

ON SPINODAL DECOMPOSITION IN CUBIC CRYSTALS*

JOHN W. CAHN†

The anisotropy of all factors influencing the mechanism of spinodal decomposition is considered for crystals of cubic symmetry. It is found that no anisotropy is introduced by the incipient surface, and that elastic anisotropy should give rise to {100} plane waves if $2C_{44} - C_{11} + C_{12} > 0$ or {111} plane waves if $2C_{44} - C_{11} + C_{12} < 0$. The limit of metastability, the kinetics, morphology and expected mean particle spacing are rederived in terms of the cubic elastic constants.

LA DECOMPOSITION SPINODALE DANS LES CRISTAUX CUBIQUES

L'auteur étudie l'anisotropie de tous les facteurs qui influencent le mécanisme de la décomposition spinodale dans les cristaux de symétrie cubique. Il conclut que l'anisotropie élastique doit donner naissance à des ondes planes {100} si $2C_{44} - C_{11} + C_{12} > 0$, ou à des ondes planes {111} si $2C_{44} - C_{11} + C_{12} < 0$. Il discute les limites de l'état métastable, la cinétique, la morphologie et l'espacement moyen des particules qu'on peut prévoir en fonction des constantes élastiques cubiques.

UBER DIE UMSETZUNG AN DER SPINODALEN IN KUBISCHEN KRISTALLEN

Die Anisotropie aller Faktoren, die den Mechanismus der Umsetzung an der Spinodalen beeinflussen, wird für Kristalle kubischer Symmetrie untersucht. Es stellt sich heraus, daß die Ausgangsfläche der Umwandlung keine Anisotropie hervorruft, und daß die elastische Anisotropie ebene Wellen verursachen sollte, und zwar in {100}-Ebenen für $2C_{44} - C_{11} + C_{12} > 0$ und in {111}-Ebenen für $2C_{44} - C_{11} + C_{12} < 0$. Die Grenze der Metastabilität, die Kinetik, die Morphologie und der zu erwartende mittlere Teilchenabstand werden wieder auf die elastischen Konstanten zurückgeführt.

INTRODUCTION

In the previous paper⁽¹⁾ the stability of an infinite isotropic solid to long-range infinitesimal composition fluctuations was considered. The elastic energy due to such a fluctuation was found to be a stabilizing factor leading to a new criterion of metastability which involves the elastic constants. In the present paper the stability of an aeolotropic solid of cubic symmetry will be examined.

The free energy of an element of volume of a system containing a composition fluctuation may be separated into three terms: (1) the free energy density $f'(c)$ of stress free homogeneous material of composition c ; (2) the free energy density due to the existence of a composition gradient, termed the gradient energy, and (3) an elastic energy density f_{el} arising from stresses resulting from changes in stress-free molar volume with composition.‡ The symmetry properties of the gradient energy in cubic crystals have already been described⁽²⁾ and are, for small gradients, isotropic and of the form $\kappa(\nabla c)^2$. Anisotropies first⁽³⁾ appear in the coefficient of the fourth order terms, and may be neglected when considering infinitesimal fluctuations. All anisotropies in the early stages of spinodal decomposition must therefore come exclusively from the

elastic anisotropy, since there is no anisotropy in the incipient surface free energy.

ELASTIC ENERGY

As before,⁽¹⁾ let us consider a sinusoidal plane wave fluctuation of the form

$$c - c_0 = A \cos \boldsymbol{\beta} \cdot \mathbf{r} \quad (1)$$

in an infinite defect-free cubic crystal in which the stress-free molar volume for small $c - c_0$ is given by

$$V(c) = V_0[1 + 3\eta(c - c_0)] = V_0(1 + 3A\eta \cos \boldsymbol{\beta} \cdot \mathbf{r}) \quad (2)$$

The stress-free strain is a pure dilation.

Choosing a co-ordinate system so that the z -axis is parallel to $\boldsymbol{\beta}$ we can determine the following about the components of the total strain (the sum of the stress-free and elastic strains):

$$\varepsilon_{xx}^T = \varepsilon_{yy}^T = \varepsilon_{zz}^T = 0 \quad (3)$$

If these components were not constant, but varied in the z -direction, then the relative displacement of two adjacent xy planes would increase without limit as we go out along the planes and give rise to ever increasing shears. That they vanish follows from the linearity between expansion and composition over a small enough composition range.

Similarly we can determine the following about the stress:

$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = 0 \quad (4)$$

The problem then reduces to finding the remaining

* This work was done during the tenure of a John Simon Guggenheim Fellowship at the Metallurgy Department, Cambridge University, Cambridge, England. Received June 23, 1961.

