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THE STATE AND HABIT OF THE Fe_{16}N_2 PRECIPITATE IN BCC IRON:
ELASTIC THEORY

M.Hong*, D.E.Wedge** and J.W.Morris,Jr.

Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
and Department of Materials Science and Mineral Engineering, University
of California, Berkeley, California 94720

SUMMARY

The linear elastic theory is used to determine the preferred habit of the α^2 Fe_{16}N_2 precipitate in α iron, assuming that the precipitate is a coherent, tetragonal phase having the form of a thin circular disc, and neglecting both surface tension effects and the difference in elastic constants between the precipitate and the iron matrix. With these approximations the precipitate habit depends on the tetragonality of the transformation strain connecting the matrix and precipitate lattices, the aspect ratio of the disc, and the elastic constants. The preferred habit of Fe_{16}N_2 in α iron is found to vary with the precipitate aspect ratio (K). The preferred habit changes continuously from $\{100\}$ for $K < 11.35$ to an asymptote near $\{102\}$ for large values of K . The results can explain the common $\{100\}$ habit of Fe_{16}N_2 , but predict that this habit is unstable when the precipitate aspect ratio is large. The theory is also used to calculate the lattice parameters of the precipitate when it is constrained within α iron. The results agree with experimental data and provide a simple explanation for discrepancies in the reported values of the lattice parameters of Fe_{16}N_2 .

*Now at Bell Telephone Laboratories, Murray Hill, N.J.

**Now at Varian Associates, Palo Alto, Calif.

INTRODUCTION

In work done recently in this laboratory (Wen, et al. [1]) the linear elastic theory [2-5] was used to determine the preferred habit of a tetragonal precipitate in a cubic matrix, given that the favored particle shape and habit minimize the total elastic energy and neglecting the difference between the elastic constants of the precipitate and those of the matrix. Under these conditions the precipitate is an arbitrarily thin plate. Its preferred habit plane can be found analytically. The preferred habit depends on the tetragonality of the precipitate and on the elastic constants, the most important of which is the elastic anisotropy factor. Despite the strength of the assumptions underlying the theory it predicts the known precipitate habits in several very different systems [1]. It correctly identifies the {100} habit of GP zones in Al-Cu and Cu-Au alloys, the {102} habit of Fe_4C carbides in α iron, and the {227} habit of $\text{V}_{0.45}\text{H}$ hydrides in vanadium.

There is, on the other hand, a well known case for which the theory fails: the intermediate $\alpha^2 \text{Fe}_{16}\text{N}_2$ precipitate in α iron. While the tetragonality of the nitride [6] is nearly equal to that of Fe_4C [1], suggesting a precipitate habit near {102}, the reported habit is {100} [7-10]. The work presented here was undertaken to clarify the source of this difference.

It is superficially appealing to dismiss this problem as an example of the limitations of the linear elastic theory itself. The assumptions underlying the application of linear elasticity to the crystallography of phase transformations are strong [3,4]. While the theory has been used with encouraging success to predict or interpret many phase transformation phenomena [5] there must be problems which lie beyond its capability.

It will, however, be surprising if the elastic theory specifically cannot predict the preferred habit of Fe_{16}N_2 in α iron, since it successfully predicts other salient features of this precipitation reaction. Mori, Cheng, and Mura [11] have shown, for example, that the microscopic elastic theory correctly identifies the structure of Fe_{16}N_2 (Figure 1) as the minimum energy configuration for interstitial nitrogen defects in BCC iron. Their analysis implies that the lattice parameters of the precipitate should be given by an extrapolation of Vegard's Law for nitrogen in martensite [12] to the composition of the precipitate, in agreement with the experimental results of Suyazov, et al. [6]. As we shall show below, the linear elastic theory also yields the proper lattice parameters for the coherent α^2 precipitate in the iron matrix, as measured by Abiko and Imai [9], and hence resolves the difference between the lattice parameters reported by Suyazov, et al. [6] and those given by Jack [13]. The theory also explains the gradual precipitate shape change during coarsening seen by Keh and Wreidt [7] and by Wagner and Brenner [8]; in fact, both the latter authors [8] and Wedge [14] have used the elastic theory to estimate the surface tension of the precipitate from the coarsening data with reasonable results. Given that the linear elastic theory correctly predicts the structure, the lattice

parameters, and relevant aspects of the coarsening behavior of Fe_{16}N_2 , it is likely that the discrepancy between the observed habit of Fe_{16}N_2 and the habit estimated from Ref. 1 is due to the additional approximations used in Ref. 1 rather than to any inherent inadequacy of the theory.

Three approximations were introduced in Ref. 1: the elastic constants of the precipitate were assumed equal to those of the matrix, surface tension anisotropy was ignored, and the precipitate was assumed to be a thin plate with an arbitrarily large aspect ratio. The first two of these approximations cannot be removed in any simple way, since neither the elastic constants nor the surface tension anisotropy of Fe_{16}N_2 are known. It is improbable, however, that either factor is responsible for a large, consistent difference between the observed and predicted habit planes. Surface tension anisotropy may affect the habit when the precipitate size is small, but will become less important as it grows. The difference in elastic moduli between the precipitate and the matrix has an effect that can be estimated from the results of Ref. 1, and is small unless the elastic constants differ dramatically in numerical value or in the sign of the elastic anisotropy ratio. The precipitate shape, on the other hand, clearly can influence the habit plane, irrespective of particle size, and its influence can be included in the elastic energy calculations which identify the preferred habit.

The available experimental data [7-9] suggest that the aspect ratio of the α^2 precipitate is its most relevant shape parameter. While well developed precipitates are invariably thin plates of very high aspect ratio, as predicted by the elastic theory, direct observation [7,8] shows that the thin plate morphology develops gradually from a more blocky initial state in which a {100} habit is already well established (Figure 2). The initial value of the aspect ratio may be relatively small. For example, Wagner and Brenner [10] measured particle aspect ratios ($K=D/Z$, where D is the particle diameter and Z is the thickness) which were less than 10 in the early stages of coarsening and were almost certainly smaller at the still earlier stage of the reaction when the {100} habit was first assumed. It is hence possible that the preference for the {100} habit is a shape effect associated with finite values of the aspect ratio.

In the work reported below the possibility that the aspect ratio of Fe_{16}N_2 influences its habit plane was tested by finding the minimum energy habit plane as a function of K . The precipitate was taken to be a coherent, tetragonal phase in the form of a circular disc of finite thickness, with isotropic surface tension and elastic moduli equal to those of the BCC iron matrix. The results do show a change in preferred habit with decreasing aspect ratio. The habit is nearly {102} for large K but shifts to {100} as K falls to about 10.

THEORY

A. The Elastic Energy of a Coherent Plate-like Precipitate

1. The Elastic Energy

The Khatchaturyan [2] relation for the elastic energy of a coherent inclusion may be briefly derived as follows.

Let a coherent inclusion, modelled as a linear elastic body, be formed in the interior of a linear elastic medium. Let the inclusion be such that an unconstrained transformation of the matrix into the inclusion would require the 'transformation strain', ϵ^0 , and assume that the difference between the elastic constants of the matrix and those of the inclusion can be neglected.

The elastic energy of the system after creation of the inclusion can be found by summing the energies associated with a series of imaginary operations leading to the same final state, as described by Eshelby [3]: (1) a subvolume having the size and shape of the inclusion is cut from the undisturbed matrix; (2) this body is transformed into the inclusion, a process that deforms it by the stress-free transformation strain, ϵ^0 ; (3) tractions are imposed to precisely reverse the transformation strain, so that (4) the inclusion can be inserted back into the matrix without misfit; then (5) the tractions are relaxed, permitting the matrix and the inclusion to strain elastically to achieve the best accommodation with one another.

