

## The Role of Misfit-Strain Energies during Precipitation of $\alpha''$ -Nitride in Fe-N Martensite

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**Abstract.** The structural changes occurring during tempering of Fe-N martensite ( $\alpha'$ ) have been investigated using X-ray diffraction and (high resolution) transmission electron microscopy. The first stage of decomposition of Fe-N martensite leads to the formation of  $\alpha''$ -nitride and ferrite ( $\alpha$ ). The formation of  $\alpha''$ -nitride involves both a local enrichment and ordering of N atoms; the Fe sublattice remains of b.c.t. type. The structural changes which take place can be largely understood as the outcome of the competition between ordering of nitrogen atoms in  $\alpha''$  precipitates and the developing of a considerable misfit between the  $\alpha''$  precipitates and the  $\alpha'/\alpha$  matrix. In the initial stage of decomposition the misfit is relatively small, and precipitation of perfect  $\alpha''$  (i.e.  $\text{Fe}_{16}\text{N}_2$ ) occurs in the martensite matrix. Upon tempering the matrix becomes ferrite and the misfit increases considerably (up to about 10 pct). This misfit is reduced by the formation of vacancies on the nitrogen sublattice in  $\alpha''$ -nitride, i.e. precipitation of imperfect  $\alpha''$  ( $\text{Fe}_{16}\text{N}_{2-x}$ ) takes place. After complete decomposition, upon continued annealing the nitrogen-concentration variations within the  $\alpha''$  precipitates disappear and the precipitates become of composition  $\text{Fe}_{16}\text{N}_2$ . Then the misfit is accommodated mainly by local deformation of the ferrite lattice.

### 1. INTRODUCTION

Iron-based interstitial martensites ( $\alpha'$ ) are supersaturated solid solutions of interstitial atoms (carbon and/or nitrogen) in an iron lattice. Precipitation in such martensites involves the formation of transition phases before the 'equilibrium' phase develops.

In binary Fe-N martensite, prior to the precipitation of an 'equilibrium' nitride, an ordered arrangement of interstitial atoms develops locally:  $\alpha''$ -nitride particles form [1-5]. However, in Fe-C martensite [6-9] no  $\alpha''$  type transition phase is observed. Within this context a comparative discussion on the development of the initial transition phases in nitrogen and carbon interstitial martensites is included at the end of this paper.

The iron sublattice of martensite and  $\alpha''$ -nitride is of b.c.t. type; the iron sublattice of ferrite is of b.c.c. type. The interstitial atoms residing in octahedral interstices of a b.c.c./b.c.t. iron sublattice severely distort their surroundings: in particular the nearest neighbour iron atoms (i.e. in the c directions of  $\alpha'$  and  $\alpha''$ ) are displaced [1]. The initial development of  $\alpha''$  precipitates (i.e. local enrichments and ordering of nitrogen atoms), which can occur without plastic deformation, can lead to a pronounced misfit between the  $\alpha''$  particle and the matrix. Hence, it is expected that elastic strain-energy effects may govern the development of  $\alpha''$  precipitates. Against this background the structural and morphological changes occurring during  $\alpha''$  precipitation for Fe-N martensites containing about 5 N/100 Fe (4.4 to 5.5 at.% N) are discussed in this paper.

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## 2. EXPERIMENTAL PROCEDURES

Iron-nitrogen martensite specimens containing 4.4 to 5.9 N/100 Fe were prepared and annealed between room temperature and 403 K as described in [4].

Specimens used for transmission electron microscopy were prepared after heat treatments (performed *ex situ*) in a temperature range between room temperature (RT) and 403 K for various tempering times as described in Ref. 10. Transmission electron microscopy was performed using a Philips CM30T microscope operated at 300 kV. High resolution images were obtained using a Philips CM30ST with a field emission gun operated at 300 kV, and a resolution of about 0.2 nm.

As prepared and annealed (at 333 K up to 110 hours and subsequently heat treated at 373 K up to 466 hours) specimens were investigated by means of X-ray diffraction using a Siemens type F diffractometer, equipped with a Cr tube and a graphite monochromator (selecting Cr  $K\alpha$  radiation) in the diffracted beam (for details see Ref. 11).

