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Cobalt-base ferromagnetic shape memory alloys

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Abstract

Single crystalline and polycrystalline CoxNiyGa100-(x+y), 41 < xCo< 62 and 19.3 < yNi < 32.7, Ferromagnetic Shape Memory Alloys have been produced in the range of the Heusler-type composition. Elasto-mechanical properties have been analyzed for the annealed and quenched states, respectively. The mechanical spectroscopy data show the occurrence of martensitic phase transformation with the transition range and characteristics depending on the state and the composition of the alloys. For XCo approximately equals 49 +/- 1 at percent, the Ni/Ga ratio was shown to be in direct relationship with the transition temperature range, from an Ms of -100 degrees C for Ni/Ga approximately equals (21/29) to a +150 degrees C for a Ni/Ga ratio of about (26/25). For Ga approximately equals 27 +/- 0.4 at percent, the Co/Ni ratio is in indirect relationship with the transition temperature, with an Ms of -125 degrees C for a (53/19) ratio to a +175 degrees C for a ratio of about (49/26). Optical and electron microscopy shows that a typical thermoelastic martensitic transformation occurs. The L21 Structurbericht parent phase transforms into monoclinic or orthohombic martensitic upon cooling. The formation of a Co-rich phase has been observed for alloys with lower Ga content and is considered to be one of the reasons for the difference in the transformation range for annealed and quenched alloys.

Keywords

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Disciplines

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Comments

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Cobalt-base ferromagnetic shape memory alloys

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ABSTRACT

Single crystalline and polycrystalline $Co_xNi_yGa_{100-(x+y)}$, $41<x_{Co}<62$ and $19.3<x_{Ni}<32.7$ [at%], Ferromagnetic Shape Memory Alloys (FMSMAs) have been produced in the range of the Heusler-type composition. Elasto-mechanical properties have been analyzed for the annealed and quenched states, respectively. The mechanical spectroscopy data show the occurrence of martensitic phase transformations with the transition range and characteristics depending on the state and the composition of the alloys. For $x_{Co}\approx 49\pm1$ at%, the Ni/Ga ratio was shown to be in direct relationship with the transition temperature range, from an Ms of –100 ^oC for a Ni/Ga ≈ (21/29) to a +150 ^oC for a Ni/Ga ratio of about (26/25). For $x_{Ga}\approx 26.3\pm1$ at%, the Co/Ni ratio is in indirect relationship with the transition temperature, with an Ms of –125 ^oC for a (53/19) ratio to a + 175 ^oC for a ratio of about (49/26). Optical and electron microscopy shows that a typical thermoelastic martensitic transformation occurs. The B2 ($L2_1$ Structurbericht) parent phase transforms into monoclinic or orthorhombic martensite upon cooling. The formation of a Co-rich phase has been observed for alloys with lower Ga content and is considered to be one of the reasons for the difference in the transformation range for annealed and quenched alloys.

Keywords: Heusler alloys, Phase transformation, Shape memory; Internal friction; Martensite; Ferromagnetism; Electron Microscopy

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1. INTRODUCTION

Ferromagnetic Shape Memory Alloys (FMSMAs) are an important member of the so-called Smart Materials group because they combine the functional properties of shape memory and magnetostrictive alloys, thus two types of energy – thermal and magnetic- can be used to control their behavior. In the effort to produce FMSMAs, the alloy components and the resulting alloys have to fulfill several conditions, such as:

- at least one of the alloy components should be magnetic;
- the alloy shows a diffusionless martensitic transformation;
- a special relationship exists between the lattice parameters of the austenite and martensite phases

Such conditions have been fulfilled by several well known FMSMAs like: FePt [1], FePd [2], NiMnGa [3, 4], but not by FeMnSi [5], and NiAl [6, 7] which are shape memory alloys but not ferromagnetic.

Recent studies have linked the search for new FMSMAs to the Heusler-type alloy family [8] and have considered the average valence electron concentration and the saturation magnetization as it appears on the Bethe-Slater curve modified to take into consideration the <s+p+d> electrons [9].

