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Publication Date

1986-11-01

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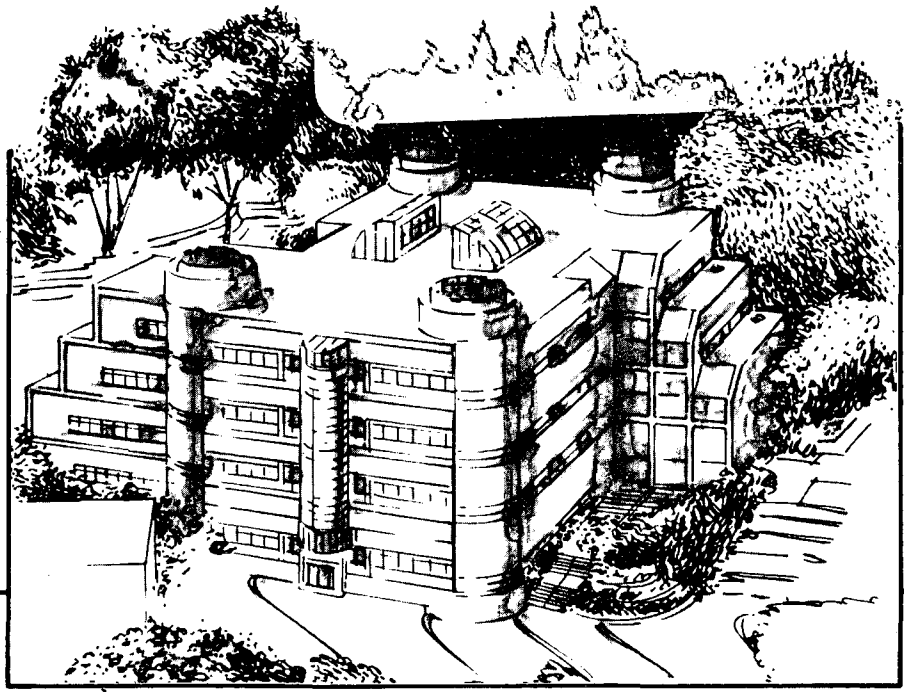
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A.G. Khachaturyan,, S.V. Semenovskaya, and
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November 1986

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-22472
c-2

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IN CUBIC PRECIPITATES DURING COARSENING**

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Abstract

The work reported here concerns the evolution of the shape of a coherent, cubic precipitate as it grows by coarsening. The work was motivated by the need to explain recent experimental observations that show that cuboidal γ' Ni₃Al precipitates in Ni-Al alloys resist coarsening and decompose into doublets of parallel rectangular plates and octets of small cubes. The theoretical model assumes a precipitate of cubic phase with negative elastic anisotropy, and neglects any difference between the elastic constants of the precipitate and the matrix. The elastic energy of the precipitate is then calculated as a function of its morphology, including the possibility of decomposition into doublets or octets of discrete particles. The results show that a cuboidal precipitate with {100} faces and edge length, $2a$, is metastable with respect to transition to a doublet of discrete plates, with dimensions $a \times 2a \times 2a$, that are separated by the distance $u \sim a$, when the edge length exceeds a characteristic distance, r_0 , that depends on the interfacial tension of the precipitate, its elastic constants, and its misfit with the parent lattice. When the edge length of the doublet, exceeds a critical value it becomes metastable with respect to transformation into an octet of cubic particles that have edge length, a , {100} interfaces,

and an interparticle separation of $0.4a$. The octet of particles becomes metastable with respect to coagulation into a thin plate on the (100) plane on further coarsening. If the interfacial tension is isotropic, the same analysis can be used to predict the transition from sphere to cube. The equilibrium transformation sizes are specifically computed for the case of γ' Ni₃Al, and are consistent with the experimental data. The possible influence of the strain energy on coarsening is also discussed.

1. Introduction

It is well known that the morphology of coherent precipitates in two-phase alloys is strongly influenced by the elastic energy associated with the misfit between the precipitate and matrix structures. The reason is that the elastic energy depends on the shape, habit and configuration of the precipitates as well as on their volume. The shape dependence of the elastic energy is treated in the original work of Eshelby [1]. Khachaturyan [2] and Roitburd [3] subsequently showed that the habit of a coherent precipitate can be predicted by minimizing its elastic energy. Khachaturyan [2] and Khachaturyan and Shatalov [4] have shown how the elastic energy of a precipitate of arbitrary shape or an arbitrary distribution of precipitates can be computed. A number of investigators [4-18] have used these and similar techniques to study or model precipitate morphologies or distributions [5-19].

Virtually all of this work implicitly assumes that the precipitates remain intact and, if they coarsen, increase monotonically in volume. However, it is clear from previous work that this is not always the case. The theory of modulated structures in decomposed alloys [5,6,17] is based on the result that appropriate periodical distributions of precipitates often have lower elastic energy than monolithic precipitates of the same volume. Khachaturyan and Airapetyan [6], showed that an isolated, coherent sphere in a cubic solid has a higher elastic energy than a periodic distribution of spheres with the same total volume.

An increasing body of experimental evidence also shows that precipitates do not always coarsen monotonically, but may subdivide after reaching some critical size. The most definitive evidence was reported by Miyazaki, Imamura and Kozaki [20] and Doi, Miyazaki and Wakatsuki [21]. They monitored the growth of γ' ($L1_2$) precipitates in Ni-Al and other Ni-based alloys and found that large, cuboidal precipitates spontaneously split into pairs or octets of γ' sub-particles. In much earlier work Westbrook [22] also observed compact octets of γ' precipitates in Ni-based alloys and concluded that they formed through the decomposition of a single coarsened particle.

Miyazaki, Nakamura and Mori [22] suggested that the decomposition was driven by the elastic energy. They used an approach that is similar to that of Khachaturyan and Airapetyan [6] to show that the elastic energy of closely separated pairs or octets of spherical inclusions may lie below that of a single spherical particle with the same total volume. As we shall show below, this analysis is correct in its ultimate conclusion. However, it does not completely prove the point since the replacement of a cuboidal inclusion by an equivalent sphere changes the elastic energy by a factor that is roughly fifty times the calculated interparticle interaction that is assumed to be the driving force for splitting.

