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D. Schryvers
L. Tanner
G. Van Tendeloo

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PREMARTENSITIC MICROSTRUCTURES AS SEEN IN THE HIGH RESOLUTION ELECTRON MICROSCOPE: A STUDY OF A Ni-AL ALLOY

D. SCHRYVERS^{1,2}, L.E. TANNER¹, G. VAN TENDELOO³

1) Chemistry and Materials Science Department, Lawrence Livermore National Laboratory, Livermore, CA 94550, U.S.A.; 2) National Center for Electron Microscopy, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, U.S.A.; 3) University of Antwerp, RUCA, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium.

1. INTRODUCTION

Recent investigations of displacive transformations in a wide range of metallic [1,2] and non-metallic materials [3,4] have been providing new insights into precursor behavior, viz., changes in parent phase properties and microstructure leading to these transformations. This behavior is viewed as evidence that the parent phase effectively "prepares itself" for the eventual transformation via related lattice displacements (usually incommensurate with the basic lattice), where the process is believed driven by anomalous temperature-dependent phonon effects [1-7]. The elucidation of this behavior is now aiding in the development of more effective models for displacive transformations, particularly those producing martensitic phases in metallic alloys [2,5-7].

Two common manifestations of the pretransformation regime in martensitic alloys are diffuse streaking in diffraction patterns and a related striated strain contrast ("tweed") in amplitude contrast TEM images [8-10], where both change continuously with temperature becoming more pronounced as the transformation temperature M_s is approached [11,12]. The diffuse streaks emanate from the Bragg reflections and are directed along $\langle 110 \rangle^*$ of the cubic parent and are perpendicular to the quasi-periodic, non-continuous tweed striations lying parallel to $\{110\}$ plane traces in the TEM image (e.g., see fig. 1 in ref. [13]). In essence, the foregoing are the signature of the lattice response to structural perturbations. This is a generic process with more than one origin and so can be found in other contexts including phase transformations of distinctly different type (e.g., in the course of thermally activated diffusional transitions such as aging, ordering, etc. [8,14-16]). However, the nature of the underlying perturbations here and the associated temperature-dependence of the effects are unique to these athermal diffusionless transformations.

The high-temperature ordered δ -phase ($B2$, $CsCl$ -type) of Ni_xAl_{1-x} ($50 < x < 65$) is one of the more extensively studied parent phases exhibiting these precursor effects [10]. In this paper we describe an additional type of TEM contrast, much finer in scale than the tweed, which is seen in high-resolution phase contrast (HREM) images of $Ni_{62.5}Al_{37.5}$. This contrast is interpreted in terms of atomic displacements similar to those leading to martensite formation. The conclusions drawn from various experimental investigations of the tweed striations and related phenomena are taken as a general basis for this interpretation [8,10-12]. These studies indicate that the effects stem from static (or quasi-static) $\langle 110 \rangle \langle \bar{1}10 \rangle$ displacement waves having a range of wavelengths up to 75 nm [9,10]. The waves, no matter what their origin, are the lattice accommodation to perturbations concentrated along particular low-energy transverse displacement paths. From elasticity measurements [17] and inelastic neutron scattering [13] such low-energy modes, without being ideally "soft modes" [18,19], do indeed exist along $\langle 110 \rangle^*$ directions in Ni-Al. Going a step further, Krumhansl [19] has recently examined

the influence of temperature-dependent competing atomic interactions and severe anisotropy on phonon dispersion curves and finds that this may well be the source of modulated domain or embryo-like pretransformation microstructures.

2. DIFFUSE INTENSITY IN RECIPROCAL SPACE

In-situ heating and cooling electron diffraction experiments by Tanner et al. [12] documented that the distribution of intensity along the diffuse streaks at the Bragg reflections is temperature dependent. Microdensitometer traces reveal weak satellites at approximately $\pm 0.16 \langle 110 \rangle^*$ which were just perceptible at room temperature and increased in amplitude as cooling approached $M_s \sim -100^\circ \text{C}$. The satellites were actually more easily observed by elastic neutron scattering experiments (see Fig. 2 of ref. [13]). This indicates that, instead of all wavelengths being equally present before the transformation, a major fraction of these waves have an incommensurate wavelength of approximately 1.3 nm (i.e., an average of 6.2 $\{110\}$ planes).

