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Elastic Energy and Metastable Phase Equilibria for Coherent Mixtures in Cubic Systems

R. O. Williams

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ELASTIC ENERGY AND METASTABLE PHASE EQUILIBRIA FOR COHERENT MIXTURES IN CUBIC SYSTEMS

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CONTENTS

ABSTRACT 1
INTRODUCTION 1
DECOMPOSITION STRUCTURES 1
ENERGY CONSIDERATIONS 4
TWO-PHASE MIXTURES 5
DISCUSSION 9
SUMMARY AND CONCLUSIONS 12
ACKNOWLEDGMENT 13
REFERENCES 13

ELASTIC ENERGY AND METASTABLE PHASE EQUILIBRIA FOR COHERENT MIXTURES IN CUBIC SYSTEMS

R. O. Williams

ABSTRACT

Expressions have been derived for the elastic energy due to coherency for cubic systems for an isotropic structure and for (100) or (111) habit planes for a lamellar structure. For the metastable equilibria the usual tangent compositions are replaced by compositions that are tangent to the elastic energy curve. For a loss of coherency there is an energy decrease due to the elastic effects and a further decrease associated with compositional changes. Information contained within this treatment permits one to calculate the x-ray diffraction effects for such structures.

INTRODUCTION

It has been known for many years that when solid solutions precipitate a new phase or decompose to a two-phase mixture in a miscibility gap, atomic coherency can cause noteworthy effects. Conventionally, the first process is called precipitation hardening; the second, spinodal decomposition. In the first place, this coherency leads to strengthening effects and in the second place it modifies the phase equilibria because the energy of the system is necessarily increased. Sometimes the new phases are themselves metastable, but in most cases they are the equilibrium phases apart from the modification caused by coherency.

Although many aspects of this problem have been considered, there does not, to our knowledge, exist any treatment that shows how the metastable phase boundaries are to be calculated. This paper provides a solution to this problem for cubic phases.

DECOMPOSITION STRUCTURES

Although many different structures are known to occur as a result of the decomposition of a supersaturated solid solution, we are primarily concerned with only two. Generally, we are concerned with the possible structures that result when both structures are cubic.

If the difference in lattice parameter between the equilibrium phases is small (around 1%) and the interfacial energy is isotropic, the structure may consist of a more or less random collection of spherical particles of the minor phase that are coherent with the matrix. We have represented this structure in Fig. 1, which illustrates precisely what we mean by coherency — an atom-to-atom matching over the interface. For this situation, both phases must be isotropically strained to a common lattice parameter, the smaller phase in tension, the other in compression. As the volume fractions of the two phases become similar, the microstructure must be more complex, perhaps an intermixed Swiss cheese structure. But, as iron-chromium alloys show, isotropy can be maintained to a high degree. Three other systems that exhibit this structure are Cu-Co, Al-Ag, and Al-Zn.