In its final state the system has an elastic displacement, $u_i(\mathbf{r})$, measured with respect to the initial state of the matrix, which gives rise to an elastic strain, $\epsilon_{ij}(\mathbf{r})$. The associated elastic stress is

$$\sigma_{ij}(\mathbf{r}) = -\sigma_{ij}^0 \Theta(\mathbf{r}) + \lambda_{ijkl} \epsilon_{lm} \quad (1)$$

where i, j, l and m are Cartesian indices, to be summed if repeated,

$$\sigma_{ij}^0 = \lambda_{ijkl} \epsilon_{lm}^0 \quad (2)$$

is the 'transformation stress', and $\Theta(\mathbf{r})$ is a form function which is equal to one inside the inclusion and to zero otherwise. The elastic energy is the sum of the elastic self-energy of the inclusion (step 3) and the relaxation energy (step 5)

$$\begin{aligned} \Delta E &= \int \left\{ \frac{1}{2} \sigma_{ij}^0 \epsilon_{ij}^0 \Theta(\mathbf{r}) - \sigma_{ij}^0 \epsilon_{ij} \Theta(\mathbf{r}) + \frac{1}{2} \lambda_{ijkl} \epsilon_{ij} \epsilon_{lm} \right\} dv \\ &= \frac{V}{2} \sigma_{ij}^0 \epsilon_{ij}^0 - \int \left[\sigma_{ij}^0 \epsilon_{ij} \Theta(\mathbf{r}) - \frac{1}{2} \lambda_{ijkl} \epsilon_{ij} \epsilon_{lm} \right] dv \\ &= \Delta E_0 - \Delta E_1 \end{aligned} \quad (3)$$

The elastic self-energy, ΔE_0 , depends on the particle volume, but is otherwise independent of the geometry. The shape and habit of the preci-

pitrate influence only the relaxation energy, ΔE_1 , which should be as large as possible to minimize the total elastic energy.

The relaxation strain field, $\epsilon_{ij}(\mathbf{r})$, is determined by the condition of static equilibrium. The stability of the elastic energy with respect to arbitrary variations of the displacement field requires the differential relation (equivalent to Cauchy's First Law):

$$\lambda_{ijkl} u_{m,lj} = \sigma_j^0 \Theta(\mathbf{r})_{hj} \quad (4)$$

the Fourier transform of which is

$$A_{im} u_m(\mathbf{k}) = -i \sigma_{ij}^0 k_j \Theta(\mathbf{k}), \quad (5)$$

where

$$A_{im}(\mathbf{k}) = \lambda_{ijkl} k_j k_l \quad (6)$$

is the dynamical matrix of the elastic medium. Defining the tensor

$$\Omega_{ij}(\mathbf{e}) = |k|^2 A_{ij}^{-1}(\mathbf{k}), \quad (7)$$

where \mathbf{e} is a unit vector in the direction of \mathbf{k} , Eq. 5 has the solution

$$u_i(\mathbf{k}) = -i |k|^{-1} \Omega_{ij} \sigma_{jl} e_l \Theta(\mathbf{k}). \quad (8)$$

It follows that

$$u_{i,j}(\mathbf{k}) = \Omega_{im}(\mathbf{e}) \sigma_{ml}^0 e_l e_j \Theta(\mathbf{k}) \quad (9)$$

If Eq. 9 is substituted into Eq. 3 and the integral replaced by an equivalent integration over reciprocal space, the relaxation energy may be written

$$\Delta E_1 = \frac{i}{2} (2\pi)^{-3} \int B_1(\mathbf{e}) |\Theta(\mathbf{k})|^2 d^3k. \quad (10)$$

where

$$B_1(\mathbf{e}) = e_i \sigma_{ij}^0 \Omega_{jk}(\mathbf{e}) \sigma_{kl}^0 e_l. \quad (11)$$

By defining the geometric function

$$H(\mathbf{e}) = (2\pi)^{-3} V^{-1} \int |\Theta(\mathbf{k})|^2 k^2 dk, \quad (12)$$

where $k=|\mathbf{k}|$, this integral may be rewritten as an integral over the unit sphere:

$$\Delta E_1 = \frac{V}{2} \int B_1(\mathbf{e}) H(\mathbf{e}) d\omega \quad (13)$$

The relaxation energy is now expressed as an integral whose kernel is the product of a geometric function, $H(\mathbf{e})$, which depends only on the particle shape and habit, and a shape-independent energy function, $B_1(\mathbf{e})$, which depends only on the elastic constants of the matrix and the

stress-free strain of the inclusion. The total energy can be written

$$\Delta E = V \int E(\mathbf{e}) H(\mathbf{e}) d\omega \quad (14)$$

where

$$E(\mathbf{e}) = \frac{1}{2} \left[\sigma_{ij}^0 \varepsilon_{ij}^0 - B_1(\mathbf{e}) \right] \quad (15)$$

2. The Elastic Energy Function

The function $B_1(\mathbf{e})$ is most easily evaluated in a coordinate system whose bases parallel the cubic axes of the matrix. The cubic matrix has three independent elastic constants, the Voigt constants c_{11} , c_{12} and c_{44} . Making the definitions

$$\begin{aligned} c_1 &= \frac{c_{11}}{c_{44}} \\ c_2 &= \frac{c_{12}}{c_{44}} \\ \Delta &= c_1 - c_2 - 2 \\ \lambda &= c_1 + 2c_2. \end{aligned} \quad (16)$$

where Δ is the 'anisotropy factor', the fourth-order elastic tensor may be written

$$\lambda_{ijkl} = c_{44}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} + c_2\delta_{ij}\delta_{kl} + \delta_{ij}\delta_{jk}\delta_{kl}). \quad (17)$$

It follows from Eqs. 6 and 7 that

$$\Omega_{ij}^{-1}(\mathbf{e}) = \lambda_{ijkl} e_k e_l \quad (18)$$

which can be inverted to give

$$\Omega_{ij}(\mathbf{e}) = F_{ij}(\mathbf{e}) \left[d(\mathbf{e}) \right]^{-1}, \quad (19)$$

where $F_{ij}(\mathbf{e})$ is the cofactor of the (ij) element of the matrix $c_{44}^{-1} \Omega^{-1}(\mathbf{e})$ and $d(\mathbf{e})$ is the determinant of this matrix.

If the principal axes of the inclusion (in its stress-free state) parallel those of the matrix, as they do in Fe_{16}N_2 , then the tetragonal stress-free strain may be written

$$\varepsilon_{ij}^0 = \varepsilon^0 (\delta_{ij} + \eta \delta_{i3} \delta_{j3}). \quad (20)$$

where the tetragonal axis is along x_3 , the principal strains are $\varepsilon_{11}^0 = \varepsilon_{22}^0 = \varepsilon^0$ and ε_{33}^0 , and η is the 'tetragonality' of the stress-free strain

$$\eta = \frac{(\varepsilon_{33}^0 - \varepsilon_{11}^0)}{\varepsilon_{11}^0} \quad (21)$$

the transformation stress is then

$$\sigma_{ij}^* = \lambda_{ijkl} \varepsilon_{kl}^* = c_{44} \varepsilon^* \left[(\lambda + c_2 \eta) \delta_{ij} + (c_1 - c_2) \eta \delta_{i3} \delta_{j3} \right] \quad (22)$$