Cobalt is obviously a serious candidate for the fabrication of FMSMAs because of its magnetic characteristics. However, only very recent research has shown promising results in the use of Co as a component for the FMSMAs.

Co-based FMSMAs have been recently produced following two paths. One has as a model the NiAl shape memory system in which Co has been added to bring out a magnetic behavior [10] . The other path has as a model the Heusler-type FMSMAs for which the unique representative was, the Ni_2MnGa system. For this system, Chernenko [11] initiated an analysis of the correlation between the Ms transformation temperatures and the valence electron/atom ratio, showing a linear relationship. Later on, Schlagel [12] summarized a series of experimental data and confirmed Chernenko's observations for the NiMnGa system.

The CoNiGa FMSMAs have been discovered [13] after a thorough analysis of Heusler –type alloys [9] and show ferromagnetic and shape memory behavior as bulk [13, 14] or thin films [15]. This paper is focused on experimental results in characterizing the structure and elasto-mechanical behavior of CoNiGa FMSMAs, while their ferromagnetic character has been previously reported [13, 16].

2. EXPERIMENTAL

CoNiGa alloys were prepared by arc melting followed by homogenization annealing at 900 ^{o}C for 10 hours. Ingots of the compositions Co_x Ni_y $Ga_{100-(x+y)}$, 41<x<62 and 18< y<33 were prepared for this investigation. For two compositions, part of the Ga and Ni respectively were replaced by up to 2% Al. The composition of the ingots was measured using energy dispersive spectroscopy (EDS). Single crystals of Co_2NiGa were grown using the modified Bridgman method. Their structure and properties were analyzed in the as-grown and quenched states.

Strips, 0.3mm thick, 4mm wide and 15mm long, were cut from the ingots and used to determine the martensitic transformation characteristics by measuring the elastic properties in an acoustic elastometer [[17]]. The temperature of measurement ranged from –180 ^{o}C to + 300 ^{o}C.

The microstructure was analyzed optically in polarized light using a heating device. Images were taken on heating and cooling in the temperature range corresponding to the phase transformation. Transmission Electron Microscopy (TEM) observations were carried out using a JEOL-4000FX microscope operated at 300 kV. The thin foils for TEM studies were prepared using mechanical thinning followed by ion-milling. All TEM structures were observed at RT.

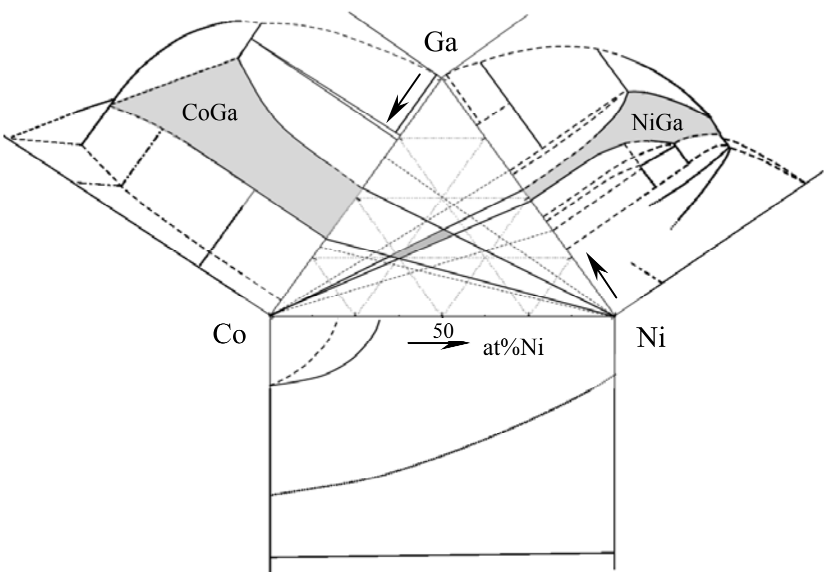

Figure 1: Schematic ternary phase diagram showing the favorable conditions for the formation of a B2 phase susceptible (center gray area) of transforming into martensite. The dotted lines show the extension of the B2 domain for solution treated alloys. Binary phase diagrams constructed after [ ].