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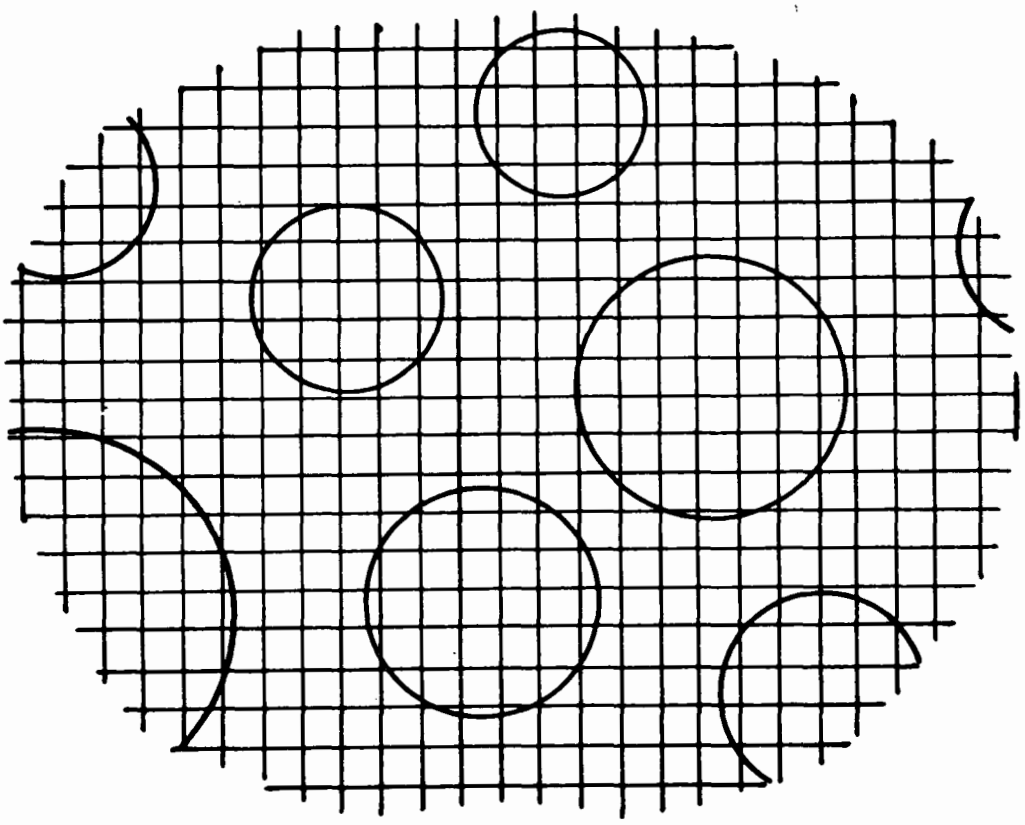

Fig. 1. Isotropic Structure Consisting of a Collection of Spherical Particles of the Minor Phase.

The ideal plate or lamellar structure forms on some habit plane for the simple reason that this drastically reduces the coherency energy, as we will show. This structure is illustrated in Fig. 2. Within a local region all the plates are parallel, but in neighboring regions the other variants will be populated. Although many habit planes may be possible, we are primarily interested in the one that minimizes the energy; thus, we need only consider the (100) and (111) habit planes for the cubic system, as these will give the extreme values for this morphology.

A third structure, called discontinuous or cellular precipitation, is of no direct concern here because its coherency energy is essentially zero. In this structure, phase separation occurs on a relatively coarse scale at a mobile high angle boundary. The process is very similar to the pearlite reaction in the iron-carbon system, being in that case a eutectoid

