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INVITED PAPER

NEW FERROMAGNETIC AND FUNCTIONALLY GRADED SHAPE MEMORY ALLOYS

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The paper summarizes recent advances in shape memory alloy investigation with focus on the path used to find new ferromagnetic shape memory alloys and on the improvement of micro-actuation by thermoelastic control of the phase transformation in graded shape memory alloy films. The first part of the paper describes experimental results and theoretical considerations concerning the search, fabrication and characterization of new Co-based Heusler-type ferromagnetic shape memory alloys with focus on the CoNiGa system. It is shown that CoNiGa alloys undergo a reversible thermoelastic martensitic transformation in a wide temperature range, depending on the composition and displaying a nickel-like saturation magnetization. The second part of the paper takes into consideration the case of layered and functionally graded microlayered films constructed by continuously changing the temperature during the deposition process of NiTi alloys on heated Si cantilever-type substrates. It is shown that – depending on the deposition temperature and sequence of deposition - high actuation can be achieved. The discussion takes into consideration the martensitic transformation in layers under constraints from the substrate and/or the neighboring microlayers. The best actuation can be obtained when transformation starts and develops gradually from the top microlayer. This was achieved in NiTi films deposited continuously on heating.

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Keywords: Shape memory alloy, Ferromagnetic, Micro-actuator

1. Introduction

Shape memory alloys (SMAs) have been intensively investigated during the past decades for their unusual properties and spectacular behavior. Currently they are actively considered for the fabrication of thermo-mechanically-controlled micro-actuators. The expansion of the SMA known properties (such as the discovery of ferromagnetism in SMAs) that would allow additional control or the use of such manufacturing technologies that would allow improved actuation are of high actuality.

While mostly known for their ability to undergo a thermally controlled reversible martensitic transformation, recent years have shown that some SMAs are also ferromagnetic. Ferromagnetic shape memory alloys (FMSMAs) are expected to show two transformations: a ferromagnetic transition and a martensitic transformation, thus creating the possibility for the occurrence of field induced phase transformation and field induced variant rearrangements [1].

Several alloy systems have shown or are potentially interesting for their ferromagnetic and shape memory properties. Ferrous FePt and FePd were known to be SMAs [e.g. 2, 3] but their magnetic behavior was studied only recently [4, 5]. The low transformation temperatures for the FePt alloys and the prohibitive cost of Pd are making these alloys of low technological interest. FeNiCoTi [6] are FMSMAs but the martensitic transformation occurs at low temperatures, while for the FeMnSiX alloys the large hysteresis also makes them of limited practical interest.

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Of special interest are the FMSMAs that form in the vicinity of the Heusler composition, like Ni_2MnGa, Co_2NiGa and Cu_2MnGa. For many years NiMnGa was the most promising Heusler system. The martensitic transformation in this system was first shown in 1984 [7], the shape memory effect was recognized in 1990 [8] and the magnetostrictive character was studied in recent years [9,10,11,12]. The recently discovered CoNiGa system [13, 14, 15] is a good alternative to known FMSMAs and expected to show better technological properties compared to NiMnGa alloys. An overview on our recent results presented in this paper proves the thermoelastic character of the transformation detected through microscopic observations, mechanical spectroscopy, neutron diffraction and macroscopic observations. The ferromagnetic behavior is also analyzed.

The fabrication of functionally graded shape memory alloy films is the second topic of this paper. Such materials composed of layers of shape memory alloys with different properties can generate different properties depending on the succession of the layers. Our results described in this paper show that in a functionally graded shape memory alloy film the martensites in the microlayers act in an interdependent way in which the constraints can be reinforced or relieved by neighboring microlayers not transformed and transformed, respectively.

2. Ferromagnetic Co-based Heusler-type FMSMAs

The paths used to discover new FMSMA was described before and Fig. 1 summarizes conceptually the formation of the FMSMAs when several conditions are satisfied [16]. The martensitic transformation is the key leading factor in this approach. SMAs form, when in addition to the martensitic transformation, a special lattice relationship exists between the parent and product phases. FeNi alloys show a magnetically driven martensitic transformation. They can be engineered by addition of Co and Ti and so the FeNiCoTi alloys fulfill the conditions for FMSMAs. FePt and FePd are other ferrous based FMSMAs.

On the other hand, some Heusler-type alloys show the shape memory effect, and the well-known Ni_2MnGa is also ferromagnetic in addition to its shape memory properties.