An alternate explanation was recently suggested by Voorhees and Johnson [24], who showed that isotropic ellipsoids whose elastic constants differ from those of the matrix may also decompose. While this work is interesting, it cannot be sufficient to explain the observed decomposition in Ni_3Al . The precipitates of interest here are cubes with {100} faces that decompose into plates or subcubes, also with {100} interfaces, that are separated along particular crystallographic directions. To analyze this case we clearly need to consider the crystallographic character of the elastic interaction, since it is the anisotropy of the elastic interaction that determines its crystallographic features.

If we neglect the elastic mismatch between the precipitate and the matrix it is possible to obtain an accurate solution for the preferred shape of a coherent cubic precipitate that includes the possibility of its decomposition into a compact array of discrete particles.

The solution is given below. It is applied to the specific case of the γ' Ni_3Al precipitate studied by Miyazaki, et al., and has the consequence that the preferred shape of the precipitate changes as the precipitate grows. With increasing size the precipitate changes from a sphere to a cube to a pair of parallel plates, to a compact octet of small cubes, and, finally, to a thin plate.

The solution draws on prior work [2,17,19] that treats the preferred shape of cubic precipitates that remain intact. The preferred shape and habit are determined by the requirement that the sum of the elastic and surface energies be minimum. The shape and habit that minimize the elastic energy depends on the elastic anisotropy of the system, which can be expressed in terms of the anisotropy factor,

$$\Delta = c_{11} - c_{12} - 2c_{44} \quad (1)$$

where the c_{ij} are the cubic elastic constants. Most systems of interest, specifically including Ni_3Al , have negative anisotropy. For such precipitates the elastic energy is minimized when the precipitate has the form of an arbitrarily thin plate with a (100) habit. If the surface tension is isotropic, as it seems to be to a reasonable approximation in most cubic systems of interest, the progression of the preferred shape during coarsening is from a sphere to a cube bounded by (100) planes to a plate with a (100) habit that progressively thins as coarsening continues. In the present work we add the possibility of a decomposition of the cube into a compact set of parallel plates or a compact octet of smaller cubes.

2. Theoretical Background

Let a cubic solid contain an arbitrary distribution of coherent cubic precipitates that are characterized by the "transformation strain",

$$\epsilon_{ij}^q = \epsilon_0 \delta_{ij} = (\Delta a/a_0) \delta_{ij} \quad (2)$$

where Δa is the lattice parameter difference between the precipitate and

matrix phases. We assume that the elastic constants of the matrix are approximately equal to those of the precipitate phase and that the anisotropy factor, Δ , is negative (equation (1)).

The elastic energy of the precipitate distribution is [2,16]

$$E^e = (1/2) \int_{\mathbf{k}} [B(\mathbf{m}) |\theta(\mathbf{k})|^2] d^3\mathbf{k} / (2\pi)^3 \quad (3)$$

where the integral is taken over reciprocal space, $\mathbf{n} = \mathbf{k}/k$ is a unit vector in the direction of \mathbf{k} , and

$$\theta(\mathbf{k}) = \int_{\mathbf{r}} \exp(-i\mathbf{k}\mathbf{r}) \tilde{\theta}(\mathbf{r}) d^3\mathbf{r} \quad (4)$$

is the Fourier transform of $\tilde{\theta}(\mathbf{r})$, which is a shape function that has the value one when the position vector, \mathbf{r} , lies within a precipitate and the value zero otherwise. The elastic energy function, $B(\mathbf{m})$, is known exactly [2,16]. As shown in reference [16], however, it can be approximated to a high degree of accuracy by the expression

$$B(\mathbf{m}) = (2\beta/c_{11}) s_0^2 \{ (c_{11} - c_{12}) - 2\beta\Delta\gamma_1(\mathbf{m}) / (2c_{11} - \Delta) - 27\beta\Delta^2\gamma_2(\mathbf{m}) / [(2c_{11} - \Delta)(3c_{11} - 2\Delta)] \} \quad (5)$$

where c_{11} , c_{12} and c_{44} are the cubic elastic constants, Δ is the anisotropy factor, β , is the bulk modulus,

$$\beta = c_{11} + 2c_{12} \quad (6)$$

and the functions $\gamma_1(\mathbf{m})$ and $\gamma_2(\mathbf{m})$ are the cubic harmonics

$$\gamma_1(\mathbf{m}) = \frac{n_x^2 n_y^2}{x} + \frac{n_x^2 n_z^2}{x} + \frac{n_y^2 n_z^2}{z} \quad (7)$$

$$\gamma_2(\mathbf{m}) = \frac{n_x^2 n_y^2 n_z^2}{x} \quad (8)$$

The representation of $B(\mathbf{m})$ that is given in equation (5) deviates by no more than one percent from the exact value and is equal to it for the symmetry directions $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$.

Using equation (5) the elastic energy can be written

$$E^e = (V\beta s_0^2/c_{11})\{(c_{11}-c_{12}) - 2\beta\Delta I_1/(2c_{11}-\Delta) - 27\beta\Delta^2 I_2/[(2c_{11}-\Delta)(3c_{11}-2\Delta)]\} \quad (9)$$

where V is the total volume of precipitate phase and I_1 and I_2 are the geometric integrals

$$I_1 = (1/V) \int_{\mathbf{k}} \gamma_1(\mathbf{m}) |\theta(\mathbf{k})|^2 d^3\mathbf{k} / (2\pi)^3 \quad (10)$$

$$I_2 = (1/V) \int_{\mathbf{k}} \gamma_2(\mathbf{m}) |\theta(\mathbf{k})|^2 d^3\mathbf{k} / (2\pi)^3 \quad (11)$$

The integrals I_1 and I_2 are dimensionless parameters whose values depend only on the shape and distribution of the precipitates.

