Abstract

The present work contains a high-resolution transmission electron microscopy study (including image simulations) of the layered martensitic structures formed in Ni–Mn–Ga alloys. The main purpose is to distinguish two structural models proposed in the literature. For the seven-layered martensite, the observations confirm its nano-twinned nature, which is inherent to the description as stacking of nearly close-packed planes derived from \{1\over2\} \text{ aust} with \((5\over2)\) sequence, i.e. the so-called 14M structure. The observed stacking sequence, however, is notably distorted (perfect \((5\ over2)\) stacking is present only in small areas), although, it preserves a predominant periodicity of seven planes. Equivalent results have been obtained for the 10-layered structure and a less frequent 12-layered phase, for which \((5\ over5)\) and \((7\over5)\) stacking sequences, respectively, have been predominantly observed. In case of the five-layered martensite, the image simulations and atom projections obtained from the two structural models fit well with the experimental images, which makes it very difficult to discern between them. Other ferromagnetic shape memory alloys present similar structures as the Ni–Mn–Ga system. Particularly, a “new” six-layered martensitic structure has been found in Ni–Fe–Ga alloys. The first observations reveal its nano-twinned nature as well, with a predominant \((4\over2)\) stacking sequence.

Keywords: High-resolution transmission electron microscopy (HRTEM); Ferromagnetic shape memory alloys (FSMA); Martensitic phase transformation; Layered structures

1. Introduction

The observation of large magnetic field induced strains caused, in the last years, a growing interest in the Ni–Mn–Ga and other ferromagnetic alloys exhibiting thermoelastic martensitic transformations [1–4]. Different martensitic phases have been reported, some of them having layered structures with periods of 5, 7 or 10 planes. The layered structures have been interpreted in the literature, in two different ways: as modulated structures with shuffling of the atomic planes derived from \{1\over10\} \text{ aust} by a function with the corresponding periodicity [5,6], or as stacking of nearly close-packed basal planes derived from \{1\over10\} \text{ aust}, as in Ni–Al alloys [7,8]. These two approaches have originated a quite big dispersion in the nomenclature of the different martensitic structures. From the first approach, the structures are usually denoted as 5M, 7M and NM (or T), for the five-, seven- and non-layered phases, respectively. Using the second approach, these phases are denoted as 10M, 14M and 2M, respectively, while the 10-layered phase is named as 10O.

In our previous paper [9], the two approaches for the structural description of the layered martensites were discussed and compared, and it was concluded that the atomic positions are close enough to be practically undistinguishable from diffraction techniques using photographic recording (as electron diffraction or the X-ray techniques used in refs. [5,6]). In the present work, a high-resolution transmission electron microscopy (HRTEM) study of the layered martensites has been performed in order to discern from the two structural models.

2. Experimental procedure

Three Ni–Mn–Ga alloys with compositions Ni$_{54.3}$Mn$_{20.5}$Ga$_{25.2}$ (alloy 1, numbers indicated of %), Ni$_{45.7}$Mn$_{37.2}$Ga$_{17.1}$ (alloy 2) and Ni$_{51.0}$Mn$_{27.9}$Ga$_{21.1}$ (alloy 3) were used in the present work, together with a Ni–Fe–Ga alloy of composition Ni$_{55}$Fe$_{18}$Ga$_{27$ (alloy 4). The selected compositions show the different martensitic structures at room temperature, which allowed the study by high-resolution transmission electron microscopy.
(HRTEM). Thin foils for electron microscopy were prepared by double-jet electropolishing in a solution of 30% nitric acid in methanol at ~15 V and 240 K (for Ni–Mn–Ga alloys) or 20% perchloric acid in ethanol at ~15 V and room temperature (for Ni–Fe–Ga).

The HRTEM observations were performed in a Jeol 2011 electron microscope equipped with a high-resolution polar piece operating at 200 kV (theoretical point resolution of 0.19 nm). Some image simulations have been performed by means of JEMS software using the multislice method. Simulated images have been calculated for the five- and seven-layered phases, in orientations, where the differences between the two models can be detected and good experimental images were obtained, i.e. along the [2 1 0] and [0 1 0] zone axes for the seven-layered martensite and [0 1 0] zone axis for the five-layered phase (Miller indexes are referred to the “monoclinic” crystallographic axes, taken along the [1 1 0], [0 0 1] and [1 1 0] directions derived from L21 austenitic lattice). More details about the image simulations and atomic positions corresponding to each structural model can be found elsewhere [10].

3. Results and discussion

In all the studied cases, the image simulations reproduce the experimental images formed by the typical arrays of white dots or their reverse contrast, depending on the particular values of defocus and foil thickness. For the present study, the white dots coincide with the atomic positions (see Fig. 1 for an example, in which the true atomic positions are superimposed on the simulated image). This means that, along the selected orientations, the experimental HRTEM images reveal the true projected structure, and then, they can be directly interpreted.

Fig. 2 shows an experimental image of the seven-layered phase formed in alloy 1, taken along the [2 1 0] zone axis, where successive blocks of five and two planes can be distinguished (marked by the inclined lines). In addition, the boundaries between these blocks form mirror planes for the two consecutive atomic planes at each side of the boundary, as shown by the additional lines marked on Fig. 2. The boundaries are marked by horizontal lines and the vertical segments show the alignment of the successive two atomic rows above and below each boundary, proving the mirror symmetry. All these features are inherent to the 14M structure, which is build up as stacking of nearly close-packed planes derived from \{1 1 0\}_{\text{aust}} planes with sequence (52) in Zhdanov notation. On its turn, the simulated images obtained with the structure modulated by a periodic shuffling with period of seven planes reveal distinctive features, such as a pseudo (43) sequence and absence of mirror planes [10], which are not demonstrated by the experimental images. Thus, the present HRTEM observations, clearly confirm the 14M structure for the seven-layered martensite and its inherent nano-twinned nature, the two nano-lamellae having five and two atomic planes in thickness.

