Experimental report

27/03/2019

Proposal: CRG-2558 **Council:** 4/2018

Title: Role of Fe and Co addition in NiMnGa shape memory alloys: site occupancy and structural stabilization ofcrystallographic phases

Research area:

This proposal is a new proposal

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Samples: NiMnGaFe

Instrument	Requested days	Allocated days	From	To
D1B	4	2	29/09/2018	01/10/2018

Abstract:

EXPERIMENT N°: CRG-D1B-18-358 **INSTRUMENTS:** D1B

DATES OF EXPERIMENT 29/09/2018-01/10/2018

TITLE: Role of Fe and Co addition in NiMnGa shape memory alloys: site occupancy and structural stabilization of crystallographic phases

REPORT 08/10/2018

Shape Memory Alloys (SMAs) are a group of active materials that undergo phase transitions (resulting in large recoverable mechanical deformations) induced by changing the temperature and/or applying a stress on them. In particular, magnetic SMAs (MSMAs) consist in metal alloys in which the actuation of the material can be induced not only by temperature or stress, but also upon the application of a magnetic field. The properties shown by MSMAs, mainly the superfast response (in the millisecond regime) and the high energy density (of the order of 105 J/m3), makes them the ideal candidates to be implemented in the field of sensors and actuators. A particularly attractive subgroup among the MSMAs is the one formed by alloys that present a large magnetic-field-induced strain (MFIS), where the application of a magnetic field deforms the material. In MSMAs the martensitic transformation goes from a cubic structure at the austenitic phase to an orthorhombic or tetragonal martensitic phase, which can be modulated in some cases. Such a variant reorientation is possible by the large magnetic anisotropy energy of the variants in the external field and the magnetoelastic coupling between lattice and spin, which allows manipulating the crystal structure by a magnetic field. Additionally, magnetic coupling between atoms will depend on their positions within the lattice. This will also have an effect on the lattice parameters.

In this regard, the aim of the proposal was to obtain the crystalline phases and atomic site occupancies of a series of alloys of $Ni_{51}Mn_{28-x}Ga_{21}Fe_x$ and $Ni_{51}Mn_{28-x}Ga_{21}Co_x$, with x=0, 1, 3 and 5 (only in the case of Fe), where we observed that the addition of Fe and Co in substitution of Mn influences the crystal structure of the martensitic phases in the alloy.

During the 48h experiment performed at the powder neutron diffractometer D1B at ILL, we managed to measure a total of six samples with the compositions and diffractogram temperatures included in the following table:

Composition	Name	T1	T2	T3	T4
$Ni_{51}Mn_{28}Ga_{21}$	M1	250K	353K	437K	-
$Ni_{51}Mn_{27}Ga_{21}Co_1$	M3(Co)	250K	361K	445K	-
$Ni_{51}Mn_{25}Ga_{21}Co_3$	M4(Co)	250K	433K	512K	-
$Ni_{51}Mn_{27}Ga_{21}Fe_1$	M3(Fe)	250K	361K	446K	-
$Ni_{51}Mn_{25}Ga_{21}Fe_3$	M4(Fe)	250K	361K	458K	500K
$Ni_{51}Mn_{23}Ga_{21}Fe_5$	M5(Fe)	250K	333K	473K	-

Table 1: Names and compositions of the six samples measured at D1B during the experiment, with the temperatures at which diffractograms were acquired.

All the diffractograms obtained in this experiment were measured working at a wavelength of λ=1.28 Å. The experimental procedure was the following: after inserting the sample in the cryofurnace at D1B we set up a routine to continuously acquire neutron diffraction data until removing the sample, setting up three different temperatures at which diffractograms were acquired for 30 min each. The three different temperatures were chosen so that we could measure a ferromagnetic martensite phase (T1), an intermediate paramagnetic martensite (if $T_C<T_A$) or ferromagnetic austenite (if $T_C>T_A$) (T2), depending on

the Curie and transformation temperatures of the sample, and a high temperature paramagnetic austenite (T3), always measured at the same temperature distance from T_C of each sample (T_C+75K). The sample M4(Fe) was also measured at a fourth temperature, T4, because it was the last sample mounted in the diffractometer and we had an extra hour to finish the experiment. Besides these standard diffractograms obtained at the aforementioned stable temperatures, we also recorded thermodiffractograms during the temperature ramps from T1 to T2, and from T2 to T3 (also T3 to T4 for M4(Fe)).

