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Microstructure, transformation temperatures, hardness and magnetic properties of $Co_{36.4+x}Ni_{33.3-x}Ga_{30.3}$ ferromagnetic SMA

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ABSTRACT

Microstructure, martensitic transformation temperatures, hardness, and magnetic properties have been studied in Co–Ni–Ga alloys for different compositions of Co and Ni. Hardness, transformation temperatures and thermal hysteresis show a decrease with Co content. On the contrary, maximal magnetization, and magnetic hysteresis both grow with cobalt composition.

1. Introduction

Ferromagnetic shape memory alloys have received much attention because they exhibit both magnetic field induced strain and magnetic shape memory effect. Magnetically induced strains up to 10% have been observed in near-stoichiometric Ni_2MnGa alloys [1,2]. This large strain results from the high anisotropy in magnetocrystalline energy of the martensite and high mobility of the interfaces between martensitic variants in Ni–Mn–Ga alloys. However, the high brittleness of these alloys restricts their applications. Studies on several candidates for ferrromagnetic shape memory alloys have been carried out: Fe–Pd [3], Fe–Pt [4], Ni–Mn–Al [5], and Co–Ni–Al [6,7] in order to find out new alternative materials with lower brittleness. Recently, Ni–Fe–Al [8] and Co–Ni–Ga [9] have been considered as good ferromagnetic shape memory alloys candidates, mainly due to the presence of a γ phase (disordered fcc A1) that improves ductility in these kind of alloys [10], but a high percentage of this phase can cause an decrease of magnetically induced strain. In contrast with Ni–Mn–Ga alloys, these new Co- and Ni-based alloys usually present dual-phase structures. This behavior was also found in Co–Ni–Al [10], Ni–Al–Fe [11] and Ni–Fe–Ga [12]. Recently, some studies have been done on the effect of a fourth element, for example Ni–Mn–Ga–Co and Ni–Fe–Ga–Co, in those alloys the addition of low quantities of Co modifies transformation temperatures and magnetic properties [13,14]. The influence of Co on the martensitic transformation in Co–Ni–Ga system for some particular heat treatments was recently published [15], but no influence on other properties has been reported.

The aim of this work is to study the correlation between composition and phase transformation temperatures, magnetization and hardness in $Co_{36.4+x}Ni_{33.3-x}Ga_{30.3}$ ($0 \leq x \leq 3.1$ at%) alloys.

2. Experimental

Four samples of polycrystalline Co–Ni–Ga alloys were prepared from pure elements Co (99.9%), Ga (99.9%), and Ni (99.9%) by arc furnace melting under argon atmosphere. The alloys were three times re-melted. After melting every alloy was vacuum sealed in a quartz capsule for heat treatments. In order to improve homogeneity, alloys were heat treated at 1273 K for 24 h, after such treatment samples were heat treated at 1173 K for 24 h in order to produce chemical ordering of structure, and finally water quenched. The specimens were cut from the ingots with a wire saw cutting machine. Chemical compositions were measured on annealed samples (Table 1) by energy dispersive spectroscopy (EDS) on a JEOL 5800 LV scanning electron microscope. Transformation temperatures were determined by differential scanning calorimetry in a DSC TA Instruments Q200. The microstructure was examined by optical microscopy using a chemical etching solution consisting of 25% HNO_3–ethanol. Magnetization measurements were carried out in a vibrating sample magnetometer (LDJ-9600-2T). Hardness was measured in a MH-001 Future-Tech instrument.

3. Results and discussion

Table 1 shows compositions obtained in studied alloys and their correspondent *e*/*a* ratio. It can be noticed that gallium contents

