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Thermodynamic study of the effect of a ternary addition on antiphase boundaries in FCC alloys

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Abstract. Antiphase boundaries play an important role when considering the mechanisms involved in the plastic deformation of a face-centred cubic alloy. We consider in this paper (100) antiphase boundaries in a binary $L1_2$ ordered alloy to which a small amount of ternary element is added. The scope of this work is to study the behaviour of the ternary element at the antiphase boundary (segregation, effect on the energy of the antiphase boundary) and to determine general simple rules that can help to predict this behaviour.

1. Introduction

When a disordered alloy exhibits a first-order transition, two kinds of interfaces between two ordered or ordered/disordered domains may occur: antiphase boundaries (APB) and interphase boundaries (IPB). An APB occurs when the interface separates two domains of the same ordered phase, whereas an IPB occurs when the interface separates two domains of different phases (either ordered/ordered or ordered/disordered). An APB may result from the ordering process having started from two different sites of the crystal without the symmetry of the crystal being kept at the interface of the two domains created. Another cause for the creation of an APB is the existence or motion of dislocations whose Burgers' vector is not a translation vector of the superlattice. These dislocations appear upon plastic deformation of the material; the first dislocation creates an APB while the trailing dislocation restores the long-range order. Because this mechanism plays an important role when considering the mechanical properties of an ordered alloy, many studies (either theoretical or experimental) on APB have been carried out on this subject.

We will consider in this study $\frac{1}{2}[110](100)$ APB occurring in an $A_3B L1_2$ ordered alloy. Such an APB is called a non-conservative APB because of the existence of AABB tetrahedra at the interface, whereas conservative APB like a $\frac{1}{2}[011](100)$ APB keep all the tetrahedra in a three A–one B configuration (figure 1). Kikuchi and Cahn (1979) studied APB and IPB using a cluster variation method (CVM) in the tetrahedron approximation. They have shown the existence of a layer of disordered phase at the APB, the thickness of which increases with temperature. They called this phenomenon the wetting of the APB by a disordered phase. They also pointed out that at temperatures close to the transition temperature T_0 the APB consisted in fact of two IPB: one IPB between one variant of the ordered phase and the disordered phase, and one IPB between the disordered phase and the other variant of the ordered phase. More recently, Finel *et al* (1990) showed that in the tetrahedron CVM approximation the wetting process consisted of what they called 'layering transitions'. As the temperature increases, one plane on each side of the APB gets disordered through a first-order transition. However, Finel (1992) pointed out that these transitions were due to

the tetrahedron approximation of the CVM and that they no longer appeared when using a tetrahedron–octahedron CVM. The properties of conservative (111) APB in $L1_2$ ordered alloys have been studied by Sanchez *et al* (1987) using a tetrahedron CVM. They have shown that at thermal equilibrium (111) APB are also wetted by a disordered phase and studied non-relaxed APB created by shearing. A following study by Wu *et al* (1989) discussed the effect of microsegregation on (111) APB in ternary $L1_2$ ordered alloys. As a matter of fact, the addition of a ternary element to a reference binary alloy may have a considerable effect on the mechanical properties of this alloy, this effect being related (among other phenomena) to the behaviour of the element with respect to the APB (segregation, variation of the APB excess free energy). However, systematic studies of this problem are still scarce owing to the amount of work involved. Since the study of Marty *et al* (1991), we know that the CVM may allow us to define some pertinent simple parameters for the purpose of predicting the effect of the addition of small quantities of a ternary element to a binary $L1_2$ ordered alloy. The purpose of this paper is to expand the previous study to APB. Its aim is to reduce the whole problem of the simulation of APB to simple general rules or statements allowing the prediction of the behaviour of the added element with respect to the APB, at least qualitatively. Owing to the amount of calculations involved in a tetrahedron–octahedron CVM when considering a ternary alloy, the APB were simulated using a tetrahedron CVM. However, the artifacts this approximation produces are only relevant to the wetting process and hence do not affect the validity of our results.