The perfect (52) stacking sequence is, however, only observed in very small areas, like that of Fig. 2. In most of the zones, the martensite is nano-twinned but the size of each twin lamella is variable, i.e. the stacking sequence is distorted (see Fig. 3a). Nevertheless, the fast fourier transform (FFT) of low magnified HRTEM images, where the stacking sequence is not perfectly periodic, still present diffuse 1/7 satellites in between the fundamental spots (Fig. 3b), which means that at larger scale there is still a predominant periodicity of seven planes. This is consistent with the presence of such satellites in the selected area diffraction patterns (SAEDPs), which involve a thin-foil area much bigger than the regions where the perfect (52) sequence is developed. The diffuse intensity often visible in such SAEDPs originates from the zones where the seven plane periodicity is locally broken.

Alloy 2 exhibits at room temperature the non-layered tetragonal phase in coexistence with the 10-layered structure, the latter one being observed in thick areas of the specimen. This fact reduced the quality of the HRTEM images obtained, the best one being shown in Fig. 4. The image seems to reveal the nano-twinned nature of the 10-layered martensite as well, although, one of the lamellae appears in reverse contrast, which hinders the confirmation of the exact mirror symmetry. The twin lamella appearing in direct contrast has five atomic planes, while the thickness of the lamella in reverse contrast is nearly the same, so the image practically demonstrates the (55) stacking sequence, in accordance with the sequence deduced from the electron diffraction patterns [9]. The thinnest zones of the specimens of this alloy exhibit a 12-layered structure, characterized by SAEDPs and FFT of HRTEM images having 11 extra satellites between two fundamental maxima. Again, as for the 7- and 10-layered martensites, the experimental HRTEM images show nano-twin arrangements (Fig. 5), which points to the structural model based
Fig. 3. (a) Experimental HRTEM image of the seven-layered martensite obtained in alloy 1, with its corresponding SAEDP. The horizontal white segments mark the boundaries between nano-lamellae. (b) FFT of a low magnified HRTEM image.

on stacking of basal planes. The stacking is not periodic throughout extended regions, but a predominance of (75) sequence can be recognized. It is worth to note that the 12-layer periodicity was also observed in a Ni$_50$Al$_{18}$Mn$_{32}$ alloy, although in that case the (5232) sequence was reported to fit the best with the experimental SAEDPs [7].

The five-layered martensite forms in alloys with composition close to the stoichiometric Ni$_2$MnGa, which usually have transformation temperatures below room temperature, but it has been found at room temperature in alloy 3, which enabled us its study by HRTEM. Fig. 6 contains an image obtained in the [0 1 0] zone axis, in which blocks of three and two planes can be distinguished. However, the true atomic projections (and consistently, the simulated images) obtained from the two structural models are very similar to each other. In fact, when superposing such atom projections on the experimental image, a good agreement is obtained for both models (see Fig. 6) and it becomes difficult to determine which one fits better than the other, resulting that, in practice, the two models can be used for this phase. It has to be remarked that, at difference with the rest of layered structures, the five-layered martensite shows a regular (almost perfectly periodic) sequence extended over the whole martensite plate.

With the aim to improve the poor ductility of the Ni–Mn–Ga alloys, other ferromagnetic alloy systems undergoing ther-

Fig. 4. Experimental HRTEM image of the 10-layered martensite obtained in alloy 2, with its corresponding SAEDP.

Fig. 5. Experimental HRTEM image of the 12-layered martensite obtained in alloy 2, with its corresponding SAEDP.

Fig. 5. Experimental HRTEM image of the 12-layered martensite obtained in alloy 2, with its corresponding SAEDP.

Fig. 6. Experimental HRTEM image of the five-layered martensite obtained in alloy 3, with its corresponding SAEDP. The atomic positions corresponding to the structural models considered are superimposed on the image.
moelastic martensitic transformations, such as Ni–Fe–Ga, Co–Ni–Al, Co–Ni–Ga are being studied since the last few years (see, for instance, ref. [4] and references therein). In the Ni–Fe–Ga system, a new martensitic structure has been found, characterized by the presence of five satellite spots in the SAEDPs, which can be denoted as six-layered martensite. This structure has been found in alloy 4, in coexistence with the well known five- and seven-layered martensites. However, the electron diffraction patterns reveal that the five satellites are quite diffuse and not equally spaced, resulting in incommensurate patterns (see upper right corner of Fig. 7). Preliminary HRTEM observations reveal the nano-twinned nature of this martensite as well, with imperfect stacking sequence over extended areas (Fig. 7). In this sense, the structure is similar to the 7-, 10- or 12-layered martensites. At a first glance, a predominance of the (42) sequence can be observed. However, more intense work is being performed in order to interpret the incommensurate diffraction patterns, which are thought to be originated from a possible combination of several stacking sequences.

As a conclusion, the present HRTEM study confirms the structural model for the layered martensites based on stacking of nearly close-packed planes (which inherently results in nano-twinned structures), with the exception of the five-layered martensite, for which the model based on modulation by periodic shuffling can not be discarded. In this particular martensite, the two models result in nearly equivalent atomic positions, which require still more powerful techniques to discern among them.

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