Using Eqs. 11 and 21, the energy function $B_1(\mathbf{e})$ can be written

$$B_1(\mathbf{e}) = c_{44} (\varepsilon^*)^2 b(\mathbf{e}). \quad (23)$$

where

$$b(\mathbf{e}) = \left[(\lambda + c_2 \eta)^2 F_1(\mathbf{e}) + 2(\Delta + 2)\eta(\lambda + c_2 \eta) F_2(\mathbf{e}) + (\Delta + 2)^2 \eta^2 F_3(\mathbf{e}) \right] [d(\mathbf{e})]^{-1} \quad (24)$$

with

$$\begin{aligned} F_1(\mathbf{e}) &= e_i F_{ij} e_j = 1 + 2\Delta \Gamma_4(\mathbf{e}) + 3\Delta^2 \Gamma_6(\mathbf{e}) \\ F_2(\mathbf{e}) &= e_i F_{i3} e_3 = e_3^2 + \Delta(1 - e_3^2) e_3^2 + \Delta^2 \Gamma_6(\mathbf{e}) \\ F_3(\mathbf{e}) &= e_3 F_{33} e_3 = e_3^4 + c_1(1 - e_3^2) e_3^2 + \Delta^2(c_1 + c_2) \Gamma_6(\mathbf{e}). \end{aligned} \quad (25)$$

$$d(\mathbf{e}) = \det [c_{44}^{-1} \Omega^{-1}(\mathbf{e})] = c_1 + \Delta(c_1 + c_2) \Gamma_4(\mathbf{e}) + \Delta^2(\lambda + 1) \Gamma_6(\mathbf{e})$$

and

$$\begin{aligned} \Gamma_4(\mathbf{e}) &= e_1^2 e_2^2 + e_2^2 e_3^2 + e_3^2 e_1^2 \\ \Gamma_6(\mathbf{e}) &= e_1^2 e_2^2 e_3^2 \end{aligned} \quad (26)$$

Substitution into Eq. 13 then gives the relaxation energy in the form

$$\Delta E_1 = \frac{1}{2} V c_{44} (\varepsilon^*)^2 \int b(\mathbf{e}) H(\mathbf{e}) d\omega \quad (27)$$

One important result can be extracted immediately from Eq. 27. The dependence of the relaxation energy on shape and habit is contained in the integral on the right, whose value depends on the structure of the inclusion only through the tetragonality, η . It follows for the inclusion of finite thickness, as for the thin plate inclusion [1], that the preferred habit is independent of the sign and magnitude of the homogeneous strain, ε^0 . It is determined by the tetragonality.

3. The Geometric Factor

It may be shown in general [14] that $H(\mathbf{e})$ is independent of the inclusion volume; it depends only on the shape and orientation. For a given cylindrically symmetric figure, for example, a circular plate, an ellipsoid, or a lens, the shape is specified by the aspect ratio, K , and the orientation is fixed by the direction, \mathbf{n} , of the axis of symmetry of the figure. It follows that for a given figure $H(\mathbf{e}) = H_K(\alpha)$, where α is the angle between the vectors \mathbf{n} and \mathbf{e} .

For the specific case of a circular disc of thickness Z and radius R [15]:

$$\begin{aligned}\Theta(k) &= V\Theta'(K, \alpha, k') \\ &= 2V \left[\frac{\sin(K^{-1}k' \cos \alpha)}{K^{-1}k' \cos \alpha} \right] \left[\frac{J_1(k' \sin \alpha)}{k' \sin \alpha} \right]\end{aligned}\quad (28)$$

where $k' = |\mathbf{k}|R$, $K = 2R/Z$, and J_1 is a Bessel function of the first kind of order one. Then

$$\begin{aligned}H(\mathbf{e}) &= H_K(\alpha) = (4\pi^2 K)^{-1} h_K(\alpha) \\ &= (4\pi^2 K)^{-1} \int |\Theta'(K, \alpha, k')|^2 (k')^2 dk'\end{aligned}\quad (29)$$

If this result is substituted into Eq. 27 and the energy function $b_1(\mathbf{e})$ is referred to the coordinates α and β , where α is the polar angle and β the azimuthal angle measured from \mathbf{n} , then

$$\begin{aligned}\Delta E_1 &= \Delta E_1(\mathbf{n}, K) \\ &= \left[\frac{1}{8\pi^2} \right] \left[\frac{V}{K} \right] c_{44}(\varepsilon^*)^2 \int_0^\pi \int_0^{2\pi} b_n(\alpha, \beta) d\beta \left\{ h_K(\alpha) \sin \alpha d\alpha \right.\end{aligned}\quad (30)$$

The kernel of this integral depends on K through $H_K(\alpha)$, and on \mathbf{n} through the function $b(\mathbf{e}) = b_n(\alpha, \beta)$. The total geometric part of the integral, $H_K(\alpha) \sin \alpha$, is plotted in Fig. 3 for various values of the aspect ratio.

B. The Preferred Habit of Fe_{16}N_2 in a Iron

To determine the preferred habit of the precipitate the elastic constants of the matrix and the stress-free strain of the precipitate must be specified.

The elastic constants of a iron are [16], in units of 10^{12} ergs/cm³, $c_{11} = 2.335$, $c_{12} = 1.355$ and $c_{44} = 1.180$. The dimensionless constants defined in Eq. 16 then have the values: $c_1 = 1.979$, $c_2 = 1.148$, $\Delta = -1.169$ and $\lambda = 4.275$.

The stress-free strain of the α^2 phase relative to a iron is the strain required to deform the BCC unit cell of iron until its lattice parameters match those of the nitride. The lattice parameters of the α^2 nitride were determined by Suyazov, et al. [6], who used a combination of x-ray and electron diffraction to confirm the Fe_{16}N_2 superlattice proposed by Jack [13] and measure its unit cell. Their experimental crystal had slightly less than the stoichiometric nitrogen content (9.36 rather than 12.5 atoms of nitrogen per 100 of iron) but was found to be homogeneously ordered in the Fe_{16}N_2 structure (Figure 1). The lattice constants of the tetragonal unit cell matched those estimated by extrapolating the linear relations of Bell and Owen [12] for nitrated martensite to the composition of the ordered phase. It follows that the stress-free strain of the α^2 precipitate can be written

$$\varepsilon_{ij} = -0.095x_N(\delta_{ij} - 10\delta_{i3}\delta_{j3}) \quad (31)$$

where x_N is the atom fraction of nitrogen relative to iron, or, equivalently, the fraction of the sites on the O_z sublattice of octahedral interstitial positions that is occupied by nitrogen. Comparing equations (31) and (20), the stress-free strain of the ordered α^2 precipitate includes a uniform distortion, ε^0 , equal to $-0.095x_N$ ($=-0.012$ at the stoichiometric composition) and a tetragonality, η , equal to -10 , that is independent of composition.

Given the elastic constants and the stress-free strain the elastic energy of the disc-shaped $Fe_{16}N_2$ precipitate can be calculated for arbitrary values of the aspect ratio, K , and the habit plane, n , from equation 14 or 30. The preferred habit is found as a function of K by varying n to achieve a minimum in the elastic energy for each value of the aspect ratio. The relevant computations are straightforward.

The results are presented in Figure 4. They show that the preferred habit plane changes continuously with the aspect ratio. The preferred habit is always a plane of type $\{h0k\}$, as it must be in the limit of large K since the elastic anisotropy factor is negative [1]. In the thin-plate limit, when K becomes arbitrarily large, the angle, θ , between the habit plane normal, n , and the tetragonal axis, x_3 , approaches 22.5 degrees. The habit plane is near (102) as predicted [1]. As K decreases, however, the habit plane changes continuously. Its normal, n , rotates toward the tetragonal axis, and becomes parallel to the tetragonal axis, $n=[001]$, for $K < 11.35$.

It follows that the linear elastic theory does predict a (001) habit for $Fe_{16}N_2$ in α iron, but only when the precipitate aspect ratio is relatively small. The preferred habit shifts toward (102) as K increases.