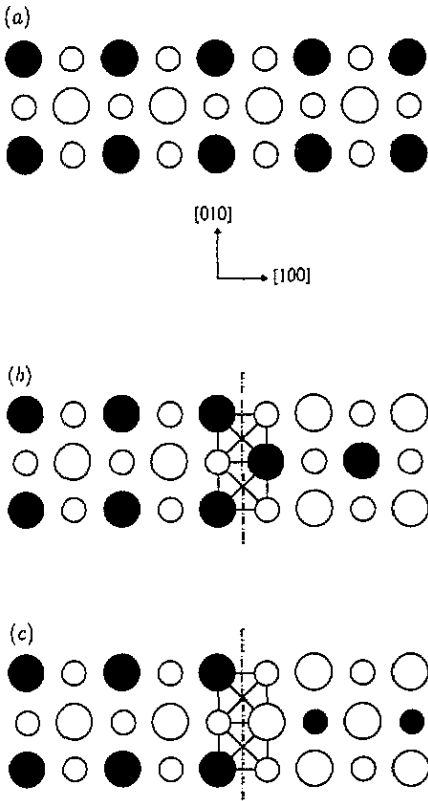


Figure 1. (a) The $L1_2$ ordered A_3B bulk. White circles represent A atoms, black circles B atoms. Small circles represent atoms at altitude $z = 0$, big circles atoms at altitude $z = 0.5$. (b) A non-conservative $\frac{1}{2}[110](100)$ APB. This APB induces AABB tetrahedra at the interface. (c) A conservative $\frac{1}{2}[011](100)$ APB. This APB does not induce any AAB tetrahedra at the interface.

2. Formalism

The APB is simulated using the cluster variation method (CVM) in the tetrahedron approximation considering first-neighbour interactions. The chain of tetrahedra shown in figure 2 is sufficient to describe the whole APB. The chemical description of any atomic position can be obtained from this chain by applying a lattice translation vector parallel to the APB interface plane. The APB is thus characterized by the probabilities of configurations of the tetrahedra, as well as the probabilities of configurations of their subclusters. We shall denote the tetrahedra configuration probabilities $t_{n,i}$, i being the i th configuration of a tetrahedron (i.e. AAAA, AAAB, etc.) and n the position of the tetrahedron in the chain of tetrahedra. The probabilities of the subclusters are denoted as shown in figure 3: $y_{n,i}$ is the probability of the i th pair configuration on the right of the n th tetrahedron, $x_{n,j,i}$ is the probability of the i th pair configuration for the j th pair inside the n th tetrahedron (j ranging from 1 to 4) and $u_{n,i}$ ($v_{n,i}$) is the probability of the i th point configuration of the n th point belonging to the lower layer of the chain of tetrahedra (upper layer). These probabilities can also be denoted as vectors; for example, t_n denotes the configuration probabilities of the n th tetrahedron.

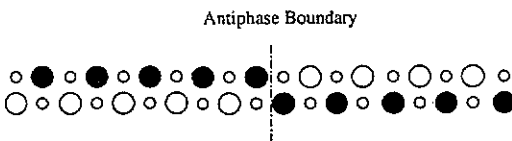


Figure 2. The tetrahedra chain forming the antiphase boundary.

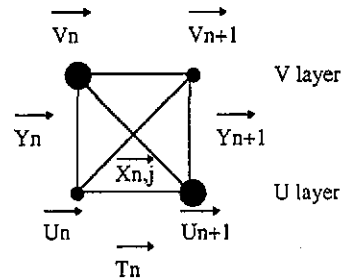


Figure 3. Notation for probabilities of each tetrahedron and its subclusters.

Considering these probabilities, the free energy of the APB is given by the following relation:

$$\beta G = 2 \sum_{n,i} \beta E t_{n,i} + 2 \sum_{n,i} L(t_{n,i}) - 2 \sum_{n,i} L(y_{n,i}) - \sum_{n,j,i} L(x_{n,j,i}) + \frac{5}{4} \sum_{n,i} L(u_{n,i}) + \frac{5}{4} \sum_{n,i} L(v_{n,i}) \quad (1)$$

where E is the energy matrix taking into account effective pair interaction energies and chemical potentials, and L the operator that associates $x(\ln(x) - 1)$ to x .

