloys: Ni_2MnAl is antiferromagnetic for a B2 (CsCl type, with Mn and Al randomly distributed in the center of the cube) structure and ferromagnetic for a $L2_1$ (BiF_3 type with Mn and Al ordered distributed in the cube center) structure. We intend to put in evidence a dependence between the applied magnetic field on a side, and the transition temperature, on other side, for the $Ni_{2-x}A_xMn_{1-y}B_yGa_{1-z}C_z$ (A, B=Co; C=Al) Heusler alloys.

Keywords: martensitic transition, transition temperature, Heusler alloys

Origin of shape memory effect in Ni_2MnGa [$Ni_{50}Mn_{25}Ga_{25}$] is based on the thermoelastic phase change which takes places at transition temperature (T_{AM}) from a cubic $L2_1$ phase to a lower symmetry phase. Structure and transition temperature of Ni_2MnGa alloy were investigated by Brown et al., which have determined each crystallographic phase between 20 and 400 K [1].

A low temperature deformed SME alloy will find its original form when heated above the transformation 7-fold martensite→5-fold martensite→austenite temperature (T_{MM}=200K; T_{MA}=260 K). Low temperature crystallographic state is a tetragonal deformation (a=b=5.922 Å; c=5.566 Å), along [100] of cubic $L2_1$ cell [1]. Diffractograms of thermally and/or stressed martensite present super-structure reflections indicating a 5-fold modulation of (110) planes.

Despite the fact that many studies concerning the structural and magnetic properties was performed on Ni_2MnGa and close as composition alloys, the metallurgical and physical phenomena concerning SME are far away of being understood. Full-Heusler Co_2MnZ (Z=Si, Ge) and $Co_2Cr_{1-x}Fe_xAl$ alloys were synthesized [2, 3]. In both cases a cubic structure was observed.

Our aim is to investigate the structure and magnetic properties, implicitly, the magnetic and crystallographic transitions in the $Ni_{2-x}A_xMn_{1-y}B_yGa_{1-z}C_z$ (A, B=Co; C=Al) Heusler alloys.

Experimental part

The $(Ni_{50-x}Co_x)(Mn_{25-y}Co_y)(Ga_{25-z}Al_z)$ (x=0; 25; y=0; 12.5; z=0; 12.5) Heusler alloys with stoichiometric compositions were melted in a furnace in Ar atmosphere, casted in a copper mold, homogenized at 1223 K for 48 hours followed by air cooling. The alloys phase composition and structural parameters (lattice constants, texture, microstrains, average size of the coherent blocks) were investigated by X-ray diffraction and optical microscopy at room temperature. The samples were prepared by standard procedure, by using Marble's reagent to put in evidence the crystallites boundaries. XRD data were handled by DICVOL, CeckCell and FullProf programs. Large microdistortions and small size coherent blocks were observed. The magnetic measurements were performed between 77 K and 673 K, by using a Foner type magnetometer (H_{max} = 4 kOe). Curie and transformation temperatures were determined from the variation of specific magnetization with the temperature.

Results and Discussions

Investigations performed by optical microscopy on samples casted and homogenized at 1223 K / 48 h in Ar indicated that the alloys where Mn was substituted with Co and, respectively, Ga with Al, contains foreign phases. Treated $Ni_{50}Mn_{25}Ga_{25}$ and $Ni_{25}Co_{25}Mn_{25}Ga_{25}$ and as cast $Ni_{50}Mn_{25}(Ga_{12.5}Al_{12.5})$ alloys are formed by a single phase (figs. 1a, 1b and 1d).

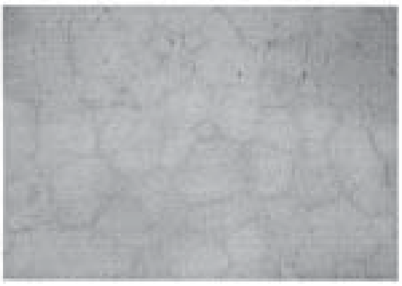

Fig. 1a $Ni_{50}Mn_{25}Ga_{25}$ alloy (treated)

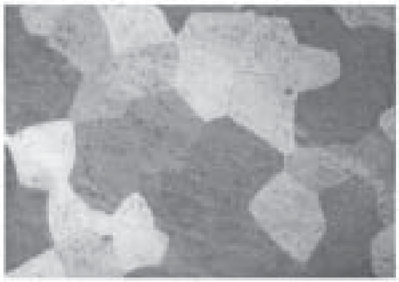

Fig. 1b $(Ni_{25}Co_{25})Mn_{25}Ga_{25}$ alloy (treated)

