J. PHYS. IV FRANCE **7** (1997)
Colloque C5, Supplément au Journal de Physique III de novembre 1997

Some Aspects of Structural Behaviour of Ni-Mn-Ga Alloys

V.A. Chernenko*, C. Seguí, E. Cesari, J. Pons and V.V. Kokorin*

Dept. Física, Universitat de les Illes Balears, 07071 Palma de Mallorca, Spain
** Institute of Magnetism, Vernadsky Str. 36-B, Kiev 252680, Ukraine*

Abstract. The temperature induced transformation of single crystalline Ni - 31.1% Mn - 17.7% Ga (at%) shape memory alloy with Ms ~ 446 K has been studied by means of dynamic mechanical analysis (DMA), calorimetry (DSC), dilatometry, three point bending tests and TEM. Two maxima in internal friction (IF) spectra on cooling and a single maximum on heating, concurrently with kink-like anomalous changes of elastic modulus (E) have been found. Corresponding changes have been observed using the other techniques. The evolution of electron diffraction patterns and microstructure during *in situ* cooling and heating experiments performed in the TEM have revealed a two-stage martensitic transformation on cooling (namely, from the cubic $L2_1$ ordered parent phase (P) to a martensitic phase with a ten-layered modulated lattice (10M) and from the latter to the monoclinic distorted martensite with seven-layer type of modulation (7M)). On heating, only one-stage transformation from 7M martensite to parent phase has been observed. The intermartensitic transformation 10M→7M and the martensitic P↔10M show the characteristics of first order transformations, such as transformation heat and transient contribution to the corresponding IF peaks.

1. INTRODUCTION

The martensitic transformation in the Ni-Mn-Ga alloy system has been extensively studied in the recent years [1-5]. Several martensitic structures have been obtained for different alloy compositions and different applied stress levels, many of them having long-period modulated lattices. As a matter of fact, single crystalline Ni-Mn-Ga alloys with Ms near room temperature undergo a sequence of stress-induced transformations upon compression along <110> axis or tension along <100>, namely from the $L2_1$ ordered cubic parent phase (P) to tetragonal martensite with 5-layered type of modulation (5M); from the latter to a 7-layered modulated martensite (7M) and, finally, to tetragonal martensite without modulation (T) [1,2,6]. Alloys with lower Ms (around 200K) have been also studied. The most remarkable result is the observation of a premartensitic transformation from the parent phase to a modulated cubic phase with a lattice parameter three times larger, before the martensitic transformation to a structure with a complex modulated lattice [5]. The premartensitic transformation behaves like a weak first order phase transition and has been discussed in terms of a soft mode condensation [7].

Few experimental data about the Ni-Mn-Ga alloys with Ms well above room temperature (about 400K) are available. At variance with Ni-Mn-Ga alloys with lower transformation temperatures, for this group of alloys Ms is usually above the Curie temperature, which is about 360K [3,4]. Previous work showed that in single-crystalline alloys, the martensite structure observed at room temperature was modulated 7M [4]. In the present paper more results concerning the transformation behaviour of high Ms Ni-Mn-Ga alloys will be presented and discussed.

2. EXPERIMENTAL PROCEDURE

A single crystal of composition (at%) Ni - 31.1%Mn - 17.7%Ga, grown by the Bridgman method, was used. The transformation start temperature, Ms, obtained by means of DSC was 433 K. Specimens of appropriate sizes were cut from the initial monocrystalline rods by means of a spark machine and polished to obtain flat surfaces. Internal friction (IF) and elastic modulus (E) spectra were recorded in three-point bending configuration using a Dynamic Mechanical Analyzer Perkin-Elmer DMA-7. The measurements were performed at oscillating stress frequency 1 Hz, oscillating stress amplitude 4 to 10 MPa (corresponding to strain amplitude in the range 10^{-4}) and cooling/heating rate dT/dt = 5 K/min. Details of the dynamic mechanical technique and treatment can be found in [5]. Martensitic transformations were also studied by a static thermomechanical test consisting of compressing cylindrical specimens (axis oriented along $[110]_P$ direction) at 77K and recording the strain recovery (elongation) during subsequent heating, using a Perkin-Elmer TMA-7 dilatometer. Finally, transmission electron microscopy (Hitachi H600, 100 kV, equipped with a single tilt heating and cooling stage) was used for structural characterization. The thin foils were prepared by double-jet electropolishing in a 50:50% mixture of nitric acid and methanol, at 240 K.