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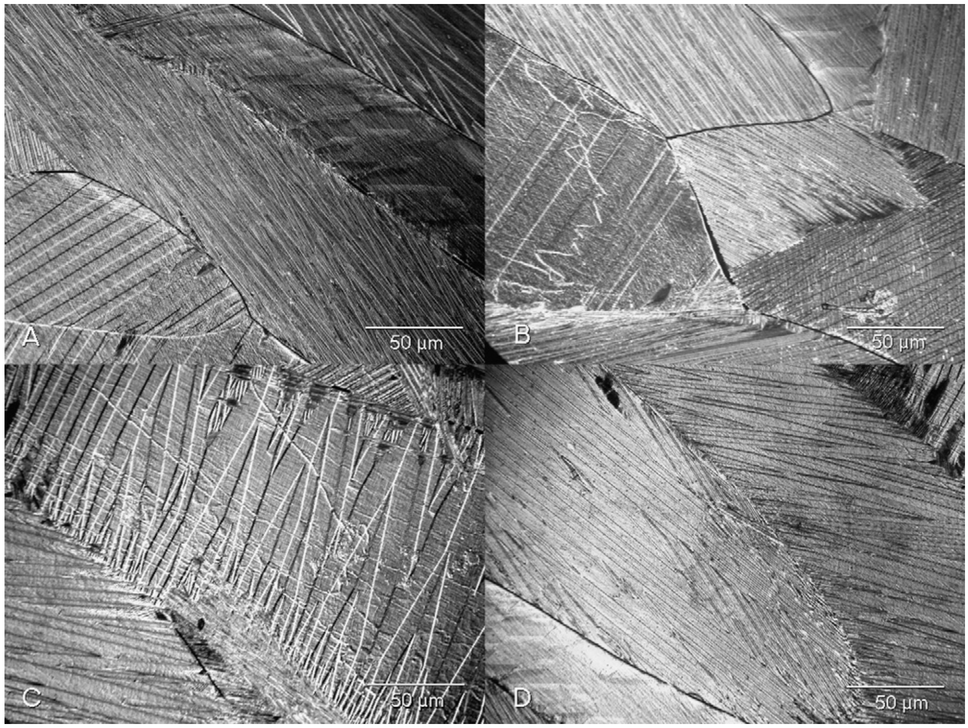

Fig. 1. Optical micrographs of alloys.

remain almost constant among four alloys and Co content varies from 36.4 to 39.5 at%. It has been assumed that atoms of Ni are replaced by those of Co, and this Co growth leads to a lower electronic concentration.

The microstructure presented by four alloys at room temperature is shown in Fig. 1. It can be noticed that the alloys present similar martensitic phase microstructure with well-defined martensite variants. No second phase was observed in any of the alloys, and this absence may be attributed to rapid solidification by arc melting processing as it has been reported [16]. In all alloys studied the morphology of austenitic grains (transforming to martensite during quenching) is columnar type on the upper part of the sample, with the presence of small grains at the bottom surface. This kind of microstructure is due to temperature gradient between top surface and the surface in contact with the copper crucible, where a process of rapid solidification takes place.

Fig. 2 shows the transformation peaks obtained in calorimetric measurements from the same alloys. It can be noticed that D-alloy presents a particular behavior, since the reverse transformation peak occurs at the lowest temperature (less than 500 K). Moreover, peaks of direct and reverse martensitic transformation are closer than those presented in other three alloys, which implies that D alloy has a lower thermal hysteresis. The other three alloys show martensite–austenite peaks at higher temperatures, so hysteresis are more important.

Table 1
Chemical composition of obtained alloys.

Alloy	Composition (at%)[a]			*e/a*
	Co	Ni	Ga	
A	36.4	33.3	30.3	7.51
B	37.6	32.1	30.3	7.50
C	39.0	30.6	30.4	7.48
D	39.5	30.1	30.4	7.47

[a] Atomic percent is ±0.1%.

The larger hysteresis in Co–Ni–Ga alloys as compared with that measured in Ni–Mn–Ga alloys, has been attributed to smaller mobility of twin interfaces. Nevertheless, for a more important Co content (D alloy: 39.47 at%) hysteresis shows a more convenient behavior for a best magnetic shape memory effect.

The transformation temperatures and hysteresis obtained from DSC measurements are presented in Table 2.