3. RESULTS AND DISCUSSION

An analysis of the ternary system for the CoNiGa shape memory alloys shown in Fig. 1 reflects the favorable conditions that exist – around the (Co_2NiGa) Heusler-type composition - for the formation of an ordered solid solution. Note that the Co-Ni phase diagram is a significant facilitator because of its large solubility between the components. Of importance is also the extended solubility that can be achieved in quenched state of the other two systems, Ni-Ga and Co-Ga.

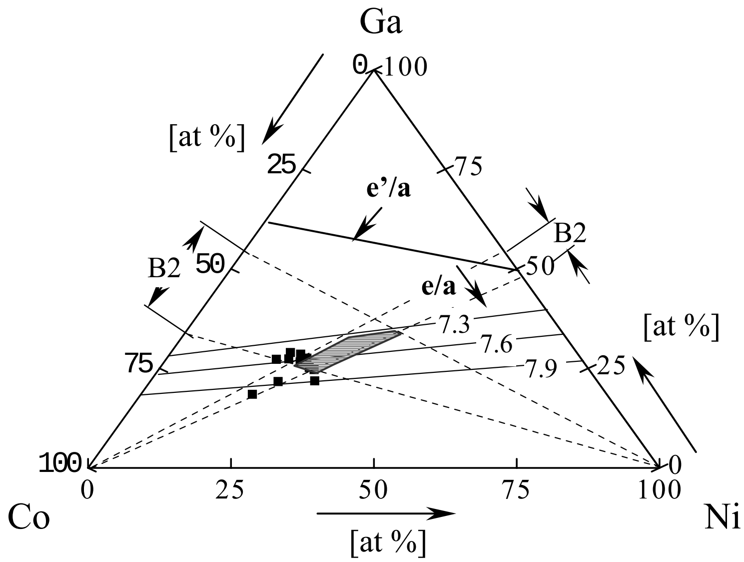

Figure 2: Compositional range for the formation of Co_2NiGa FMSMAs (see text for details). The black dots mark the alloys investigated in this study.

The composition of the alloys studied in this paper and for which a phase transformation has been observed are presented in Fig.2 and fall around the compositional range of the B2 phase of the binary Ni-Ga and Co-Ga systems of alloys.

The Bethe-Slater curve suggests that high values of the saturation magnetization can be obtained for electron / atom (e/a) ratios larger than 7.3. If we take into consideration both the metallurgical observations and the electron / atom lines (Figure 2), it can be observed that the CoNiGa alloys analyzed in this study fulfill the above-mentioned conditions.

Figure 3a shows the microstructure of a $Co_{50}Ni_{23.5}Ga_{26.5}$ alloy. The structure is composed of Co-rich (up to 60 at%) dendrites in a Ga-rich (around 29 at%) matrix. The examination in polarized light of a thermally cycled sample suggests that the martensite structure develops in the Ga-rich phase rather than in the Co-rich one. A typical shape memory martensitic structure has been observed in a Ga-rich alloy (Fig. 3b), while further examinations revealed typical hierarchical variants.

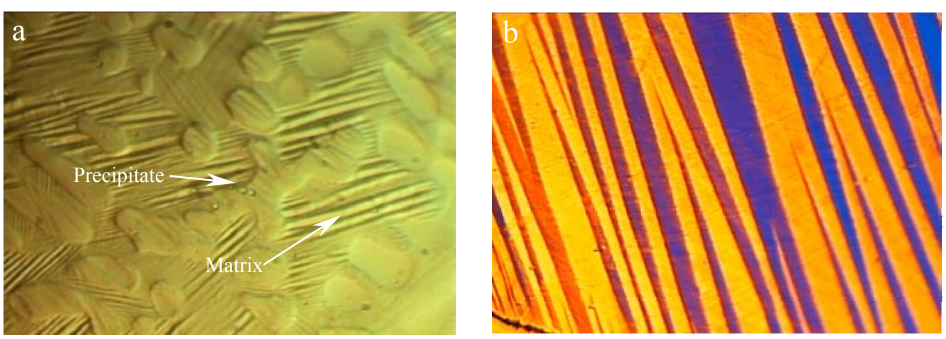

Figure 3: Microstructure of Co_2NiGa alloys:
a. Co rich precipitates and Ga-rich matrix with martensite formations in a $Co_{50}Ni_{23.5}Ga_{26.5}$ alloy;
b. typical martensitic structure in a $Co_{50}Ni_{22.25}Ga_{27.75}$ alloy