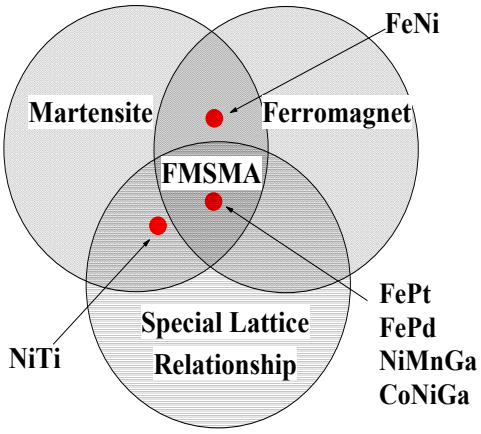


Fig. 1. Conceptual position of several alloy systems in the Martensite, Ferromagnetic and Special Lattice Relationship groups. Alloys in the overlap group of all three are FMSMAs.

The study of the (s+p) electron/atom ratio (e/a) showed that a structural stability occurs in FMSMAs at a critical e/a around 7.3. In addition, a finite value for the saturation magnetization can be obtained - according to the Slater-Pauling curve [17] - for (d+s+p) electron/atom ratios larger than e'/a≈11.5. Both these conditions are fulfilled by the Heusler composition in the CoNiGa system (Fig.2). The CoNiGa ternary phase diagram shown in Fig. 3 delimits a region in which the conditions for the formation of the B2 phase are favorable. This region is in the range in which the e/a and e'/a ratios are also favorable for the occurrence of FMSMA (Fig. 2).

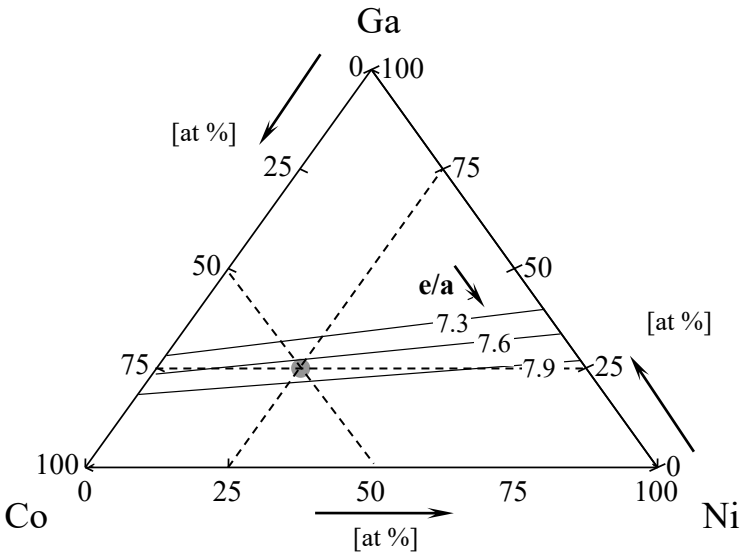


Fig. 2. Compositional range for the formation of Co_2NiGa FMSMAs (see text for details). The black dots mark the alloys investigated in this study.

A single crystal growth in the compositional range of the Heusler composition shows a typical martensitic structure like the one described in Fig. 4. The two phases involved in the transformation were also investigated. The neutron diffraction data for the Co_2NiGa single-crystal shown in Fig. 5 was taken at 350 and 150 K respectively. The high temperature phase is cubic, with a $L2_1$ symmetry.

