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High resolution TEM study of Ni_4Ti_3 precipitates in austenitic $Ni_{51}Ti_{49}$

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Abstract

Binary NiTi with a composition of 51 at.% Ni was heat treated to form lens-shaped Ni_4Ti_3 precipitates that are coherent or semi-coherent with the B2 matrix. High resolution transmission electron microscopy (HRTEM) was used to study the internal structure of the precipitates, precipitate–precipitate and matrix–precipitate interfaces and the deformation of the B2 matrix near a precipitate. Observations were made in the $\langle 1\,1\,0\rangle_{B2}$ and $\langle 1\,1\,1\rangle_{B2}$ zones and compared with computer simulated high resolution images. The $\langle 1\,1\,1\rangle_{B2}$ observations made it possible to study the $[0\,0\,1]_H$ zone orientation of Ni_4Ti_3 (direction defined according to the hexagonal unit cell of Ni_4Ti_3) which corresponds to the normal of the central plane of the discs. In these images the superperiodicity of the 4:3 ordering is clearly visible confirming the known atomic structure. Close to the precipitate the B2 matrix is deformed, as determined by measuring the interplanar spacing from the HRTEM images. The observed deformations are compared with theoretical models for the stress field.

Keywords: Ni–Ti; HRTEM; Precipitates; Strain field

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1. Introduction

The presence of Ni_4Ti_3 precipitates in the austenitic B2 matrix of almost equiatomic NiTi alloys has a great influence on the features of the martensitic transformation and therefore alters the properties of the shape memory effect. The structure and morphology of these lens-shaped precipitates have been thoroughly investigated and are well known [1,2]. Their influence on the transformation temperatures and the occurrence of multiple step transformations was mainly investigated by DSC measurements and TEM observations [3,4]. An important result is that when these precipitates are coherent or semi-coherent they are nucleation centres for the formation of the R-phase [3]. Therefore, the M_S temperature changes with different heat treatments, which are responsible for the growth of these precipitates [4]. This behaviour is explained by the fact that the lattice mismatch between precipitate and matrix induces a stress field in the surrounding matrix. Also the change of Ni concentration in the matrix, due to the Ni enriched precipitates, has its influence on the transformation temperatures [3,5]. On the other hand, the growth of new precipitates and the occurrence of a favourite variant is influenced by the internal stress fields but also by those externally applied [4]. Theoretical models are used to calculate which martensite variant is favoured and to predict the growth of precipitate variants [5,6]. These seem to confirm the experimental results but are typically all based on a theoretical model for the stress field around the precipitate. In this research, high resolution transmission electron microscopy (HRTEM) is used to determine the matrix deformation around a Ni_4Ti_3 precipitate.

2. Experiments

2.1. Sample preparation

Samples were made out of a 3 mm diameter $Ni_{51}Ti_{49}$ rod, from which 300 μm thick discs were cut. These discs were given the appropriate heat treatment to form coherent and semi-coherent Ni_4Ti_3 precipitates in the B2 matrix: (1) annealing at 950 °C in vacuum for 1 h followed by water quenching; (2) ageing at 500 °C for 4 h in vacuum followed by water quenching. After the heat treatment, these discs were mechanically ground followed by electropolishing with a solution of 93% acetic acid and 7% perchloric acid. For the high resolution investigation a top-entry JEOL 4000EX electron microscope was used operating at 400 kV.

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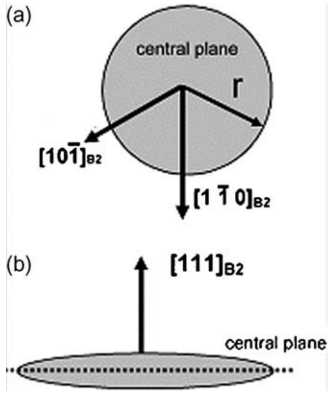

Fig. 1. (a) Precipitate projection in $[1\,1\,1]_{B2}$ zone orientation; (b) precipitate projection in $[1,-1,0]_{B2}$ zone orientation.

Following parameters were used as a reference for the crystal structure of the matrix and the precipitate. The matrix has the B2 structure with lattice parameter $a = 3.01$ Å [6]. For the precipitate the hexagonal description will be used with lattice parameters: $a = b = 11.24$ Å, $c = 5.077$ Å [7]. Eight precipitate variants are possible, the conventional orientation relationship being:

$$(1\,1\,1)_{B2}//(0\,0\,1)_{H};\ [3, -2, -1]_{B2}//[1\,0\,0]_{H}$$

the $[1\,1\,1]_{B2}$ being the normal to the central plane of the lens-shaped precipitate of Fig. 1.