The first term on the right hand side of (9) is independent of the precipitate shape or distribution. It is, in fact, the elastic energy of a precipitate that has the form of a thin plate in a (100) habit, as can be seen immediately by recognizing that $\gamma_1(100) = \gamma_2(100) = 0$. To determine the preferred shape it is sufficient to consider the elastic energy relative to that of the thin plate, which can be written in the compact form

$$\Delta E^e = E^1 V [4I_1 + 54\Delta I_2 / (3c_{11} - 2\Delta)] \quad (12)$$

where

$$E^1 = -(1/2)\beta^2 \Delta s_0^2 / [c_{11}(2c_{11} - \Delta)] \quad (13)$$

since we have assumed $\Delta \leq 0$, $E^1 > 0$. Since E^1 is a material constant, the relative energy of the precipitate configuration can be written

$$\Delta E^* = \Delta E^e / VE^1 = 4I_1 + 54\Delta I_2 / (3c_{11} - 2\Delta) \quad (14)$$

The relative energy depends on the elastic constants only through the second term on the right hand side of equation (14). As we shall see, this term is very small for the cases of interest to us; the relative energy of a distribution of cubic phase precipitates in a cubic matrix is very nearly a universal function.

The shape is characterized by the function $\Theta(\mathbf{k})$ that influences the elastic energy through the integrals I_1 and I_2 . We shall consider cases in which the precipitate decomposes into two or more discrete particles of similar geometry. If \mathbf{R}^α denotes the center of the α th particle the shape function for the distribution can be written

$$\Theta(\mathbf{r}) = \sum_{\alpha} \tilde{\Theta}^{\circ}(\mathbf{r}-\mathbf{R}^{\alpha}) \quad (15)$$

where $\tilde{\Theta}^{\circ}(\mathbf{r})$ is the shape function of an individual particle. The Fourier transform of (15) is

$$\Theta(\mathbf{k}) = \Theta^{\circ}(\mathbf{k}) \sum_{\alpha} \exp[-i\mathbf{k} \cdot \mathbf{R}^{\alpha}] \quad (16)$$

where

$$\Theta^{\circ}(\mathbf{k}) = \int_{\mathbf{r}} \tilde{\Theta}^{\circ}(\mathbf{r}) \exp[-i\mathbf{k} \cdot \mathbf{r}] \quad (17)$$

is the shape function of a single particle. When the particles are rectangular parallelepipeds with edge lengths a , b and c ,

$$\begin{aligned} \Theta^{\circ}(\mathbf{k}) &= \Theta^{\circ}(k_x, k_y, k_z) \\ &= [(2/k_x) \sin(k_x a/2)] [(2/k_y) \sin(k_y b/2)] [(2/k_z) \sin(k_z c/2)] \end{aligned} \quad (18)$$

It is useful to note the analogy between the shape function that is defined here and that used in the theory of diffraction. The function $\Theta(\mathbf{k})$ is the shape function that governs the amplitude of diffraction from a set of particles. The squared modulus, $|\Theta(\mathbf{k})|^2$, is just the Laue interference function that gives the intensity distribution around a reciprocal lattice point due to diffraction by the particles. The function $\Theta^{\circ}(\mathbf{k})$ is the single-particle scattering factor; the summation, $\sum_{\alpha} \exp[-i\mathbf{k} \cdot \mathbf{R}^{\alpha}]$ is the structure amplitude that describes the mutual interference of several scattering centers.

3. The Dependence of the Elastic Energy on the Morphology

In this section we solve the integrals (10) and (11) to determine the elastic energies of various precipitate morphologies. The

precipitate shapes of interest are the sphere, the cube, doublet and octet groups of particles derived from the cube, and the platelet.

The elastic energy is specifically evaluated for each shape for the elastic constants of γ' Ni₃Al: $c_{11} = 1.986$, $c_{12} = 1.266$, and $c_{44} = 1.179$ in units of 10^{12} dyne/cm² [12].

a. Elastic Energy of a Sphere

When the precipitate is spherical the integrals (10) and (11) can be found analytically. Since the shape function of a sphere, $\theta(\mathbf{k})$, does not depend on the direction of the vector \mathbf{k} ,

$$\begin{aligned} I_1 &= (1/V) \int \gamma_1(\mathbf{m}) |\theta(\mathbf{k})|^2 d^3\mathbf{k} / (2\pi)^3 \\ &= (1/V) \int d\omega_n \gamma_1(\mathbf{m}) \{ (2\pi)^{-3} \int |\theta(\mathbf{k})|^2 k^2 dk \} \end{aligned} \quad (19)$$

where $k = |\mathbf{k}|$ and $d\omega_n$ is the element of solid angle in the direction of the unit vector $\mathbf{n} = \mathbf{k}/k$. Since, for a sphere,

$$\int |\theta(\mathbf{k})|^2 k^2 dk = V/4\pi \quad (20)$$

$$\begin{aligned} I_1 &= (4\pi)^{-1} \int d\omega_n \gamma_1(\mathbf{m}) = \langle \gamma_1(\mathbf{m}) \rangle \\ &= 1/5 \end{aligned} \quad (21)$$

where $\langle \gamma_1(\mathbf{m}) \rangle$ is the average of $\gamma_1(\mathbf{m})$ over the sphere. The same analysis yields

$$I_2 = \langle \gamma_2(\mathbf{m}) \rangle = 1/105 \quad (22)$$

Assuming the elastic constants of γ' Ni₃Al, it follows from equations (21), (22) and (12) that the elastic energy of a sphere relative to that of a thin plate on (100) is

$$\Delta E^{\circ}(\text{sphere}) = 0.709(V E_1) \quad (23)$$

b. Elastic Energy of a Cube

According to equation (18) the shape function of a single cuboidal particle with edge length (2a) is

$$\begin{aligned}\theta(\mathbf{k}) &= \theta(hk1) \\ &= (2a)^3 [\sin(2\pi h)/2\pi h] [\sin(2\pi k)/2\pi k] [\sin(2\pi l)/2\pi l]\end{aligned}\quad (24)$$

where the variables (h,k,l) are determined by the identities $k_x a = 2\pi h$, $k_y a = 2\pi k$, $k_z a = 2\pi l$. The geometrical integrals I_1 and I_2 must be evaluated numerically. They are

$$\begin{aligned}I_1 &= (8/V^2) \iiint [(h^2 k^2 + h^2 l^2 + k^2 l^2) / (h^2 + k^2 + l^2)^2] |\theta(hk1)|^2 dh dk dl \\ &= 0.1578\end{aligned}\quad (25)$$

and

$$\begin{aligned}I_2 &= (8/V^2) \iiint [(h^2 k^2 l^2) / (h^2 + k^2 + l^2)^3] |\theta(hk1)|^2 dh dk dl \\ &= 0.007664\end{aligned}\quad (26)$$