## 3. SUMMARY OF RESULTS

In the as-prepared condition all the specimens investigated consist of plate martensite and retained austenite.

From the X-ray diffraction data it is concluded [11] that during heat treatment at 333 K an ordered  $\alpha''$  transition nitride develops as indicated by the continuous decrease of the integrated intensity of the martensite reflections (in particular the  $\{002\}\alpha'$ - $\{200\}\alpha'$  martensite doublet has been analysed) and the observation of the  $\{004\}\alpha''$  main reflection and also the  $\{112\}\alpha''$ - $\{211\}\alpha''$  superstructure reflections (distinct after 9 hours of annealing at 333 K). These superstructure reflections are due to the occupation of specific c-type octahedral sites ('order' sites) which results in a unit cell composed of  $2 \times 2 \times 2$  unit cells of the parent martensite [1]. The decrease upon annealing of the  $c_{\alpha''}$  lattice parameter suggests that the overall nitrogen content of the precipitates gradually becomes less. After 110 hours at 333 K the precipitates contain about 10.75 N/100 Fe as calculated from the  $c_{\alpha''}$  lattice parameter taking into account the misfit-induced strain [11,12].

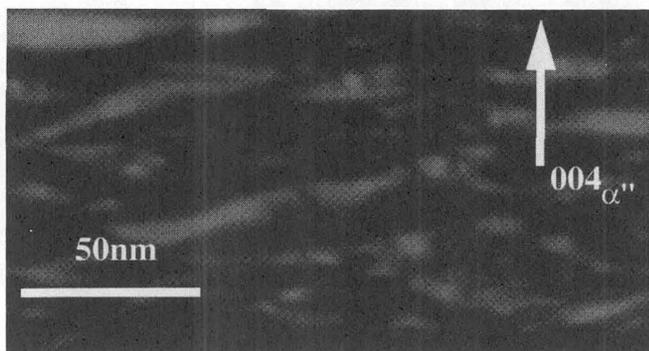


**Figure 1:** Dark field image (using the  $(004)\alpha''$  reflection; foil normal  $[001]\alpha'/\alpha'$ ) of a Fe-N martensitic specimen (composition 4.6 N/100 Fe) aged at room temperature for 11 months. Plate-like precipitates (viewed edge-on) oriented approximately parallel to the  $(001)\alpha'/\alpha'$  matrix planes are visible. Contrast variations due to variations in nitrogen content occur in particular at the edges of the precipitates.

Up to this stage of tempering electron diffraction patterns show intensity between the  $(002)\alpha'$  and  $(004)\alpha''$  diffraction spots. This intensity is caused partly by streaking through  $(002)\alpha'$  caused by the limited size of the precipitates and partly by the presence of nitrogen deficient regions in the  $\alpha''$  phase. The presence of such nitrogen deficient regions was demonstrated by making dark field images for various positions of the objective aperture along the streak mentioned [10]. The nitrogen deficient regions are

associated with a smaller ( $c_{\alpha''}$ ) lattice parameter than for perfect  $\alpha''$  which leads to diffracted intensity between the  $(002)\alpha'$  and  $(004)\alpha''$  diffraction spots. The dark field image given in Fig. 1 shows precipitates formed at RT (after 11 months of aging). The precipitates are platelike and they are oriented approximately parallel with the  $(001)\alpha/\alpha'$  matrix planes. Contrast variations occur especially near the edges of the precipitates which give them a mottled appearance. These contrast variations reflect the variations in the nitrogen content.