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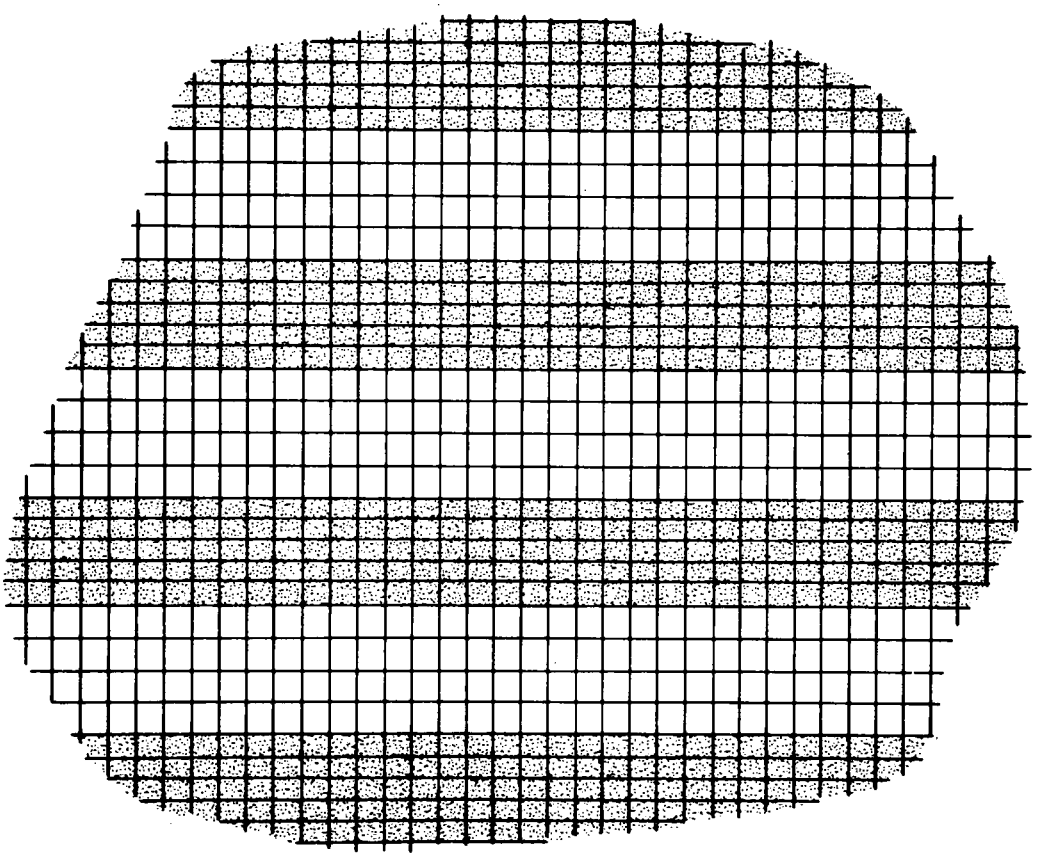

Fig. 2. A Lamellar Structure Consisting of Alternating Plates of the Two Phases. The other variants of the habit plane would be populated in adjacent regions.

reaction. Cellular decomposition may take place in the two-phase field at temperatures above which metastable coherent structures are possible. Cases are also known in which coherent structures are eliminated by this reaction, the driving force being, in part, coherency energy.

ENERGY CONSIDERATIONS

As a starting point we consider the elastic energy density in terms of the strains for the two morphologies.

For the isotropic system the three strains are equal, as are the stresses, such that the stress is given as

$$\sigma = (C_{11} + 2C_{12})\varepsilon \tag{1}$$

and the energy density is given as

$$E = \frac{3}{2}\sigma\varepsilon = \frac{3}{2}(C_{11} + 2C_{12})\varepsilon^2 \ . \tag{2}$$

For the (100) habit plane the cube axes are also the principal stress axes. The two stresses in the habit plane are equal, but the stress normal to the habit plane is zero. This later condition gives the normal strain ε_z as

$$\varepsilon_z = -2\,\frac{C_{12}}{C_{11}}\,\varepsilon_x \tag{3}$$

such that the habit plane stress, σ_x, is given as

$$\sigma_x = [C_{11} + C_{12}(1 - \frac{2C_{12}}{C_{11}})]\varepsilon_x \tag{4}$$

and the energy density as

$$E = [C_{11} + C_{12}(1 - \frac{2C_{12}}{C_{11}})]\varepsilon_x{}^2 \ . \tag{5}$$

For the (111) habit plane, the normal direction is again a principal stress direction (of zero magnitude). Using the set of elastic constants corresponding to this geometry, the solution is given as

$$\varepsilon_z = -2 \frac{C_{12} - H/3}{C_{11} + 2H/3} \varepsilon_x , \tag{6}$$

and

$$\sigma_x = \left[C_{11} + C_{12} + H/3 - 2 \frac{(C_{12} - H/3)^2}{C_{11} + 2H/3}\right]\varepsilon_x , \tag{7}$$

where H, the measure of the elastic anisotropy, is defined as

$$H = 2C_{44} + C_{12} - C_{11} . \tag{8}$$

The energy density is given as

$$E = \sigma_x \varepsilon_x , \tag{9}$$

which can be expressed in terms of the elastic constants and ε_x similar to Eq. 5. For H equal to zero, the equations for the (100) and (111) cases become identical.

