

In situ transmission electron microscopy investigations of the kinetics of α'' -Fe₁₆N₂ precipitation during the ageing of nitrogen–ferrite

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In situ transmission electron microscopy investigations were carried out on a supersaturated nitrogen–ferrite to characterise the precipitation kinetics of α'' -Fe₁₆N₂ nitrides at 85 °C. The coarsening behaviour consists of two stages. The first stage obeys the LSW theory and the coarsening rate was determined as 11.2 nm³ s⁻¹. The second stage corresponds to the stabilization of coarsening, and was assumed to be related to the coherency loss between the precipitates and the matrix.

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The solubility of nitrogen in α -ferrite decreases as temperature decreases. During the quenching–ageing of nitrogen–ferrite, the metastable nitride α'' -Fe₁₆N₂ formed as thin disc-shaped plates on the three sets of α -ferrite matrix {0 0 1} planes. This precipitation behaviour is accompanied of changes in the hardness [1–3].

Transmission electron microscopy (TEM) has been widely employed to investigate α'' -Fe₁₆N₂ precipitates in nitrogen–ferrite via both bulk and in situ ageing procedures. Much effort has been expended to study the crystallographic aspects of α'' -Fe₁₆N₂ nitride, e.g. the crystal structure, position of atoms, precipitate morphology and the orientation relationships with the matrix [1,3–8]. However, to our knowledge, no information appears to have been reported on the precipitation kinetics of α'' -Fe₁₆N₂ nitride from supersaturated nitrogen–ferrite.

In the present study, in situ TEM characterisation was carried out on the precipitation kinetics of

α'' -Fe₁₆N₂ during low-temperature ageing. Emphasis is given to determining the precipitation sequence and to establishing the size evolution of α'' -Fe₁₆N₂ precipitates as a function of time.

Pure iron sheets (1 mm thick) were nitrided at 840 °C for 120 min in ammonia–hydrogen gas mixtures, the composition of which was NH₃:H₂ = 1.3%:98.7%. After nitriding, the specimens were maintained at 840 °C for 100 min to allow a uniform nitrogen distribution. The resulting Fe–0.5 wt.% N alloy was annealed in the ferrite–austenite biphasic region at 620 °C for 5 min, followed by quenching into water at 25 °C. The microstructure thus obtained, which consisted of small amounts of martensite islands and a ferrite matrix (the volume fraction of the two phases was martensite:ferrite = 18%:82%), is a so-called dual-phase. The ageing behaviour of the supersaturated ferrite matrix was the object of this investigation. The specimen was cut into two parts, one for bulk ageing and one for the preparation of thin foils for in situ ageing.

Bulk ageing was performed at 85 °C in order to test the evolution of Vickers hardness (HV) with ageing time. Every 5 min during ageing, the sample was taken out of the furnace, quenched to room temperature and 20 hardness indentations were made on ferrite matrix.

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A low load of 50 g was used and the resulting indentations were very small compared with the ferrite grains. These small indentations were made completely within ferrite grains in such a way that the distance between indentations and martensite islands was at least three times the diagonal of indentations. Consequently the influence of martensite on the hardness of ferrite could be minimised.

The preparation of thin foils for in situ TEM examination was achieved by using the double-jet technique with a 95% glacial acetic acid/5% perchloric acid electrolyte. Before and after the preparation of thin foils, materials were kept at $-20\text{ }^{\circ}\text{C}$ to prevent room temperature ageing. The microscope used in this investigation was a Philips CM12 operated at 120 kV.

In situ ageing of thin foils was carried out at $85\text{ }^{\circ}\text{C}$ using a simple-tilt heating stage. All micrographs were recorded successively with small time intervals on only one selected ferrite grain. On each micrograph, the mean radius of 20–25 precipitates was measured.

