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THE MICROSTRUCTURE OF NITRIDED Fe-0.3Wt%Ti ALLOY ANNEALED AT 800°C

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Following the initial work on nitriding Fe-Ti alloys between 550° and 700°C which showed exceptional resistance to softening at higher temperatures[(1)] the present paper describes an electron microscope study of the coarsening and coherency strains associated with precipitation in this system. The alloy chosen was Fe-0.27Wt%Ti, in order to reduce the volume fraction of precipitates so as to avoid complications of overlapping strain fields. This alloy was nitrided in pure ammonia at 600°C, held at 600°C in pure argon to remove excess nitrogen in solution and quenched into silicon oil[(2)]. These denitrogenised specimens were annealed in argon at 800°C for various times of aging up to two weeks, followed by quenching. Electron microscopy contrast and diffraction experiments were performed on thin foils prepared from these heat-treated specimens by jet polishing of discs in chromic-acetic acid at 25 v.

Figures 1 and 2 show bright and dark field images obtained after two weeks aging at 800°C. The electron diffraction patterns of all nitrided specimens used in this investigation showed streaks in <100>α directions indicating the presence of fine platelets lying parallel to {100}α planes (see inset, Fig. 1). These platelets were imaged in dark field structure factor contrast as described in Ref 3 by tilting the beam to bring the streak into the microscope optical axis in order to provide high resolution (Fig. 2) without the confusion introduced by strain fields (Fig. 1). Many such images were used to obtain information on the average diameters and thicknesses of the platelets after different annealing times. The results are presented in Table 1, along with hardness measurements for each specimen.

In the denitrogenised specimen which had no annealing treatment at 800°C, extremely fine particles were present of about 30Å diameter, although much coarser particles could be observed on dislocations in sub-grain boundaries. After 1 hr. at 800°C, the diffraction streaks show a definite maximum. Analysis of many diffraction patterns and comparison to the earlier results[1] shows that this maximum is due to the 200 reflection of the f.c.c. TiN structure. At earlier times than this, it is impossible to be certain from the diffraction evidence whether the plates are mixed substitutional-interstitial solute atom zones of the type proposed by Spiers et al.[5], or very thin plates. The strain contrast analyses (Table 1) also support the existence of TiN, since the observed strain of 45% agrees well with the misfit expected from coherent TiN plates.

Continued aging at 800°C produces a slow growth in the plate size. After 8 hrs. a small drop in hardness is detected, accompanied by a reduction in coherency strain. After 3 days the plates are still only 55Å in diameter but the coherency strain has dropped to one third of its original value. By 7 days the average diameter has grown to 80Å, the hardness has fallen appreciably and a few of the larger plates (>120Å) show little strain field contrast. Many of the plates in the

14 day specimen (Fig. 1) show no strain fields whatsoever, and these have diameters of 150Å and larger.

In the as-nitrided specimens it is apparent that very fine platelets exist similar to those in the denitrogenised specimen before annealing. However, a coarser precipitate is also present which has the appearance of clusters of plates some 500Å in length lying on $\{100\}\alpha$ planes. It is suggested that these are α''-$Fe_{16}N_2$ precipitates, because iron specimens fully nitrided at 600°C in ammonia and quenched will be greatly supersaturated in nitrogen with respect to this nitride. The appearance and orientation of these plates are similar to the α'' precipitates observed by Keh and Wriedt[6] in pure iron specimens aged around room temperature. This explanation would also account for their virtual dissappearance on subsequent denitrogenising in argon at 600°C.

No great accuracy is claimed for the magnitude of the coherency strains given in Table 1, and it has been estimated[7] that errors arising from the theoretical analysis of Ashby and Brown (which ignores effects of anisotropy and shear strains at the precipitate interface) limit the accuracy of the effective Burger's vector determination to ± 50%. However, in the specimen annealed for 2 weeks it was possible to measure the strain field, diameter, and thickness of each particle, and from the analysis of 14 particles the standard deviation in measurements of b and ε were obtained (given in Table 1). This result indicates that the error arising from measurement is less than 30%.

It has been established that TiN precipitates are formed in ferrite with the Bain orientation[1]. Thus by taking the lattice parameter of TiN as a_0=4.24Å, coherent precipitates of TiN should have a misfit of

48% normal to the plate surface along [001]. In the case of $\alpha''-Fe_{16}N_2$, the c dimension normal to the plate of this structure is 6.29Å[9], and produces a misfit of 10% with two unit cells of ferrite. The same α'' structure with some of the Fe atoms replaced by Ti will cause a slightly larger misfit. Therefore, the evidence of an observed misfit of around 45%, even accepting a 50% error, and the maxima on the diffracting streaks strongly point to the platelets having a TiN structure after short times at 800°C. Unfortunately, there were no micrographs suitable for strain field measurements in the non-annealed nitrided specimens so no direct evidence is available on whether TiN is the initial product of nitriding or not.