TWO-PHASE MIXTURES

Having obtained the required energy density equations in terms of the elastic constants and the strains, our next problem is that of obtaining the strains in the two phases such that we can evaluate the total energy.

Considering first the lamellar structure, if we define the parameter Z in terms of the lattice parameters as

$$Z = \frac{2(a_2 - a_1)}{a_1 + a_2} , \tag{10}$$

where subscripts 1 and 2 identify the two phases, it follows that

$$\varepsilon_1 - \varepsilon_2 = Z \quad , \tag{11}$$

for the strains in the habit plane where for example, if phase 2 has the larger parameter, Z is positive, phase 1 is extended (a positive strain), and phase 2 is compressed so as to obtain the common lattice parameter in the habit plane. Further, the sum of the normal forces across a cut normal to the habit plane is zero, that is,

$$v_1\sigma_1 + v_2\sigma_2 = 0 \quad , \tag{12}$$

where v is the volume fraction of the subscribed phase. If we represent the dependence on the elastic constants as w, that is,

$$\sigma = w\varepsilon \quad , \tag{13}$$

the values of the habit plane strains for the two phases are given as

$$\varepsilon_1 = \frac{v_2 w_2 Z}{v_1 w_1 + v_2 w_2} \tag{14}$$

and

$$\varepsilon_2 = \frac{-v_1 w_1 Z}{v_1 w_1 + v_2 w_2} \quad . \tag{15}$$

The energy density is given as

$$E = v_1 w_1 \varepsilon_1{}^2 + v_2 w_2 \varepsilon_2{}^2 \tag{16}$$

which results in

$$E = \frac{v_1 v_2 w_1 w_1{}^2 Z^2}{v_1 w_1 + v_2 w_2} \tag{17}$$

when the substitution is made.

For the isotropic case, the above equations remain unchanged provided that the value of w is increased by a factor of 3/2.

We show in Fig. 3 the construction which now gives the metastable equilibrium. The free energy curve corresponds to immiscibility and the composition of the equilibrium phases is given as A and B by the common tangent. For the coherent state the equilibrium is determined by the common tangent to the elastic energy curve. Specifically, the elastic energy as given by Eq. 17 is just the height of the shaded area in Fig. 3. That this is the correct construction for the coherent equilibrium results from the fact that no other pair of compositions can result in a lower total free energy. This has been demonstrated analytically.

