Nucleation and Growth of the Ni_5Al_3 Phase in Ni-Al Austenite and Martensite

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Abstract: The nucleation and growth mechanisms of Ni_5Al_3 precipitates and microtwinned plates in B2 austenite and 2M (3R) martensite phases are described on the basis of conventional and high resolution electron microscopy. In the $\text{Ni}_{62.5}\text{Al}_{37.5}$ B2 austenite matrix short annealings at 550°C introduce three-pointed star shaped precipitates consisting of twin related parts of different variants of the Ni_5Al_3 structure. Longer annealings result in plates growing separately from these wings and developing microtwinning in order to accommodate stress built-up at the interfaces with the surrounding matrix. Annealing of $\text{Ni}_{65}\text{Al}_{35}$ 2M martensite plates induces simple reordering into the Ni_5Al_3 phase, increasing the fct c/a ratio by about 1%. As a result stracking faults are introduced in the smallest twin variants.

1. INTRODUCTION

The Ni_5Al_3 phase, further on abbreviated as 5:3, was first observed in a $\text{Ni}_{63.8}\text{Al}_{35.2}\text{Co}_1$ alloy by Enami and Nenno [1]. They suggested an ordered orthorhombic unit cell based on an fct lattice and with space group D^{19}_{2h} (Cmmm), schematically presented in fig. 1a. This unit cell was later confirmed in pure $\text{Ni}_{65.3}\text{Al}_{34.7}$ by Khadkikar and Vedula who determined the lattice parameters to be $a = 0.7475$ nm, $b = 0.3732$ nm and $c = 0.6727$ nm [2]. At this composition the sample is in the martensite state at room temperature and annealing at 550°C will induce the 5:3 ordering in the 2M plates (new notation [3] for 3R). Since the a-parameter of the 5:3 unit cell is extremely close to twice its b-parameter, a simple reordering of the L1₀ ordering of the 2M martensite can be expected. In the case of the 5:3 precipitating in the cubic B2 matrix, again by annealing at 550°C, the necessary distortion accompanying the reordering is the reverse bcc to fct Bain distortion, i.e. the same distortion known to yield the 2M martensite structure. Thus the 2M to 5:3 transformation is purely diffusive while the B2 to 5:3 transformation is a coupled displacive-diffusive transformation. Since for the latter the nominal bulk composition of the presently used material also has, to within 0.5 at. %, a 5:3 ratio, the diffusive component is expected to be limited to local atom exchanges. The

aim of this work is to elucidate the nucleation and growth characteristics of both transformation paths at the atomic level using different electron microscopy (EM) techniques.

Figure 1 - (a) Unit cell of the 5:3 structure in relation to the basic bcc lattice of the B2 austenite.
(b) Six possible variants of the 5:3 structure in a bcc matrix.

2. RESULTS

2.1. B2 to 5:3 transformation

The reverse Bain distortion consists of the elongation of one B2 cubic axis (usually chosen as c-axis for the product phase) and the equal contraction of the remaining two B2 cubic axes. As a result the fct a- and b-axes are chosen along the $[110]_{B2}$ and $[1\bar{1}0]_{B2}$ directions. Thus, with each chosen elongated c-axis two possibilities exist for the ordering. When disregarding accompanying rotations, a single B2 grain can then accommodate six different variants of this new structure (M_i , $i = 1 \dots 6$). These are schematically shown in fig. 1b. As a result of the martensitic type of distortion the new phase will be expected to accommodate the stress built-up by multiple stacking faults or twinning. As with regular twinned martensite, a given set of twins will consist of two perpendicular Bain distortions. In the present case, however, the existence of two ordered variants for each chosen elongation complicates the possible combinations.

After a two hour period of annealing at 550°C, followed by a water quench, numerous 5:3 precipitates are observed embedded in the B2 matrix as well as decorating the grain boundaries. Variations in bright field contrast in TEM indicate that in most cases these precipitates consist of different distortion and/or ordering variants. An example of a very symmetric three-pointed star shaped precipitate is shown in the low magnification HREM image of fig. 2a. Here the B2 matrix is observed along a $[\bar{1}11]$ zone axis. The central axis or midribs of each of the three wings of the star are observed edge-on and are parallel with the three equivalent $\{110\}_{B2}$ planes visible in the matrix. The Bain variants B_α (with $\alpha = a, b$ or c , the elongating cubic axis) are indicated on the image and are in twin relation at each midrib. The entire precipitate is formed by equal portions of all three possible Bain distortions. The twin plane is a close packed $\{212\}_{5:3}$ type plane and belongs to both segments. Note that there are no other twins observed in the different segments. In other cases, wings consisting of more twin variants are also found [4].