C. The Lattice Strain of the Embedded $Fe_{16}N_2$ Precipitate

A precipitate that is coherently connected to its matrix is internally strained, and hence has lattice constants which differ from those of its stress-free crystal. The latter are the lattice parameters measured by x-ray or electron diffraction from the embedded precipitate. They may be computed from the elastic theory if the stress-free strain is known, and are constant within the precipitate if its shape is an ellipsoid or a thin plate [2,4]. From Eq. 9,

$$\varepsilon_{ij}(k) = \frac{1}{2}(e_j\Omega_{im} + e_i\Omega_{jm})\sigma_{mi}^{\circ}e_l\Theta(k). \quad (32)$$

where the strains are measured relative to the relaxed state of the matrix. When the precipitate is a thin plate having normal n , the shape function is non-zero only when e is very close to n . Then

$$\varepsilon_{ij}(r) \simeq \frac{1}{2}(\pi_j\Omega_{im} + \pi_i\Omega_{jm})\sigma_{mi}^{\circ}\pi_l\Theta(r). \quad (33)$$

It follows that the state of strain within the precipitate depends on

the shape and habit plane as well as on the stress-free strain.

For an Fe_{16}N_2 precipitate in the form of a thin plate with a (001) habit, Eq. 33 simplifies to

$$\begin{aligned}\varepsilon_{ij}(\mathbf{r}) &= \Omega_{333}\sigma_{33}^0\Theta(\mathbf{r})\delta_{i3}\delta_{j3} \\ &= \varepsilon^0 \left[1 + \eta + 2 \left(\frac{c_2}{c_1} \right) \right]\end{aligned}\quad (34)$$

The precipitate is, therefore, epitaxial in its habit plane. The strain along its normal is 0.094 relative to the iron lattice.

DISCUSSION

A. The Internal Strain

1. Comparison between Theory and Experiment

The internal strain within a thin, stoichiometric α^2 precipitate in a (001) habit was computed from the stress-free strain given by Suyazov, et.al [6]. The theory predicts that the constrained precipitate is perfectly coherent with the iron matrix in the (001) plane (as it must be in the thin-plate limit [2,4]) and is strained relative to the iron lattice by 0.094 perpendicular to the habit plane. Hence the lattice constants of the embedded precipitate should be twice those of iron in the basal plane, $a_1=a_2=5.73\text{\AA}$, and elongated with respect to iron in the perpendicular direction, $a_3=6.27\text{\AA}$, in contrast to the projected lattice parameters of the stoichiometric phase in its relaxed state: $a_1=a_2=5.66\text{\AA}$, $a_3=6.35\text{\AA}$. The computed lattice parameters agree closely with those found by Abiko and Imai [9] from the electron diffraction patterns of constrained precipitates and with those reported by Jack [13] from x-ray diffraction studies on nitrated powders: $a=5.73\text{\AA}$, $c=6.29\text{\AA}$. The computed strain in the x_3 -direction agrees with that measured by Garwood and Thomas [10] by x-ray diffraction from precipitates embedded in the bulk.

The apparent agreement between theory and experiment is called into question, however, by Jack's [13,19] conclusion that the lattice constants measured in his work represent the stress-free state of the precipitate phase. While some features of his experimental results [13], such as the observation of strong nitride peaks coupled with relatively weak iron peaks, suggest that the precipitates were stress-free, there are at least two aspects of the data which are very difficult to interpret unless the precipitates were embedded in iron. These are the values of the measured lattice parameters and the insensitivity of the lattice parameters to the nitrogen content.

Jack's [13] proposed α^2 unit cell has basal plane lattice constants equal to those of BCC iron. In contrast, the dissolution of nitrogen in iron causes a tetragonal distortion which contracts the BCC unit cell in the basal plane. It is generally accepted that the tetragonal distortion results from the segregation of nitrogen atoms to a single set (O_z) of octahedral interstitial sites. The formation of stoichiometric Fe_{16}N_2 hence involves only the ordering of the O_z nitrogen into the pattern shown in Figure 1. It would be surprising if such an ordering caused a significant change in the lattice, and would require a remarkable coincidence for the ordering to expand the basal plane of the nitride so that it precisely regenerated the lattice parameters of nitrogen-free BCC iron. If, on the other hand, the precipitate is a thin coherent plate with a (001) habit in iron, the elastic theory requires that it be strained so that it is epitaxial in the basal plane.

Jack [13] also reported that the lattice parameters of α^2 are unaltered by substantial variations in nitrogen content (from 5.3 to 9.5

atom percent nitrogen relative to iron). This behavior contrasts strikingly with that of Fe-N solid solutions, whose cell dimensions depend linearly on nitrogen content up to at least 10 atom percent [12,20,21]. To accept Jack's interpretation one must adopt his assumption, that the simple act of ordering the O_z nitrogen atoms creates a lattice so rigid that it is impervious to deviations from stoichiometry. If this assumption is true it is remarkable and unique, and has powerful theoretical implications. If, on the other hand, Jack [13] was seeing embedded precipitates whose volume fraction changed with the nitrogen content then his results are obvious.

While Jack's [13] values for the stress-free lattice constants of $Fe_{16}N_2$ challenge the imagination, those of Snyazov, et al [6] are intuitively plausible. They found, as expected, that the lattice is not significantly distorted when the O_z nitrogen orders into the α^2 structure. Their results imply that the lattice constants of α^2 vary in the usual way with changes in composition. Moreover, if their values are used in the elastic theory the results of Abiko and Imai [9] and Garwood and Thomas [10] are predicted, and those of Jack [13] can be easily interpreted.

2. The Change in Internal Strain with the Habit Plane

It follows from Eq. 33 that the internal strain of a coherent thin-plate precipitate varies with its habit. This not only changes the constrained lattice parameters of the precipitate, but may also alter its apparent crystal structure. In the case of $Fe_{16}N_2$, a rotation away from (001) toward (102) causes a small monoclinic distortion of the tetragonal phase. The lattice strain in the (102) habit can be easily computed. The lattice constants are: $a_1=5.59A$, $a_2=5.73A$, $a_3=6.34A$. The angle between the a_1 and a_3 axes is predicted to increase by about 0.3 degrees. Electron diffraction studies by Shih [18] on rotated precipitates have demonstrated the contraction of a_1 and the rotation of a_3 relative to a_1 , and are hence in qualitative agreement with the theoretical prediction.

3. The Influence of Precipitate Stoichiometry and Order

The stress-free strain of the α^2 precipitate is linear in the nitrogen concentration, x_N , and varies according to Eq. 31 [6,12]. It follows from Eq. 33 that the strain in an embedded precipitate, relative to the matrix, is also linear in x_N , and will hence change in proportion to any deviation from stoichiometry. The associated change in the apparent lattice constants of the embedded precipitate is more subtle. When the precipitate is a thin plate its strain may be resolved onto principal axes in and perpendicular to the habit plane. The strain in the habit plane is necessarily zero; hence the components of the cell axes which lie in the habit plane are insensitive to stoichiometry. However, the perpendicular dimension of the unit cell changes linearly with x_N . If the habit is (001), for example, a deviation from stoichiometry should change a_3 , but leaves a_1 and a_2 unaltered. If the habit normal does not parallel a crystal axis, then two or more lattice parameters should be affected.

