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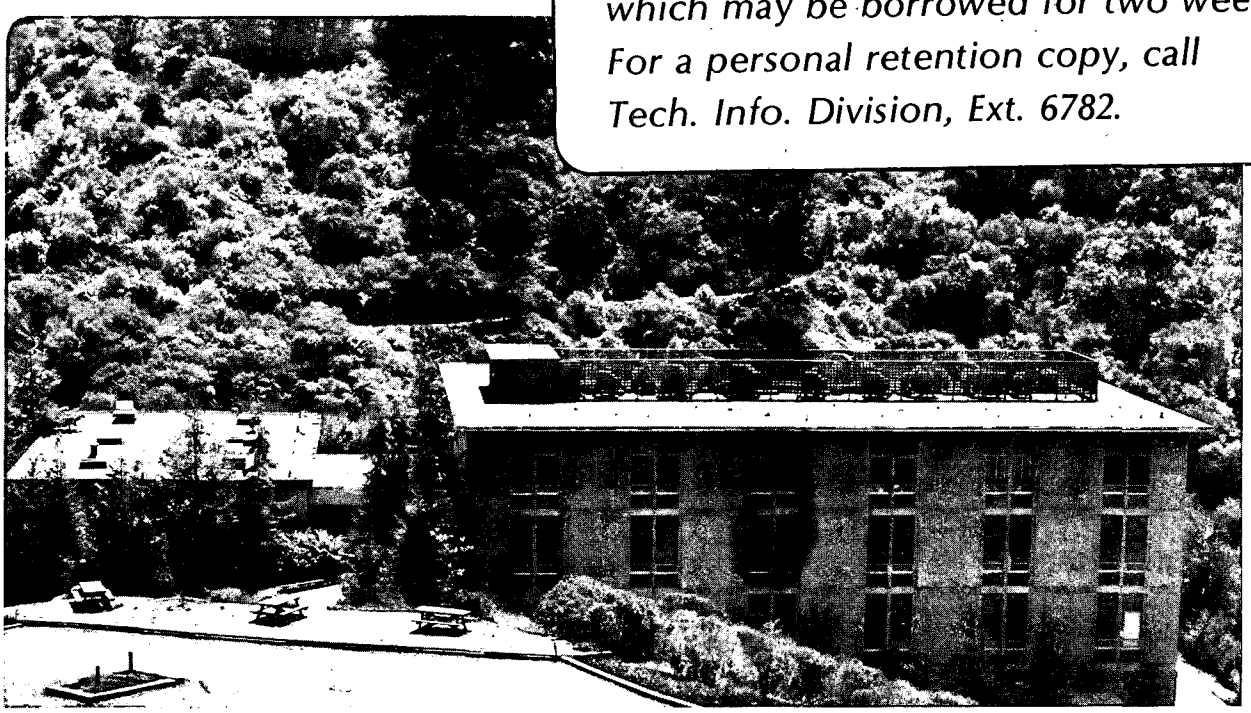

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MORPHOLOGICAL ASPECTS OF α''-$Fe_{16}N_2$ PRECIPITATION IN α-Fe

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Introduction

The intermediate precipitate α''-$Fe_{16}N_2$ formed during the quench-aging of nitrogen-ferrite occurs via a nitrogen GP zone stage as thin disc-shaped plates on the three sets of matrix {001} planes (1). Its b.c. tetragonal structure (2) shown in Fig. 1 can be considered as a tetragonal distortion of ferrite with an expansion (9.7%) in the c-direction and a slight contraction (0.2%) in the a-direction due to the ordered occupation by nitrogen atoms of two of the sixteen octahedral interstices whose tetrad axes are parallel with one of the cube directions, i.e. the c-edge.

Previous TEM studies on α'' precipitation have been performed using bulk-aging (3,4,5) and in-situ aging (6,7) procedures and, irrespective of which aging treatment is adopted, individual disc-shaped α'' particles always have a characteristic "rosette" contrast when viewed normal to the plate surface. This effect has not been explained but was thought to originate through variations of the plate thickness (3) or anisotropy of surface energy (8). The present TEM analysis using high-angle tilting shows that this contrast arises because individual α'' particles are comprised of several inclined segments near the same {001} plane.