3. RESULTS

Examples of the obtained DSC cooling and heating curves are shown in Figure 1. As it can be seen in the cooling curve, the main exothermic peak around 430K is followed by a second peak, much smaller, around 340K. In contrast, the heating curve shows only one endothermic peak at about 440K. The exchanged heats corresponding to the peaks observed on cooling are -11.8±0.2 J/g and -1.3±0.4 J/g, while for the single peak observed on heating it is 13.0±0.2 J/g. Thus, from the DSC data the occurrence of two temperature-induced first order transformations on cooling and only one reverse transformation on heating can be inferred. This behaviour is also observed in the internal friction (IF) and elastic modulus (E) spectra recorded in the DMA (Figure 2). Two IF (tan δ) peaks, accompanied by two corresponding E minima can be seen in the cooling run. After the second peak, the IF level gradually decreases to zero as the temperature decreases. On heating, the IF gradually rises until it reaches a constant value at about 320K. On further heating, a big IF peak related to the reverse martensitic transformation occurs. Although the decrease in IF level after the second peak on cooling and the subsequent increase on heating look like additional flattened peaks, further experiments that will be discussed later showed that this behaviour of IF at low temperatures is not related to a phase transformation.

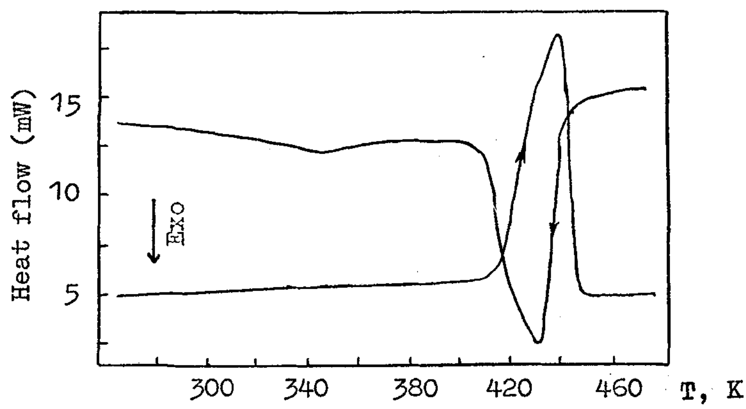

Figure 1. DSC curves obtained for a cooling/heating rate of 10K/min.

The strain recovery after static compression (Figure 3) serves as further evidence for the above mentioned sequence of martensitic transformations. Namely, the strain stored by martensite after releasing the compressive stress at 77 K is entirely recovered during subsequent heating throughout the reverse martensitic transformation in one-step manner, displaying a conventional shape memory effect which is characteristic for Ni-Mn-Ga alloys [3]. Moreover, subsequently cooling the unloaded specimen, a well pronounced two-step strain accumulation, related to the two successive transformations, is observed. The spontaneous shape change on cooling indicates the induction of the two-way shape memory effect accounting for the influence of the first transformation under compression (being the training procedure in this case) on the nucleation and growth of the two martensites formed separately.

It has to be emphasized that a single martensitic transformation and retransformation can be easily obtained by uncompleted cooling, as it has been experimentally proven by DSC and DMA measurements. The intermediate martensitic phase formed in that way undergoes during subsequent heating the reverse transformation to the parent phase, in the same temperature interval than the sample cooled to the lowest temperature martensitic phase. The heat exchanges during uncompleted cooling and subsequent heating are very similar in value (11.8±0.2 J/g).

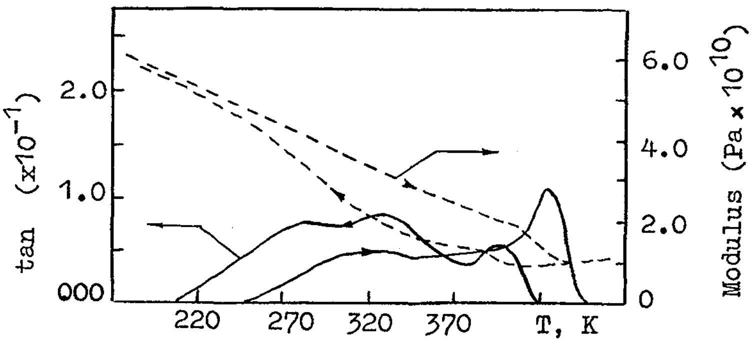

Figure 2. Internal friction (tan δ) and elastic modulus as a function of temperature. dT/dt = 5 K/min ; f = 1 Hz ; amplitude of oscillating stress 6 MPa.