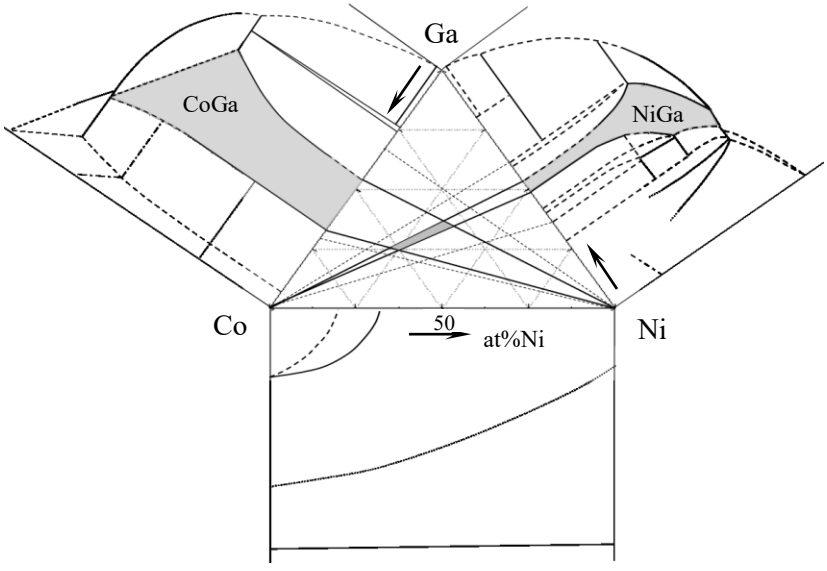


Fig. 3. Schematic ternary phase diagram showing the favorable conditions for the formation of a B2 phase susceptible (center gray area) of transforming into martensite. The dotted lines show the extension of the B2 domain for solution treated alloys. Binary phase diagrams constructed after [18].

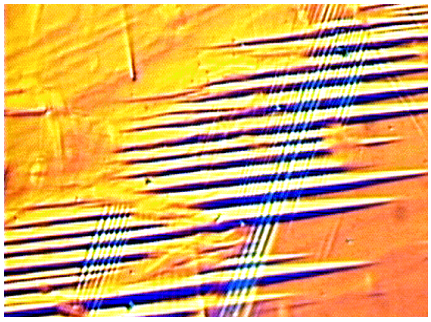


Fig. 4. Martensitic structure in a Co_2NiGa single crystal.

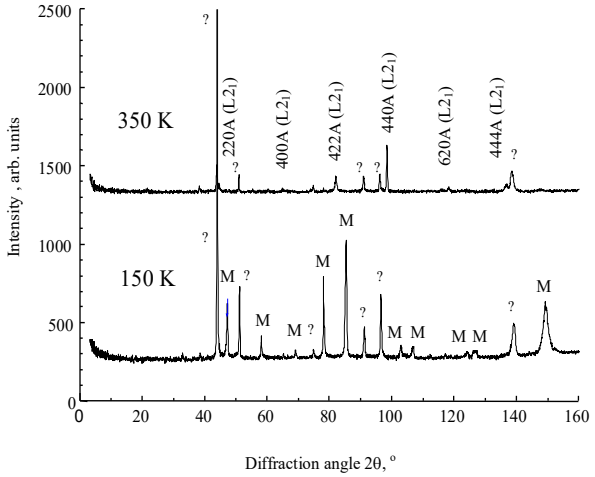


Fig. 5. Neutron diffraction data for a Co_2NiGa. Single crystal recorded at 250 and 150 K, respectively.

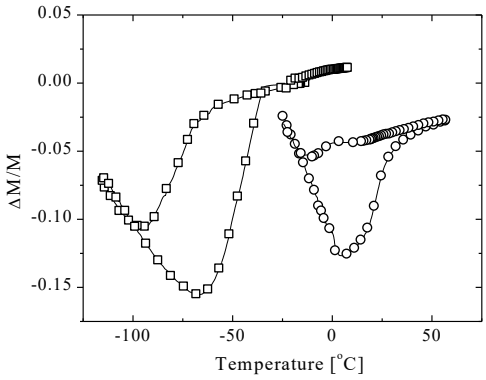


Fig. 6. The influence of quenching on the martensitic phase transformation of a $Co_{50}Ni_{25}Ga_{25}$ single crystal (before quenching and after annealing followed by slow cooling (□), and after quenching (○)).

The additional peaks that do not transform appear because the composition of the alloy falls slightly outside the gray area in Fig. 3. A solution treatment followed by quenching enlarges the region in Fig. 3 and affects the phase transformation, as shown in Fig. 6. The change in the modulus defect ΔM/M as a function of temperature observed in Fig. 6 proves that the phase transformation is thermoelastic reversible. As a result of the solution treatment an increase in the transformation temperature range occurred, suggesting that the precipitates were dissolved in the B2 phase matrix. An additional solution treatment followed by slow cooling reverted the transformation toward its original values.

The series of micrographs in Fig. 7 show the microstructural changes associated with the phase transformation in a Co_2NiGa polycrystal similar to those observed in known shape memory alloys. This confirms once more the character of the phase transformation.