In summary, the conclusions from this work are:

1) No pattern of precipitation could be detected in the nitrided alloys, but preferential nucleation on dislocations was seen.
2) After short annealing times at 800°C very large values of misfit of the coherent platelets with the matrix were measured. This misfit is consistent with the platelets having a f.c.c. TiN structure and a Bain orientation relationship to the matrix.
3) After annealing at 800°C for some days, the precipitates began to lose their coherency. Coherency strain contrast is not observed from plates of diameter >150Å.

TABLE I

Data on TiN platelets as a function of annealing, including corresponding hardness of the alloys.

Annealing time at 800°C	Average diam. Å	Average thickness Å	Effective Burger's vector b Å	Coherency strain ε %	Vickers hardness
0, as nitrided					541
0, denitrogenized	~30				491,465*
1/2 hr	30	5	2.3	45	475
1 hr	40				439
4 hr	45	5			441
8 hr	40	6	1.7	30	375
3 days	55	7	1.2	17	
7 days	80	10	1.1	11	268
14 days	130	11±1	0.54±0.13	5.0±1.4	271

*Measurements from two specimens.

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FIGURE CAPTIONS

Fig. 1. Fe-0.27%Ti aged 2 weeks at 800°C. Bright field micrograph, showing strain field contrast around small precipitates. Inset shows electron diffraction pattern with TiN streaks and diffuse arcs from Fe_3O_4. The moiré pattern is due to double diffraction from the Fe_3O_4 surface film and the underlying metal. Foil normal [001], $\vec{g} = 200$.

Fig. 2. Similar area as Fig. 1 showing dark field structure factor contrast micrograph of TiN precipitates. Dark field image (gun tilt) of the [100] streak shown in Fig. 1. Foil normal [001].