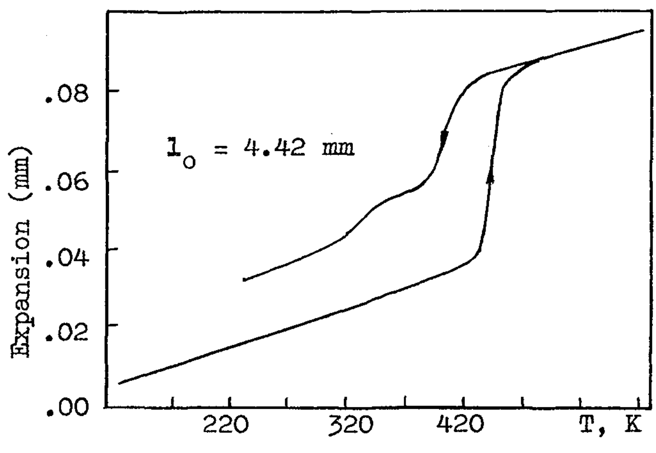

Figure 3. Temperature dependence of the height of a cylindrical specimen cut along <110>$_P$ direction. The specimen was previously compressed by a stress of 45 MPa and unloaded at 77K. l_o stands for the initial sample height.

To examine the nature of the phases involved in the above transformations, transmission electron microscopy observations were performed using cooling and heating sample holders. Figure 4 shows the selected area electron diffraction patterns (SAEDP) obtained at different temperatures in the following sequence: room temperature, heating up until completing the reverse transformation to the parent phase and cooling back. The changes in the diffraction patterns indicate that the temperature anomalies of the physical properties shown above are originated from the crystal structure variations accounting for the martensitic and intermartensitic transformations. Fig. 4a (room temperature) corresponds to the low temperature martensite, Fig. 4b to the parent phase and Fig. 4c to the intermediate martensite. The SAEDP at room temperature shows a modulated commensurate lattice characterized by periodic stacking sequences of $\{110\}_P$ planes along the $<110>_P$ direction with a periodicity of 7 planes (since the unit reciprocal lattice distance along the $[110]_P$ direction is divided in 7 equal parts by 6 extra spots indicated by arrows in Fig. 4a) which will be denoted as martensite 7M. The high temperature parent phase (P) structure has a cubic $L2_1$ ordered lattice modulated by dynamic waves of atomic displacements propagating mainly along the $<110>_P$ direction, producing diffuse scattering streaks of the fundamental reflections [4]. On cooling from the parent phase the specimen transforms to a modulated structure similar to the martensite 7M, but with different periodicity equal to 10 (9 extra spots along [110] direction, Fig. 4c), denoted as martensite 10M. During further cooling the initially described martensite was formed, thus confirming the two-step forward transformation, P→10M→7M. *In-situ* TEM observations were also performed on heating after both completed and uncompleted cooling (that is, starting from 7M and 10M martensite respectively). In the latter case the 10M to P transformation was observed, but in the former the 10M martensite was not detected, indicating that a one-step reverse transformation 7M→P takes place.