Assuming the elastic constants of γ' Ni₃Al, the relative elastic energy of a cuboid is, then

$$\Delta E^e(\text{cube}) = 0.558(V E_1) \quad (27)$$

c. Elastic Energy of a Doublet of Parallel Plates

Now consider a doublet of particles that is formed by the decomposition of a sphere of edge length (2a) into parallel plates with dimensions $2a \times a \times 2a$ that are separated by the distance u in the [010] direction (Figure 1). Given equation (18) and defining the triplet (h,k,l) as in equation (24), the shape function of a single plate is

$$\begin{aligned}\theta^o(\mathbf{k}) &= \theta^o(hk1) \\ &= 4a^3 [\sin(2\pi h)/2\pi h] [\sin(\pi k/\pi k)] [\sin(2\pi l)/2\pi l]\end{aligned}\quad (28)$$

The vectors that locate the two plates within the doublet with respect to its center are

$$R^{\alpha} = \pm(a/2)(1+\xi)e_y \quad (29)$$

where e_y is a unit vector along [010] and $\xi = u/a$. The shape function of the doublet is, from equation (16),

$$\Theta(hkl) = 2\Theta^{\circ}(hkl)\cos[\pi k(1+\xi)] \quad (30)$$

The geometric integrals I_1 and I_2 have the form given in equations (25) and (26), where $V = (2a)^3$ is the total volume of the doublet particle, but they are now functions of the dimensionless separation, ξ , and, given a set of elastic constants, can be used to compute the elastic energy of the doublet as a function of the separation, ξ , from equation (12).

The function $\Delta E^{\circ}(\text{doublet})$ for Ni_3Al is plotted in Figure 2. The results show that the elastic energy decreases when the cube decomposes into parallel plates, and reaches a minimum when the separation is $\xi = \xi_m = 0.8$, that is, when the separation, u , is

$$u_m = 0.8a \quad (31)$$

The values of the geometric integrals at this separation are

$$\begin{aligned} I_1(0.8) &= 0.134 \\ I_2(0.8) &= 0.00548 \end{aligned} \quad (32)$$

so that the relative energy of the platelet pair at equilibrium is

$$\Delta E^{\circ}(\text{doublet}) = 0.483(VE_1) \quad (33)$$

where $V=(2a)^3$ is the total volume of the pair.

It follows from equations (27) and (33) that the decomposition of a cube into a set of parallel plates with equilibrium separation causes a net decrease in the elastic energy,

$$\delta E^{\circ} = - 0.0753(VE_1) \quad (34)$$

d. Elastic Energy of an Octet of Cubes

Now consider an octet of particles that is formed by the decomposition of a cube of edge length, $2a$, into eight cuboidal subparticles of edge length, a , that are separated along the $\langle 111 \rangle$ directions of the lattice (Figure 3). The positions of the subparticles with respect to the center of the cluster are given by the vectors

$$\mathbf{R}^{\alpha} = \pm(a/2)(1+\xi)\mathbf{e}_x \pm (a/2)(1+\xi)\mathbf{e}_y \pm (a/2)(1+\xi)\mathbf{e}_z \quad (35)$$

where \mathbf{e}_x , \mathbf{e}_y and \mathbf{e}_z are unit vectors in the $[100]$, $[010]$ and $[001]$ directions. The shape function of a single cube of side a is

$$\Theta^{\circ}(hkl) = 4a^3 [\sin(\pi h)/\pi h] [\sin(\pi k)/\pi k] [\sin(\pi l)/\pi l] \quad (36)$$

so the shape function of the octet of cubes is

$$\Theta(hkl) = 8\Theta^{\circ}(hkl) \cos[\pi h(1+\xi)] \cos[\pi k(1+\xi)] \cos[\pi l(1+\xi)] \quad (37)$$

The integrals I_1 and I_2 again have the form given in equations (25) and (26). They were evaluated numerically and used to evaluate the relative elastic energy as a function of the dimensionless separation, ξ , for the specific case of Ni_3Al . The results are plotted in Figure 2. They show that the elastic energy decreases as the cubic subparticles are separated in the $\langle 111 \rangle$ directions, and reaches a minimum when $\xi = \xi_m = 0.35$, or

$$u_m = 0.35a \quad (38)$$

For this value of the separation the values of the geometric integrals are

$$\begin{aligned} I_1 &= 0.120 \\ I_2 &= 0.00456 \end{aligned} \quad (39)$$

The relative elastic energy is

$$\Delta E^e(\text{octet}) = 0.436(V E_1) \quad (40)$$

e. **The Elastic Energy of a Platelet with Optimal Aspect Ratio**

Finally, let the precipitate take the form of a circular platelet with a (100) habit, diameter D, thickness h, and aspect ratio

$$\kappa = h/D \quad (41)$$

The elastic energy of a platelet precipitate of cubic phase was found by Khachaturyan and Airapetyan [7,16], and depends on the aspect ratio as well as on the volume. To find the optimal value of the aspect ratio of a platelet of given volume it is necessary to consider the interfacial contribution to the energy as well, since the optimal value minimizes the sum of the elastic and interfacial energies. The total free energy (elastic plus interfacial) relative to the elastic energy of an arbitrarily thin plate (in the limit $\kappa \rightarrow 0$) can be written

$$\Delta F = -(\eta V E_1 / \pi) \kappa \ln(\kappa) + \sigma (2\pi V / \kappa)^{2/3} \quad (42)$$