According to the phase diagrams (Figs.1,2) the presence of a Co-rich phase in a Ga-rich matrix is likely to occur in alloys situated at low Ga contents, while higher Ga contents seem to favor a single B2 phase that transforms into martensite, especially in the quenched state. This conclusion is strengthened by neutron diffraction studies that suggests the presence of a Co phase for the stoechiometric composition.

Figure 4 shows a typical TEM images taken from CoNiGa martensites. The analysis of selected area electron diffraction (SAED) patterns suggests that the parent phase transforms to tetragonal or orthorhombic martensites, in agreement with the neutron and X-ray studies. High-density striations are observed in the bright field image. SAED pattern and dark field image revealed that they are composed of thin twin plates. Preliminary neutron scattering and X-ray diffraction profiles suggest that Heusler-type cubic austenites transform into tetragonal and/or orthorhombic martensites [18]. The profiles allow an estimation of the lattice constant of the parent phase, 0.575 nm. The tetragonal and orthorhombic distortion are estimated at $c/a \approx 0.86$ and $c/b \approx 0.88$.

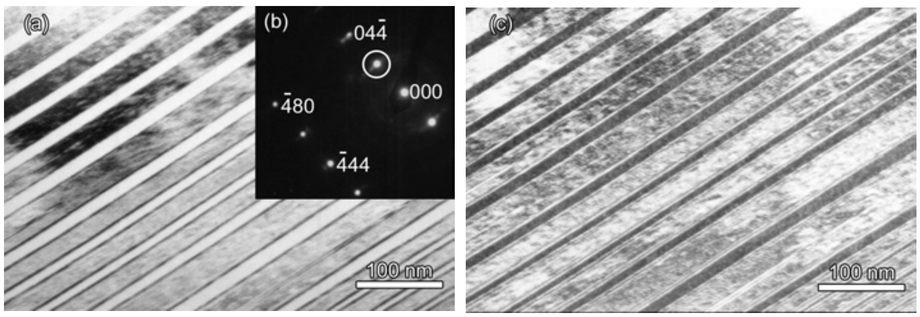

Figure 4: Internal twins and the corresponding SAED pattern of CoNiGa martensites:
(a) Bright field image, (b) SAED pattern taken of (b),
(c) Dark field image using the circled reflections in (b).

Figure 5 shows a TEM micrograph taken of the $Co_{50.1}Ni_{20.9}Ga_{29.0}$ alloy, with the M_s temperature lower than room temperature. Tweed contrast was frequently observed in the parent-phase. It is generally known that precursor phenomenon of martensitic transformation [19], e.g. tweed contrast in TEM microstructure, lattice softening and diffuse scattering of X-rays and electrons, can be observed in β-phase alloys. It is proposed that the broad inflections of the modulus defect versus T curves were caused by the precursor phenomenon.

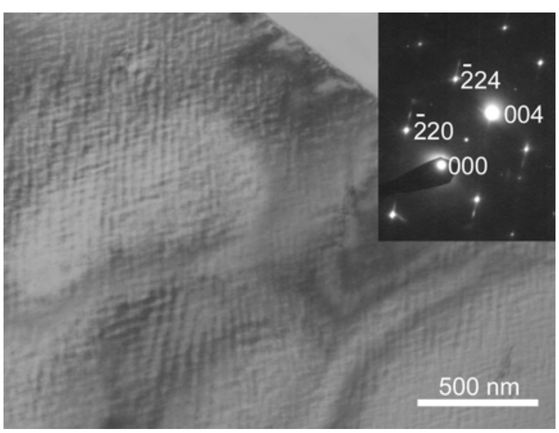

Figure 5: Tweed contrast and the correspondent SAED pattern of the CoNiGa parent-phase