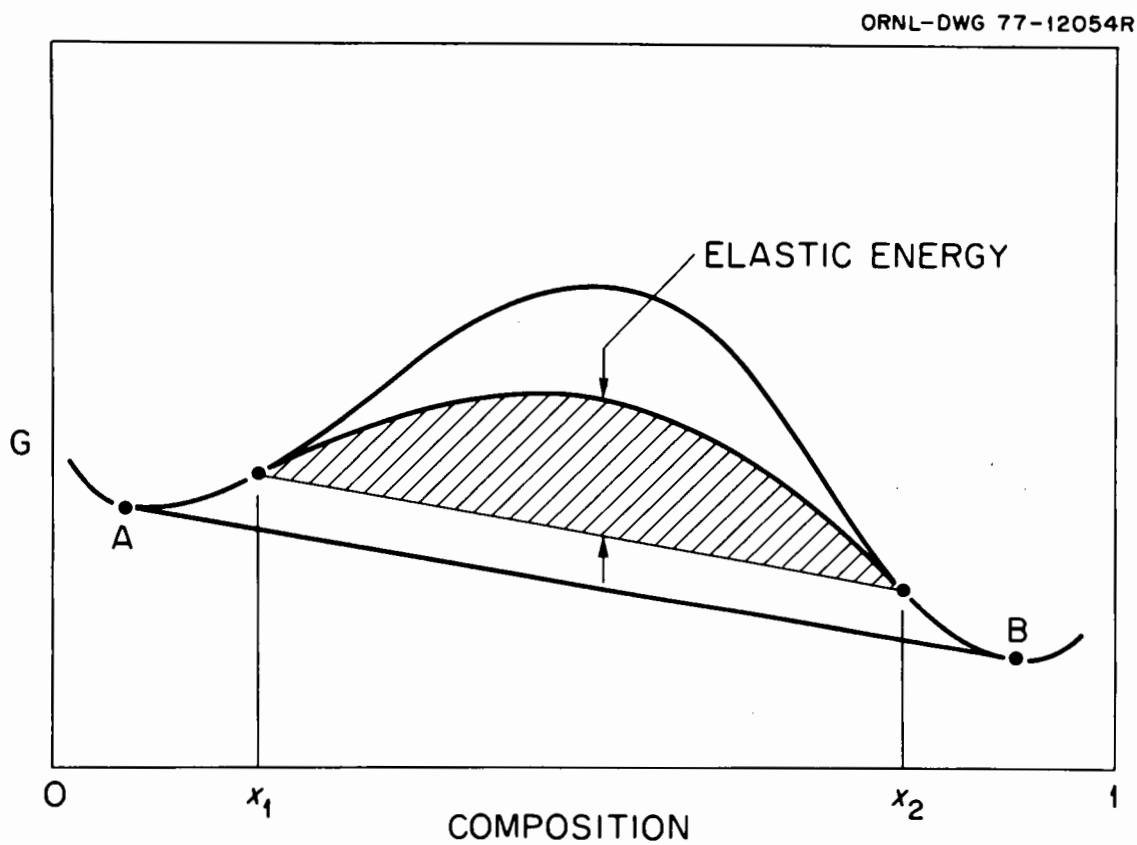

Fig. 3. Construction for Determining the Equilibrium for Coherent Structures. The true equilibrium is given as points A and B determined by the common tangent. The metastable equilibrium is given by the tangents to the elastic energy curve, points X_1 and X_2. The height of the shaded region represents the elastic energy.

Figure 3 further shows that there are two energy changes when coherency is lost. There is the loss of elastic energy and a further free energy decrease that occurs as the equilibrium compositions are obtained.

Analytically, the condition of equilibrium is given as

$$\frac{dG}{dX} - V\frac{dE}{dX} = \frac{G_2 - G_1}{X_2 - X_1} \tag{18}$$

which applies at compositions X_1 and X_2 and where V is the atomic volume. The value of dE/dX may be obtained from Eq. 17, and when valuated at X_1 gives

$$\frac{dE}{dX} = \frac{w_2 Z^2}{X_2 - X_1} \tag{19}$$

and at X_2,

$$\frac{dE}{dX} = \frac{-w_1 Z^2}{X_2 - X_1} \tag{20}$$

when we use

$$v_1 = (X_2 - X)/(X_2 - X_1) \tag{21}$$

and $v_2 = 1 - v_1$. Thus, the evaluation of the metastable equilibrium is not materially more difficult than the general case where one must use an iterative approach to establish the common tangent.

For binary cases where Vegard's law holds, Z may be expressed in terms of X_1 and X_2 such that the evaluation of Eqs. 19 and 20 is somewhat simplified.

The case which we illustrated corresponds to a common free energy curve but nothing in the treatment is changed if the free energy curves are distinct. This occurs, for example, when one of the phases is ordered.

DISCUSSION

What this analysis shows, when applied to a system showing a miscibility gap, is that there are three coherent miscibility gaps which divide the equilibrium gap into four regions as in Fig. 4. Only discontinuous precipitation is possible in region I, precipitation on the (100) and (111) habit planes is only possible within the respective gaps, and the isotropic structure is only possible within the lowest gap. Taking the elastic constants as composition independent, the relative position of the (100) and (111) gaps are determined by the anisotropy factor; for the isotropic materials they coincide. Based upon the data of Simmons and Wang[1] all cubic metals favor the (100) habit plane except V, Cr, Nb, and Mo, all of which are bcc and occur together in the periodic table.