All nitrogen has been taken up in imperfect (i.e. nitrogen deficient)  $\alpha''$  precipitates after annealing 110 hours at 333 K and subsequent annealing for 5 hours at 373 K. Further tempering (i.e. at 373 K) causes the vacancies on the nitrogen sublattice to fill up as indicated by the increase of the  $c_{\alpha''}$  lattice parameter which reaches a value of that of perfect  $\alpha''$  after prolonged tempering (up to 446 hours at 373 K). The filling up of the vacancies is also reflected in the changes of the integrated intensities of the precipitate reflections. After full decomposition of the martensite into  $\alpha + \alpha''$  the integrated intensity of the precipitate reflections is affected in two ways by the filling up of vacancies : a decrease of the number of  $\alpha''$  unit cells and a change in the structure factor. The structure factor depends on the nitrogen content because the occupancy of the octahedral interstices of the iron sublattice is associated with a systematic displacement of the iron atoms constituting the octahedral interstice containing the nitrogen atom. Consequently the changes of the integrated intensities depend on the  $\{hkl\}$  reflection considered. Thereby the average changes of the positions of specific iron atoms in the unit cell can be determined e.g. from the ratio of the integrated intensity of the  $\{002\}\alpha''$  superstructure reflection and that of the  $\{004\}\alpha''$  main reflection. The number of unit cells was calculated from the  $\alpha''$  composition indicated by the measured ( $c_{\alpha''}$ ) lattice parameter after correction for the misfit-induced strain. After 6.5 hours at 373 K the composition is almost that of perfect  $\alpha''$  (12.45 N/100 Fe vs. 12.5 N/100 Fe for perfect  $\alpha''$ ) and the Fe-N nearest neighbour distance has been calculated as 0.187 nm [11].

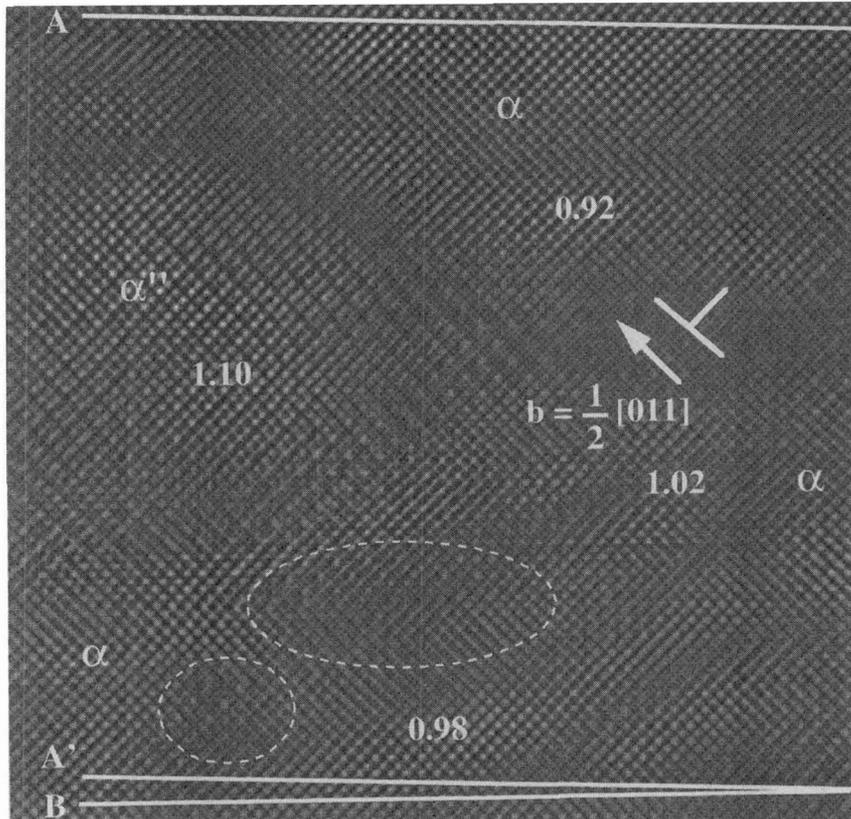


**Figure 2:** Dark field image (using the  $(004)\alpha''$  reflection; foil normal  $[001]\alpha$ ) of a Fe-N martensitic specimen (composition 5.6 N/100 Fe) tempered at 403 K for 1.5 hour. The precipitates have formed lamellae oriented approximately parallel to the  $(001)\alpha$  matrix planes. At this stage of tempering the contrast within the precipitates appears more homogeneous than at the initial stage (see Fig. 1).