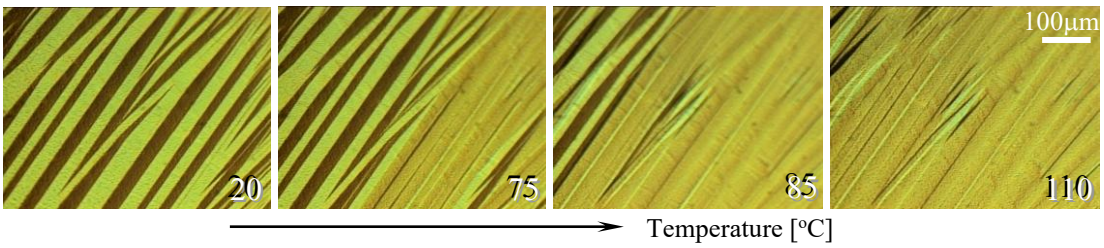


Fig. 7. Microstructural changes observed on heating a $Co_{50}Ni_{22}Ga_{28}$ shape memory alloy.

The ferromagnetic character of the Co_2NiGa alloys is described by the magnetization curves in as solidified and quenched state (Fig. 8). The saturation magnetization depends on the state of the alloy and, in quenched state, is comparable to the one of Ni.

The results summarized in this paper show that Co_2NiGa are a new class of Heusler-type FMSMAs, similar to Ni_2MnGa and with very good perspectives for practical use.

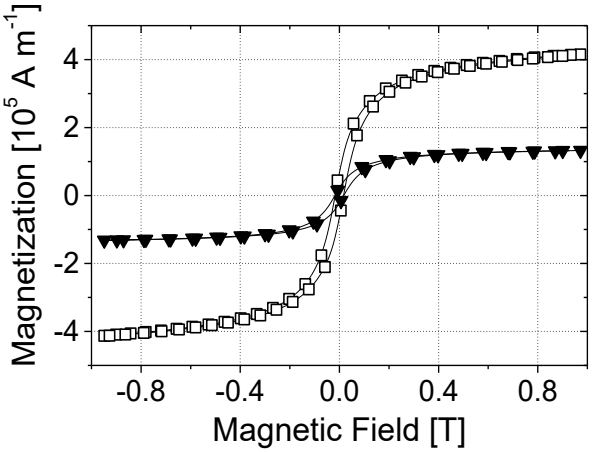


Fig. 8. Magnetization curves of $Co_{50}Ni_{0.22}Ga_{0.22}$ determined at room temperature, as -solidified (▼), annealed 3 hrs at 850 °C and quenched (□).

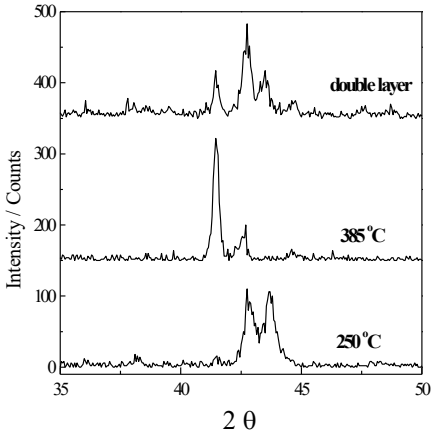


Fig. 9. X-ray diffraction data for NiTi films deposited at 250 and 385°C and for a film with one layer deposited at 250 °C and the other at 385°C.

3. Interaction between microlayers in NiTi functionally graded SMA films

Ni-rich NiTi alloys are known to show a two-step B2→R-phase→B19' transition with the sequence influenced by the stress. Stachowiak and McCormick have demonstrated that the B2→R-phase→B19' sequence that occurs at low stress becomes only a B2→B19' at higher stress [18]. A similar observation was made for Ni-rich NiTi films deposited on heated Si cantilever-type substrates [19]. A film deposited at 250 °C is subject to a lower thermoelastic stress, on cooling from the deposition temperature, as compared to a film of the same composition deposited at 385 °C. According to the above-mentioned observations the 250 °C film shows a B2→R-phase→B19' while the 385 °C film shows only a B2→B19' transition. This difference is proven by the X-ray data of individual films deposited at 250 and 385 °C respectively, and of a corresponding double layer film showing the features of the component layers, in which each layer was half of the thickness of the monolayers (Fig. 9). The transition from one sequence to another is gradual, i.e. the transformations coalesce and shift gradually as the deposition temperature and thermoelastic stresses changes [19].