where σ is the interfacial energy, which we shall assume isotropic, and the dimensionless constant, η , is

$$\eta = 2(2c_{11} - \Delta)(c_{11} - c_{12}) / (c_{11} c_{44}) \quad (43)$$

The constant η is of the order of a few units. In the case of Ni_3Al ,

$$\eta = 3.46 \quad (44)$$

Defining the effective size of the precipitate by the relation $(2a)^3 = V$, equation (42) can be rewritten in the dimensionless form

$$\Delta F / V E_1 = -1.1 \kappa \ln(\kappa) + 1.845 \kappa^{-2/3} (r_0 / 2a) \quad (45)$$

where

$$r_0 = \sigma / E_1 \quad (46)$$

is a characteristic length for the material. The minimum value of ΔF for a plate of given volume occurs when the aspect ratio satisfies the relation

$$-0.894\kappa_0^{5/3}[1+\ln(\kappa_0)] = r_0/2a \quad (47)$$

At this value of the aspect ratio the free energy relative to that of the thin plate is

$$\Delta F(\kappa_0)/VE_1 = -[2.75\kappa_0\ln(\kappa_0) + 1.65\kappa_0] \quad (48)$$

f. Other Sets of Elastic Constants

The energies and equilibrium separations cited above were computed for the specific case of Ni_3Al . However, the results are a good approximation for most materials of interest. The reason is that, according to equation (14), the dimensionless form of the relative energy, $\Delta E^* = \Delta E^0/(VE_1)$, depends on the specific material properties only through the term that is proportional to the integral I_2 . This integral is always small compared to I_1 , as illustrated by the values cited above. The term proportional to I_2 in equation (14) contributes only 5-10% of the energy change in the cases studied.

4. Morphological Transformations During Coarsening

The results of the previous section show that there is a monotonic decrease in the elastic energy as a sphere changes to a cube, and as a cube decomposes into doublet and octet forms. It seems clear that the same analysis can be repeated indefinitely; the elastic energy of each cube within an octet of cubes would be decreased by decomposing it into subcubes, each of those would preferentially decompose into subcubes, and the process might be continued until the particle size reached atomic dimensions. The reason this is not expected to happen is the interfacial energy, which increases monotonically as the precipitate morphology becomes less compact. Of the shapes we have considered,

while the elastic energy decreases as the shape changes from sphere to cube to doublet to octet to plate, the surface energy increases in the same sequence. Since the preferred morphology is that which minimizes the sum of the elastic and the surface energy, and since the surface energy becomes less important as the particle volume increases, the preferred shape of the precipitate evolves during coarsening through the sequence of possible shapes in order of decreasing elastic energy. The particle sizes at which equilibrium transitions occur between the shapes considered in the previous section are computed below.

a. **Transition from Sphere to Cube**

If the interfacial tension (σ) is nearly isotropic, as we shall assume, the preferred shape of a precipitate is spherical when its size is arbitrarily small. If the volume of the sphere is written $(2a)^3$ for ease of comparison with a cube, its surface area is

$$S = 4a^2(36\pi)^{1/3} \quad (49)$$

Using equation (23) its total energy is (relative to the elastic energy of a thin plate in a (100) habit),

$$\Delta F(\text{sphere}) = 0.709E_1(2a)^3 + \sigma(36\pi)^{1/3}(2a)^2 \quad (50)$$

The relative energy of a cuboid of the same volume is, using equation (27),

$$\Delta F(\text{cube}) = 0.558E_1(2a)^3 + 6\sigma(2a)^2 \quad (51)$$

It follows that the sphere becomes metastable with respect to transition into a cube when

$$0.222E_1(2a) \geq \sigma[6-(36\pi)^{1/3}] \quad (52)$$

The inequality (52) is satisfied when

$$2a \geq 7.7(\sigma/E_1) = 7.7r_0 \quad (53)$$

where $r_0 = \sigma/E_1$ is the characteristic length of the material that was defined in equation (46).

b. Transformations between Cube, Doublet and Octet

Now consider the decomposition of a cube of edge length $2a$ into a pair of particles of dimensions $2a \times a \times 2a$ (Figure 1). It follows with the help of equation (33) that the relative energy of the doublet is

$$\Delta F(\text{doublet}) = 0.483E_1(2a)^3 + 8\sigma(2a)^2 \quad (54)$$

Comparing this value to the relative energy of the cube (equation (51)) shows that the cube is metastable with respect to decomposition into a doublet when

$$2a \geq 27r_0 \quad (55)$$

An octet of identical cubes of edge length a has the same volume as a cube of edge length $2a$, but has surface area $12(2a)^2$. It follows from equation (40) that its relative energy is

$$\Delta F(\text{octet}) = 0.436E_1(2a)^3 + 12\sigma(2a)^2 \quad (56)$$

The octet configuration is stable with respect to the cube when

$$2a \geq 50r_0 \quad (57)$$

and is stable with respect to the doublet configuration when

$$2a \geq 82r_0 \quad (58)$$

c. Transformation from an Octet to a Platelet

Equation (40) shows that the elastic energy of an octet of cuboidal precipitates is positive when it is measured with respect to that of an arbitrarily thin plate. For Ni_3Al , $\Delta E^{\circ}(\text{octet}) = 0.436VE_1$, which, as we have discussed, should be a reasonable approximation for most cubic systems with negative anisotropy. Since ΔE° is positive there must be a precipitate volume that is large enough that the octet is at least metastable with respect to transformation into a disc-like thin plate.