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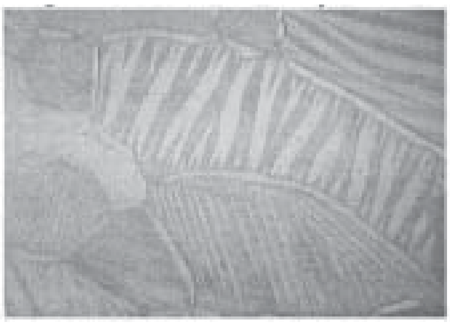

Fig. 1c $Ni_{50}(Co_{12.5}Mn_{12.5})Ga_{25}$ alloy (treated)

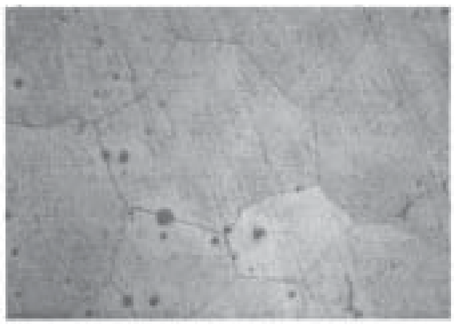

Fig. 1d $Ni_{50}Mn_{25}(Ga_{12.5}Al_{12.5})$ alloy (as cast)

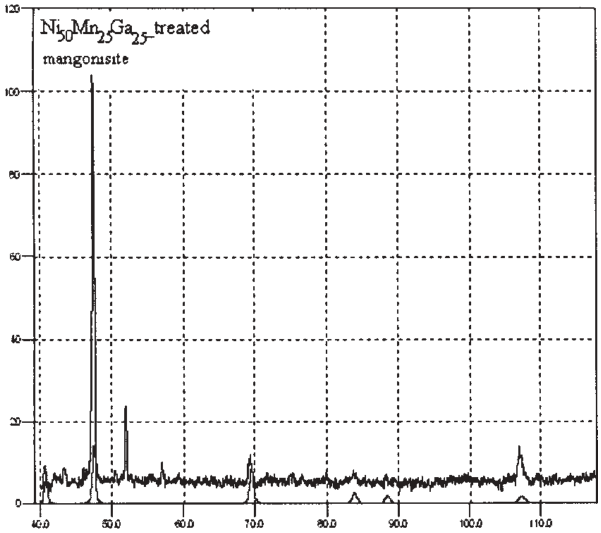

Fig. 2a A small concentration of manganese oxide is present at the surface of the treated $Ni_{50}Mn_{25}Ga_{25}$ alloy

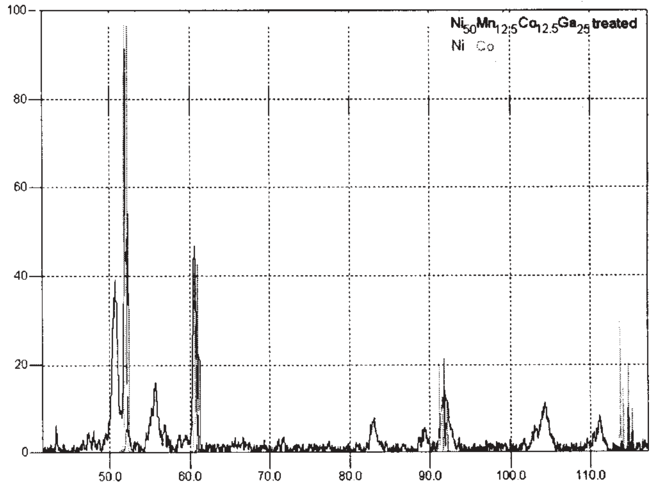

Fig. 2b Possible (Ni)/(Co) solid solutions present in the treated $Ni_{50}Mn_{12.5}Co_{12.5}Ga_{25}$ alloy