The CVM approximation consists then of minimizing (1) over the set of tetrahedra configuration probabilities. All subcluster configuration probabilities can be calculated from the tetrahedra configuration probabilities through a matrix relationship (for example, to calculate a pair configuration probability, one has to sum all the tetrahedra configuration probabilities for the tetrahedron configurations containing the considered pair configuration). Nonetheless, a problem arises from the choice of probabilities of tetrahedra configurations as the variable working set. Since two tetrahedra overlap by a pair, there exists a constraint on

the probabilities of next-neighbour tetrahedra configurations. This problem could be solved by introducing Lagrange multipliers, but this would reduce the efficiency of the minimization process as well as its accuracy. Considering the overlapping pair configuration probabilities, it is possible to define a set of unconstrained variables consisting of probabilities of tetrahedra configurations and of overlapping pair configurations y_n . This set is made explicit in the appendix. The only constraint existing is due to the fact that long-range order far from the APB must meet the one observed in the bulk. For this reason, the first and last pair configuration probabilities y_1 and y_{p+1} (where p is the total number of tetrahedra along the chain) are set to values calculated from homogeneous CVM calculations carried out for the ordered phase. These probabilities are removed from the set of variables and kept constant during the minimization process, thus ensuring that the chemical profile of the APB meets the bulk at the end of the chain of tetrahedra. The minimization process of the free energy of the APB is carried out in the grand canonical ensemble with constant chemical potentials. The composition of the ternary ordered alloy is chosen when calculating the homogeneous CVM, this calculation giving out as a result the tetrahedra configuration probabilities for the bulk and the chemical potentials corresponding to the chosen composition. The energy matrix E is then calculated using these values of the chemical potentials, and after the minimization process (a Newton–Raphson algorithm) the chosen concentrations are equal to the concentrations found at both ends of the chain of tetrahedra. To ensure that no artifact comes out from this constraint, it has been checked for every calculation that the values found for the ordered bulk tetrahedron configuration probabilities did not vary for a few tetrahedra on each side of the chain, i.e. that the number of tetrahedra taken into account was sufficient for the APB chemical description to meet the bulk at both ends of the chain without forcing the system to do so. Typically, the length of the chain ranges from 40 tetrahedra to 80, depending on the temperature. Nonetheless, since in the grand canonical ensemble the bulk is considered as an endless source of each element, the energy parameters considered have to be realistic. If not, a considerable amount of ternary element may segregate at the APB (and the calculations diverge) or, on the contrary, such a small amount of ternary element is present at the APB that the logarithm of probabilities diverges. The physical meaning of this consideration is that the transition temperature of the binary alloys AC and BC must be realistic and not differ from each other by more than approximately 1000 K. The excess free energy of the APB is then calculated as the difference of the free energy of the APB minus the free energy of a chain of tetrahedra of the same length in the ordered phase. As for this excess free energy, the absorption of an element is the sum of point occupancies for the whole chain of tetrahedra minus the sum of point occupancies for the same chain considered in the ordered bulk. The absorption is thus expressed in excess number of atoms per surface unit.

3. Results

The study carried out by Marty *et al* (1991) on the thermodynamics of dilute ternary FCC alloys involves a virial expansion of the CVM. Rewriting this formalism in the case of an APB is difficult, and as we shall demonstrate later, many properties of an APB depend only on homogeneous phase characteristics for which the virial expansion has been fully developed. Nonetheless, there is little difficulty in applying the basic principle of the virial expansion to the case of the APB. If we consider a very small amount of added ternary element C, then we can assume that only the probabilities of configurations involving at most one atom C are non-negligible. It is in fact necessary to proceed to such an expansion when considering

small concentrations since the probability for the CCCC tetrahedron configuration is so close to zero that the calculation diverges. It has then been pointed out by Marty *et al* (1991) that all the energies of the tetrahedron configurations involving one atom C could be rewritten in terms of symmetric and antisymmetric variables. Let us consider the three effective ordering pair interaction energies J_{AB} , J_{AC} and J_{BC} defined from the pair interaction potentials from the following equation:

$$J_{XY} = (V_{XX}^1 + V_{YY}^1 - 2V_{XY}^1)/4 \quad (2)$$

where V^1 is a first-neighbour pair interaction potential.