† General Electric Research Laboratory, Schenectady, N.Y.

‡ This separation of the last two terms should cause no difficulty because the introduction of a constant composition gradient into a finite crystal gives rise to no elastic energy.

strain and stress components and the elastic energy for an arbitrary orientation of β relative to the cubic axes.

Equations (2), (3) and (4) are sufficient to determine all remaining stress and strain components, but the algebra involved is formidable. A quite good approximate solution can be readily obtained. In the isotropic case ε_{yz}^T and ε_{xz}^T are also zero. This follows directly from equation (4). If we make the assumption that in the cubic case also, ε_{zz}^T is the only non-vanishing component, we can determine it as follows: Deduct the stress-free strain to obtain the elastic strain, rotate the co-ordinate system to coincide with the cube axes and insert the elastic-strain components into the equation for the elastic-energy density. This gives

$$f_{el} = \varepsilon^2 \left[\frac{C_{11}}{2} \left\{ 3 + \frac{2\varepsilon_{zz}^T}{\varepsilon} + \left(\frac{\varepsilon_{zz}^T}{\varepsilon} \right)^2 \right\} + C_{12} \left(3 + \frac{2\varepsilon_{zz}^T}{\varepsilon} \right) + (2C_{44} - C_{11} + C_{12}) \times (l^2m^2 + m^2n^2 + n^2l^2) \left(\frac{\varepsilon_{zz}^T}{\varepsilon} \right)^2 \right]$$

where $\varepsilon = A\eta \cos \beta \cdot \mathbf{r}$ and l, m and n are the directional cosines between β and the three cube axes. This may then be minimized with respect to ε_{zz}^T to give

$$\varepsilon_{zz}^T = - \frac{\varepsilon(C_{11} + 2C_{12})}{C_{11} + 2(2C_{44} - C_{11} + C_{12})(l^2m^2 + m^2n^2 + n^2l^2)} \quad (6)$$

and

$$f_{el} = \varepsilon^2 Y \quad (7)$$

where

$$Y = \frac{1}{2}(C_{11} + 2C_{12}) \times \left[3 - \frac{C_{11} + 2C_{12}}{C_{11} + 2(2C_{44} - C_{11} + C_{12})(l^2m^2 + m^2n^2 + n^2l^2)} \right] \quad (8)$$

The assumption $\varepsilon_{xz}^T = \varepsilon_{yz}^T = 0$ is valid for certain symmetry direction of β , $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$. For these directions the results obtained above are exact. For other directions, by permitting some shearing along β , the elastic energy can be reduced by a term of order

$$\frac{(2C_{44} - C_{11} + C_{12})^2}{8C_{44}} [(l^6 + m^6 + n^6) - (l^4 + m^4 + n^4)^2] \quad (9)$$

The magnitude of $(\varepsilon_{xz}^T)^2 + (\varepsilon_{yz}^T)^2$ is approximately

$$\frac{(2C_{44} - C_{11} + C_{12})^2}{16(C_{44})^2} [(l^6 + m^6 + n^6) - (l^4 + m^4 + n^4)^2] \quad (10)$$

These quantities reduce to zero for the symmetry direc-

TABLE 1. Elastic constant* for spinodal decomposition

Material	$\frac{2C_{44}}{C_{11} - C_{12}}$	$\times 10^{12} \text{ dyn/cm}^2$			
		$Y(100)$	$Y(110)$	$Y(111)$	$E/(1-\nu)$
Al	1.2	0.99	1.12	1.14	1.08
Fe(α)	2.4	2.10	3.38	3.68	2.8
Pb	3.9	0.19	0.51	0.59	0.33
Cu	3.3	1.15	2.33	2.62	1.75
Mo	0.78	5.0	4.5	4.3	

* Cubic elastic constants from Boas and Mackenzie⁽⁴⁾.

tions, or for isotropic elastic constants, and for most purposes are sufficiently small to justify their neglect.

An examination of equation (8) shows that the elastic coefficient Y reduces to $E/(1-\nu)$ as the anisotropy $2C_{44} - C_{11} + C_{12}$ reduces to zero. The elastic coefficient is least for the β parallel to $\langle 100 \rangle$ and maximum for β parallel to $\langle 111 \rangle$ when $2C_{44} - C_{11} + C_{12} > 0$ which is the usual case. When $2C_{44} - C_{11} + C_{12} < 0$ the reverse is true. Table 1 gives the magnitude of the elastic constants for several metals. The anisotropy is small for aluminum and molybdenum and large for iron, lead and copper. It is interesting to note that, for a $\{100\}$ habit, copper is as soft as aluminum.