Fig. 3 shows the influence of cobalt content on the transformation temperatures and transformation hysteresis. It can be noted from Fig. 3(a) that composition has an important influence on the transformation temperatures: those temperatures undergo a decrement with Co content. Moreover it can be observed that in general the thermal hysteresis present an increase; however the alloy with a higher Co content has shown a particular low hysteresis. This behavior has firstly associated to a precipitation process, but the optical analysis of D alloy has not revealed a second phase.

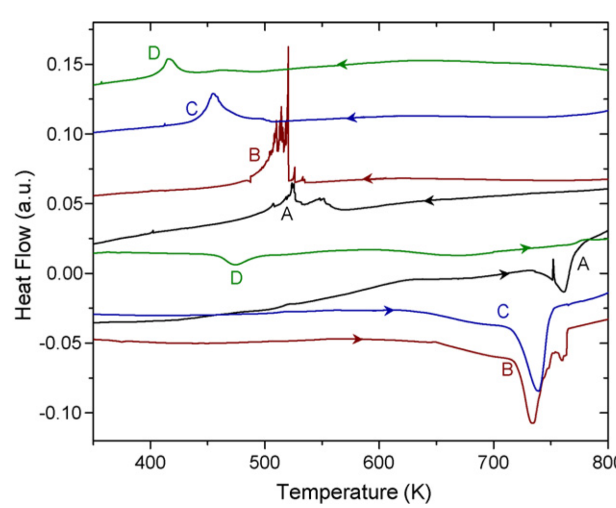

Fig. 2. DSC measurements for different Co contents.

Table 2
Transformation temperatures of different alloys.

Alloy	Temperature (K)				Hysteresis
	M_S	M_f	A_S	A_f	
A	526	514	740	771	217
B	520	500	718	755	251
C	470	444	716	750	256
D	427	406	460	495	40

New studies should be done to find out the presence of second phase small precipitates, and also the evolution of transformation temperatures with higher cobalt contents.

The magnetic hysteresis loops obtained in four alloys are presented in Fig. 4, showing very narrow hysteresis. It can be noticed that maximal magnetization of the alloys increases with Co content (i.e. decreases with e/a ratio). This behavior can be attributed to an increase in magnetic anisotropy with Co content as it has been argued elsewhere [17].

The maximal magnetization at 15 000 Oe as a function of Co content is presented in Fig. 5. Magnetization presents a linear behavior with Co content. On the other hand, spite the very narrow hysteresis presented in Fig. 4 in those materials, the magnetic hysteresis presents an increase with Co content, as it can be noticed in Fig. 6. The hysteresis value of D alloy for higher Co content is more important than for the other alloys.

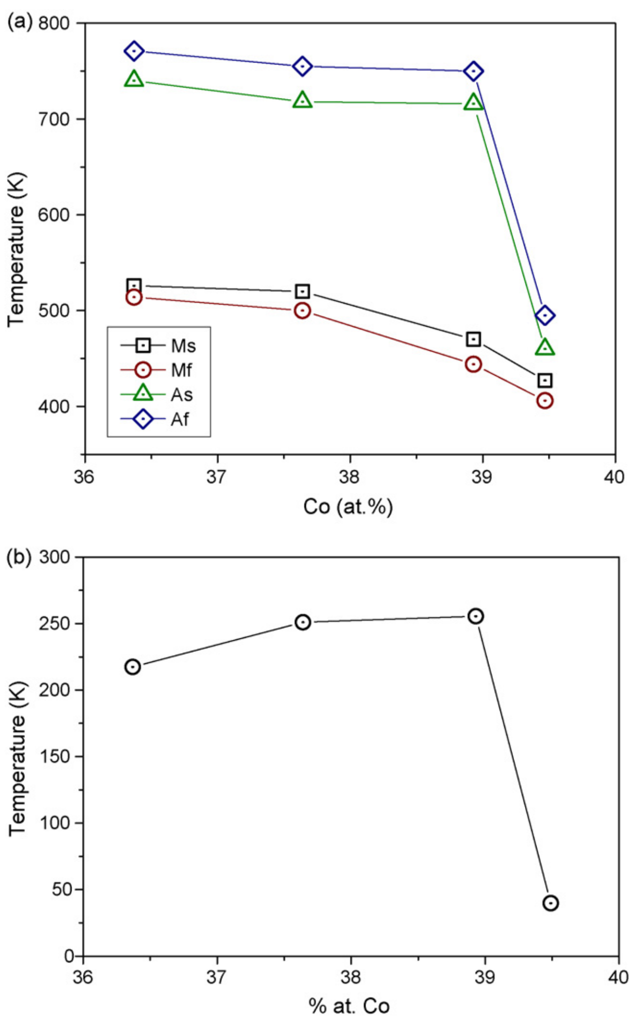

Fig. 3. (a) Transformation temperatures and (b) thermal hysteresis with Co content.