J_{AB} is a constant parameter characterizing the binary A_3B alloy to which the C element is added. Symmetric and antisymmetric pair energies can then be defined as follows:

$$\begin{aligned} S &= J_{AC} + J_{BC} \\ D &= J_{AC} - J_{BC}. \end{aligned} \quad (3)$$

The energy dependence of the tetrahedron configurations including one atom C is summarized in table 1. The first column express the energy contribution from pair interactions of a configuration with respect to the effective ordering pair energies, the second column with respect to J_{AB} , S and D .

Table 1. Energy contributions of tetrahedron configurations including one atom C.

Configuration	Energy contribution
AAAC	$-3J_{AC} \quad -3S/2 - 3D/2$
AABC	$-2J_{AC} - J_{BC} - 2J_{AB} \quad -3S/2 - D/2 - 2J_{AB}$
ABBC	$-J_{AC} - 2J_{BC} - 2J_{AB} \quad -3S/2 + D/2 - 2J_{AB}$
BBBC	$-3J_{BC} \quad -3S/2 + 3D/2$

Each of these configurations involves a term $-3S/2$ and, whatever the value of S , it cannot stabilize one configuration more than another one. Thus, when considering a small amount of added element, the behaviour of C will only depend on the antisymmetric variable D . From this conclusion, Marty *et al* (1991) defined an energy parameter J controlling the behaviour of the added element, this parameter being the antisymmetric variable normalized by J_{AB} :

$$J = (J_{AC} - J_{BC})/J_{AB}. \quad (4)$$

From now on the symmetric variable S will be redefined as:

$$S = (J_{AC} + J_{BC})/J_{AB} \quad (5)$$

for coherency purpose.

For any further calculation, the effective ordering pair interaction energy of the reference binary alloy A_3B will have the value $J_{AB} = 1.0$. In the tetrahedron approximation, the ordering temperature is given by $kT_0 = 1.94J_{AB}$. Except when noted explicitly, the temperature considered for the calculations is $kT = 1.6J_{AB}$.

The ratio of the calculated values of the absorption of the added ternary element C (from now on denoted Γ_c) to C_c^\dagger are plotted against J on figure 4 for two concentrations of C in the ordered bulk. The derivatives of Γ_c with respect to S and J have been analytically calculated for $C_c = 0.1\%$, and were found respectively to be of the order of 10^{-9} and 10^{-2} , thus proving what was previously asserted. The behaviour of C varies with respect to J ; when Γ_c is positive (domain centred on $J \sim 0$) the ternary element segregates at the APB; on the contrary, when Γ_c is negative the ternary element is rejected outside the APB in the ordered bulk. A maximum of the absorption is obtained for $J \sim 0$ for the stoichiometric A_3B case. To study the change of behaviour of the C element when considering off-stoichiometric cases, Γ_c has been calculated for a binary alloy with an A element depletion. The absorption maximum is shifted to higher values of J (for a B element depletion it is shifted to lower values of J) but the points where $\Gamma_c = 0$ are obtained for approximately the same values of J . To check if this phenomenon depends on the configuration expansion, the absorption Γ_c has been calculated for $C_c = 3\%$ by considering the whole set of tetrahedra configurations. The absorption profile does not essentially differ from the ones presented previously, and the points where $\Gamma_c = 0$ are found at the same values of J .

- Γ_c/C_c for $C_c=3\%$, stoichiometry A_3B
- ◻ Γ_c/C_c for $C_c=0.1\%$, binary composition: $C_a=0.74$; $C_b=0.26$
- Γ_c/C_c for $C_c=0.1\%$, stoichiometry A_3B