Comparing equation (48) for the relative energy of a disc of optimal aspect ratio to that of the octet shows that the disc is preferred when

$$-[2.75\kappa_0 \ln(\kappa_0) + 1.65\kappa_0] \leq 0.436 + 12(r_0/2a) \quad (59)$$

The preferred value of the aspect ratio is given in terms of the ratio $(r_0/2a)$ in equation (47). It follows that the disc shape is preferred when

$$\kappa_0 \leq 0.38 \quad (60)$$

which corresponds to a precipitate size

$$2a = (V)^{1/3} = 377r_0 \quad (61)$$

The dimensions of the disc that is just stable with respect to the octet are

$$\begin{aligned} h_0 &= (4V\kappa_0^2/\pi)^{1/3} = 207r_0 \\ D_0 &= h_0/\kappa_0 = 572r_0 \end{aligned} \quad (62)$$

Note, however, that the computed results for the platelet configuration are only approximate since they are based on an expression, equation (48), that is only strictly valid when the plate is very thin ($\kappa \ll 1$).

5. Comparison with Experiment

The analysis presented above is written for coherent precipitates of cubic phase that are sufficiently disperse to be approximately isolated from one another. The only experimental data known to us that may satisfy these conditions, and for which we have sufficient information to complete the calculations, concerns the morphological changes during coarsening in alloys that contain relatively low volume fractions of γ' Ni_3Al . Ardell and Nicholson [25] found that γ' precipitates are spherical when their size is very small. Phillips [26] observed cuboidal precipitates with a minimum size slightly above 50 Å. Miyazaki, Imamura and Kozaki [19] found cuboids at sizes up to about 0.7 μm , which began to split into doublets when their size reached about 0.8 μm (see Figures 1 and 2 of reference [20]). Westbrook [22] found octets of cubic precipitates that apparently result from the decomposition of a single precipitate. Doi, et al., [21] observed octets of precipitates in Ni-Si-Al, but did not find them in Ni-Al. Hence there is no critical size available for direct comparison.

To compare the experimental observations to the theoretical results of section 5 we require values for the misfit strain, ϵ_0 , and the interfacial tension, σ . The misfit strain has been variously reported by a number of authors [27-29]. The most complete set of measurements seem to be the x-ray single crystal data of Corey and Lisowski [29], who find $\epsilon_0 = 0.0079$. Then taking $\sigma \sim 10 \text{ erg/cm}^2$, the characteristic length for Ni_3Al is

$$r_0 \approx 11 \text{ \AA} \quad (63)$$

The morphological transitions are then predicted at the effective radii:

(1) sphere \rightarrow cube:

$$2a = v^{1/3} = 77 \text{ \AA} \quad (64)$$

(2) cube \rightarrow doublet

$$2a = v^{1/3} \approx 300 \text{ \AA} \quad (65)$$

(3) doublet \rightarrow octet

$$2a = v^{1/3} \cong 900 \text{ \AA} \quad (66)$$

which corresponds to a thickness of 450 \AA of each doublet plate. If the doublet does not appear, the cube is metastable with respect to the octet when $2a \cong 550 \text{ \AA}$; (4) octet \rightarrow plate

$$2a = v^{1/3} \cong 4100 \text{ \AA} \quad (67)$$

which corresponds to an edge length of each elementary cube of the octet of 0.2 μm .

The theoretical and experimental values are in reasonable agreement for the sphere \rightarrow cube transition. However, the subsequent transitions, from cube to doublet, octet or plate, are all predicted to occur at sizes well below those at which the transitions are experimentally found. The reason for the discrepancy may be straightforward. The sizes we have calculated are those at which the precipitate shape first becomes metastable. Since a finite perturbation is required to deform a cube into a doublet, octet or platelet, the cuboidal shape may be retained to significantly larger sizes, eventually transforming at the size at which the cube becomes unstable with respect to an infinitesimal shape perturbation that alters its shape. Since a sphere can deform into a cube by progressively flattening its {100} surfaces, the transition size between the sphere and the cube should be very close to the equilibrium value, and a close agreement between the theory and experiment is expected.

6. Discussion and Conclusion

a. Results

Perhaps the most important result of this investigation is the demonstration that large, cubic precipitates are at least metastable with respect to splitting into arrays of subparticles, even when the

precipitates are cubic and do not differ significantly from the matrix in their elastic constants. The preference for decomposition has its source in elastic anisotropy, which introduces an effective elastic repulsion between the elementary subvolumes of the precipitate. A spherical or cubic precipitate is held together by interfacial tension. As the precipitate coarsens the interfacial contribution to the free energy decreases in importance, and decomposition is favored.

The decomposition described in this paper is formally similar to that which governs the formation of "bubble domains" in ferromagnetic and ferroelectric solids. Like the elastic energy, the magnetostatic and electrostatic energies also depend on the morphology of the domains as well as on their volume. The mutual repulsion of parallel magnetic or electric dipoles within a domain is opposed by the effective surface tension of the domain boundary, which has the consequence that there is a critical size or field at which domains subdivide into discrete subvolumes [17].

By considering the anisotropic elastic interaction and the surface tension alone it is possible to predict the effective sizes at which a cube is metastable with respect to decomposition into a pair of parallel plates or an octet of smaller cubes. It is also possible to predict the equilibrium separation between the discrete elements of the composite precipitate. Specific results were presented for the case of the γ' , Ni_3Al precipitate phase. However, the nature of the equations is such that, if the result is given in terms of the dimensionless radius, r_0 , it should be a good approximation for most cubic phase precipitates with negative anisotropy.

Using the same analysis the decomposition of cuboidal precipitates can be placed in a morphological sequence that governs the shape transition of a precipitate from a spherical initial shape to a final shape as a thin platelet. The sequence is sphere \rightarrow cube \rightarrow doublet \rightarrow octet \rightarrow platelet, and the shape transitions become preferred at particular values of the dimensionless radius, r_0 . The equilibrium transition radii were computed for the particular case of Ni_3Al . Because the elastic constants enter in a non-negligible way in the cube \rightarrow octet \rightarrow platelet transition, the specific value of the equilibrium radius for this transition may vary significantly from one system to another.

Moreover, a platelet precipitate is almost certainly metastable with respect to decomposition into an array of discrete particles in the plane; the decomposition of platelet precipitates is under investigation.