First of all, it is worth mentioning that for a TEM investigation of this type it is preferable if the ferrite grain is oriented in the $\langle 001 \rangle$ direction. The reason is that under such conditions one set of disc-shaped $\alpha''\text{-Fe}_{16}\text{N}_2$ precipitates are viewed face-on and the other two sets edge-on [1,3], enabling direct and simple measurement of the radius of the precipitates. In this study, double-tilt heating stages were unfortunately unavailable and a simple-tilt heating stage was used. As a consequence, tilting ferrite grains into one of the $\langle 001 \rangle$ directions was not always possible. This inconvenience did not cause any problem because in directions other than $\langle 001 \rangle$ the precipitates appears as ellipses on screen and the major diameter of ellipses is always equal to the real diameter of disc-shaped precipitates (fortunately, this holds only for disc-shaped precipitates). As can be seen in Figure 1, our observations were made on only one ferrite grain, in the $[112]$ direction, and all $\alpha''\text{-Fe}_{16}\text{N}_2$ precipitates were recorded as ellipses.

The first $\alpha''\text{-Fe}_{16}\text{N}_2$ precipitates were detected 80 min after the onset of ageing and their mean radius was estimated as 24 nm. Three successive TEM micrographs, corresponding to $t = 90, 100$ and 110 min, are shown in Figure 1. From these micrographs, which demonstrate the ageing sequence of $\alpha''\text{-Fe}_{16}\text{N}_2$, we noticed two things:

- the total number of $\alpha''\text{-Fe}_{16}\text{N}_2$ precipitates decreases;
- smaller precipitates (highlighted by arrows) dissolve with time in favour of larger precipitates.

This is the Gibbs–Thomson effect and reflects the coarsening behaviour of $\alpha''\text{-Fe}_{16}\text{N}_2$ nitrides. It is therefore clear that in the present study using conventional TEM, only the coarsening stage was detected; the nucleation and growth stages were ignored due to the small size of the precipitates.

The evolution of the mean size of $\alpha''\text{-Fe}_{16}\text{N}_2$ precipitates during coarsening is shown in Figure 2, by plotting the cube of the mean radius of precipitates as a function of ageing time ($r^3 = f(t)$). The data can be divided into two parts:

- The first part follows the classical LSW [9,10] law, which is written as:

$$r^3 - r_0^3 = K(t - t_0)$$

where r and r_0 are the mean radius at time t , and at the onset of coarsening t_0 , respectively. K is a measure of the coarsening rate and corresponds to the slope of the experimental data, which was determined as $11.2\text{ nm}^3\text{ s}^{-1}$. This very high coarsening rate results from the high diffusivity of nitrogen in iron.

- The second part is a plateau, starting from approximately 4 h of ageing. This plateau clearly corresponds to the stabilisation of coarsening, during which the mean radius of precipitates remains almost constant (about 50 nm).

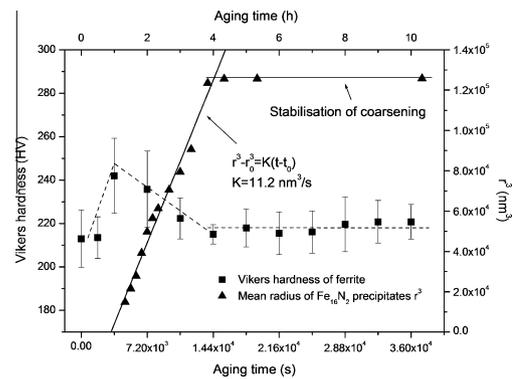


Figure 2. Evolution of the mean radius of $\alpha''\text{-Fe}_{16}\text{N}_2$ precipitates (triangle symbol) and of the Vickers hardness of nitrogen–ferrite (square symbol) as a function of time.

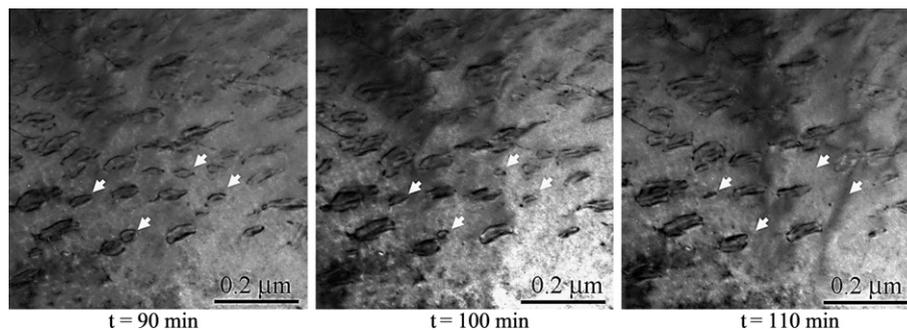


Figure 1. In situ TEM micrographs, corresponding to ageing times $t = 90, 100$ and 110 min, showing $\alpha''\text{-Fe}_{16}\text{N}_2$ precipitates in nitrogen–ferrite matrix at $85\text{ }^{\circ}\text{C}$. Four precipitates of small size highlighted by arrows dissolve with time.