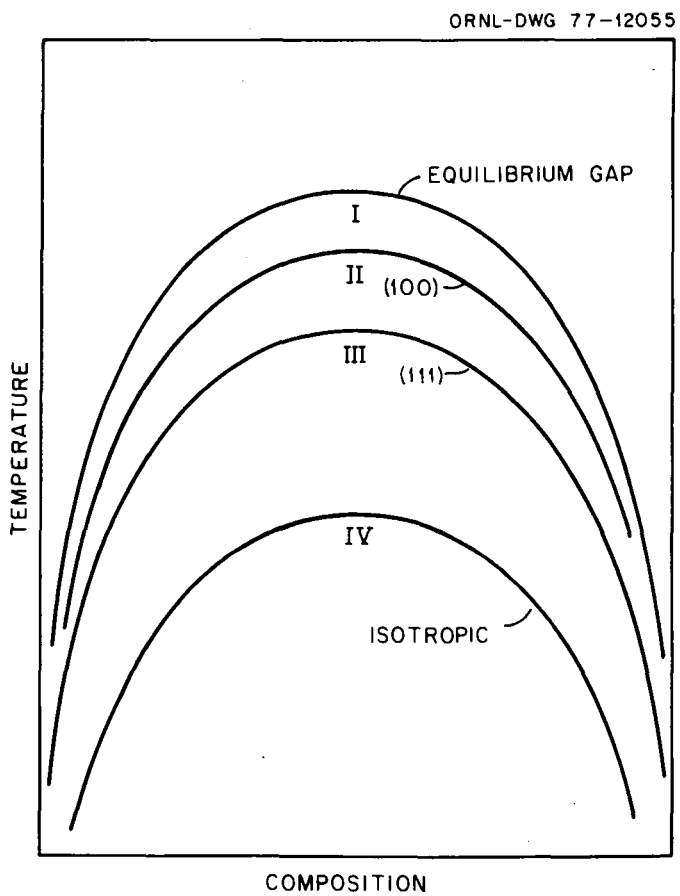

Fig. 4. The Three Coherent Miscibility Gaps. The drawing is scaled to correspond to the elastic constants of copper, but the results are reasonably typical.

The energy of either the (100) or (111) structures relative to the isotropic case is somewhat more complicated. Specifically, this ratio is between 0.15 and 0.18 for Ag, Au, Cu, Pd, and Pt for E_{100}/E_{iso}. A value of 0.19 was calculated for E_{111}/E_{iso} for niobium. Chromium exhibits near extremes for both ratios, 0.54 and 0.45, respectively. In terms of isotropic elasticity, a small ratio corresponds to a low Poisson's ratio.

For a miscibility gap for metals for which the sign of the anisotropy differs, the (100) and (111) curves will cross such that the predicted habit plane differs on the two ends of the diagram. Because it contains a disproportionate fraction of the energy, the minor phase determines the habit plane. Specifically for the uranium-niobium system that exhibits a miscibility gap in the bcc phase, the uranium-rich alloys should exhibit a (111) habit and the (100) habit should be favored for niobium-rich alloys.[2]

The method which we have given is applicable to higher order systems provided that the composition differences are now recognized as being tie line lengths. Specifically, one picks two compositions defining a tie line which passes through a fixed point in the two-phase region which minimizes the free energy at that point when the elastic energy is included. If one has a program which determines tie lines in this manner, the inclusion of the elastic energy is a very minor complication.

Phase equilibria studies for the bcc phase in the ternary system U-Zr-Nb have been conducted.[2] Each binary contains an assymetric miscibility gap and the elastic energy is of importance in each case, particularly for the zirconium-niobium system. Calculations in the ternary system which include the elastic energy have been carried out. It is interesting that in ternary and higher order systems, thermodynamic stability can be investigated along tie lines of constant lattice parameter where the elastic energy is zero. Such tie lines must always exist. Such calculations for the U-Zr-Nb system indicated a large central region in the ternary system where decomposition is possible.

Earlier, Cahn[3] had considered the importance of elastic anisotropy on the nature of spinodal decomposition. The elastic density equations that can be obtained from his work are exactly the same as ours but for a

factor of 1/2. This factor arises from his considering the average energy density for a sine composition fluctuation in terms of the maximum strain. Cahn's treatment provided the expression which gave the spinodal compositions.