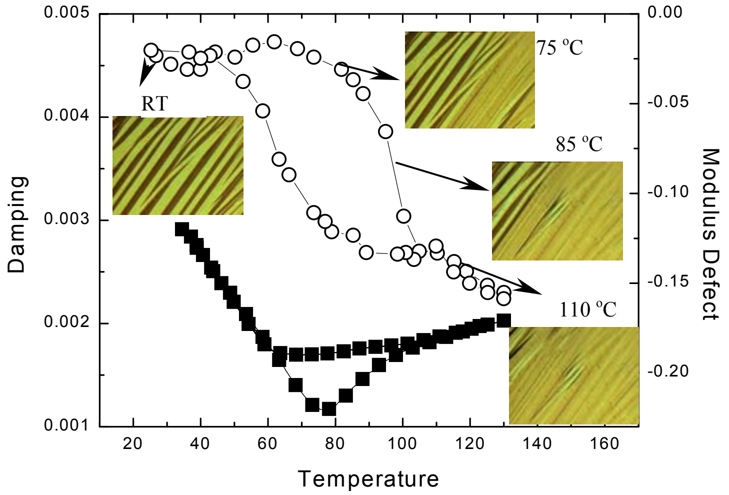

Figure 5: Elasto-mechanical (damping (■) and modulus defect (○)) and microstructural changes (inserts taken on heating) observed during the thermal cycling of a $Co_{50}Ni_{22}Ga_{28}$ FMSMA.

The thermoelastic character of the martensite has been obseved on heating and cooling the Ga-rich specimen. The corresponding elasto-mechanical behavior of a sample prepared from the same alloy shows a phase transition detected by both the internal friction and modulus defect. The results are associated in fig. 5. It can be seen that the transition is typical for shape memory alloys in that it associates the structural and elastomechanical changes to changes in the temperature, in a reversible manner. A similar microstructural change has been observed in a sample with Co-rich precipitates but only for the Ga-rich matrix. The transition temperature was slightly higher than the one observed in the sample without precipitates (with lower Ga content).

The change in the modulus defect associated with the martensitic transformation in Co_2NiGa alloys is shown in figs. 6a and b. Figure 6a describes the behavior of alloys with a 49.3±0.8 at% Co while fig. 6b describes the behavior

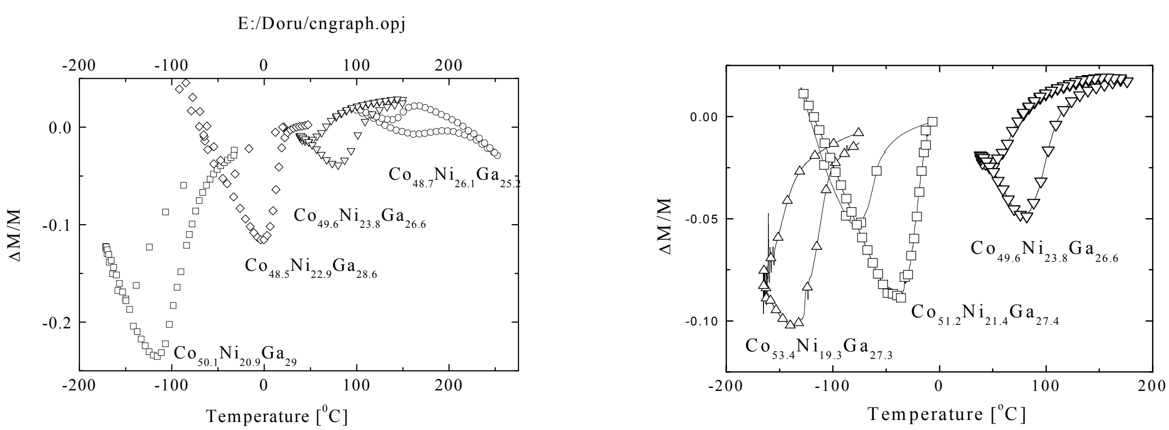

Figure 6: Phase transformations observed in the CoNiGa FMSMA system by changes in the modulus defect as a function of temperature for alloys with: (a) Co= 49.3±0.8 at % and (b) Ga = 27±0.4 at %.

of alloys with 27±0.4 at% Ga. In both cases it can be seen that the transition temperature and the amplitude of the transformation are composition-dependent (fig.7).