A change in the state of order of the nitrogen atoms within the nitride precipitate may affect the lattice in either of two ways. First, it may change the net elastic interaction between the nitrogen interstitial defects. This interaction energy contributes to the internal energy of the precipitate phase. Its minimization led Mori, et al [11] to their prediction of the structure of Fe_{16}N_2 . But the internal elastic energy does not influence the precipitate strain or habit. Second, the state of order may modify the internal strain, and hence the elastic energy, of the embedded precipitate. However, it will do this only if it varies the stress-free strain of the precipitate. The stress-free strain of α^2 is apparently insensitive to the state of order of the nitrogen [6], as long as the nitrogen remains confined to a single set of octahedral interstitial sites. It follows that, barring a redistribution of nitrogen onto the O_x and O_y interstitial sites, the lattice constants and habit plane of α^2 should not depend significantly on the state of order.

B. The Habit Plane

1. Comparison between Theory and Experiment

The theoretical results suggest that α^2 prefers the (001) habit when its aspect ratio is small. The available experimental evidence indicates that the precipitate has both a {100} habit and a relatively low aspect ratio in its initial state. Wagner and Brenner [8] measured particle aspect ratios less than 10 in the early stages of coarsening of α^2 in Fe-Mo alloys. Driver and Papazian [17] report well-defined crystallites with K near 20 in similar alloys. Both Keh and Wriedt [7] and Abiko and Imai [9] found aspect ratios near 30 for partially coarsened precipitates; since K increased monotonically during growth, their results imply a lower aspect ratio at the starting particle size. There is, hence, a reasonable agreement between the experimental observations and the predictions of the linear elastic theory for the initial habit of the α^2 nitride.

The theory is less successful in specifying the habits of well coarsened precipitates. The theory predicts a gradual habit shift toward (102) and argues that the (001) habit is unstable when the aspect ratio is large, while the experimental data [7-10] suggest that the (001) habit is preserved. On the other hand, there is evidence of habit plane instability in electron micrographs of well coarsened α^2 precipitates such as those published by Keh and Wriedt [7] and by Abiko and Imai [9]; while the precipitates generally follow {100} planes they are irregular, and have occasional steps, kinks, and branches that deviate from {100}. Further electron microscopic studies were recently undertaken [18] to clarify the habit of large nitride precipitates in a low-nitrogen alloy. The micrographs show that large α^2 precipitates with high aspect ratios frequently retain the {100} habit. However, they also reveal a clear, though sluggish, tendency for rotation of the habit plane. The rotation occurs through the agglomeration of adjacent precipitates or the formation of branches which radiate from the central precipitate at a slight angle. The magnitude of the habit shift tends to increase with the aspect ratio and is near that predicted by the theory.

When the (001) habit is retained its preservation may be a simple kinetic phenomenon. If the precipitate already has a (001) habit then it can decrease both its elastic and its surface energy per unit volume by coarsening on that plane with an appropriate increase in its aspect ratio. Its continued growth on (001) is only unfavorable if a population of large precipitates with the rotated habit already exists. But habit plane rotation is not easy to accomplish. It can only plausibly occur through the periodic nucleation of layers of Fe_{16}N_2 at the precipitate interface to create stepped surfaces that are angled to (001). Since the difference in elastic energy between the (001) and the rotated habit is relatively small even in the thin-plate limit (Figure 5), there is only a modest driving force available to impel formation of the appropriate periodic distribution of steps. This driving force must not only overcome the contribution to surface energy from the periodic distribution of interfacial ledges, but must also compete with that which promotes continued growth in the (001) plane. It is therefore reasonable that the (001) habit is often preserved.

2. The Source of the Habit Plane Shift

The physical reason for the rotation of the preferred habit plane can be roughly understood by comparing Figs. 3 and 5. The elastic energy of a precipitate of finite thickness is determined by an integral over the unit sphere (Eq. 15) whose kernel is the elastic energy of a thin plate of orientation e multiplied by the geometric weight of orientation e in the precipitate shape. The thin-plate elastic energy is plotted in Fig. 5 as a function of the angle, θ between the vector e and the x_3 axis for directions of the type $e=[h0k]$. The function has a weak minimum at $\theta=22.5^\circ$ (e is close to $[102]$), a weak maximum at $\theta=0^\circ$ ($e=[001]$), and a strong maximum at $\theta=90^\circ$ ($e=[100]$). Fig. 3 is a plot of the geometric factor as a function of the angle, α , between e and the normal n to the habit plane. It is peaked at $\alpha=0^\circ$, i.e., at $e=n$, to a degree that increases with K .

When K is very large the geometric factor is sharply spiked at $\alpha=0^\circ$. The habit is then determined by the minimum of the thin-plate elastic energy and falls at $\theta=22.5^\circ$. As K decreases the geometric function broadens, adding weighted energy contributions from e near n . The anharmonicity of the function $E(e)$ has the consequence that the most favorable orientation (n) is rotated toward $[001]$. When K is relatively small the geometric function is broad, and favors the (001) habit since the major contributions to the elastic energy then come from the wide valley in $E(e)$ centered on $[001]$.

3. The Significance of Approximations in the Theory

The theory employs three relevant physical approximations: the precipitate is given a disc shape, its elastic constants are taken to be equal to those of the matrix, and its surface tension anisotropy is ignored. Each of these approximations will, of course, affect the quantitative precision of the theory.

The disc shape was chosen for mathematical simplicity in light of the fact that those who have investigated the precipitate [7-10,17] have reported that its shape is a thin disc. More recent work [18] suggests that well-developed α^2 precipitates have a rosette morphology whose best axisymmetric representation may be a thin lens. Wedge [14] computed the elastic energy of a lens-shaped nitride precipitate and found that this shape is, in fact, always favored over both the disc and the ellipsoid. The quantitative relation between n and K may be changed somewhat if a lens shape is assumed; however, the lens has the same preferred habit as the disc for both small and large values of K .

The elastic moduli of the Fe_{16}N_2 precipitate are unknown, but must not differ too greatly from those of iron since both the stress-free strain of the precipitate and its internal strain in the embedded condition can be found from computations which employ the iron moduli. It is, therefore, unlikely that the difference in elastic constants will significantly influence the preferred habit plane. In the thin-plate limit the theory can be corrected for the modulus change by simply substituting the elastic constants of the precipitate for those of iron [4]. It can then be shown [1] that the habit plane of a precipitate of given tetragonality is relatively insensitive to the precise values of the elastic constants, provided that the sign of the elastic anisotropy factor does not change.

The surface tension anisotropy of the α^2 -iron interface is also unknown, but there are experimental indications that it is significant. Both Wagner and Brenner [8] and Wedge [14] have used the coarsening data for α^2 to calculate values of the interfacial tension. The results are very sensitive to details of the model employed [14], but do suggest that the effective surface tension around the periphery of the precipitate plate is substantially higher than that in the (001) habit plane. If these conclusions are correct then the surface tension will promote the (001) habit when the particle is small (and hence has a small aspect ratio). Surface tension anisotropy will not affect the habit of large precipitates (high aspect ratio) since the surface contribution to the total energy is then negligible. The net effect of surface tension anisotropy should be to delay the assumption of a rotated habit plane until the particle size is large. This factor cannot change the preference for an eventual shift to a rotated habit near (102).

It follows that the three approximations explicitly added to the theory in the present treatment may influence quantitative aspects of the results, but should not change their qualitative features. The inclusion of a more accurate precipitate shape and an appropriately anisotropic surface tension may change the value of the aspect ratio at which the (001) habit becomes energetically unstable with respect to rotation and the subsequent variation of the preferred habit with K , but should not affect the eventual preference for (102). A correction of the elastic constants may have an effect on the asymptotic habit, but the change should be small.

It is not necessary to assume that the nitride is either stoichiometric or ideally ordered. The preferred habit depends only on the

tetragonality, η , which, given its definition in Eq. 21, is independent of the nitrogen content or state of order within the precipitate so long as the stress-free strain of the precipitate obeys the Bell-Owen [12] relations. It is hence only necessary that the nitrogen be gathered locally into a region that defines a nitride (of whatever composition) within an iron matrix, and that the nitrogen be internally distributed (in whatever state of order) over the O_z sublattice of interstitial sites.