Figure 2 - (a) A three-pointed star shaped 5:3 precipitate embedded in a B2 matrix viewed along a $[111]_{B2}$ zone. (b) HREM image of a single wing observed in an $\langle 021 \rangle_{5:3}$ zone. Black arrows indicate dislocations.

Although the net shape change is presumably accommodated to a certain extent by the twinning with different variants, the distortion to a close packed structure and accompanying rotation still introduce dislocations at the interfaces between each variant or segment and the matrix. The density of the dislocations, indicated by black arrows in the HREM image of a single wing in fig. 2b, can be determined as one for every 7 $\{110\}_{B2}$ planes that become close packed. In this particular precipitate the HREM pattern strongly suggests an $\langle 021 \rangle$ type zone of the 5:3, which corresponds with M_4 and M_5 variants, as indicated. When the interplanar spacings of the 5:3 lattice are measured from this HREM image, using the $\{110\}_{B2}$ lattice fringes as internal reference with $a_{B2} = 0.2856$ nm for the present $x = 62.5$ composition [5], one finds $d_{001} = 0.359$ nm and $d_{012} = 0.249$ nm with a precision of about 0.5%.

Figure 3 - a) Multiply twinned thin plate growing out on both sides of a broader nucleus. b) Separately growing segments of a single wing.

In fig. 3 a large but thin plate, observed after annealing for one day at 550°C and consisting of multiple parallel planar faults seems to be growing out of a somewhat broader nucleus. Inside this nucleus the zig-zag

lattice fringes as well as the strong contrast difference indicate that these planar faults are microtwin planes. This means that the plate consists of those two Bain variants that are present in the nucleus. Careful measurements of the orientations of the traces of the microtwin planes show that those in the plate deviate by about 3° from those inside the nucleus, the latter being parallel with the corresponding $(110)_{B2}$ fringes. This again suggests that the alleged nucleus is a former wing. The need for continuing microtwins is probably related with stress accommodations at the plate-matrix interface, since the partial balancing effect of the other wings with respect to the total strain in the matrix becomes less effective. Another possible growth mechanism is shown in fig. 3b. Here each segment of a given wing grows out separately and starts to twin, using the remaining Bain variant [4].

So far, the twinned nature of the 5:3 plates strongly resembles that of 2M martensite plates. However, as mentioned above, the choice of twin variants can be affected by the 5:3 ordering. Indeed, for a given close packed plane chosen as twin plane between two Bain variants, the 5:3 ordering induces a loss of sixfold symmetry for this plane [4]. As a result, only specific combinations of the ordering variants are possible. For example, only combinations 3-2 and 3-6 are expected when starting with variant M_3 , each combination yielding its own choice of habit plane. The 3-2 microtwin will have a $(01\bar{1})_{B2}$ habit plane, while 3-6 a $(110)_{B2}$ one. These relations are confirmed by SAED patterns [4].

Since HREM lattice fringes or SAED patterns of both parent and product phases are obtained in single micrographs during different stages of the growth, the evolution of the lattice parameters of the 5:3 structure can be followed with a good precision. For the large plates all lattice parameters were experimentally obtained from SAED patterns of different zones. From this the tetragonal symmetry for the basic lattice of the 5:3 structure was confirmed. For the smallest precipitates the lattice parameters were calculated assuming a tetragonal symmetry for the basic lattice. From these parameters the corresponding lattice distortions η_1 (<1) and η_3 (>1) can be found. The large plates show values close to these of 2M with the nearest composition [6]. However, from the c/a ratio found in the small precipitates it must be concluded that the fct lattice of the 5:3 structure in the segments of fig. 2 is close to face centred cubic (fcc), which means a very strong distortion with respect to the original bcc lattice of the austenite. Such a large distortion explains the high density of dislocations at the precipitate-matrix interfaces. Apparently this large distortion is lowered as the segments develop multiple microtwinning to accommodate the stress at the growing habit planes.