Experimental

An Fe-0.08wt%N alloy was prepared by homogenizing zone-refined iron foils (0.1mm thick) in a flowing ($0.6 cm.s^{-1}$) gas mixture of $10.5NH_3$:$89.5H_2$ at 590°C followed by quenching into iced brine. Specimens for TEM were prepared by the window technique using standard procedures. Bulk material was aged in a vacuum furnace (< 1.3 cPa). In-situ aging of thin foils at a pressure < 0.3mPa was performed by using the double tilt heating stage ($1°C.s^{-1}$) of a Kratos 1.5MeV HVEM. Electron microscopy was performed using a Siemens 102 and the HVEM operating at 100 and 400kV respectively.

Results

Figure 2 shows a typical micrograph of α"-$Fe_{16}N_2$ precipitates in a [100] projection formed by bulk-aging a specimen 100 min. at 200°C. Three sets of disc-shaped plates on the {001} matrix planes are visible as is the "rosette" contrast of the plates which are perpendicular to the electron beam. Similar contrast behaviour is observed for α" precipitates formed by in-situ aging 3 min. at 250°C as shown in Fig. 3. The contrast of individual segments changes from bright to dark as the foil is tilted slightly about a constant diffraction vector of the ferrite matrix. This suggests that each "rosette" is made up of a number of orientation variants and is confirmed in Fig. 4 by the high angle tilting analysis on a precipitate formed by bulk-aging 10 min. at 250°C. When viewed in a [113] beam direction (Fig. 4a) the large inclined precipitate intersecting one foil surface exhibits contrast typical of the rosette plates. The large dark segment is diffracting strongly and when tilted edge-on in a [120] beam direction (Fig. 4b), clearly shows an inclination of ~ 10° with respect to the rest of the particle. The segments which appear light in Fig. 4a are not edge-on in the [120] orientation (Fig. 4b) and hence are also inclined with respect to the overall (001) habit of the particle with a different axis of inclination relative to the darker central segment. In Fig. 4a the perimeter of the plate can be seen to follow a zig-zag path which is straight along each individual segment. The contrast exhibited by these segments is similar to the larger areas and indicates that these small regions are associated with the growth of additional new variants at the plate periphery, presumably with the same angle of inclination (~10°) to the (001) habit plane. The boundaries between different segments in each particle tend to lie along radial directions with no apparent crystallographic preference as shown in Fig. 3.

The model of α" rosette particles resulting from this contrast analysis is illustrated schematically in Fig. 5. Each of the segments comprising the particle is

an orientation variant inclined about 10° with respect to the overall (001) plane. This leads to a puckered sheet whose overall habit is the (001) plane. Small segments near the perimeter as seen in Fig. 4 are secondary kinks made up of individual orientation variants. This model is consistent with the observed difficulty of tilting a plate edge-on, the appearance of undulating plates when viewed nearly edge-on and the rosette contrast of plates seen face-on.

Discussion

The proposed puckered sheet morphology for the rosette α''-$Fe_{16}N_2$ plates solves the discrepancy between the experimentally observed (001) habit (3-7) and the (h01) plane predicted on the basis of the linear elastic theory (9) which was pointed out recently (10). Wen et al. (9) calculated a habit plane 22° off the 001 plane for Fe_4C in α-iron assuming a flat plate precipitate with a tetragonality ratio of η = -10. For the present case of α''-$Fe_{16}N_2$ in ferrite using the lattice parameters measured by Jack (2), becomes ~ 45 and the theory outlined by Wen et al. (9) predicts a misorientation of ~ 9° from {001} in good agreement with the ~10° inclination of segments found in the present work. Individual segments in the particles observe the predicted inclination and all of them group together with an overall habit of (001) presumably in order to lower the strain energy. It is thus not necessary to invoke an effect of aspect ratio to explain the observed habit plane shift (10).