3. HIGH RESOLUTION IMAGES

When HREM images are obtained from the parent B2 phase at room temperature, the most informative viewing direction is along $[001]$. A suitable choice of the experimental parameters (e.g., defocus) will then result in a square pattern of white dots, resembling the configuration of the projected Ni (or Al) sublattice. In order to obtain such an image, the thin-foil specimen must be tilted into a symmetric zone axis orientation. Figure 1a shows such an image from a relatively thick region of a sample. In addition to the expected square white dot pattern, a diffuse contrast modulation along both $\{110\}$ and $\{1\bar{1}0\}$ directions is observed. The average period of this modulation (indicated in the figure) agrees with the ~ 1.3 nm determined from the satellite positions in the SAED pattern. No clear shift of the white dots can be observed between each $\{110\}$ strip of differing contrast. It is emphasized once again that this modulation, as observed in these multi-beam phase contrast HREM images, is not to be confused with the two-beam amplitude contrast tweed pattern of the same orientation, but of much coarser spacing [8-10]. Since the basic white dot pattern is only slightly perturbed, one can look for a structural origin for these phase-contrast "micromodulations" in terms of small distortions of the ordered B2 parent lattice.

FIGURE 1a) $[001]$ HR image showing the white dot lattice contrast together with the $\{110\}$ "micromodulation". The inset is a calculated image (thickness = 5.7 nm, defocus = -80 nm) for the modulated parent B2 phase. b) $[010]$ projection of the monoclinic unit cell of the final 7R martensitic phase. The arrows indicate the displacement with respect to the previous $\{110\}$ B2 plane.

4. INTERPRETATION OF THE IMAGES

In general, computer simulations calculating the expected HREM phase contrast images for a given type of model unit cell have to be performed in order to interpret the observed images of a real structure. These calculated images are then compared with the micrographs and, if necessary, the model unit cell is modified to obtain suitable agreement. Our calculated images show the same square pattern of white dots as the HREM images for the undistorted B2 structure. However, the simulation incorporating the introduction of transverse displacements is much more complicated owing to the large number of parameters involved and the large unit cell dimensions.

A $\langle 110 \rangle \langle 110 \rangle$ transverse displacement wave may be applied to the basic crystal since the micromodulation contrast is related to the diffuse intensity distribution in reciprocal space. Although a number of different possibilities can be explored, due to space limitations we will confine the present discussion to the image simulations plus diffraction evidence that gave the most successful results. We use the approach suggested by Morii and Iizumi [20] in which the pretransformation state is viewed as a microstructural assembly "in which the stacking of the (110) planes is shuffled in a similar fashion as in the stacking structure of the (final martensite)". In the present case, the final structure is a 7-layer monoclinic cell denoted as 7R [21]. Our HREM images, as well as diffraction results [21], indicate that this phase has a (52) stacking sequence (Zhdanov notation), which can be seen as a long-period microtwinned superstructure based on the FCT $L1_0$ unit cell (3R-type) [22]. The [010] projection of the 7R structure is schematically represented in fig. 1b, including arrows indicating the relative displacements of the (110) planes of cubic B2 to produce this new close-packed monoclinic phase.

If HREM images of the asymmetric stacking arrangement are calculated using the multislice method [23], it becomes clear that the wide (5 plane) and narrow (2 plane) portions of the modulation will produce differing contrast arising from the small spacings between successive twin planes in the latter. Using a model unit cell for the premartensitic state with an atomic shuffling distortion of only 30% of that required for 7R, but still resembling the displacements towards its (52) stacking, gives simulated images as shown in the inset of fig. 1a. The actual atomic displacements are too small to markedly affect the structure image of the basic B2 lattice (i.e., the square white dot pattern), but the change in local environment results in an apparent difference in background between the wide and narrow modulation subunits. Moreover, when viewing the simulated image at a grazing incidence along the [110] direction, the white dots are seen *not* to be perfectly aligned; an effect also discernable in the experimentally obtained image.