Upon tempering at higher temperatures the intensity between the  $(002)\alpha'$  and  $(004)\alpha''$  diffraction spots in the electron diffraction pattern gradually disappears. The shape of the precipitates changes as shown by comparing the dark field TEM images obtained for an initial stage (11 months RT; Fig. 1) and for prolonged tempering (1.5 hours at 403 K; Fig.2). The precipitates coarsen and form lamellae during further tempering. Also, the contrast variations within the precipitates are reduced upon further tempering which indicates that the nitrogen content has become approximately homogeneous within the precipitates.

In Fig. 3 an interface parallel to the plate normal ( $(010)\alpha/\alpha''$  interface region) of a specimen tempered at 393 K for 288 hours is imaged edge on. The  $\alpha''$  precipitate (located at the upper left side of the image) can be distinguished by the presence of the superstructure fringes and the ratio of the  $c_{\alpha''}$ - and  $a_{\alpha''}$ -

lattice parameters which equals about 1.10 (indicated in the figure). Despite the large misfit between the precipitate and the matrix only one dislocation with a Burgers vector of 0.1 nm (result of making a Burgers circuit) on the iron lattice is detected in this area. The dislocation core cannot readily be observed due to the strain contrast occurring in this region.



**Figure 3:** A high resolution transmission electron image (foil normal  $[001]_{\alpha}$ ) of a Fe-N martensitic specimen (composition 5.8 N/100 Fe) tempered at 393 K for 288 hours. A (010) type  $\alpha''/\alpha$  interface between a precipitate and the matrix (at an  $\alpha''$  plate edge) is shown. A dislocation with Burgers vector of 0.1 nm is present but not readily visible because of the strain contrast. The misfit between matrix and precipitate is accommodated by local distortions of the ferrite lattice (see the variation of the  $c/a$  lattice-parameter ratio). The lines A (with  $A'/A$ ) and B, parallel to  $(001)_{\alpha}$  planes, are not parallel to each other indicating that the ferrite lattice exhibits local orientation differences.

Lattice distortions of the ferrite matrix can be observed in the vicinity of the precipitate : see the heavily distorted regions in Fig. 3 (encircled regions). Locally the ferrite matrix is tetragonally distorted: varying  $c$  to a lattice-parameter ratios have been observed as indicated by the numbers close to one in Fig. 3 (these ratios concern the  $c$  to a ratio of a few unit cells). Also a tilt of the  $(001)_{\alpha}$  atomic planes could be observed near the interface. The lines A ( $A'$  is parallel to A) and B in Fig. 3 both are parallel to a  $(001)_{\alpha}$  plane: their orientations differ slightly. Because of the severe distortion of the ferrite matrix the actual precipitate-matrix interface cannot be indicated precisely.

## 4. DISCUSSION

### 4.1 The role of elastic energy in the decomposition of Fe-N martensite

The X-ray diffraction experiments and the transmission electron microscopy results given above could be explained on the basis of the elastic misfit between precipitate and matrix and the local distortion of the iron sublattice by the presence of nitrogen in octahedral interstices.

The concentration of the nitrogen atoms in the  $\alpha''$  precipitates gives rise to a considerable misfit between the precipitate and the eventually ferrite matrix : about 10 pct in the direction of the (c-)axis and about -0.3 pct in the direction of the (a-)axes for  $\text{Fe}_{16}\text{N}_2$ . Initially the misfit is small because the matrix is (still) a tetragonal martensite (containing 5.9 N/100 Fe) which allows the formation of almost perfect  $\text{Fe}_{16}\text{N}_2$  (about 12.5N/100 Fe). Upon further tempering (at 333 K) depletion of the matrix surrounding the precipitates continues and thus the misfit increases from about 3 to 4 pct ( $\alpha''$  in the martensite matrix) to about 10 pct ( $\alpha''$  in the ferrite matrix). The precipitate-matrix misfit can be reduced by the development of nitrogen deficient  $\alpha''$  because the c-lattice parameter of  $\alpha''$  decreases with decreasing nitrogen content.

The elastic energy contained in the  $\alpha''$  particles-matrix system not only consists of (i) the elastic (precipitate-matrix) misfit energy but involves also an internal elastic energy contribution caused by (ii) the (static) distortion of the iron sublattice around interstitial nitrogen atoms and (iii) the interaction of these local distortion fields due to different nitrogen atoms [13]. The first contribution favours the formation of nitrogen deficient  $\alpha''$  and the second two terms favour the formation of perfect  $\alpha''$ .