It was suggested that due to the elastic anisotropy of the ferrite, the preferred habit of a flat plate should be of the type h01 (9), i.e. the inclination should be around an <010> axis. Considering each segment as an individual flat plate leads to a crystallographic appearance of the rosette as observed by Shih and Morris (11) who found branches in <010> and <110> directions. However, in the present study no such crystallographic preference was apparent probably due to the

slightly higher aging temperature (200°C). Thus at this temperature elastic anisotropy does not seem to be a major influence in the selection of variants. Further, even though the degree of inclination of the segments from the overall (001) habit of the plate may vary, the non-planar morphology of the plate does not change with the degree of tetragonality as the nitrogen GP zones which precede the α" precipitate also have an undulating appearance (12).

The grouping of several precipitate variants into a cluster such as the observed α" rosettes is not limited to the precipitation of $Fe_{16}N_2$ in nitrogen-ferrite. Similar fine structure has been observed in precipitates of Ta_2C in tantalum (13). The clustering of two twin-related variants in a single self-accommodating precipitate is familiar in twinned martensite plates (14) and has also been observed in the precipitation of V_3N from vanadium (15) and even in order-disorder transformations as reported for Ni_3V (16). In nitrogen-ferrite two mirror-related variants of γ'-Fe_4N from 'V'-shaped clusters rather than twinned plates (17) and even more complex groups of four variants have been found to occur in shape-memory alloys (18). Although quite different in appearance the cruciform particles found in the early stages of aging carbon-ferrite (19) are likely to be similar groups of variants. It is therefore suggested that the observed rosette morphology is just one more example of precipitate self-accommodation.

Conclusion

Based on a detailed analysis by TEM, it is suggested that the rosette-type plates of α" in Fe-N are puckered sheets made up of flat segments inclined ~10° with respect to the overall {001} habit plane. This model is consistent with all the observed contrast features and is in basic agreement with the predictions of the theory of coherent elastic inclusions.

Acknowledgements

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FIG. 1. The crystal structure of α''-$Fe_{16}N_2$.

FIG. 2. Brightfield micrograph of $\alpha''Fe_{16}N_2$ precipitates in Fe0.08wt%N bulk-aged 100 min. at 200°C.

FIG. 3. Contrast changes exhibited by rosette α'' plates during tilting along g $01\bar{1}$.

FIG. 4 Morphology of an α'' precipitate as revealed by high angle tilting.

FIG. 5 Schematic representation of the proposed puckered sheet morphology for an $\alpha''Fe_{16}N_2$ precipitate.