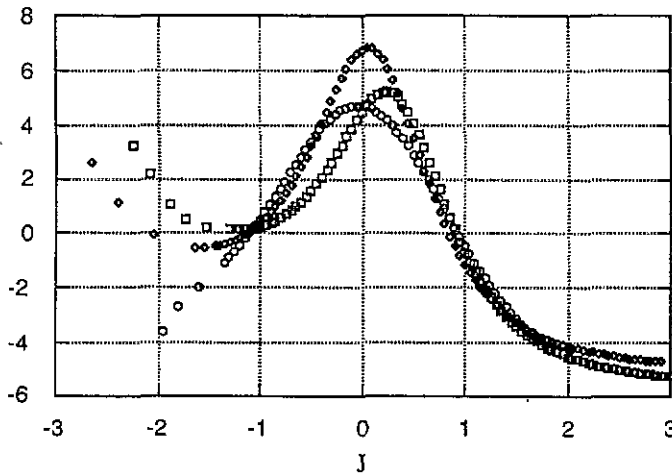


Figure 4. Absorption Γ_c calculated as a function of J for several values of the C element concentration in the ordered bulk. The plot calculated at $C_c = 3\%$ has been calculated over the whole set of tetrahedron configurations with $S = 1$. Spaced dots point out the domains where the calculations diverge.

A chemical profile calculated at $C_c = 3\%$ and $J = 0.725$ is shown on figure 5. The APB takes place at the 21st tetrahedron. The point occupancies of the element C follow the $L1_2$ symmetry, the nature of the occupancy of the two layers U and V swapping at the APB. A mean occupancy has been calculated for each tetrahedron in order to define a concentration

† We have divided by C_c so as to compare different plots on a more equal basis. The absorption is, however, expressed in terms of excess number of atoms per surface unit of the APB and is not a concentration.

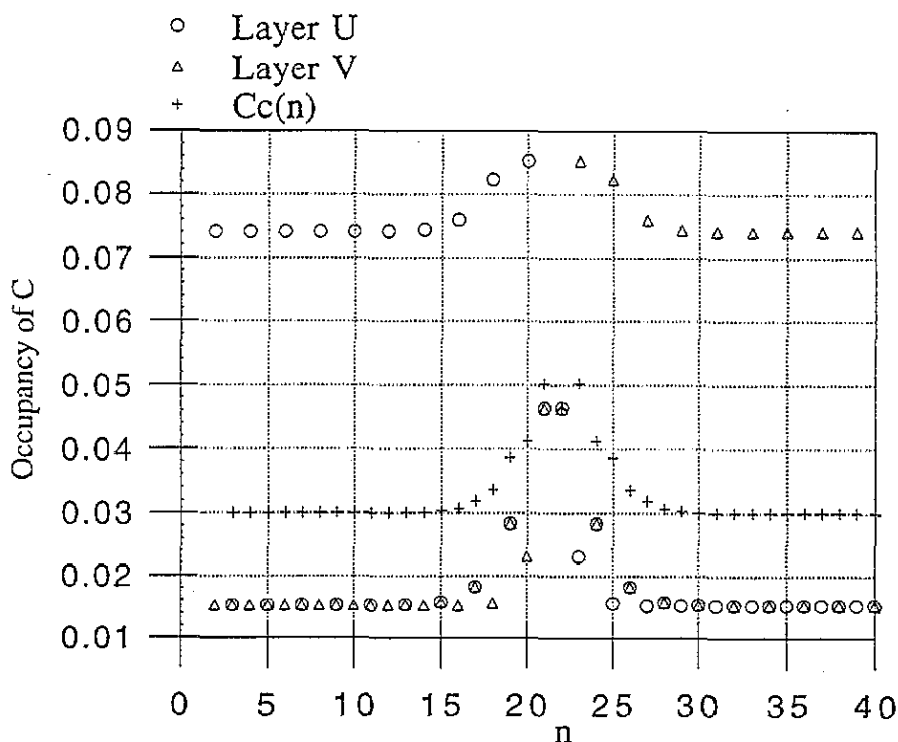


Figure 5. Chemical profile calculated for $C_c = 3\%$ and $J = 0.725$. The point occupancies of the element C have been plotted for the two layers U and V as a function of n (see figure 3). A mean occupancy $C_c(n)$ has been calculated for each tetrahedron from the formula: $C_c(n) = (U_{n,3} + U_{n+1,3} + V_{n,3} + V_{n+1,3})/4$.

profile at the APB. This result illustrates what happens at the APB although a concentration profile would require a much larger APB in order to be able to define a local concentration.