The change in hardness of nitrogen–ferrite tested during bulk ageing is also presented in Figure 2. The coupled microstructure–hardness data show a logical result and can be summarised as follows:

- The increase in the hardness of ferrite from 213 to 242 HV (0–1 h) could be attributed to the nucleation and growth stages of α'' -Fe₁₆N₂ precipitates, which were not detectable by TEM.
- The subsequent decrease in hardness of ferrite from 242 to 215 HV (1–4 h) is clearly caused by the coarsening of α'' -Fe₁₆N₂ precipitates, during which the total number of precipitates decreases and the resultant strengthening effect deteriorates.
- During the stabilization of coarsening (4–10 h), the hardness remains unchanged and maintains almost the same level as that of the precipitate-free state.

This result suggests that nitrogen–ferrite is a coarsening-resistant material. Although the diffusivity of nitrogen and the resulted coarsening rate are very high, the stabilization of coarsening is achieved rapidly and the mechanical properties do not deteriorate uncontrollably.

The knowledge of the coarsening rate at 85 °C allowed us to estimate the coarsening rate at room temperature by using the modified LSW equation for disc-shaped precipitates [11] as follows:

$$\frac{r^3 - r_0^3}{t - t_0} = K = \frac{32}{9q\pi} \cdot \frac{\gamma C_\infty V_m^2 D}{RT}$$

where C_∞ is the solubility of nitrogen in ferrite matrix, D is the diffusivity of nitrogen in ferrite matrix, γ is the precipitate–matrix interfacial energy, V_m is the volume per mol of precipitates, R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the ageing temperature in Kelvin and q is the aspect ratio $q = e/r$, where e is the thickness of precipitates.

The temperature-dependent parameters in the equation are C_∞ and D . In the Fe–N system, the solubility of nitrogen in ferrite at both 85 and at 25 °C is very low and the two values could be supposed equal. D can be determined by the equation $D = 7.8 \times 10^{-7} \exp\left(\frac{-79,100}{RT}\right)$ [12]. Hence the coarsening rate K at 25 °C is simply given by $K_{25^\circ\text{C}} = K_{85^\circ\text{C}} \frac{D_{25^\circ\text{C}} \cdot 358}{D_{85^\circ\text{C}} \cdot 298}$ and estimated as 0.064 nm³ s⁻¹. A rough calculation suggests that even at room temperature, coarsening of α'' -Fe₁₆N₂ will proceed rather rapidly and cause a decrease in the mechanical properties. Fortunately, the stabilization of coarsening can be predicted for any ageing temperature. Figure 3 presents an ex situ TEM micrograph of a ferrite specimen aged at room temperature for 15 months. If the LSW theory holds throughout such a long ageing time, the mean size of α'' -Fe₁₆N₂ precipitates will reach a gigantic value. The reality is that the mean radius of precipitates shown in Figure 3 is estimated to be only 56 nm, which does not differ considerably from the value for ageing at 85 °C (50 nm). This fact strongly supports the prediction described above.

The stabilization of coarsening has been reported by many authors in precipitation-strengthened alloys [11,13–19]. Paris et al. [17] proposed that the elastic inhomogeneity could be the origin of the stabilization of coarsening, and predicted that a strong reduction in

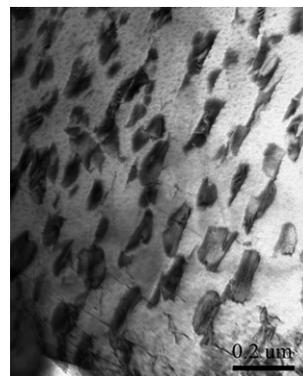


Figure 3. TEM micrograph of a nitrogen–ferrite aged at room temperature for 15 months showing α'' -Fe₁₆N₂ precipitates, the mean radius of which estimated as 60 nm.