From the lattice distortions the habit plane orientation as well as angles between given planes in the precipitates and plates with respect to their original planes in the $B2$ matrix can be calculated using crystallographic theory [7]. These values indicate a good agreement between theory and experiment [4]. The direction cosines of a habit plane close to a $(101)_{B2}$ plane are calculated to be $(0.657, 0.146, 0.740)_{B2}$ yielding an angle of 4.9° to be compared with a measured angle of 5° . However, the measured volume fractions are larger by more than 10 % when compared to the calculated ones (0.380 versus 0.335 [4]).

Measurements and calculations like this can yield information on the relative importance of the displacive versus diffusive character of the transformation. It is clear that the slow growth of the precipitates can only be explained by including the diffusion, although at the present composition this does not imply a decomposition. On the other hand, the microtwinning is a typical feature of a distorted lattice accommodating

to the surrounding matrix. If this twinning is indeed used to obtain as little stress as possible at this habit plane, then the relation between the lattice distortions, volume fraction, orientation relationships etc. as calculated from continuum theory should indeed apply. The result on the volume fraction could indicate that the purely displacive character of the stress-free habit plane condition is not sufficient to explain all features or parameters of the 5:3 plates.

2.2. 2M to 5:3 transformation [8]

In fig. 4 a sequence of SAED $[101]_{2M}$ patterns obtained during in-situ annealing of a $\text{Ni}_{65}\text{Al}_{35}$ martensite plate from room temperature up to 630°C is shown. The appearance of diffuse spots later on sharpening into strong ordering $h0h_{5:3}$ and $0k0_{5:3}$ reflections of two 5:3 twinned variants is apparent. The sharpness of these superreflections can be related with the size of different translation and orientation variants of the 5:3 in each martensite twin. Due to the simple relation between the 5:3 and L1_0 structures, the ordering is expected to take place on the mixed Ni-Al (001) planes of the fct. The only effect on the basic lattice is an increase by about 1% of the fct c/a ratio. [001] SAED patterns show extra spots that can be explained by the crossing of the Ewald sphere with $\langle 111 \rangle_{\text{fct}}$ streaks through new ordering reflections [8].

Figure 4 - The evolution of 5:3 ordering reflections during in-situ heating of a 2M plate: (a) RT (b) 480°C and (c) 530°C . At 630°C the superreflections in the last pattern sharpen up.

Fig. 5 shows a $[\bar{1}\bar{2}0]_{5:3}$ HREM image obtained in 2M $\text{Ni}_{65}\text{Al}_{35}$ material annealed for 5 min. at 550°C . The martensite plate is now completely converted into the 5:3 ordering. As a result, some stacking faults on close packed $(212)_{5:3}$ planes are found (arrow in fig. 5). These stacking faults can be limited to a single microtwin variant but are also seen to be continuous over several twins, thus changing orientation at each twin plane. In some cases these stacking faults end inside a given twin. Intrinsic as well as extrinsic one are observed. No domain interfaces violating the expected ordering scheme are observed. The 5:3 ordering is also seen to be coherent over the martensite twin interfaces.

Figure 5 - $[120]_{5:3}$ HREM image of a fully ordered 5:3 plate, formed by annealing 2M material and showing a new SF in a small martensite twin variant (look along arrow).

3. CONCLUSIONS

The nucleation and growth of the 5:3 phase in a B2 austenite matrix of $\text{Ni}_{62.5}\text{Al}_{37.5}$ material is accompanied by the formation of different types of twin constructions. In an early stage, the different variants of the Bain distortion are used to form three-pointed stars, with or without internal defects. These nano-scale precipitates also accommodate the expected ordering of the 5:3 structure and the lattice is close to fcc, which indicates a large distortion. In a later stage the wings of this star can grow into single plate-shaped precipitates strongly resembling classic 2M plates and exhibiting fine microtwinning parallel with existing twin planes in the wing. Alternatively, an extra family of twins can be introduced into each segment of a wing to form a plate with a different habit plane. In all cases, the habit planes are arranged four by four around each 110 pole of the austenite. In 2M martensite samples the 5:3 phase is formed by simple reordering of the atoms, inducing stacking faults inside the smallest martensite twin variants.

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