This result would tend to show that the knowledge of J is sufficient to determine at least qualitatively whether the added element will segregate at the APB or if it will be rejected in the ordered bulk. Nonetheless, it must be pointed out that J itself is not necessarily a good parameter for the purpose of predicting the behaviour of the added element at the APB:

(i) The case considered for the full tetrahedra configuration probabilities involved antiferromagnetic interactions for AC and BC pairs (i.e. $S > 0$). In the case where both AC and BC pair interactions are ferromagnetic (i.e. $S < 0$), C will have a tendency to cluster and the probabilities of the configurations involving one atom C might be smaller than the probabilities of configurations involving more atoms C. This means that the configuration expansion carried out is not necessarily valid when considering ferromagnetic AC and BC pair interactions.

(ii) J is a parameter calculated from effective pair interaction potentials in a ternary alloy. It is possible to determine these pair potentials from measurements of the atomic correlation functions using special experimental techniques (neutron diffraction on single crystals with different isotopic compositions or x-ray anomalous scattering using a synchrotron radiation source), but the data available are restricted to very few alloys, thus drastically restricting the general use of J for any ternary alloy.

However, the pertinence of J in the considered cases will allow us to draw more general conclusions from our study, these conclusions making it possible to predict the behaviour of the added element without the knowledge of any particular pair interaction data.

Let us consider a hypothetical chemical profile across the APB as shown on figure 6. This profile implies that it is possible to define a concentration anywhere in the APB. For the moment, we will assume that the APB is wide enough for the definition of local concentration to be meaningful. In the previous calculations (figure 5) the APB was too narrow for this to be the case, but it is anticipated that in the limit the two descriptions will converge. On both sides of the APB, the concentration of an element is equal to the concentration of this element in the ordered bulk. At the APB, it is equal to the concentration in the disordered phase (in figure 6, the concentration in the disordered phase is higher than the concentration in the bulk). Between the two, a reorganization takes place. The number of planes occupied by the disordered phase will be denoted n , and the number of planes for which the reorganization occurs will be denoted l .

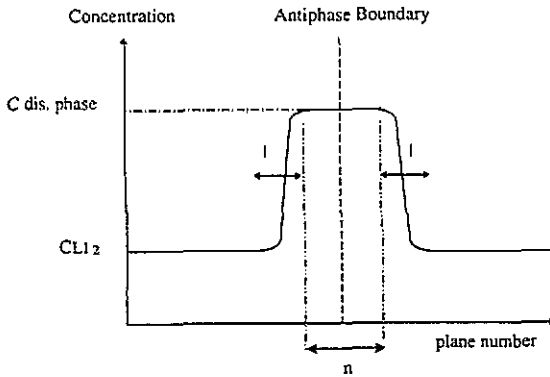


Figure 6. Simplified chemical profile at the APB: n is the number of planes occupied by the disordered phase and l the number of planes for which the reorganization takes place.

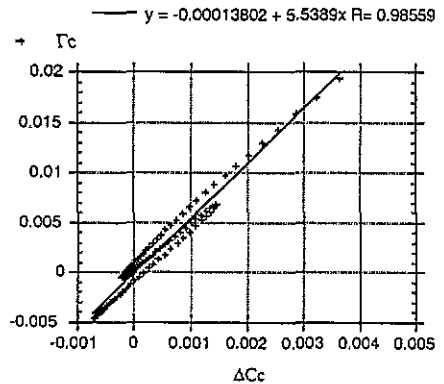


Figure 7. Γ_c as a function of ΔC_c . The curve consists of three line segments whose slopes are nearly equal. The linear regression shows that the constant term is equal to zero, i.e. $\Gamma_c(0) = 0$.

We assume that:

(i) the disordered phase at the APB is the disordered phase whose energy is the closest to the one of the ordered phase—in that case, we will consider that the disordered phase is the FCC phase;

(ii) there is no reorganization between the disordered phase at the APB and the bulk (i.e. the chemical profile is a top-hat function).