The microstructural analysis suggests that the cause for the decrease in the amplitude resides in the presence of the Co-rich precipitates. The higher the Co/Ga ratio, the more precipitates form and the less the matrix. The latter one is the one that transforms and causes the change observed in the modulus defect.

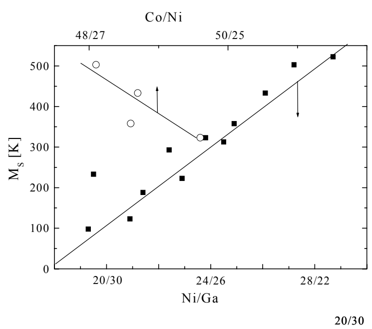

Figure 7: Changes in the martensitic start (M_s) temperature as a function of the component ratio for the investigated CoNiGa alloys.

The change in the transition temperature is tentatively attributed to the Ga content of the matrix. The lower the Ga content is, the higher the transition temperature. The analysis of the binary Co-Ga and Ni-Ga phase diagrams suggests that Ga content of the matrix can be reduced by solution treatment followed by quenching. Accordingly the quenched state of a Co-rich two-phase alloy in the CoNiGa system should show a higher transition temperature compared to the unquenched one because of the higher solubility at high temperatures. This assumption is verified by the experimental data presented in fig. 8 that shows the phase transitions for a two-phase $Co_{50}Ni_{25}Ga_{25}$ single crystal before and after quenching. An increase in the transformation temperatures has been observed after water-quenching from 900 ^oC. Upon further annealing of the quenched sample, followed by slow cooling, the transformation reverted toward the low temperatures while a subsequent solution treatment followed by quenching shifted the transformation toward high temperatures again.

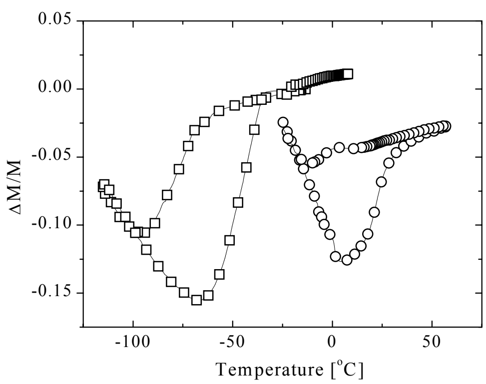

Figure 8: The influence of quenching on the martensitic phase transformation of a $Co_{50}Ni_{25}Ga_{25}$ single crystal (before quenching and after annealing followed by slow cooling (□), and after quenching (○)).

A similar shift in the transition temperature range has been observed in quaternary Co-Ni-Ga-Al alloys as a result of replacing part of Ga or Ni by Al. Figure 9 shows that a slightly higher transition temperature can be reached for alloys in which a part of Ga has been substituted by Al, and a lower transition temperature when Ni was substituted by

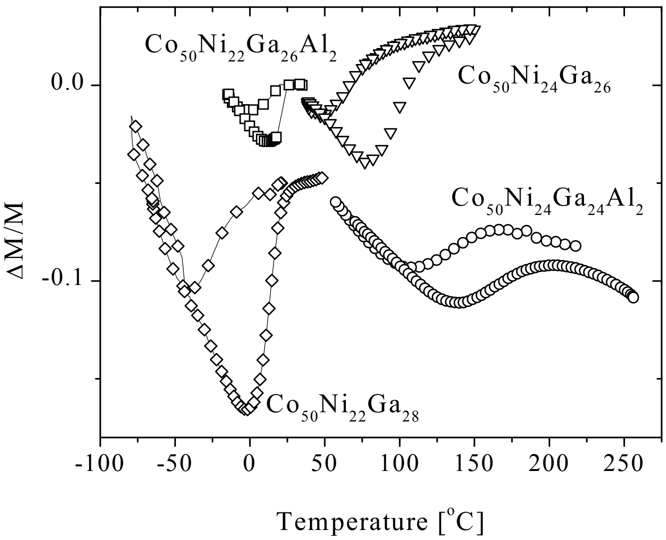

Figure 9: The effect of Al addition on the martensitic transformation in Co_2NiGa FMSMAs.