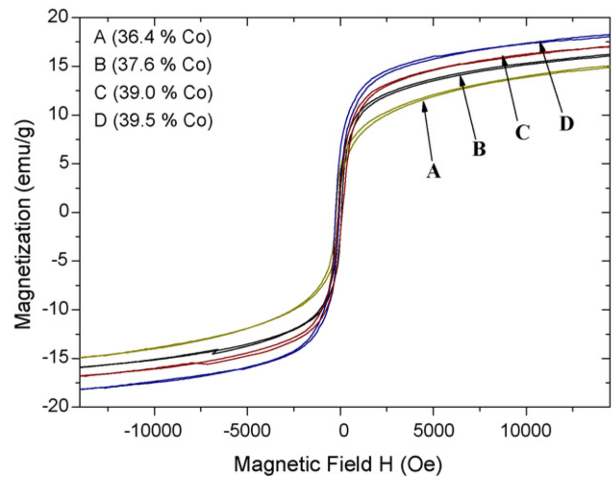

Fig. 4. Magnetization curves for $Co_{36.4+x}Ni_{33.3-x}Ga_{30.3}$ alloys.

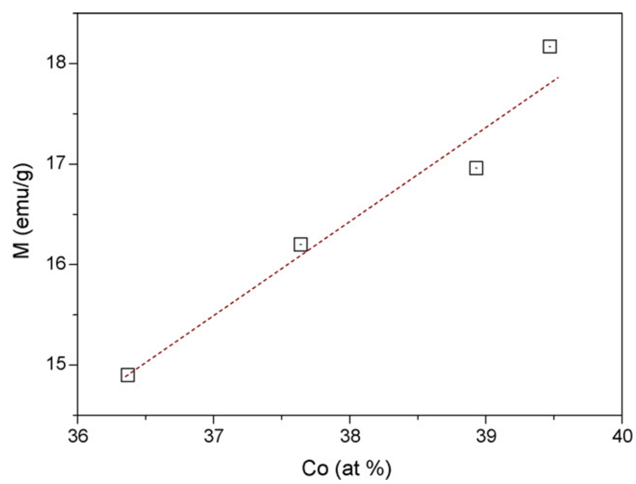

Fig. 5. Magnetization at 15 000 Oe for different Co contents.

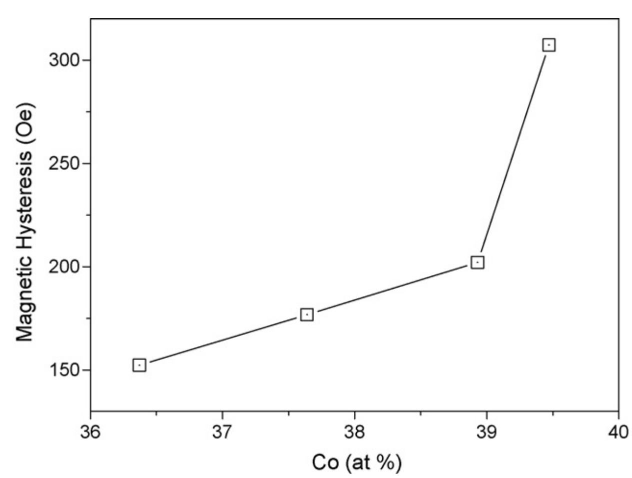

Fig. 6. Magnetic hysteresis versus Co content.

Hardness in Fig. 7, decreases with cobalt content, but the value for the alloy with higher cobalt content shows a recovery. This last result suggests that this composition produces an important structural change on this alloy.