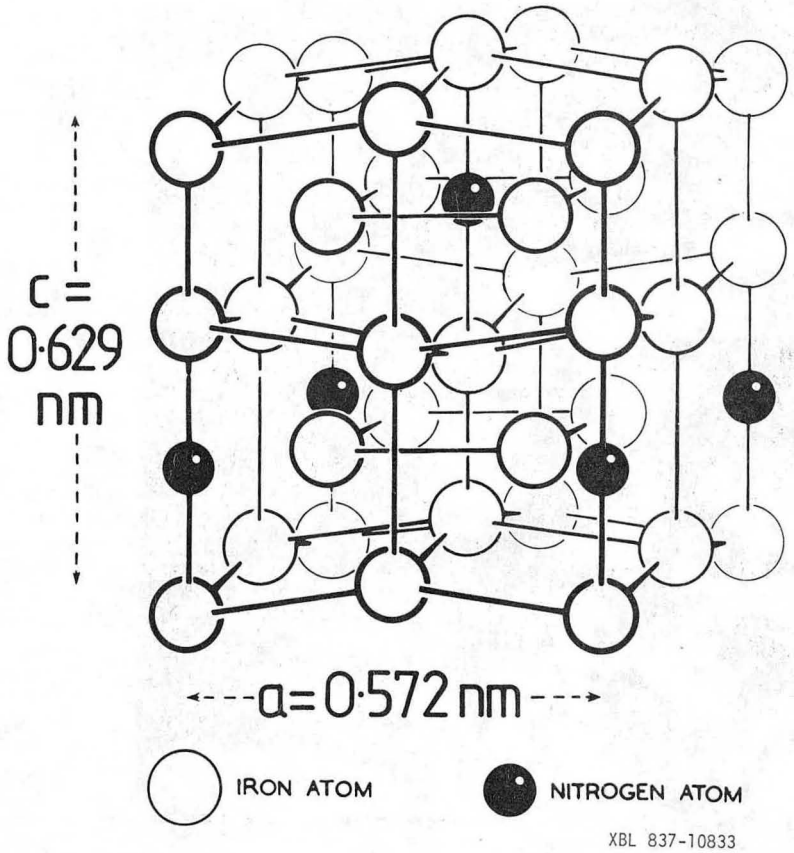

Fig. 1

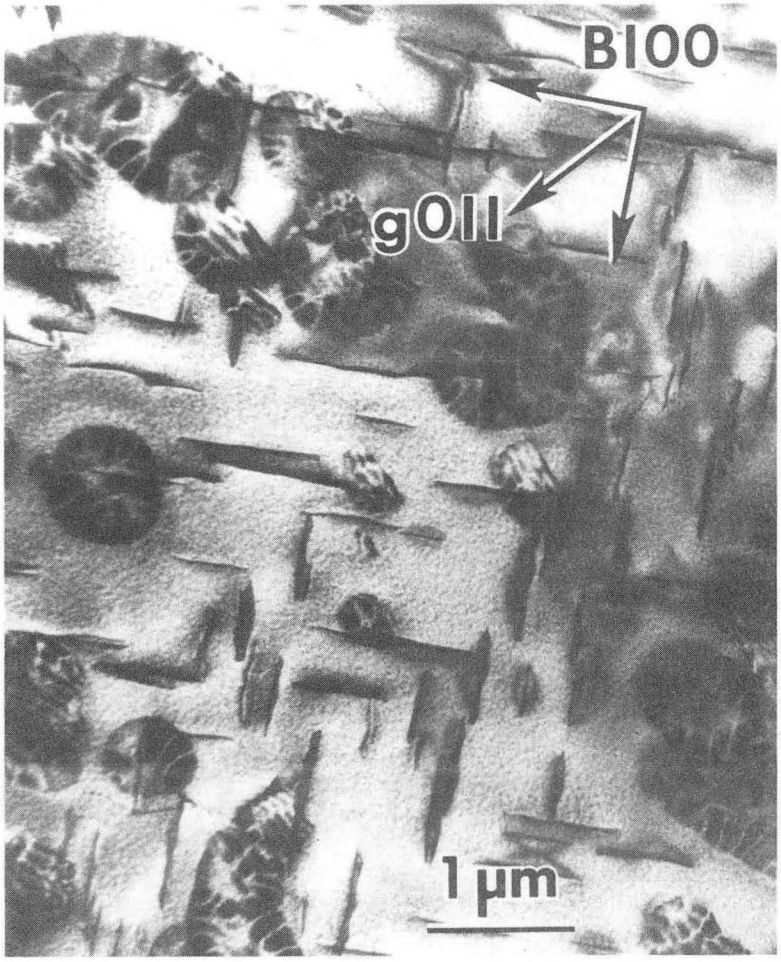

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Fig. 2