Al. However, the amplitude of the transformation seems to diminish when Ga is replaced by Al. It can be concluded – for the compositional range investigated - that while Al can be used to shift the transformation temperature, it also has negative effects on the amplitude of the transformation, very likely because it favors the formation of new precipitates.

Recent studies of the NiMnGa system [11, 12] showed a relationship between the electron / atom ratio (e/a) and the transformation temperatures. The comparative experimental data presented in fig. 10 proves that a similar relationship seems to exist for the Co-base FMSMAs, and therefore the transformation mechanisms could be the same for both systems. However a theoretical analysis of the e/a ratio for stoechiometric Ni_2MnGa and Co_2NiGa alloys shows that while the influence of the ratio between the last two components for each alloy family – Mn/Ga and Ni/Ga respectively – is similar, the influence of the ratio of the first two components is totally different. Figure shows that - for NiMnGa – higher e/a – hence higher transition temperatures – can be achieved by increasing the Ni/Mn ratio. The same goal can be obtained for CoNiGa alloys by reducing the Co/Ni ratio. This observation is consistent with the experimental data showed in figs. 6 and 7.

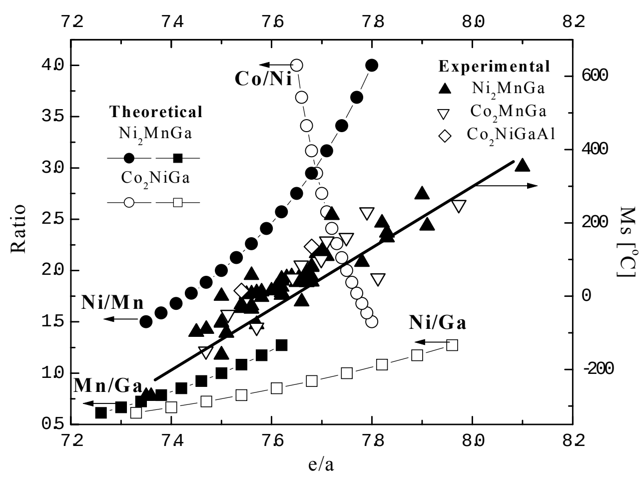

Figure 10: Theoretical evaluation of the relationship between the components ratio and e/a for stoichiometric Heusler-type FMSMAs associated with experimental data showing the M_s vs. e/a dependence for NiMnGa [ ] and CoNiGa (Al) alloys.

4. CONCLUSIONS

CoNiGa FMSMA system has been investigated from microstructural and elasto-mechanical perspectives. The phase transition observed resembles the one known for NiMnGa FMSMAs. It also benefits from the favorable conditions that exist in the ternary Co-Ni-Ga system for the formation of a solid solution in the vicinity of the Heusler-type composition. This B2 phase transforms into martensite in a thermoelastic and reversible manner, and as proved by both structural and elasto-mechanical data.

The microstructural analysis shows that for lower Ga content (x_{Ga}<26at%), the formation of Co-rich precipitates is diminishing the output of the transformation. The martensite seems to develop in areas richer in Ga than the stoichiometric composition. A solution treatment followed by quenching for an alloy with Co-rich precipitates increased the transition temperatures by 75 ^{o}C, while a subsequent annealing reverted the transformation toward the initial temperature values. It is therefore suggested that the Co and Ni enriched matrix are the cause for the increase in the transformation temperatures upon quenching.

The increase in the Ni/Ga ratio has been shown to be effective in increasing the transformation temperatures, while the increase in the Co/Ni ratio is in indirect relationship with the transformation temperature. These observations have been confirmed by both theoretical and calculated values of the e/a vs. ratio dependence and experimental data of the Ms vs. e/a and Ms vs. composition respectively.

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