On the basis of an estimate of all the above mentioned elastic energy contributions (and the configurational entropy) involved during precipitation of both perfect and nitrogen-deficient  $\alpha''$  in a ferrite or a martensite matrix, it is argued in [11] that indeed in a martensite matrix (initially) a perfect  $\alpha''$  is preferred over nitrogen-deficient  $\alpha''$ -nitride and that in a ferrite matrix a nitrogen deficient  $\alpha''$ -nitride is preferred over perfect  $\alpha''$ .

The large misfit in the c-direction also explains the development of precipitates with a platelike shape and oriented along the (001)-planes of the matrix.

The X-ray and electron diffraction results indicate that tempering (after full decomposition of the martensite into ferrite and  $\alpha''$ -nitride) at higher temperatures results in the formation of 'perfect'  $\alpha''$ -nitride. This indicates that the elastic misfit energy is reduced in some way. Reduction of the misfit could be accomplished by plastic deformation. However, high resolution electron microscopy images of the precipitate-matrix interfaces show that very few dislocations are present even after prolonged annealing. The major part of the misfit seems to be accommodated by local deformation of the ferrite matrix as indicated in Fig. 3. The matrix is heavily distorted in some regions, other areas are tetragonally distorted and (001) matrix planes show locally different orientations. Thus it should be concluded that the misfit remains accommodated elastically predominantly.

### 4.2 Initial decomposition behaviour in Fe-N and Fe-C martensite

Interstitial atoms in c-type octahedral interstices in martensite induce locally a state of stress by displacement of surrounding iron atoms. The system can reduce its elastic energy by appropriate alignment of strain fields surrounding the interstitial atoms i.e. if the interstitial atoms order as in an  $\alpha''$  [13]. So a driving force for the formation of  $\alpha''$ -like precipitates could be this relaxation of elastic energy. It is interesting to note that the initial steps in the decomposition of Fe-N martensite can be understood on the basis of elastic energy considerations only (i.e. misfit between precipitate and matrix, and displacement of surrounding iron atoms by interstitial atoms).

In binary Fe-N and Fe-C martensites the deformation of the iron lattice by an interstitial atom is about the same for a nitrogen atom and a carbon atom (the lattice parameter dependencies on the interstitial content for Fe-N and Fe-C are comparable). Also the strain effects due to misfit between interstitial enrichments and matrix are similar. So, on the basis of elastic energy effects a similar decomposition behaviour is expected for Fe-N and Fe-C martensites. However, in Fe-C martensite no ordering of  $\alpha''$  type occurs [4]. Initially the carbon atoms form local enrichments in which the carbon atoms are most

likely distributed randomly (no superstructure reflections could be observed [4]). These experimental observations suggest that net interactions between interstitial atoms are different for N-N and C-C. The elastic interaction that promotes long-range ordering of the interstitials apparently governs the N-N interaction. Also, the chemical N-N interaction is reported to be repulsive [14]. On the contrary, the chemical C-C interaction is attractive [15] and apparently it causes the formation of clusters instead of  $\alpha''$ -like ordered arrangements of C atoms.

## 5. CONCLUSIONS

The structural changes occurring during the initial stage of decomposition of Fe-N martensite are controlled by elastic energy changes. The following elastic energy contributions occur: (i) elastic accommodation of the misfit between the matrix and the  $\alpha''$  precipitates, (ii) distortion of the iron lattice around the nitrogen interstitial atoms and (iii) the elastic interactions of these local distortion fields.

The competition of these energy contributions leads to the formation of perfect  $\alpha''$  and subsequently to the formation of nitrogen deficient  $\alpha''$  in a matrix that changes from martensite to ferrite.

Upon continued annealing the vacancies on the nitrogen sublattice fill up and perfect  $\alpha''$  develops (again). Then the elastic accommodation of the considerable precipitate/matrix misfit (up to 10 pct) is attained by severe deformation of the ferrite matrix surrounding the precipitate.

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