There is, however, an additional assumption involved in applying the theory to the Fe-Mo system, since it is known [8,17] that Mo tends to accumulate within the α^2 phase. The theory is applicable under the approximations made by Driver and Papazian [17], who estimated the lattice parameters of $(Fe,Mo)_{16}N_2$ by summing the homogeneous distortion of Fe due to Mo and the tetragonal distortion due to N. In this case the tetragonality of the precipitate is identical to that of $Fe_{16}N_2$ in iron.

C. Implications for Other Precipitation Reactions

If the preferred habit of a precipitate is determined by the need to minimize its elastic energy then the habit may depend on the shape of the precipitate as well as on its relaxed structure, and the apparent structure of the precipitate may depend on its preferred habit plane. This behavior is most likely when the normal to the preferred habit does not lie on a joint symmetry axis of the precipitate and matrix crystals.

In the case of a coherent tetragonal precipitate in an anisotropic cubic crystal, the results of Ref. 1 show that there is generally only one true minimum, $E(n)$, of $E(e)$ within the segment of the unit sphere in reciprocal space defined by the directions [001], [100] and [110]. The symmetry of $E(e)$ about the minimum need be no more than is required by the symmetry of the crystal. If $E(e)$ is asymmetric about n then a precipitate having finite thickness can usually lower its total elastic energy by assuming a habit away from n which spreads its geometric intensity so as to minimize the weighted average of $E(e)$. When the aspect ratio is small n will tend to lie along a symmetry axis (such as [001]) so that the elastic energy function may spread over the several symmetrically disposed minima of $E(e)$.

It follows that precipitates that form through a discrete nucleation or three-dimensional spinodal mechanism will tend to have low index habit planes whatever the identity of the asymptotic thin-plate habit. If rotation of the habit plane is kinetically difficult, as it will generally be, then the low index plane will be retained until the precipitate size is large, and will hence be the habit plane reported for the system. High index habit planes are expected only when the asymptotic habit is high-index and when the precipitate either is the product of a one-dimensional spinodal decomposition (the normal to the asymptotic habit is also the preferred direction for the spinodal wave [4]) or is so malleable that it can easily adjust its habit as the aspect ratio increases.

The same reasoning should extend to crystallographies other than

the tetragonal-in-cubic case considered here. For example, following the initial work leading to this paper [15], Mayo and Tsakalacos [22] showed that a similar analysis explains the habit of hexagonal $MgZn_2$ precipitates in aluminum.