Since the thermoelastic stress is considered one of the leading factors in the occurrence of one of the other sequence of transformation, it follows that in a multilayer in which each layer transforms under a different stress, the transformation becomes stress graded. For NiTi films as those described before the continuous interaction between the martensites is expected to led to interesting behavior when the thermoelastic stress is the gradient factor. Double layer films deposited on Si substrates out of NiTi targets have already shown an extraordinary damping peak when the first layer was deposited at 385 °C and the second at 250 °C [20].

The idea that a certain interaction between the martensites occurs in these films suggests that if the temperature is continuously changed during the deposition, the microlayers that form in this process would also interact in a continuos manner.

Fig. 10 shows the displacement of the end of NiTi films / Si bimorph cantilevers deposited under the following conditions: (1) a film deposited at constant (385°C) temperature; (2) a film deposited on cooling by continuously changing the temperature between 385 °C and 250 °C and (3) a

film deposited on heating by continuously changing the temperature between 250 °C and 385 °C. All other deposition parameters (time, power, Ar pressure) were kept the same during the depositions.

It can be observed that films deposited on heating show a higher displacement compared to those deposited at constant temperature and that the films deposited on cooling show an insignificant change in the displacement as a result of the phase transformation.

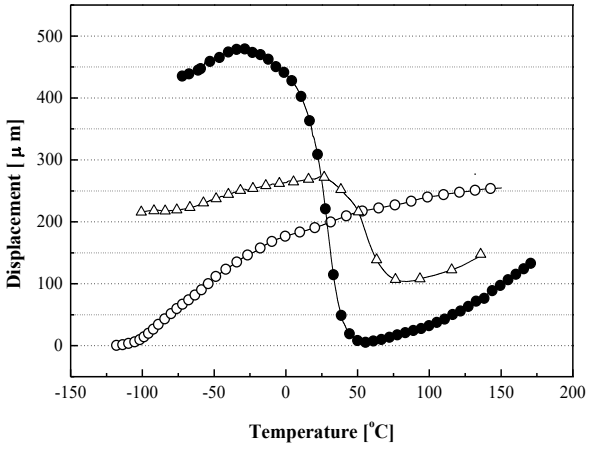


Fig. 10. Displacement vs. temperature curves for NiTi films deposited at 385 °C (Δ), on cooling from 385 to 250 °C (o) and on heating from 250 to 385 °C (•).

One possible explanation is suggested in Fig. 11.

The stress and transitional graded films are analyzed for two cases- heating and cooling –and three sub-cases –the temperature of the experiment T_x is higher or lower than the transition temperature of any microlayer or equal to the transition temperature of a Δt microlayer.

For the depositions on heating, as long as the temperature T_x is higher than the transformation temperature of any microlayer, the only displacement observed for the bimorph is the one produced by the thermoelastic stress that arises on cooling from the deposition temperature. As the temperature reaches the transformation temperature of the first microlayer, this one transforms under constraint only from the bottom untransformed layer. As the top microlayer transforms it relieves the stress and, as the temperature is lowered, it allows the next layer to transform under similar conditions (i.e. with constrains only from one side because the already transformed microlayers do not act as constraints). This step transformation allows an orderly and complete transformation of the film from top to bottom, therefore giving the maximum stress relief and associated displacement in the bimorph.

A different situation appears when the films are deposited on cooling. The first microlayer to transform finds itself constrained from two sides – the substrate and the top untransformed layer. This situation continues as the temperature is lowered, until the last microlayer starts to transform. Since this layer is not constrained from any part it can relieve part of the total stress. However this stress relief is low because it is only associated with a small amount of transforming microlayer.

In these films, the grading parameter is the thermoelastic stress coupled with the stress transition that occurs at a different temperature in each microlayer. By conveniently using these two parameters the film can be engineered in such a way to give optimal functional properties for the bimorph.