Then we can calculate Γ_a , Γ_b and Γ_c from the concentrations of the two homogeneous phases L_{12} and FCC:

$$\begin{pmatrix} \Gamma_a \\ \Gamma_b \\ \Gamma_c \end{pmatrix} = n \begin{pmatrix} C_a(\text{FCC}) - C_a(L_{12}) \\ C_b(\text{FCC}) - C_b(L_{12}) \\ C_c(\text{FCC}) - C_c(L_{12}) \end{pmatrix} = n \begin{pmatrix} \Delta C_a \\ \Delta C_b \\ \Delta C_c \end{pmatrix}. \quad (6)$$

Since the considered temperature is below the transition temperature, the FCC phase is metastable. It is possible to calculate the characteristics of this homogeneous FCC metastable

phase for the same temperature and chemical potentials at which the APB has been calculated. This makes it possible to calculate the difference of concentrations appearing in (6) as a function of J . Since J yields Γ_c and ΔC_c , Γ_c as a function of ΔC_c can be plotted by considering J as a curvilinear abscissa (figure 7). The curve consists of three line segments whose slopes are nearly equal, and as the temperature increases, the curve tends towards an exact line. A linear regression over the whole set of points shows that the relation $\Gamma_c = n\Delta C_c$ is satisfied apart from the fact that the coefficient is not an integer but a real coefficient taking into account the influence of reorganization. Hence, this real coefficient will be denoted k . The relation (6) has now to be verified for Γ_b and Γ_a . A plot of Γ_b against ΔC_b is shown on figure 8. If (6) was fully satisfied, the constant term of the linear regression should be zero. This constant term being non-zero is due to the reorganization neglected in expression (6), and we shall write the relation between Γ_b and ΔC_b as follows:

$$\Gamma_b = k\Delta C_b + X_b \tag{7}$$

where X_b is the constant term.

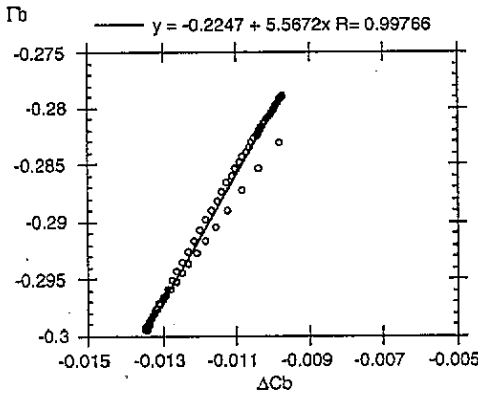


Figure 8. Γ_b as a function of ΔC_b . The linear regression shows that the slope is the same as the coefficient k obtained in figure 6 and that the constant term is non-zero.

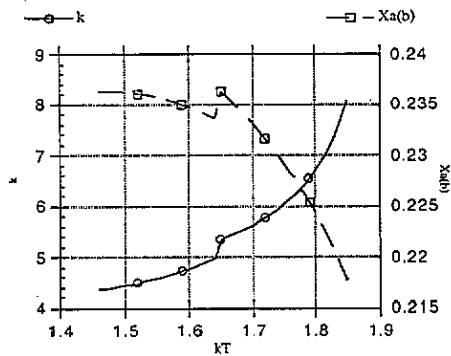


Figure 9. $k^0 = \Gamma_c/\Delta C_c$ and X_a^0 as functions of temperature. Discontinuities are due to a layering transition.

Since we have $\Gamma_a + \Gamma_b + \Gamma_c = 0$ and $\Delta C_a + \Delta C_b + \Delta C_c = 0$, necessarily $X_a + X_b + X_c = 0$ and since $X_c = 0$ we have then:

$$X_a = -X_b. \tag{8}$$

Moreover, if the amount of ternary element added to the reference binary alloy is small enough to consider that its influence on Γ_a and Γ_b is negligible, then the values of the coefficients k and X_x are imposed by the APB chemical profile in the binary reference alloy, and we can write:

$$\begin{pmatrix} \Gamma_a \\ \Gamma_b \\ \Gamma_c \end{pmatrix} = k^0 \begin{pmatrix} \Delta C_a \\ \Delta C_b \\ \Delta C_c \end{pmatrix} + \begin{pmatrix} X_a^0 \\ X_b^0 \\ 0 \end{pmatrix} \tag{9}$$

where k^0 , X_a^0 and X_b^0 are calculated considering an APB in the reference binary alloy, k^0 being a coefficient related to the number of planes occupied by the disordered phase and

X_x^0 a term related to the reorganization between the ordered phase and the disordered FCC phase.