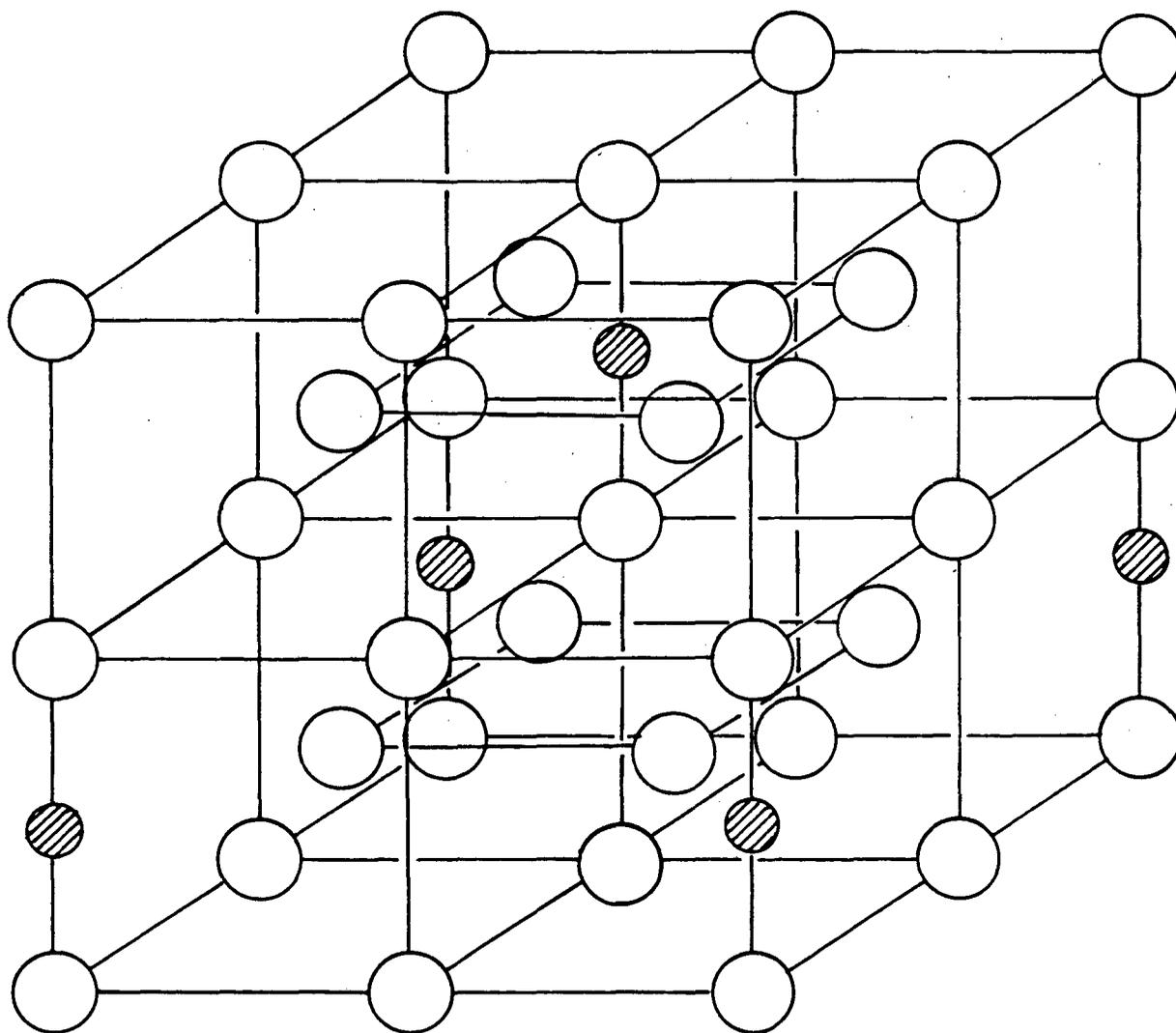
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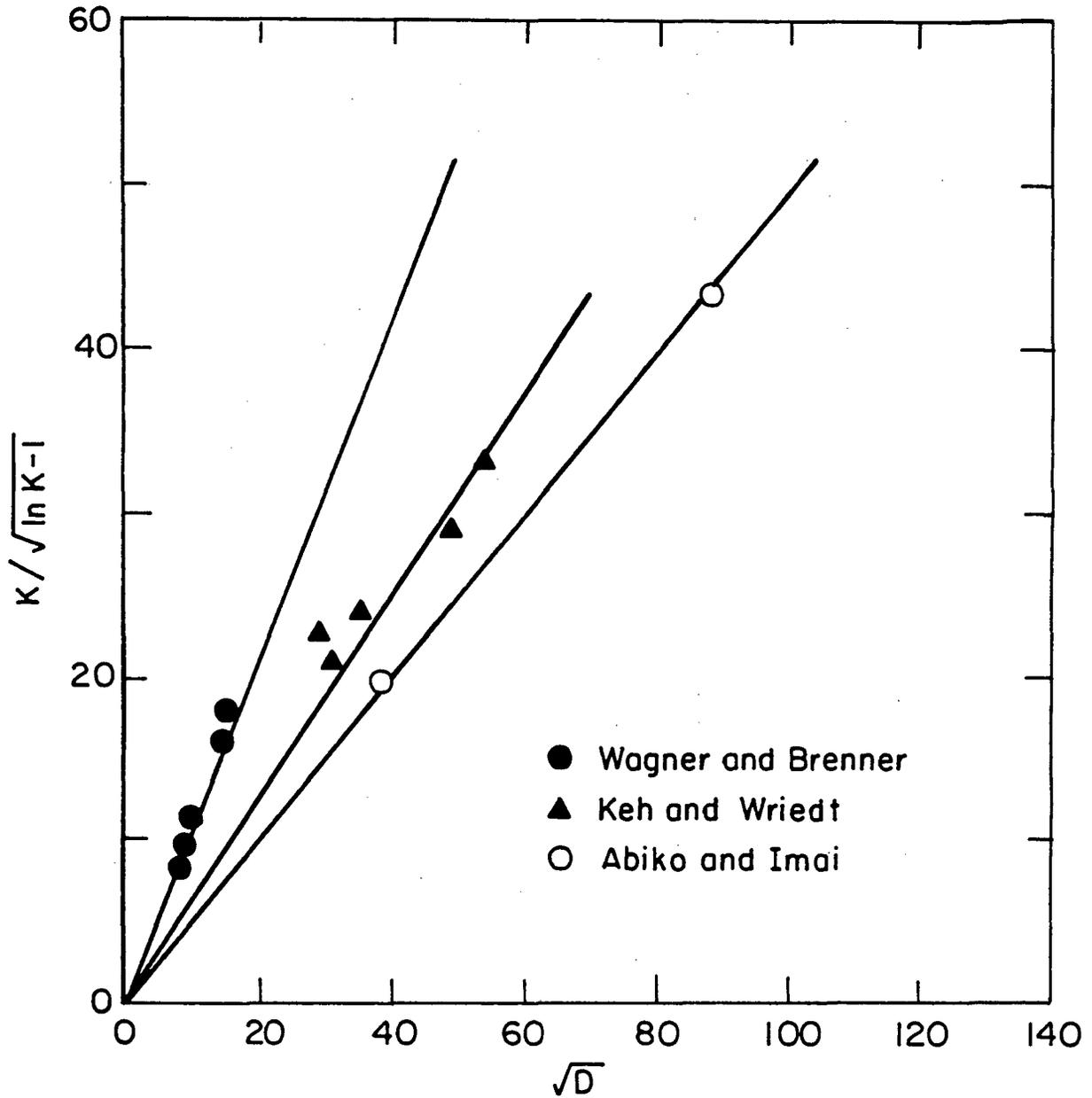
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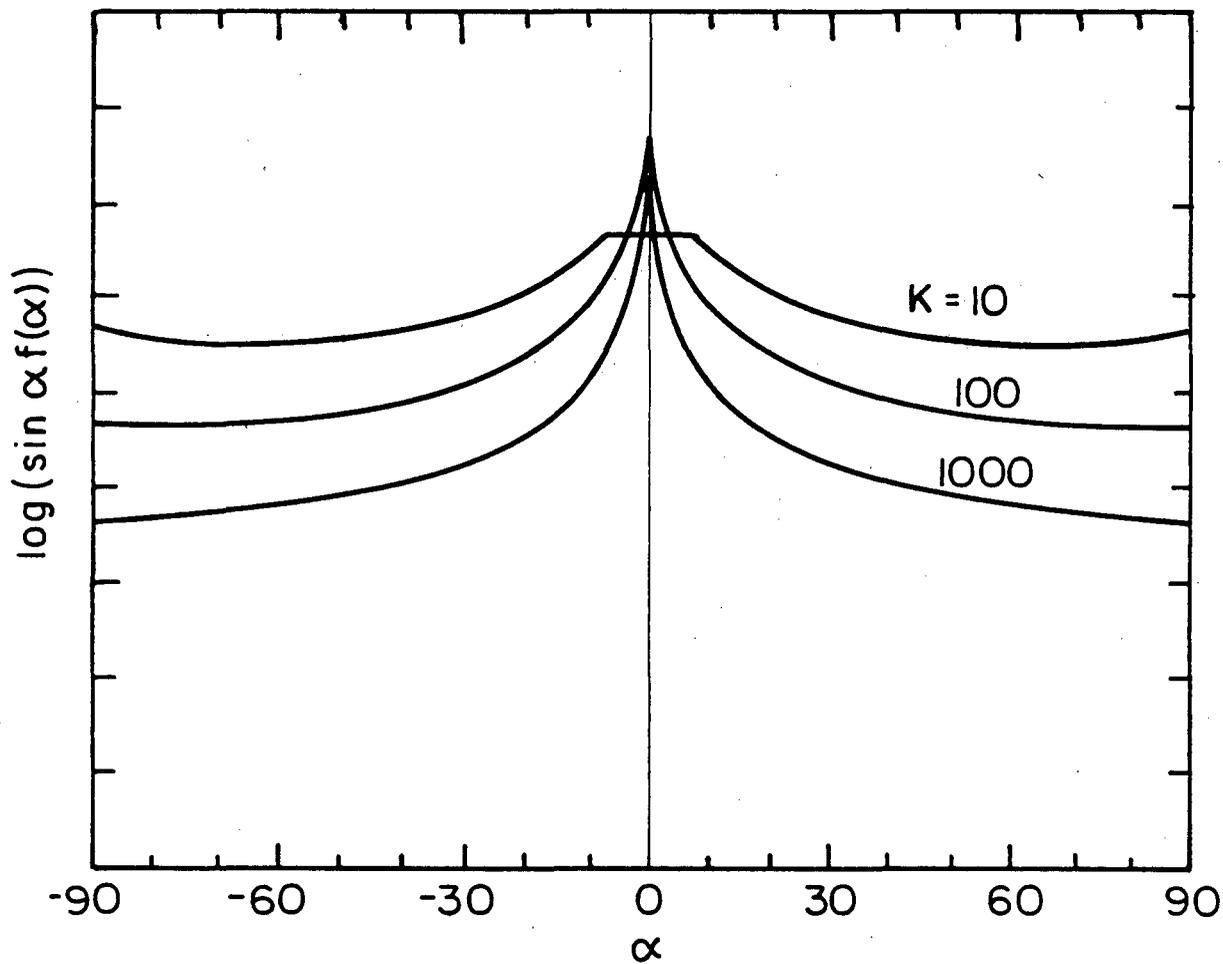
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Figure 1: The crystal structure of Fe_{16}N_2 (after Jack [13]).