THE LIMIT OF METASTABILITY

Since for $2C_{44} - C_{11} + C_{12} > 0$ the elastic energy is minimum for β parallel to $\langle 100 \rangle$, we can expect that the solution will first become unstable to $\{100\}$ plane waves. For these the free energy change per unit volume is given by

$$\frac{\Delta F}{V} = \frac{A^2}{4} \left[\frac{\partial^2 f'}{\partial c^2} + 2\eta^2 Y(100) + 2\kappa\beta^2 \right] \quad (11)$$

where

$$Y(100) = (C_{11} + 2C_{12})(C_{11} - C_{12})/C_{11} \quad (12)$$

The limit of metastability if thus given by the locus of

$$\frac{\partial^2 f'}{\partial c^2} + 2\eta^2 Y(100) = 0 \quad (13)$$

Similarly for $2C_{44} - C_{11} + C_{12} < 0$, it will be given by

$$\frac{\partial^2 f'}{\partial c^2} + 2\eta^2 Y(111) = 0 \quad (14)$$

where

$$Y(111) = \frac{6(C_{11} + 2C_{12})C_{44}}{4C_{44} + C_{11} + 2C_{12}} \quad (15)$$

As before, these conditions are obviously sufficient for instability to infinitesimal fluctuation. That they are also necessary can again be shown from the lack of interaction among the Fourier components of an arbitrary fluctuation. Thus the free energy change of an

arbitrary fluctuation is the sum of the free energy changes due to each Fourier component alone. If none of these individually are negative, then no arbitrary infinitesimal fluctuation can give a negative free energy change.

THE HABIT PLANE AND THE KINETICS OF DECOMPOSITION

In the unstable region in the vicinity of the limit of metastability the solution is only unstable to long wave-length fluctuations in the neighbourhood of the $\langle 100 \rangle$ directions if $2C_{44} - C_{11} + C_{12} > 0$, or the $\langle 111 \rangle$ directions if $2C_{44} - C_{11} + C_{12} < 0$. Only these Fourier components of an arbitrary fluctuation will grow, the remaining components will disappear. Thus spinodal decomposition will, in this region, give rise to strong preferred orientations.

As we consider increasingly more unstable solutions more and more orientations become unstable. However the orientations of lowest elastic energy will always be able to decompose with the smallest wavelength and hence most rapidly, although the anisotropy should diminish with increasing instability.

In order to consider this effect in more detail we write the equation for the kinetics of amplification of a fluctuation of wavelength β . Proceeding exactly as in the previous paper we obtain for the change in amplitude with time

$$A(\beta, t) = A(\beta, 0)e^{R(\beta)t} \quad (16)$$

where the amplification factor

$$R(\beta) = -M\beta^2 \left(\frac{\partial^2 f'}{\partial c^2} + 2\eta^2 Y + 2\kappa\beta^2 \right) \quad (17)$$

Again M is the mobility, which is isotropic in cubic crystals. As before, the amplification factor is negative when the solution is stable to that fluctuation and positive if not. If the solution is unstable to some wavelengths, then there exists a critical value of β for which the amplification factor is zero. This is given by

$$\beta_c^2 = -\frac{1}{2\kappa} \left(\frac{\partial^2 f'}{\partial c^2} + 2\eta^2 Y \right) \quad (18)$$

and is a function of orientation because of its dependence on Y . For some orientations β_c does not exist and the solution is stable to all fluctuations in that direction.

The maximum value of $R(\beta)$ for a given orientation occurs for

$$\beta = \beta_c/\sqrt{2} \quad (19)$$

and is given by

$$R_{\max} = R(\beta_c/\sqrt{2}) = \frac{M\kappa}{2} \beta_c^4 \quad (20)$$

It is therefore extremely sensitive to any anisotropy in β_c .

The determination of the amplification factor and wavelength of the most rapidly growing wave can serve to determine for that temperature and composition the parameters β_c and κ (strictly $M\kappa$) through equation (19) and (20) and hence $\partial^2 f'/\partial c^2$ through equation (18), and therefore determine the amplification factor for all orientations and wavelengths.

Alternatively determination of the wavelength of the most rapidly growing waves in two non-equivalent directions can, through equations (18) and (19), serve to determine κ and $\partial^2 f'/\partial c^2$ for that temperature and composition, thereby determining β_c for all orientations and give, through equation (17), a knowledge of M the amplification factor for all orientations and wavelengths.