The dependence of the elastic interaction distance on the separation distance as diagrammed in Figure 3 has the consequence that precipitates repel one another when they are close and attract when they are well separated. This phenomenon has fundamental significance for the coarsening of elastic particles. The repulsive interaction opposes their aggregation into particles of large size; once the particles reach appreciable size they should resist further coarsening, as is observed experimentally [25]. On the other hand, the attraction of elastic particles that are well separated should result in their condensation into groups of neighboring precipitates, such as doublets, octets and segmented plates.

Finally, note that the results presented here do not preclude the direct precipitation of particles that have cubic or platelet shape. The size parameter, r_0 , depends on the balance between the interfacial tension, misfit strain, and elastic constants of the precipitate. If the equilibrium value of r_0 for the cubic or platelet shape is less than the radius of the critical nucleus, the initial particles should have the form of cubes or platelets.

b. Limitations of the Theory

Several limitations of the theoretical analysis should be noted.

First, the analysis is written for coherent precipitates of cubic phase with negative anisotropy that are sufficiently dispersed to be approximately isolated from one another. It should, hence, apply to coarsening in cubic systems that have relatively low precipitate volume fractions, and is no longer valid when the precipitates lose coherency with the matrix. The assumption of a low volume fraction limits the practical applicability of the theory, since age-hardened alloys often contain very high volume fractions of the hardening phase. The driving force for loss of coherency increases with the misfit parameter, ϵ_0 ; it

is, hence, expected that precipitates lose coherency with the matrix at increasingly smaller sizes as the misfit parameter increases. The predicted sizes for the sphere \rightarrow cube and cube \rightarrow doublet transitions also decreases as the misfit parameter grows. Whether these morphological transitions occur depends on the competition between the two effects.

Second, the theory ignores the difference between the elastic constants of the precipitate and the matrix. While we know of no detailed analysis of the importance of the elastic mismatch in systems that have non-ellipsoidal geometry, previous work [13,14,19] has shown that models that account for anisotropy without the elastic mismatch generate reasonably accurate results for shapes and habits of typical precipitate phases, and the present analysis provides a fairly close match to experiment in the case of γ' Ni₃Al. The neglect of the elastic constant difference also appears reasonable in light of the recent results of Voorhees and Johnson [24] who specifically studied the contribution of the modulus mismatch to decomposition in an ellipsoidal approximation. While they found that the modulus mismatch promotes the decomposition of a monolithic precipitate, the magnitude of the driving force for Ni₃Al is small compared to the driving force that results from the elastic anisotropy, as computed above.

Third, the shape transition criteria that are presented here were computed for equilibrium between the initial and final shapes. From a thermodynamic perspective, the shape transitions are first order transitions. They may proceed through intermediate states of higher energy, and may, hence, be kinetically suppressed. This is presumably the reason that the computed transition sizes are significantly smaller than those observed experimentally. The experimental observations [20,21] include examples of continuous splitting of Ni₃Al precipitates. These observations are expected if the actual transformation occurs at a critical size at which the particle becomes unstable with respect to infinitesimal variations of its shape rather than at the point of equilibrium between alternative shapes.

Fourth, the shapes considered here include only a few particular ones whose relevance is suggested by the experimental data. Other

shapes that were not considered may also be preferred over some range of sizes and may, therefore, intrude during coarsening.

c. **Implications**

We conclude by noting two implications of the work reported here. The first is to the theory of coarsening. The results suggest that one should be cautious in applying conventional coarsening models, such as the Lifshitz-Slyozov-Wagner [30,31] model, to the coarsening of coherent precipitates. While such models should work when the size range of the particles is such that a single shape is stable, they do not account for changes in the preferred shape, and specifically do not predict the "reverse coarsening" that occurs when a large precipitate decomposes into a set of smaller particles.

It is possible to sketch the qualitative outlines of a coarsening theory that takes the elastic interaction into account. The coarsening process can be divided into two distinct stages, which we shall call "interface-controlled" and "strain-controlled". Coarsening is interface-controlled when the particles are very small ($a \ll r_0$). Then the surface tension dominates their energy, they have spherical shape, and the LSW theory of coarsening should apply. Interestingly, this theory predicts that the particles coarsen with a constant size distribution about the mean. To the extent that this is true the elastic energy is unaffected by coarsening and influences the coarsening rate only through its effect on the diffusivity.

When the particles become larger ($a \gg r_0$) the elastic energy predominates over the interfacial contribution and coarsening is "strain-controlled". The particles take on cuboidal or compound shapes and resist further growth. As shown in the body of this paper, as their size increases they decompose back into smaller particles so that the individual particle size remains nearly the same.

We can infer from these results that when the elastic mismatch between the precipitate and matrix is significant a distribution of precipitates is likely to be trapped in a thermoelastic "quasi-equilibrium" in which the precipitate size coarsens very slowly, if at all. Significant further coarsening would require a loss of coherency or a

significant reconfiguration of the precipitate distribution. Coarsening theories of the LSW type are of little value in treating this behavior.

Second, the free energy of a solid that contains a distribution of coherent precipitates is determined by their size, shape and distribution, in addition to their identity. Because of the elastic interaction the size, shape and distribution of the precipitates are internal thermodynamic parameters whose particular values constrain the local equilibrium of the system. These parameters must be specifically taken into account in any attempt to construct a "coherent phase diagram" for the system.

Acknowledgments

The authors are grateful to T. Edgecumbe-Summers, Lawrence Berkeley Laboratory, for helpful discussions. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