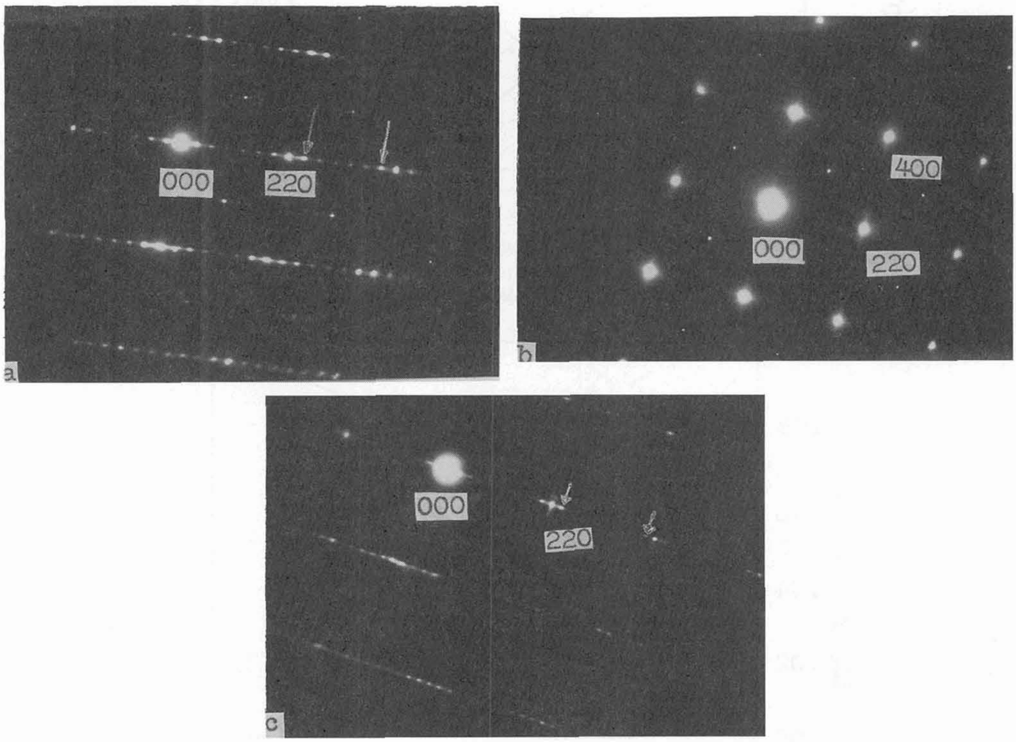

Figure 4. Selected area electron diffraction patterns obtained at different temperatures.
(a) Room temperature, martensite 7M; (b) T = 470 K, parent phase and (c) T = 370 K, martensite 10M

4. DISCUSSION

It was already known that, at room temperature, the crystal structure of martensites formed in single crystalline high Ms Ni-Mn-Ga alloys is modulated 7M, as reported in [4]. However, as follows from the present results, a new behaviour characterized by a temperature induced intermartensitic transformation to the equilibrium martensitic phase has been observed in these alloys. The above in-situ electron microscopy observations clearly proved that the two peaks observed in DSC and IF cooling curves, concurrently with modulus and strain anomalies, are due to two different successive temperature-induced martensitic transformations. It is worth to note that intermartensitic transformations involving similar martensitic structures as those described in the present work were already observed in single-crystalline alloys with other compositions (Ms near room temperature), but only in stress-induced transformations with uniaxial compression along <110>$_P$ or tension along <100>$_P$ [1,2,6], and not in temperature-induced transformations. The order of magnitude of transformation heats accompanying the intermartensitic transformations and the values of the accumulated strain are in agreement with previous data of stress-induced martensites in lower Ms alloys [1,6], which gives an idea about the closeness of the free energies of the different martensites. The observed one-step character of the reverse martensitic transformation can be interpreted as due to a comparatively larger temperature hysteresis for the 7M→10M transformation than for the 7M→P one.

In order to clarify the origin of the IF detected at low temperatures, experiments were performed in which the temperature change was stopped at different temperatures during both the cooling and heating runs. It was found that while IF in the temperature range corresponding to the identified martensitic and intermartensitic transformations have a dominant temperature rate (as called transient) contribution, in the low temperature region IF was practically temperature rate independent. Furthermore, such IF resulted to increase with increasing stress amplitude, pointing out to an intrinsic origin. It can be therefore concluded that no other phase transition takes place after the 7M martensite has been formed, this conclusion being supported by the TEM observations. However, the reason why IF in the martensitic state is temperature dependent is still a subject under discussion, more experimental work being needed to elucidate this point.

Acknowledgments

Authors gratefully acknowledge Zasimchuk I.K. for his help in crystal growth. Chernenko V.A. is grateful to the Universitat de les Illes Balears for financing his stay at the Departament de Fisica, UIB. Partial financial support from DGES-MEC, Spain (project num. PB 95-0340) is acknowledged.

References

1. Kokorin V.V., Martynov V.V. and Chernenko V.A., *Scripta Met. Mat.* **26** (1992) 175
2. Martynov V.V. and Kokorin V.V., *J. de Physique III*, Vol. 2 (1992) 739
3. Chernenko V.A., Cesari E., Kokorin V.V. and Vitenko I.N., *Scripta Met. Mat.* **33** (1995) 1239
4. Fritsch G., Kokorin V.V., Chernenko V.A., Kempf A. and Zasimchuk I.K., *Phase Transitions* **57** (1996) 233
5. Cesari E., Chernenko V.A., Kokorin V.V., Pons J. and Seguí C., *Acta Mat.* **45** (1997) 999.
6. Chernenko V.A., Amengual A., Cesari E., Kokorin V.V. and Zasimchuk I.K., *J. de Physique IV*, Vol. 5 (1995) C2-95
7. Kokorin V.V., Chernenko V.A., Cesari E., Pons J. and Seguí C., *J. Phys.: Condens. Matter* **8** (1996) 6457