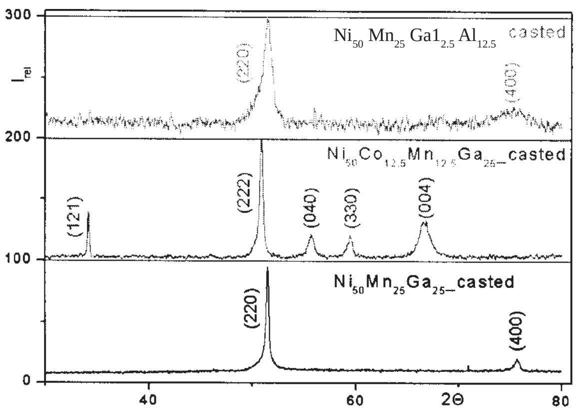

Fig. 3a Diffractograms of as cast alloys

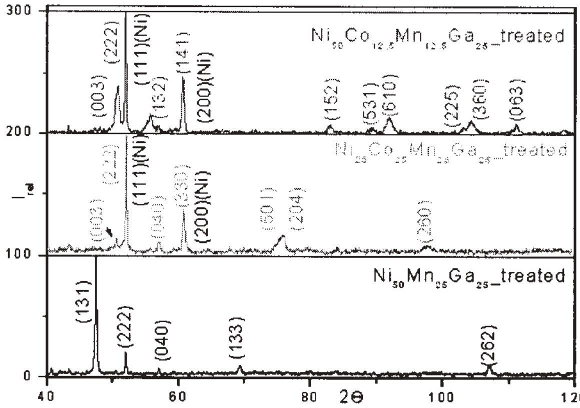

Fig. 3b Diffractograms of treated alloys

$Ni_{50}(Co_{12.5}Mn_{12.5})Ga_{25}$ treated alloy contains probably three phases: 1) a white phase was observed at the crystallite boundary; 2) second and third phases (black/ white stripes) were observed into the crystallite (fig. 1c).

Due to the treatment, a small quantity of manganese oxide can appear on the alloys surface as small black points (fig.1a, 1b and 1d). This supposition was confirmed by XRD data (fig.2a). On other hand, by X-ray measurements we observed that treated $Ni_{50}Mn_{12.5}Co_{12.5}Ga_{25}$ alloy could contain a Ni/Co based solid solution, into an orthorhombic matrix (fig.3b).

$Ni_{50}Mn_{25}Ga_{25}$ and $Ni_{50}Mn_{25}Ga_{12.5}Al_{12.5}$ casted alloys contain only a $L2_1$ phase (fig. 3a), while casted $Ni_{25}Mn_{12.5}Co_{12.5}Ga_{25}$ alloy has an orthorhombic structure (fig.3a and table 1). The partial replacement of Ga with Al leads to a lattice constant larger as $Ni_{50}Mn_{25}Ga_{25}$ alloy, smaller average size of the coherent blocks and larger microstrains (table 1 and fig.3a).

Substitution of Mn with Co leads to the formation of an orthorhombic (intermetallic) phase without complementary thermal treatment (fig.3a). By means of thermal treatment we obtained $Ni_{50}Mn_{25}Ga_{25}$ alloy in martensite state (orthorhombic structure), without foreign phases (fig. 3b). The substitution of Ni and Mn with Co in treated alloys leads to a decrease of unit cell volume of orthorhombic structure (table1). Average size of the coherent blocks, determined by means of Rietveld method, have a decrease with the decrease of unit cell volume (fig.4).

Ni_2MnGa treated alloys have a Curie temperature around 360 K and a transformation point from austenite to martensite below room temperature (223 K) (s.Tab.2). Substitution of Ni with Co in investigated Heusler alloys leads to an increase of the Curie temperature, but in these alloys, in the investigated range of temperatures no martensite-austenite transition was observed (fig.5). The observed value of specific magnetization of treated

Table 1
VARIATION OF LATTICE CONSTANTS (a, b, c) AND OF AVERAGE SIZE OF COHERENT BLOCKS (D) WITH CHEMICAL COMPOSITION AND THERMAL TREATMENT

	Chemical composition	Structure	A (Å)	B (Å)	C (Å)	V ($Å^3$)	D (Å)
as cast	$Ni_{50}Mn_{25}Ga_{25}$	$L2_1$	5.845	5.845	5.845	199.689	288
	$Ni_{25}Co_{1.25}Mn_{1.25}Ga_{25}$	orthorhombic	7.606	7.613	6.479	375.163	644
	$Ni_{50}Mn_{25}Ga_{12.5}Al_{12.5}$	$L2_1$	5.850	5.850	5.850	200.202	111
treated	$Ni_{50}Mn_{25}Ga_{25}$	orthorhombic	7.679	7.511	6.307	363.769	10134
	$Ni_{25}Co_{25}Mn_{25}Ga_{25}$	orthorhombic	7.599	7.536	6.344	363.296	6924
	$Ni_{50}Mn_{12.5}Co_{12.5}Ga_{25}$	orthorhombic	7.602	7.555	6.284	360.910	285