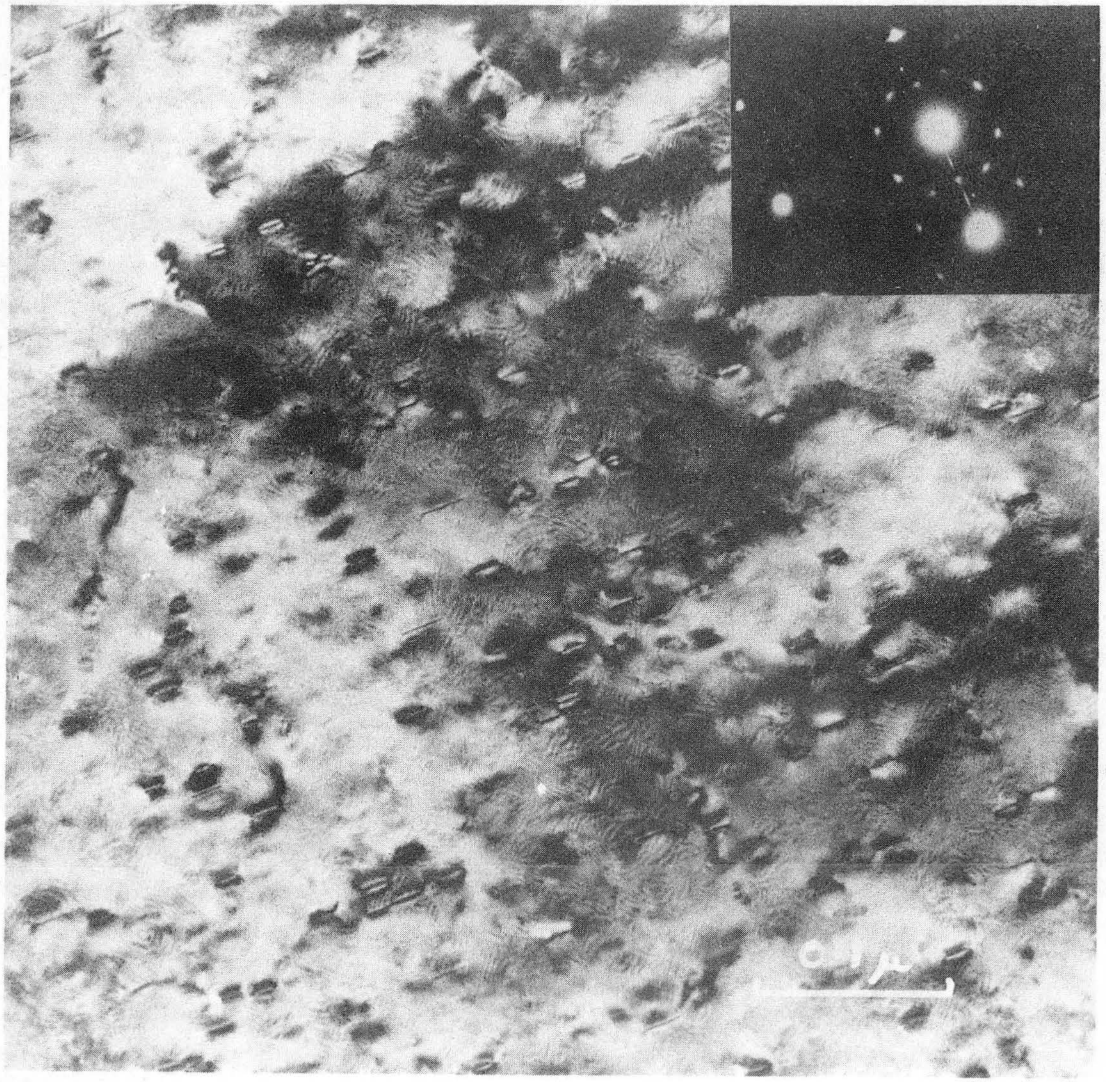

Fig. 1

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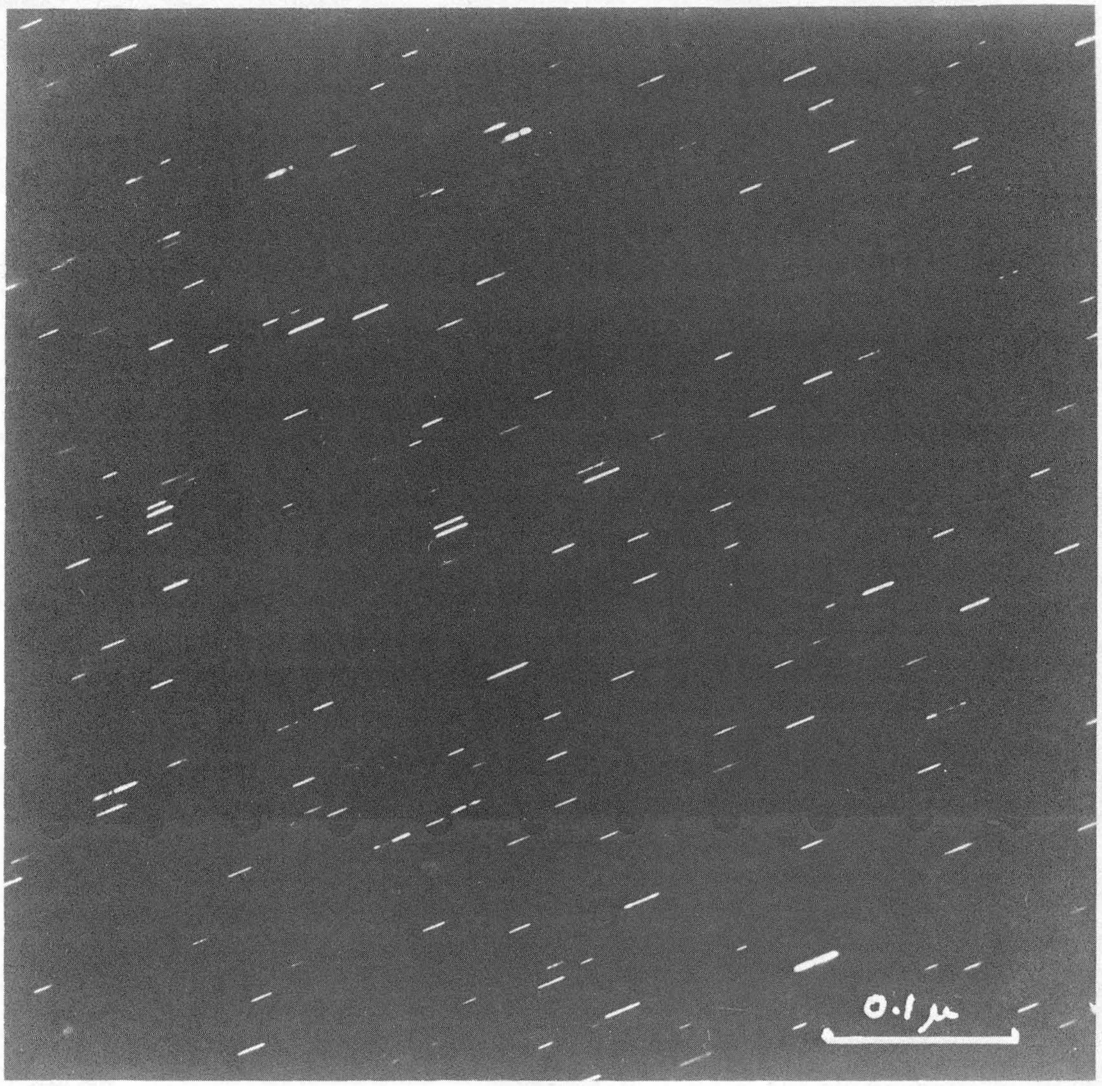

Fig. 2

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