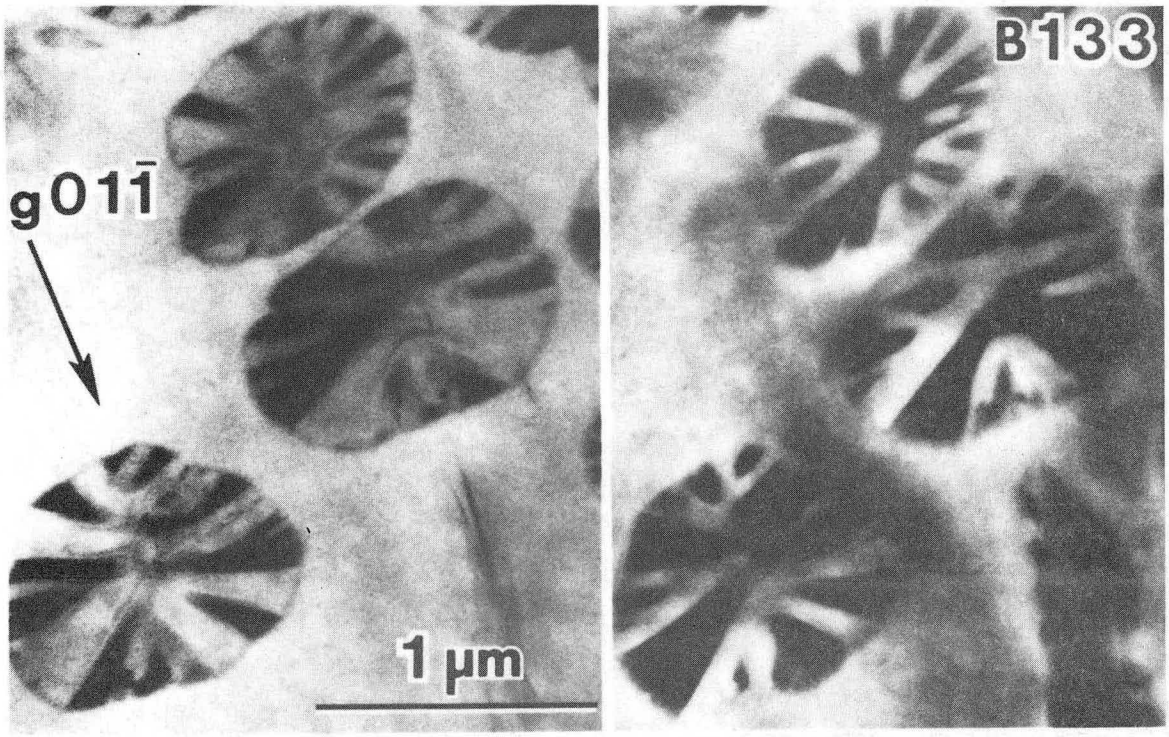

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Fig. 3

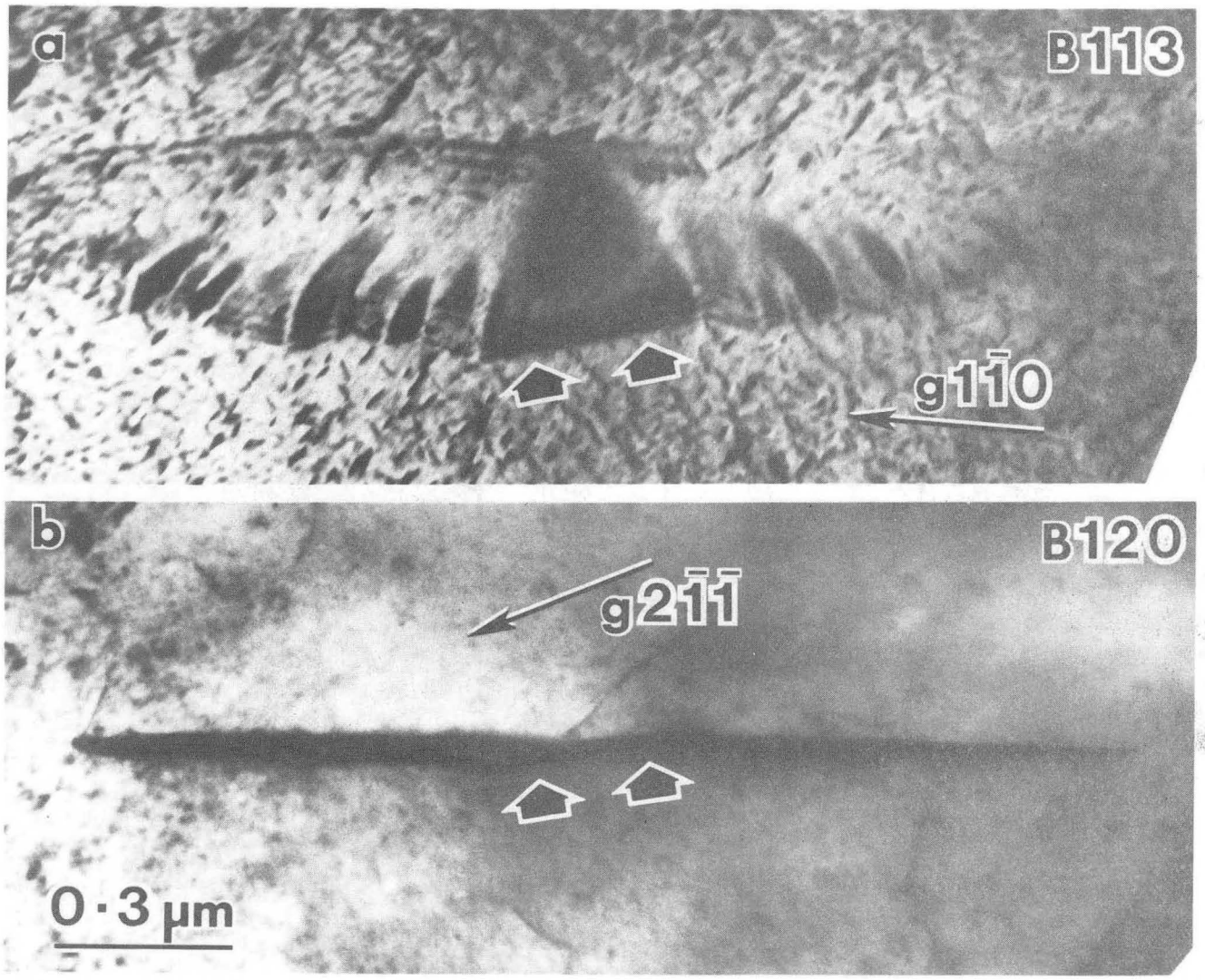

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Fig. 4