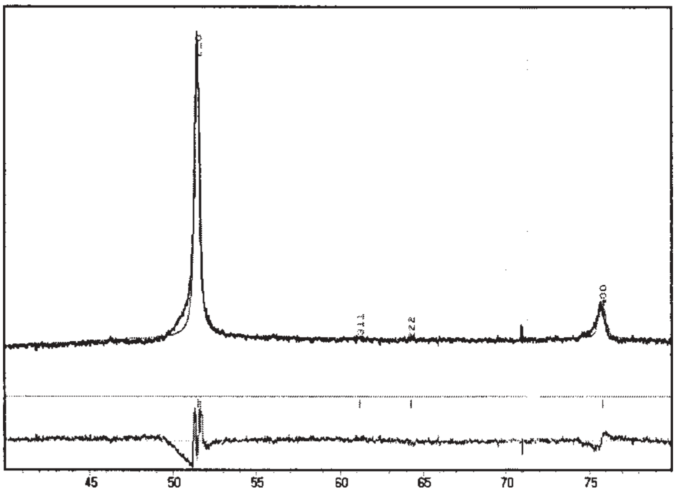

Fig. 4. Difractogram of as cast $Ni_{50}Mn_{25}Ga_{25}$ alloy (observed data-black; calculated-red; difference-green)

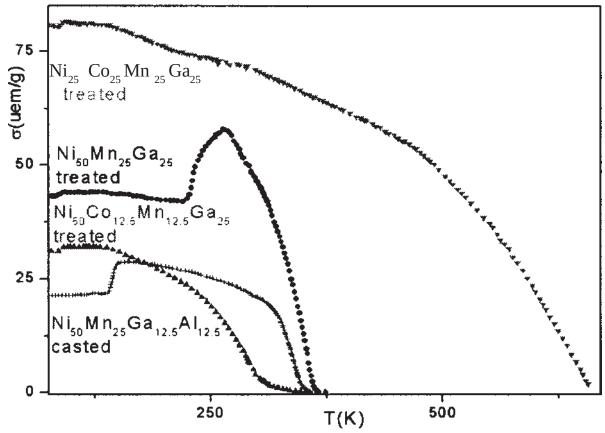

Fig. 5 Variation of specific magnetization with the temperature and nominal composition for treated/as cast alloys

Table 2
CURIE AND TRANSITION TEMPERATURES (T_C, T_{AM}(AND SPECIFIC MAGNETIZATIONS ($\sigma_{90 K}$) FOR $Ni_{2-x}A_xMn_{1-y}B_yGa_{1-z}C_z$(A, B= Co; C= A1) HEUSLER ALLOYS

Nominal composition	Treatment	T_C (K)	T_{AM} (K)	$\sigma_{90 K}$ (uem/g)
$Ni_{50}Mn_{25}Ga_{25}$	950°C/48h/Ar	360	223	43.9
$(Ni_{25}Co_{25})Mn_{25}Ga_{25}$	950°C/48h/Ar	662	-	81.1
$Ni_{50}(Mn_{12.5}Co_{12.5})Ga_{25}$	950°C/48h/Ar	316	-	32.3
$Ni_{50}Mn_{25}(Ga_{12.5}Al_{12.5})$	as cast	350	139	21.3

$(Ni_{25}Co_{25})Mn_{25}Ga_{25}$ alloy implies a contribution of magnetic moment of Co to the total magnetic moment of the sample, when Ni is the substituted atom. The substitution of Mn with Co and Ga with Al led to a decrease of the magnetic moment and of the Curie temperature (table 2). Because foreign phases are not present in the as cast $Ni_{50}Mn_{25}(Ga_{12.5}Al_{12.5})$ alloy, we suppose that Mn, Ga and Al atoms are chaotically distributed in the $L2_1$ unit cell.

Conclusions

$Ni_{50}Mn_{25}Ga_{25}$, $(Ni_{25}Co_{25})Mn_{25}Ga_{25}$, $Ni_{50}(Mn_{12.5}Co_{12.5})Ga_{25}$ and $Ni_{50}Mn_{25}(Ga_{12.5}Al_{12.5})$ alloys were as cast and treated. At room temperature treated alloys are formed by a mixture of orthorhombic and cubic structure. Alloys obtained by substitution of Ni/Mn with Co present no austenite-martensite transition, while the Ga substitution with Al leads to a decrease of specific magnetic moment and of the transition temperature.

References

1. P. J.BROWN, J.CRANGLE, T.KANOMATA, M.MATSUMOTO, K.-U. NEUMANN, B.OULADDIAF , K.R.A.ZIEBECK, J. Phys.: Condens. Matter, **14**, 2002, 10159
2. K.R.A.ZIEBECK, P.J. WEBSTER, J. Phys. F: Met. Phys. **5**, 1984, 1756
3. K.INOMATA, S.OKAMURA, A.MIYAZAKI, M.KIKUCHI, N.TEZUKA, M.WOJCIK, E.JEDRYKA, J. Phys. D: Appl. Phys., **39,** 2006, 816

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