A quick initial FULLPROF analysis of the diffractograms obtained in the experiment shows that the parent M1 sample has a mixture of modulated orthorhombic and tetragonal phases; the Co-rich samples tend to stabilize the tetragonal phase towards a non-modulated one; and the Fe-rich samples tend to stabilize the orthorhombic phase. This can be observed in the diffractogram figures attached to the report, but also in the differences of the thermodiffractograms, where the phase change is evident around the transformation temperature T_A. A more detailed analysis of the obtained diffractograms at the different temperatures measured, by means of Lebai ND FULLPROF refinements, will give us the detailed crystalline phases present at each alloy for the aforementioned temperatures. A further analysis of the ND data performing Rietveld refinements with FULLPROF will allow us to unravel the specific site occupancies of each phase in the six alloys measured at each temperature. Finally, although the neutron beam hitting our samples at D1B is not polarized, because of the magnetic scattering produced between our samples below their TC and the incoming neutrons, by means of exhaustive Rietveld refinements of the diffractograms below and above TC in the same crystallographic phases of each sample (T1 and T2 for samples with $T_C<T_A$; T2 and T3 for samples with $T_C>T_A$), we will try to obtain the magnetic moments at each atomic site.

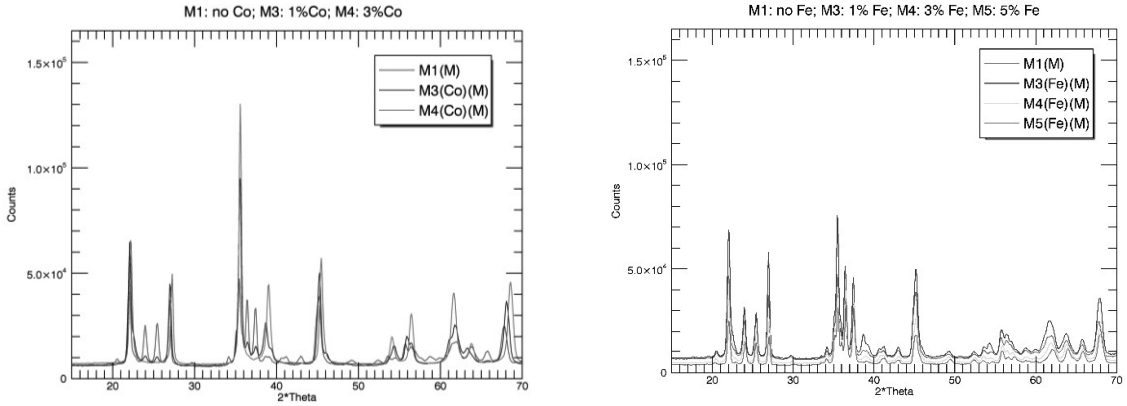

Fig. 1: Neutron diffractograms measured for the Co rich (left) and Fe rich (right) samples, together with the parent sample without any Co or Fe (M1).

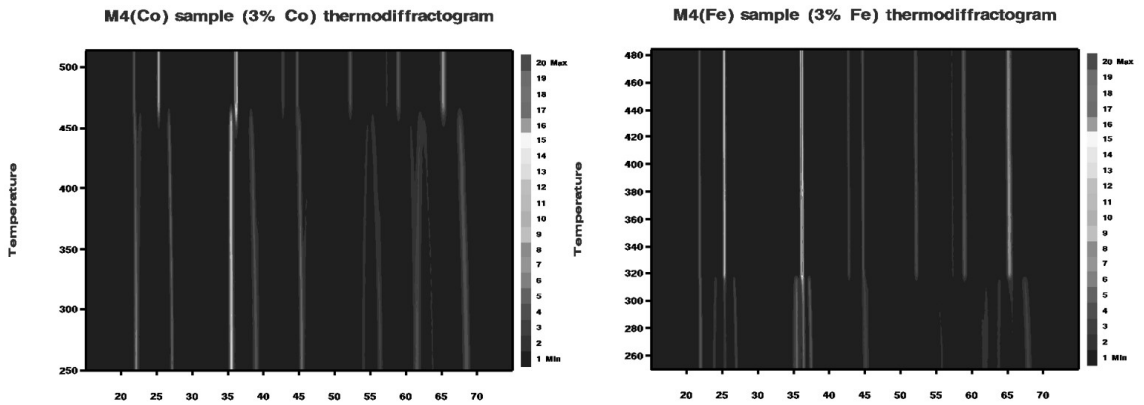

Fig. 2: Thermodiffractograms measured for the M4(Co) (left) and M4(Fe) (rich) samples showing the different phase stabilizations below the transformation temperatura in each case.