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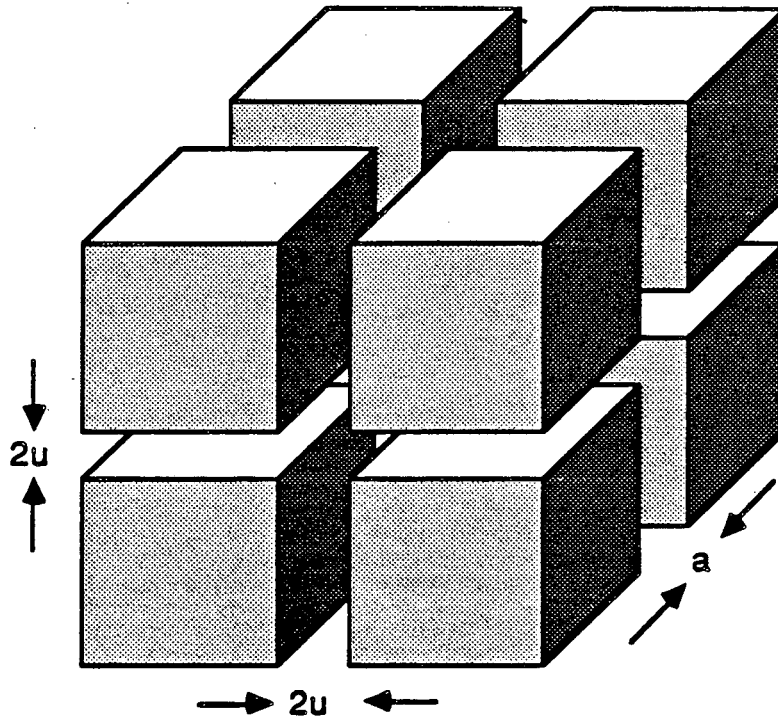


Fig. 1 Schematic drawing of octet that results from the decomposition of a cuboidal particle.

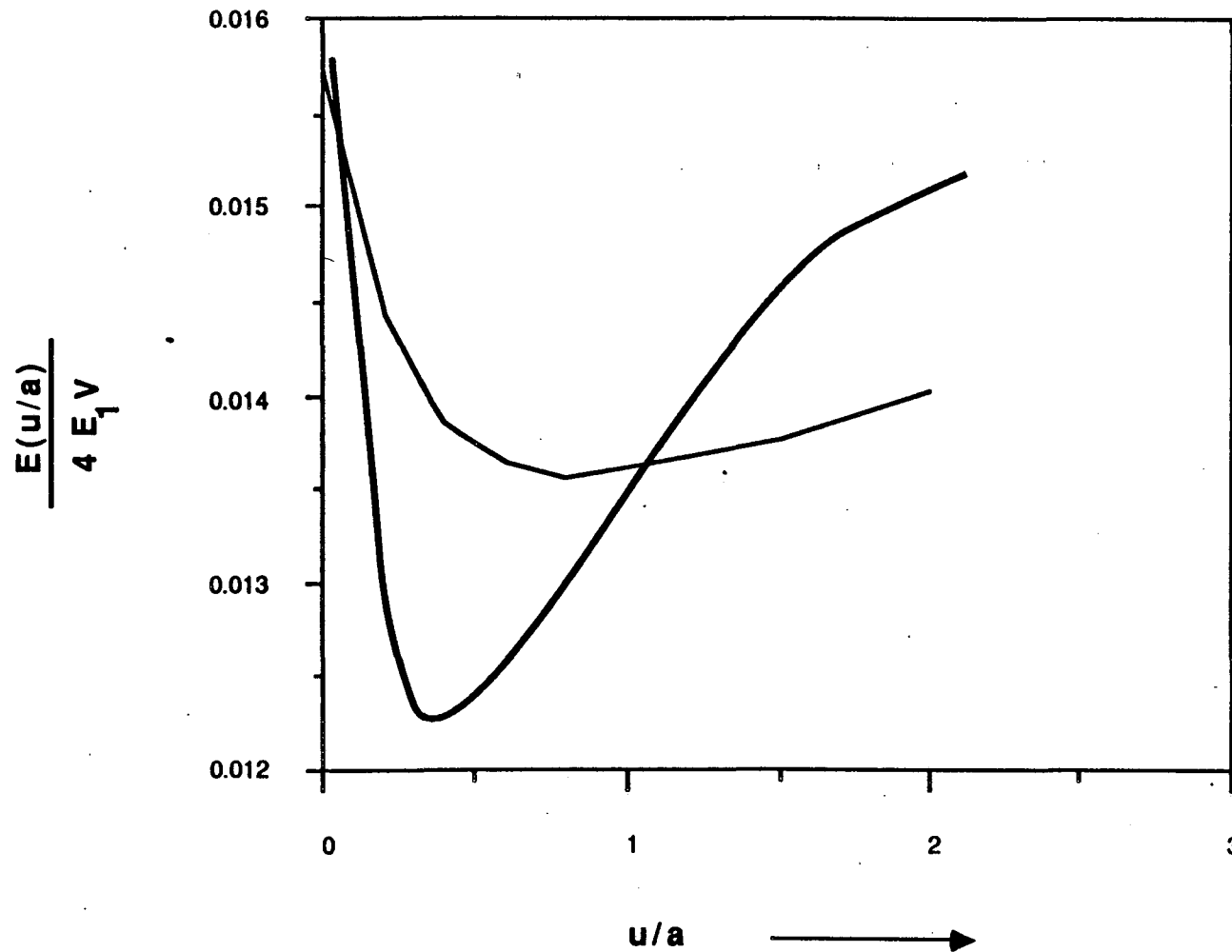


Fig. 2 Configurational elastic energy, in dimensionless form, as a function of dimensionless particle spacing (u/a) for an octet of cubes (dark line) and a doublet of plates (light line).

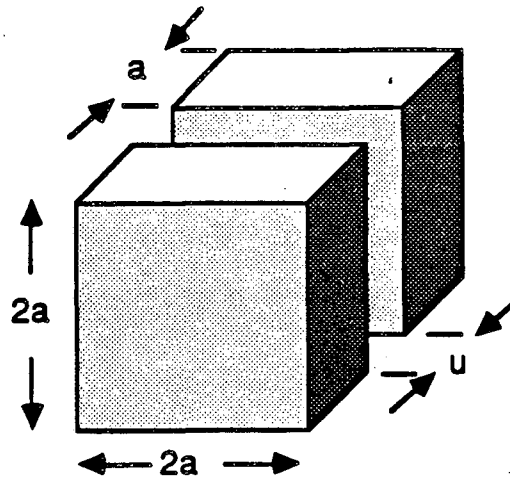


Fig. 3 Schematic drawing of doublet of plates that results from the decomposition of a cuboidal particle.

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