High resolution observations of this precipitate variant and the matrix were made in $[1\,1\,1]_{B2}$, $[1,1,-1]_{B2}$ and $[1,-1,0]_{B2}$ zone orientations. In the $[1\,1\,1]_{B2}$ observation the electron beam is perpendicular to the central plane of the precipitate. High resolution images reveal the 4:3 superstructure of the precipitate and curved interfaces between precipitates could be observed. Deformation of the matrix in this zone is expected to be very small since the corresponding directions remain relatively undistorted (<0.3%), so these observations are not used to determine the strain in the matrix. Images of and further comments on these observations are given in [8]. The largest deformations of the matrix are expected to be observed in the $[1,-1,0]_{B2}$ orientation; more precisely along the $[1\,1\,1]_{B2}$ direction which has the largest lattice mismatch of 2.9% [6]. However, as it is experimentally more difficult to make good observations of the atom columns in the $[1,-1,0]_{B2}$ zone, most observations to retrieve strain information were made in the $[1,1,-1]_{B2}$ zone. In this orientation, the interface

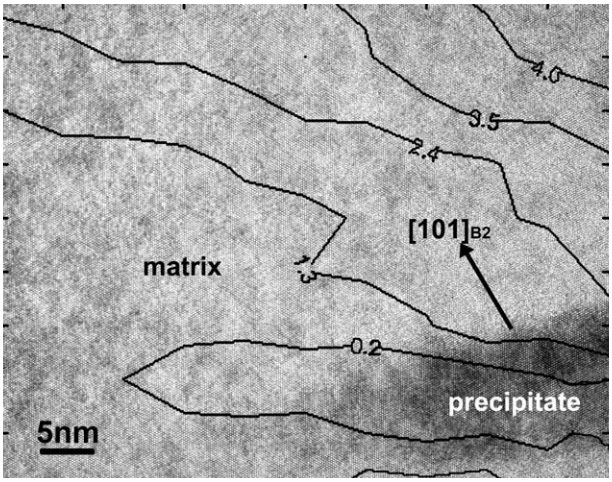

Fig. 3. HRTEM image of the tip of a Ni_4Ti_3 precipitate in $[1,1,-1]_{B2}$ zone orientation. The contours give the Δd (%) for the $(1\,0\,1)_{B2}$ planes.

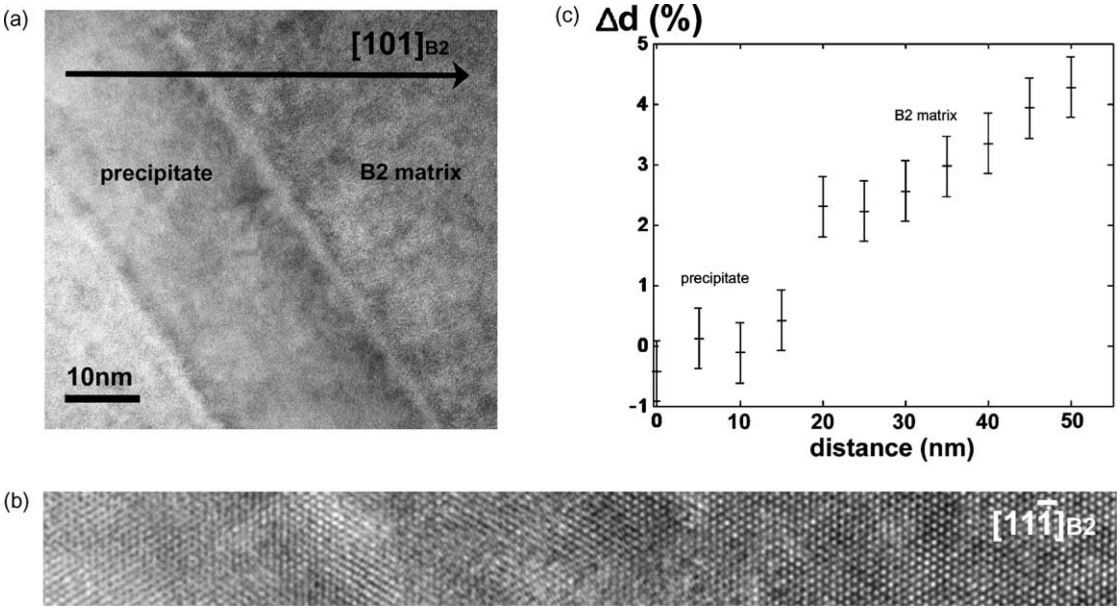

Fig. 2. (a) HRTEM image of a Ni_4Ti_3 precipitate in $[1,1,-1]_{B2}$ zone orientation of which an enlargement is given in (b). The vertical rows are the $(1\,0\,1)_{B2}$ planes from which relative differences in interplanar spacings are calculated: Δd (%) and plotted in graph (c).