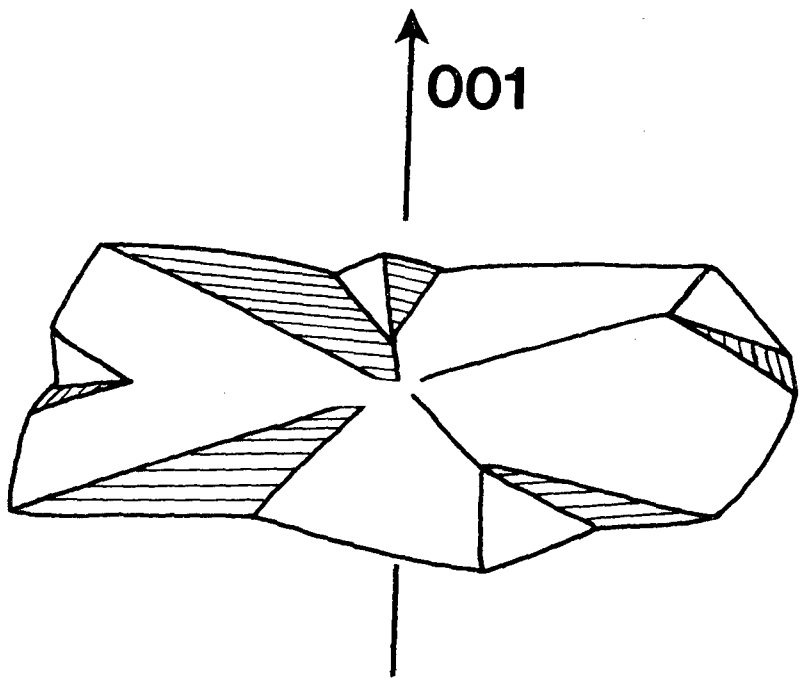

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Fig. 5

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