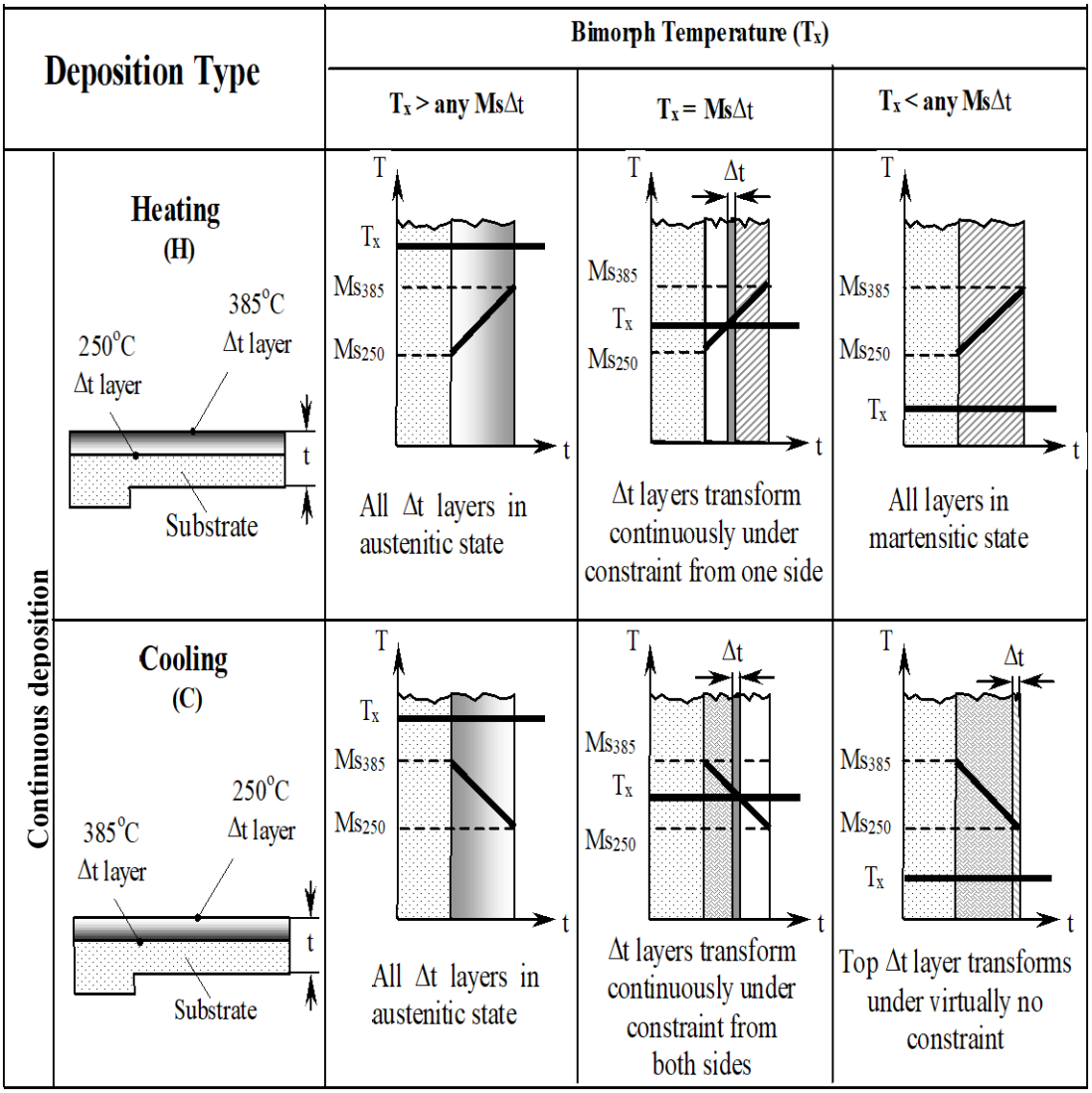


Fig. 11. Specific transitions in films deposited on heating and on cooling (see text for details).

4. Conclusions

The area of shape memory alloys is subject of continuous innovation resulted from an oriented effort to expand the limits of a material with huge potential for high tech applications. The ferromagnetic and functionally grading aspects are two of the most recently studied.

The new research path developed during the last few years allowed the discovery of a new CoNiGa Heusler-type FMSMA, with a very promising future. The martensitic transformation in CoNiGa alloys is similar to the one known in shape memory alloys and the ferromagnetic behavior is expected to be better than the one known for NiMnGa alloys. The compositional field in which CoNiGa alloys show the memory effect is large and so is the transformation temperature range (from –150 to +200 ºC).

The functionally graded NiTi films produced by continuously changing the deposition temperature were thermo-elastically engineered in such a way to give the highest actuation by favoring a complete and ordered transformation, when the film deposition was made with the substrate gradually cooled between 385 and 250 ºC.

The transformation of the microlayers under constraint discussed in the paper proves that a microlayer transforms differently when is subjected to constraints coming from transformed and untransformed layers, respectively.

The two aspects discussed in this paper are both of high importance for the development of SMA's actuation function. They have favorable perspectives for use in the fabrication of micro-actuators.

Acknowledgements

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