As already indicated, there are a few systems known that give the isotropic structure. Such systems are limited to those having a small difference in lattice parameter (less than two percent). There are a number of systems, including Au-Pt, Cu-Ni-Co, and Cu-Ni-Fe, that appear to closely approximate the ideal (100) structure. There are many systems that form plates, but the tendency for adjacent plates to be parallel is not too great. Such structures must have an elastic energy higher than for the ideal plate structure, but the difference may be modest. In particular, the importance of parallelism decreases as the volume fraction of the minor phase decreases. The simple cubic arrays of cubes which is commonly seen in nickel-base alloys which form Ni_3Al must also have an elastic energy greater than predicted for the (100) habit plane. Cahn considered this to be the structure that his analysis predicts for the (100) softness or habit plane.[3]

We have not included the thermoelastic effect in our calculations. To a first approximation this effect cancels, being of similar magnitude but of opposite sign in the two phases. Further, this effect is linear with stress and becomes relatively less important at high stresses compared to elastic energy which is quadratic with stress.

In our derivation we have given the expressions required to calcuate strains normal to the habit planes. These are important for calculating the x-ray diffraction effects from such structures. X-ray calculations can be done rather simply by considering a large unit cell of the usual dimensions in the habit plane but extending through one or more periods of the structure normal to the habit plane. The normal strains are used to position the atoms in this structure and the average scattering power is determined by the compositions. Possible ordering in one of the phases is easily accommodated. The intensity is calculated by standard methods. However, the final intensity results from averaging the intensities for all variants of the habit plane.

One can translate such structures into sets of parameters that describe the short-range order and the displacements and can calculate the intensity using the standard expression for the diffuse scattering for alloys. There is nothing wrong with this approach, but the above method is much easier. In particular, the first method does not suffer from termination effects which will surely be encountered using diffuse scattering calculations. For the isotropic structure, the later method is more attractive because, ideally, the displacements are zero.

Tien and Copley[4] have considered the effect of stress on changing the morphology of the Ni-Ni_3Al structure at elevated temperatures. The anologous predictions for the plate structures are made in terms of the parameter

$$(v\varepsilon_z)_1 + (v\varepsilon_z)_2 \quad . \tag{23}$$

The size of this term will be very small compared to the magnitude of its components, but it need not be zero. If, for example, this parameter is negative, a normal compressive stress would enhance the amount of material populating this particular habit plane among its variants. The effect should operate during decomposition or during subsequent annealing.

SUMMARY AND CONCLUSIONS

1. Equations for calculating the elastic energy due to coherency have been derived for cubic phases.

2. Cases considered are the isotropic structure, and the (100) and (111) habit planes for plate structures.

3. The plate structures will always be of lowest energy, the particular habit plane being determined by the anisotropy factor in agreement with the work of Cahn.[3]

4. Because of the compositional dependence of the elastic constants, it is possible that in some systems the habit plane will change with composition.

5. When the lattice parameter difference is sufficiently small, the isotropic structure can form.

6. For the metastable equilibria the common tangent construction is replaced by the anologuous construction using the elastic energy curve. This calculation is not materially more difficult than the standard calculation. It also applies to systems of higher order.

7. From the parameters used in this formulation it is possible to carry out calculations of x-ray diffraction using a unit cell sufficiently large to represent the structure.

8. Loss of coherency is accompanied by an elastic energy decrease plus a free energy change resulting from compositional changes.

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REFERENCES

1. G. Simmons and H. Wang, *Single Crystal Elastic Constants,* MIT Press, Cambridge, Mass., 1971.
2. R. O. Williams, to be published in *Journal of Nuclear Material.*
3. J. H. Cahn, *Acta Metall.* 22: 179 (1962).
4. J. K. Tien and S. M. Copley, *Metall. Trans.* 2: 215 (1971).

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