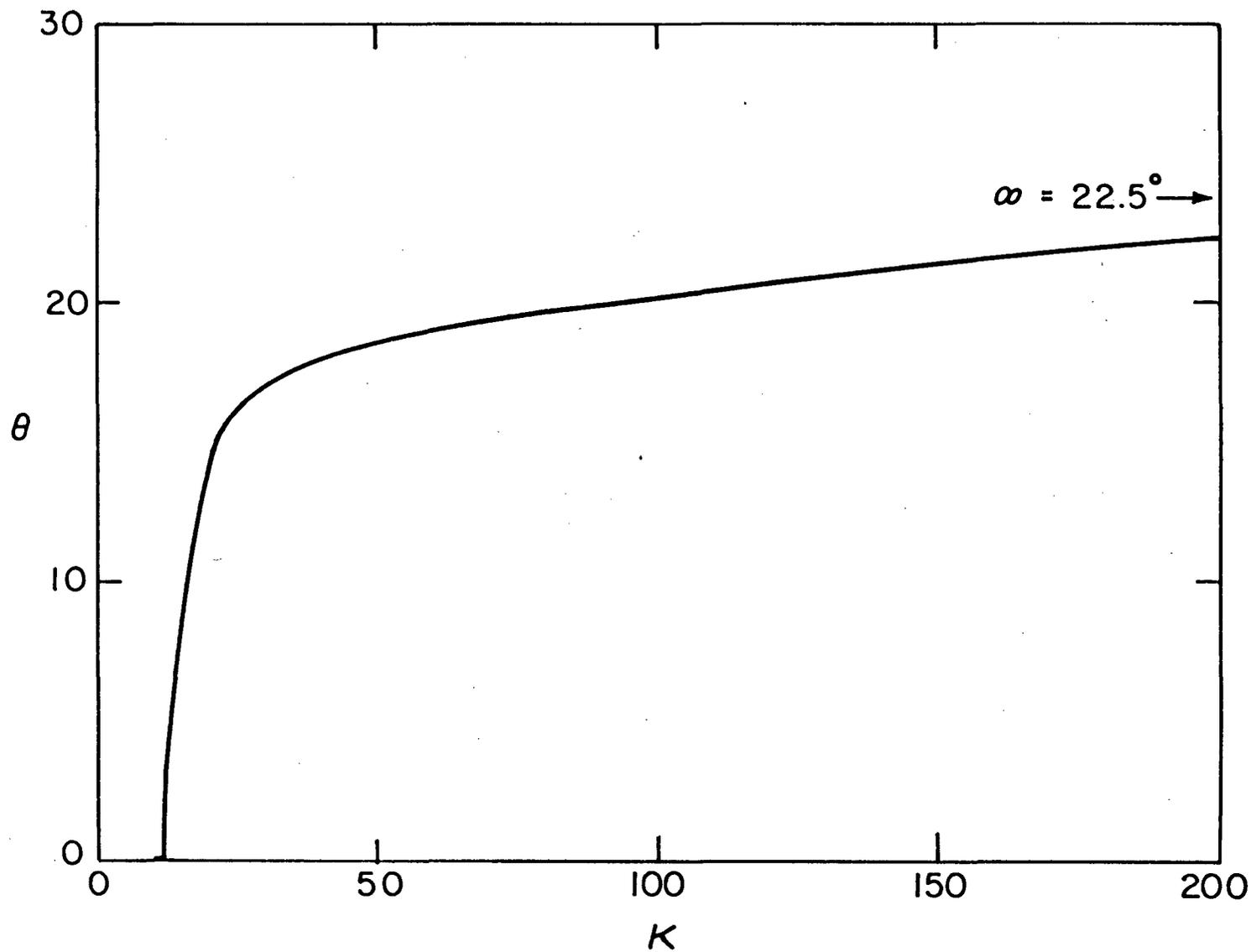
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Figure 2: The variation of aspect ratio (K) with particle size (D) during the coarsening of $Fe_{16}N_2$. The aspect ratio is plotted in the appropriate form to give a linear relation with D in the thin-plate limit [4]. The data are taken from the continuous coarsening experiments of Keh and Wriedt [7] and Wagner and Brenner [8]. The data of Abiko and Imai [9] are also included; however, their data represent two different coarsening conditions.



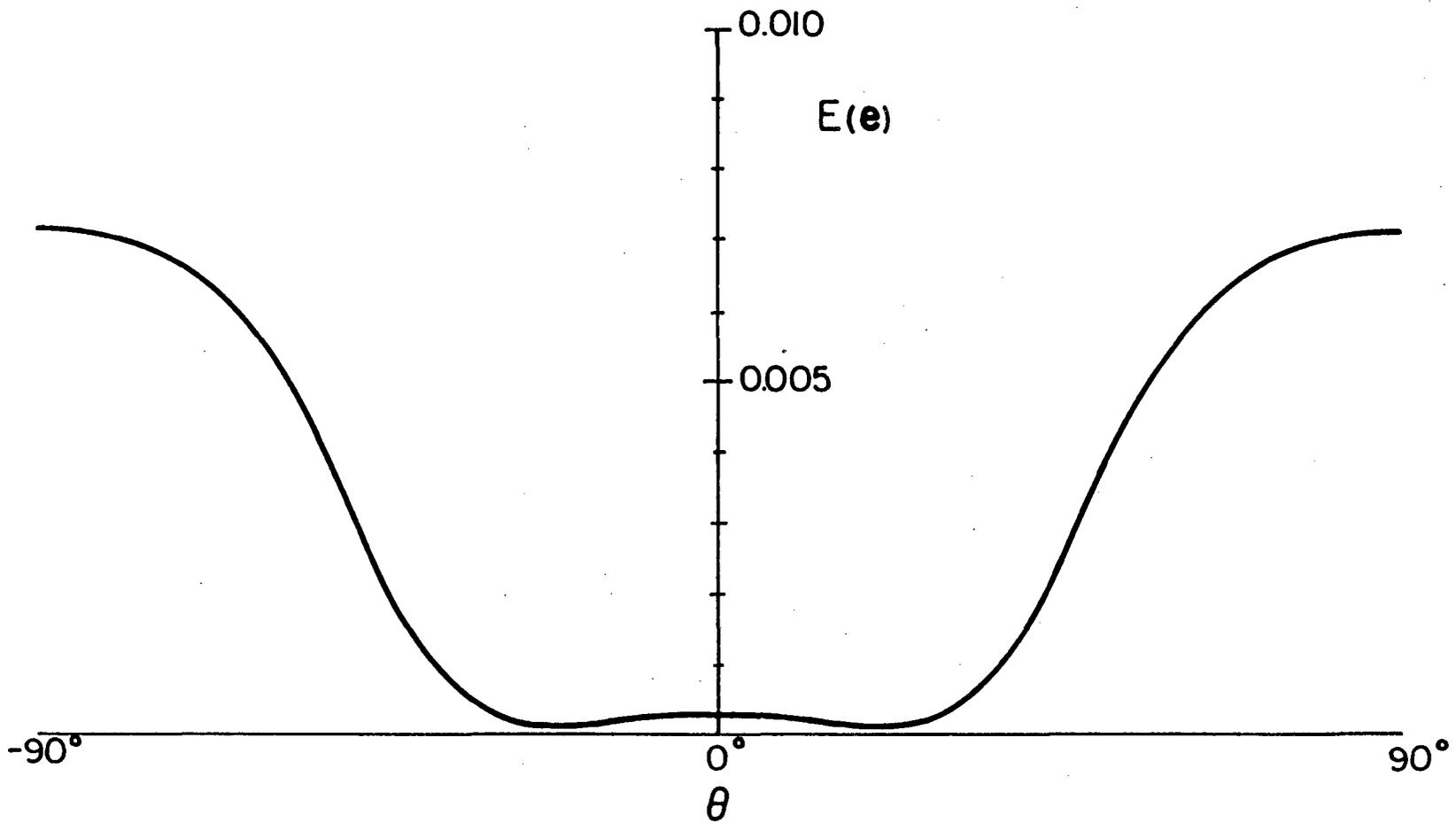
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Figure 3: The variation of the geometric factor in the elastic energy integral with angle, alpha (measured from the habit plane normal), for various values of the aspect ratio (K).



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Figure 4: The variation of the preferred habit with aspect ratio. The preferred habit is always of the type $\{h0k\}$. Theta is the angle between the normal (n) to the habit plane and the tetragonal axis of the precipitate (the $[001]$ direction of the Fe matrix).



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Figure 5: The elastic energy function $E(e)$, plotted for the directions $[h0k]$ about $[001]$. Theta is the angle between the direction (e) and $[001]$. E is in units of $c_{44}(e^\circ)^2$.

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