DISCUSSION

The initial kinetics and mechanism of spinodal decomposition in cubic crystals has been completely described in terms of the seven parameters, $\partial^2 f'/\partial c^2$, κ , M , η and the three elastic constants and is otherwise independent of crystal structure. Of these, all but $\partial^2 f'/\partial c^2$ and κ are readily determined. The quantity $\partial^2 f'/\partial c^2$ may be determined by extrapolation of free energy data and κ has been estimated^(2,3) from statistical mechanics and, in the case of fluids, from surface tension data. These two can also be determined in a spinodal decomposition experiment as outlined above. The following predictions can be made:

(1) If $2C_{44} - C_{11} + C_{12} > 0$, spinodal decomposition should give plane waves primarily on all three $\{100\}$ planes. If $2C_{44} - C_{11} + C_{12} < 0$, these should lie about the four $\{111\}$ planes. For most metals the former is true and indeed the $\{100\}$ habit is usually observed⁽⁵⁻⁷⁾. It would be interesting if the $\{111\}$ habit is found in systems such as those based on molybdenum, in which the second inequality is true. This anisotropy is not due to surface anisotropy for the surface free energy of the incipient surface is completely isotropic in cubic crystals.

(2) The initial kinetics of decomposition are described by an exponential increase (or decrease) in amplitude of each Fourier component. For a given composition and temperature the amplification factor as a function of wavelength and orientation is completely described by the above parameters. Only two suitably chosen measurements need be made to fix the two parameters $\partial^2 f'/\partial c^2$ and κ (three, if M is not known either). These could then be checked against estimates from other sources. The theory can be checked for self-consistency by measuring the

amplification factors for other wavelengths or orientations, or by measuring the wavelengths of the most rapidly growing waves for other orientations. The cubic aeolotropy thus introduces one further experimental variable, orientation, which permits easier experimental verification than was available in the isotropic case.

(3) The kinetics are such (exponential growth) that after a while the fastest growing waves predominate, giving rise to almost pure sinusoidal fluctuations which lie in the $\langle 100 \rangle$ or $\langle 111 \rangle$ directions and have the wavelength $\sqrt{2}$ times the critical wavelength $2\pi/\beta_c$ which does not grow.

(4) The amplification factor should be independent of the previous history of the sample, except for any effects on M such as non-equilibrium vacancy concentration. Thus thermal cycling experiments should enable one to study the amplification factor of wavelengths which are not the fastest growing, including the wavelengths with negative amplification factors.

(5) The kinetics and wavelengths of the fastest growing waves as a function of temperature and composition are described by the temperature and composition dependence of the various parameters. Statistical mechanical estimates of κ indicate that it is not very sensitive to composition or temperature changes. So far the only experimental estimates of κ are those obtained from surface tension measurements and are therefore averages over the entire composition range. Similarly $\partial^2 f' / \partial c^2$ has only been estimated by extrapolation or from a theoretical solution model. Spinodal decomposition seems to offer the first possibility of a direct measurement of both the quantities as a function of composition throughout the unstable region.

(6) The limit of metastability in aeolotropic cubic crystals occurs sooner than one would expect if one used the result of the isotropic calculation (see Table 1). The spinodal mechanism seeks out the softest plane, which can be considerably softer than indicated by the average elastic constants. It should be pointed out again that the limit of metastability is still defined by equations (13) or (14). Unless $\eta = 0$ this does not coincide with the spinodal.

(7) Since various plane waves do not interact with each other, the structure at this stage will be approximately represented by the three $\{100\}$ waves or the four $\{111\}$ waves. The former resembles a simple cubic array of regions rich in one component connected along the $\langle 100 \rangle$ directions by rods similarly enriched. The body centers of this array are regions depleted in this component connected by similarly depleted $\langle 100 \rangle$ rods. This gives two interlocking continuous lattice works of

$\langle 100 \rangle$ rods, one enriched and the other depleted, in one of the components. On the other hand, the $\{111\}$ habit gives an "NaCl structure" in which cubes of enriched and depleted material alternate along the $\langle 100 \rangle$ directions.

Of all these, the main one which can currently be checked in the published literature is the $\{100\}$ habit. That this habit is indeed observed is a strong confirmation for the role which elastic energies play in spinodal decomposition. The Al-Zn system in which the elastic energy is small, but not negligible, would be an interesting system in which to study the growth of the waves not in the $\langle 100 \rangle$ direction. These should grow more slowly and with longer mean wavelengths but should still be detectable.

So far in this paper, only the initial stages of spinodal decomposition were considered. Most of the experimental results in the literature seem to be concerned with the later stages. The extension of the theory to the amplitudes where higher order terms in the free energy or where non-linear elasticity theory must be used is difficult indeed, but has been considered in one dimension by Hillert.⁽⁸⁾ His results are useful as a next approximation in which one takes into account interaction among plane waves of the same orientation but neglects interaction among plane waves of different orientations, bearing in mind that one must replace his $\partial^2 F / \partial^2 X$ by $\partial^2 f' / \partial c^2 + 2\eta^2 Y$ to take care of the elastic effects.