Maximal magnetization and hardness obtained in this study are shown in Table 3. It is well known that transformation temper-

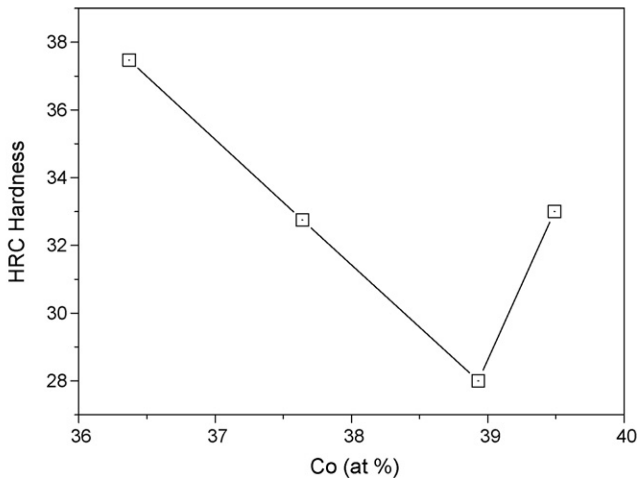

Fig. 7. Dependence of the hardness on Co content.

Table 3
Magnetization, hardness and hysteresis for different alloys.

Alloy	Co at%	e/a	Magnetization (emu/g)	Hardness (HRC)
A	36.4	7.51	14.90	37.47
B	37.6	7.50	16.20	32.75
C	38.9	7.48	16.96	28.18
D	39.5	7.47	18.17	33.13

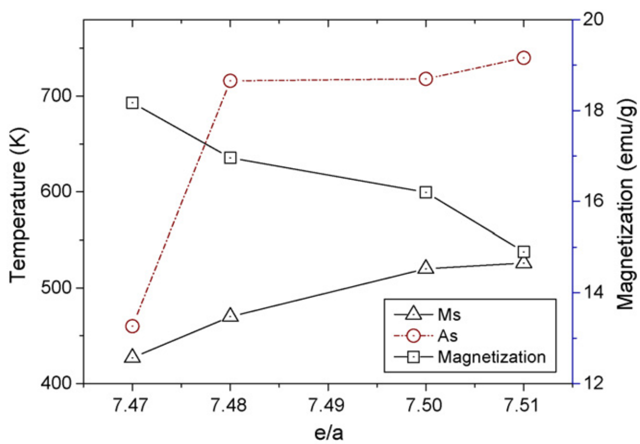

Fig. 8. Transformation temperatures and maximal magnetization at 15 000 Oe as a function of *e*/*a* ratio.

atures in ferromagnetic shape memory alloys are very sensible to changes in composition, and consequently on the electronic concentration (*e*/*a*). Fig. 8 shows the main transformation temperatures and the maximal magnetization (at 15 000 Oe) as a function of electronic concentration.

From this figure it can be noticed that M_S temperature grows with electronic concentration, besides the A_S temperature grows more rapidly for the low values, but for higher values of *e*/*a* this transformation temperature grows slowly. On the other hand, the magnetization decreases with electronic ratio.

4. Summary

In this work, studies of the relationship between composition and phase transformation temperatures, magnetization and hardness in Co–Ni–Ga alloys have been carried out. The characteristic martensitic transformation temperatures show a decrease with cobalt content. The martensitic transformation hysteresis shows a particular behavior for higher Co contents, i.e. the hysteresis is comparatively lower, and this fact may improve the magnetic shape memory effect in those alloys. On the other hand, the magnetization increases with cobalt content, increasing the magnetic anisotropy. The magnetic hysteresis increases with cobalt content. The hardness of alloys shows a general decrease with cobalt content. This measured decrease in hardness about 20% might be associated with an increase in ductility that should be of interest for applications. Those results suggest that a structural change may occur at high Co content, probably a different type of martensite, or a precipitation not detectable in optic microscopy. More work about this is actually in progress by transmission electron microscopy in order to find out a different martensite structure or the presence of small precipitates of a second phase.

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