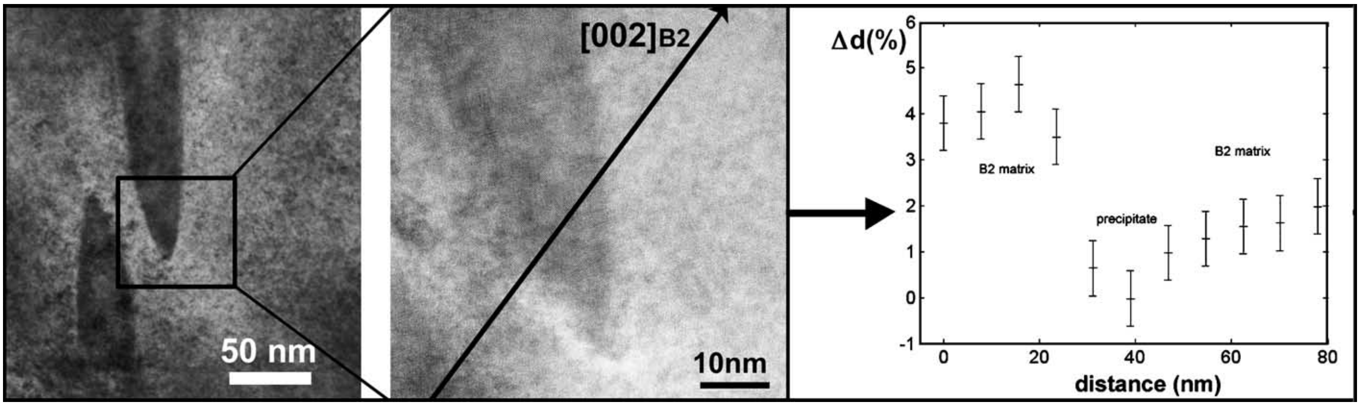

Fig. 4. HRTEM image in $[1,-1,0]_{B2}$ zone orientation of two precipitates. As seen in the graph the Δd for the $(0\,0\,2)_{B2}$ planes is significantly larger between the two precipitates.

plane makes an angle of 19.47° with the incident electron beam causing some overlap between matrix and precipitate, but deformations are still observable.

2.2. Method to determine lattice deformations

From high resolution images, relative differences in interplanar spacing for a specific plane can be determined by fast Fourier transform (FFT) procedures. Since the expected differences in interplanar spacing between precipitate and strained matrix are smaller than 6%, an area of 5 nm × 5 nm at least is needed to measure the relative distance for interplanar spacing with sufficient precision. To determine relative differences, a reference measure is chosen. This is the interplanar spacing of the corresponding plane in the precipitate. The relative difference of interplanar spacing in reference to this plane is called Δd (%), which can be determined with a precision of 0.6% Δd. This can be done to see the variation for a chosen plane in a chosen direction. Fig. 2 shows the procedure for an observation in the $[1,1,-1]_{B2}$ zone and gives a graph for the change in $(1\,0\,1)_{B2}$ interplanar distance in the $[1\,0\,1]_{B2}$ direction.

3. Results and discussion

Precipitates with a diameter of less than 300 nm were used for the observations; if they grow larger, they become less coherent with the matrix and the misfit is relaxed by introduction of dislocations [5,9].

From the observations it could be determined that, close to the interface, the Δd (%) difference for the matrix is almost equal to the calculated lattice mismatch. In a $[1,1,-1]_{B2}$ orientation two of the three $\{1\,1\,0\}_{B2}$ planes have a calculated lattice mismatch of 2.02%. Close to the interface this corresponds to the measured Δd, but the measured deformation increases with increasing distance from the interface, as seen in Fig. 2c. Differences up to 6% were measured at distances around 50 nm from the precipitate. The other $(1,-1,0)_{B2}$ plane has a calculated Δd of only 0.38% and this is confirmed by the observations in which no difference was measured. Observations at the tip of a precipitate showed that, for such planes, the Δd can even be smaller than the calculated lattice mismatch. Fig. 3 shows an example of the contours giving the Δd for the $(1\,0\,1)_{B2}$ planes, and also here they are larger further from the precipitate. (No dislocations or defects that would relax the stress were observed in this case.) Observations in the $[1,-1,0]_{B2}$ zone give similar results. At the interface, the Δd is equal to the expected lattice mismatch. Between two precipitates the deformation of the matrix is much larger even at the tip (Fig. 4).

From these observations, it is clear that there is no matrix strain at the interface itself while it increases further away from it. The strain should reach the maximum and then relax back to zero, but this could not yet be observed. This seems in contradiction to the most commonly assumed curve for the stress field around a precipitate in which the maximum is close to the interface and decreases further away from it [3,10]. In order to understand the present observations, it might be necessary to take into account a concentration gradient, as differences in composition may also result in a change in lattice parameter. Such combined effect on stress might give a curve as measured.

4. Conclusion

By using HRTEM, it was possible to measure differences in interplanar spacings around a Ni_4Ti_3 precipitate. The matrix strain (in reference to the crystal parameters) is zero at the interface and increases further away from it. It is not yet clear whether this is only the result of stress to compensate the lattice mismatch or also because of a concentration gradient.

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