It is possible to make some qualitative predictions about the later stages of spinodal decomposition:

(1) When the amplitude of the plane waves becomes such that higher order terms in the expansion of f' about c_0 become important, there will be an interaction⁽¹⁾ among the plane waves which causes a slowing down of the rate of growth to the equilibrium compositions and distorts the plane waves.

(2) Depending on the relative volumes of the two phases in equilibrium, we expect imperfect versions of the following morphology:

(a) If the volume fraction of one phase is much smaller than the other, the $\{100\}$ habit will give a simple cubic array of octahedral particles whose corners are aligned along the $\langle 100 \rangle$ directions. As we consider systems with increasing volume fraction, these octahedra will come in contact along their corners giving a continuous simple cubic-lattice work of truncated octahedra (tetrakaidecahedra).

(b) The $\{111\}$ habit will give a face-centered cubic array of particles of the minor phase. These particles should vary from spheres to cubes as the volume fraction increases.

(3) The initial spacing of the particles in the $\{100\}$

habit is equal to the wavelength of the most rapidly growing wave; in the $\{111\}$ habit, the near-neighbor spacing of particles (in the $\langle 110 \rangle$) is $\sqrt{3}/2$ times the wavelength of the most rapidly growing wave.

(4) During the initial stages, the amplitude of the individual plane waves is only about one third (or one quarter for the $\{111\}$ habit) of the maximum composition difference in the sample. A similar fraction ($< 7/8$) persists as long as coherency is maintained, so that the observed separation of the side bands will represent only a fraction of the actual composition difference. Furthermore, the actual composition difference will be less than it will be for the final equilibrium incoherent phases for at least two reasons. One is a surface effect and is quite apparent from Hillert's results; the other is due to coherency strains altering the conditions of equilibrium.

(5) The maximum elastic shear strain is at the corners of the particles (or in the center of the square faces of the truncated octahedra) and is of the order of the fractional lattice parameter difference. If it exceeds the theoretical limit, plastic flow should originate there and coherency will be lost.

(6) The reported increase in wavelength with time is probably due to resolution of some of the particles or rods and growth of others. The driving force for it is reduction in surface-free energy. The three-dimensional aspect of this stage is quite important and there is some question of the meaning of Hillert's one-dimensional model for it.

Spinodal decomposition differs from nucleation and growth in that it proceeds from a stage small in degree but large in extent, passing through stages of primarily increasing amplitude, whereas a nucleation and growth mechanism proceeds from a stage small in extent but large in degree, passing through stages of primarily increasing extent. In spinodal decomposi-

tion there is no clear division where one can say the new phase has appeared; in nucleation and growth this is the important nucleation event.

Let us consider the transition between nucleation and growth and spinodal decomposition. Nucleation and growth can obviously occur in the unstable region as a competing mechanism, but spinodal decomposition cannot occur in the metastable region. This latter statement is to some extent a matter of definition. Consider, for example, a solid solution which would be metastable, were it not for the presence of defects. It would decompose continuously in the vicinity of the defects giving rise to the new phase, which would then spread by growth into the remainder of the sample. Let us consider this to fall within our definition of a nucleation and growth process, with heterogeneous nucleation. We see from this example that for spinodal decomposition to occur in real crystals, the bulk-defect free material must be unstable, and it was such material which was considered here.

ACKNOWLEDGMENTS

I would like to thank Drs. J. W. Christian, J. D. Eshelby and especially R. B. Nicholson for stimulating discussions, and express my sincere appreciation to the John Simon Guggenheim Memorial Foundation for the fellowship during which this work was done.

REFERENCES

1. J. W. CAHN, *Acta Met.*, **9**, 795 (1961).
2. J. W. CAHN and J. E. HILLIARD, *J. Chem. Phys.* **28**, 258 (1958).
3. R. KIKUCHI and J. W. CAHN, *J. Phys. Chem. Solids*, in press.
4. W. BOAS and J. K. MACKENZIE, *Progr. Met. Phys.* **2**, 90 (1950).
5. V. DANIEL and H. LIPSON, *Proc. Roy. Soc.* **A181**, 368 (1943); **A182**, 378 (1944).
6. T. J. TIEDEMA, J. BOUMAN and W. G. BURGERS, *Acta Met.* **5**, 310 (1957).
7. L. J. VAN DER TOORN, *Acta Met.* **8**, 715 (1960).
8. M. HILLERT, *Acta Met.* **9**, 525 (1961).