When comparing the above results with similar calculations using other distortional wave models we conclude that the shuffling of B2 {110} planes to mimic 7R gives the best agreement with the observed contrast. Since the periodicity of the 7R martensitic structure is retained in this model, the simulated modulation results in satellites at commensurate positions of $\pm 1/7 \langle 110 \rangle^*$. As indicated above, diffraction shows satellites at $\pm 0.16 \langle 110 \rangle^*$, hence, the distortion is actually incommensurate with the B2 lattice involving a non-integral or averaged modulation periodicity close to 6 (110) planes (between 6 and 7 planes) with a domain or embryo-like pattern as discussed recently by Krumhansl [19] and others [7].

We are well aware that under normal circumstances, conclusions from image simulations of HREM micrographs should be based on the comparison of a set of images taken and calculated at different defocus and thickness values, rather than on the possible fortuitous correspondence of a single image. For our purposes here, however, we are more concerned with the disposition of the atomic displacements rather than the actual atomic coordinates and lattice parameters. A full comparison with other possible models and a discussion of different causes affecting the contrast modulation will be published in detail elsewhere.

5. DOMAIN STRUCTURE OR NOT?

From previous low-magnification and low-resolution amplitude contrast TEM experiments no firm evidence for a well-defined domain structure could be presented. However, since the twinned modulation is seen as a precursor effect to the martensitic transformation in Ni-Al, it is attractive to

visualize an assembly of very small domains, with each domain only being distorted by one wave instead of six. At this point, it is important to note that no indication for fully martensitically transformed domains was found in the HREM images. Moreover, the $[110]$ and $[1\bar{1}0]$ micromodulations do intersect with one another, indicating the possibilities that: (a) an atom can be displaced by more than one wave, or (b) that small domains overlap with one another.

From careful examination of the HREM images it is clear that, while the entire crystal is modulated, any set of the 1.3 nm micromodulations does not extend over a very large area. This may be explained by the existence of numerous phase shifts (or perhaps discommensurations) [7] resulting in different wave packets arrayed along one particular lattice direction. From the observed images, the size of these packets, or domains, may be roughly estimated as a few wavelengths, i.e., 3 to 8 nm (see arrows in fig. 1). This is in reasonable agreement with the correlation length of local distortional fluctuations of about 4 nm determined from the breadth of the satellites observed with elastic neutron scattering by Shapiro et al. [13]. According to this view, the waves in different packets will then be out of phase. Since these regions are still relatively small, they can be considered as out-of-phase domains of a long-period structure, much as in the case of microdomains in short-range ordered alloys [24,25]. This ill-defined long-period will contribute to the streaking in regions between Bragg peaks and their satellites.

6. CONCLUDING REMARKS

The present study indicates that the B2 β -phase in quenched $\text{Ni}_{62.5}\text{Al}_{37.5}$ is distorted by displacement waves involving a planar shuffling of atoms resembling the final 7R martensite structure and with wavelengths of the order of 1.3 nm. The appearance of a $\langle 110 \rangle \langle 1\bar{1}0 \rangle$ type modulation with the indicated periodicity corresponds well with recent inelastic neutron scattering results which reveal nonlinear behavior in the TA $\langle 110 \rangle$ phonon dispersion curve around the same wavelengths indicating a partial lattice softening for such waves [13]. In bulk material all six equivalent wave-vectors are equally present.

These distortional modulations are configured in some form of three-dimensional assembly. Following the interpretation given above, it can be concluded that a one-dimensional domain structure along one of six $\langle 110 \rangle$ directions may exist. However, the beating of six displacement waves with apparently uncorrelated phase and wavelengths rules out the existence of a "conventional" three-dimensional domain structure [26]. For this reason it is uncertain whether much more information can be gained from image simulations as presented above.

There are now numerous indications that the underlying structure to the twinned contrast in this alloy is a precursor effect of the martensitic transformation. However, a detailed description of the effective correlation between the distorted parent phase and the martensitic product phase has yet to be developed. Recent HREM results reveal the existence of a sequence of different structures in the transition region between the modulated β -phase and the martensitic phase, depending on parameters such as the local composition and stress. Such transition structures include modulated β -phase in which only one $[110]$ modulation is preferred or in which the periodicity differs from the above described 1.3 nm and the FCT $L1_0$ martensite with single shear defects. Details of these transformation microstructures and transitions will be described in a forthcoming paper.

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