coarsening kinetics may be expected in materials where the shear moduli of the matrix and precipitates differ significantly. In the Fe–N system, it is commonly accepted that a α'' -Fe₁₆N₂ lattice (body-centred tetragonal) is an ensemble of eight slightly deformed ferrite lattices (body-centred cubic) plus two nitrogen atoms. In other words, α'' -Fe₁₆N₂ could be considered simply as ferrite supersaturated in nitrogen. For this reason, although the shear modulus of α'' -Fe₁₆N₂ is currently unknown, we think that it should not differ much from that of ferrite and the prediction of Paris et al. [17] could not be valid in our case.

Barlow et al. [20] related the stabilization of coarsening to the elimination of short-circuit diffusion paths such as dislocations during ageing. This explanation is again not valid in our case because we found that the dislocation density increases with ageing time. A TEM micrograph recorded when $t = 10$ h is shown in Figure 4. One can see clearly that many dislocations are attached with precipitates and the dislocation density is remarkably higher than those shown in Figure 1.

Perez and Lewis [18], according to their calculations, pointed out that the interface misfit and atomic-scale elasticity are among the most important factors causing the stabilization of coarsening. Following our observations, we agree with Perez and Lewis [18] that studies on the interface properties including misfits, interface dislocations and coherency strain energy, are the right approach. Figure 4 shows that almost every larger precipitate is associated with dislocations but vanishing

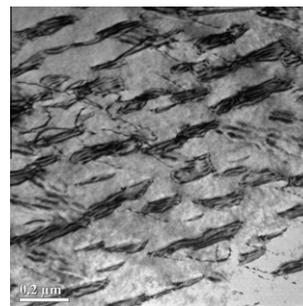


Figure 4. TEM micrograph of a nitrogen–ferrite aged at 85 °C for 10 h showing dislocations attached to α'' -Fe₁₆N₂ precipitates.

smaller precipitates are not associated with dislocations. This fact made us relate the present situation to the coherency loss of large precipitates caused by the dislocation loop punching mechanism [21]. According to this mechanism, when the size of a coherent precipitate reaches a critical value, the coherency strain energy becomes so high that a pair of dislocation loops, one interstitial and the other of the vacancy type, form at the interphase boundary. One will be left at the boundary (the coherency is thus lost) and the other one will be expelled into the matrix as can be seen in Figure 3. The interface dislocation formation process is difficult to achieve and requires that the stresses exceed the strength of the matrix. A question that arises here is whether this process slows down the coarsening kinetics? Iwamura and Miura [22] studied the coarsening behaviour of Al₃Sc precipitates in Al–0.2 wt.% Sc alloy and reported the acceleration of the coarsening kinetics due to the loss of coherency. However, Watanabe et al. [23] found that the transition in precipitate coherency causes no changes in the coarsening rates of Co and γ -Fe precipitates in the Cu matrix. There are to date few reports on this issue, but it seems that the answer to this question depends on the systems involved and requires detailed study.

In situ TEM investigations of the kinetics of α'' -Fe₁₆N₂ precipitation in nitrogen–ferrite matrix yielded the following conclusions:

- (1) The coarsening behaviour of disc-shaped α'' -Fe₁₆N₂ nitrides precipitated from supersaturated nitrogen–ferrite at 85 °C was observed by in situ TEM, which allowed a “real-time” characterisation of the global microstructure transition and a precise tracking of individual particles.
- (2) The coarsening kinetics consists of two stages. During the first stage (ageing time = 80 min–4 h): the cube of the mean radius of α'' -Fe₁₆N₂ increased linearly with time. The coarsening rate was determined as 11.2 nm³ s^{−1}. This behaviour, accompanied by a hardness decrease, obeys the classical LSW theory.
- (3) During the second stage (ageing time = 4–10 h) the coarsening rate was completely constant: the mean radius of α'' -Fe₁₆N₂ remained at 50 nm and the hardness was unchanged with time.

- (4) Dislocations attached on α'' -Fe₁₆N₂ precipitates were observed and a believed to relate to the stabilization of coarsening.

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