The two coefficients k^0 and X_a^0 have been plotted as functions of temperature on figure 9 for a stoichiometry A_3B of the binary reference alloy with k^0 calculated from the relation $k = \Gamma_c/\Delta C_c$. Calculations start at the spinodal ordering temperature for the binary A_3B alloy, which is $T_s = 1.451J$ (below this temperature, considering a homogeneous disordered phase has no physical meaning). Both curves show a logarithmic shape. When the temperature increases, the number of planes occupied by the disordered plane increases and so does the coefficient k^0 . The reorganization length l also increases but remains finite, this being due to the first-order character of the transition. Since the reorganization length l remains finite while the width of the APB diverges, its effect tends to be smaller and thus X_a^0 decreases when the temperature increases. The logarithmic divergence of these quantities when approaching the transition temperature is characteristic of the wetting process, as shown by Finel *et al* (1990).

The most important information implied by (9) is the following: at the transition temperature, the difference ($\Delta C_a, \Delta C_b, \Delta C_c$) is the difference of concentrations between the ordered phase and the stable disordered FCC phase. Thus the difference ($\Delta C_a, \Delta C_b, \Delta C_c$) is the tie-line relating the ordered $L1_2$ phase to the FCC phase on the A,B,C phase diagram. If the temperature at which the APB is considered is not too distant from the transition temperature and since the coefficient k^0 is always positive, the behaviour of the added element can be directly known from reading the tie-line on the phase diagram.

Another aspect of the effect of the ternary addition on an APB is the stabilization of the APB, i.e. does the ternary addition decrease or increase the APB excess free energy? The difference of excess free energies $\beta G(t) - \beta G(b)$ (where $\beta G(t)$ and $\beta G(b)$ are the excess free energies of the APB in the ternary and binary alloys) has been plotted in figure 10 against J for two concentrations $C_c = 0.1\%$ and $C_c = 3\%$. It can be noted that for values of J above 0.5 the APB is destabilized by the addition for $C_c = 0.1\%$ (positive difference of excess free energies) whereas it is stabilized (negative difference of excess free energies) for $C_c = 3\%$. However, the added element segregates at the APB in both cases, as can be seen from figure 4. This leads to the conclusion that the behaviour of the added element cannot be directly related to the stabilization or destabilization of the APB. As a matter of fact, whereas the symmetric energy variable S has no influence on the behaviour of the added element, it still modifies the energies of the tetrahedron configurations including at least one atom C. The probabilities of these configurations increases with the concentration C_c . Thus the energy of the defect varies with the amount of added element whereas the behaviour does not. Nonetheless, if we consider that the APB is indeed an equilibrium between the ordered and disordered phases separated by two interphase boundaries, the variation of the excess free energy of the APB upon adding the ternary element can be approximated as follows:

$$\beta G(t) - \beta G(b) \sim k\{[\beta G_{FCC}(t) - \beta G_{L1_2}(t)] - [\beta G_{FCC}(b) - \beta G_{L1_2}(b)]\} \quad (10)$$

where k is the coefficient appearing in (7) and βG_x is the free energy per unit area of a $[100]$ plane of the phase x .

The expression (10) is exact only if the chemical profile is a top-hat function. $\beta G(t) - \beta G(b)$ and $k\{[\beta G_{FCC}(t) - \beta G_{L1_2}(t)] - [\beta G_{FCC}(b) - \beta G_{L1_2}(b)]\}$ have been plotted against J in figure 11. The two curves are nearly identical apart from the small discrepancies due to the reorganization which has been neglected. Thus, the knowledge of the free energies of the homogeneous ordered and disordered phases of the binary and ternary alloys is sufficient to conclude whether the APB is stabilized or destabilized by the ternary addition.

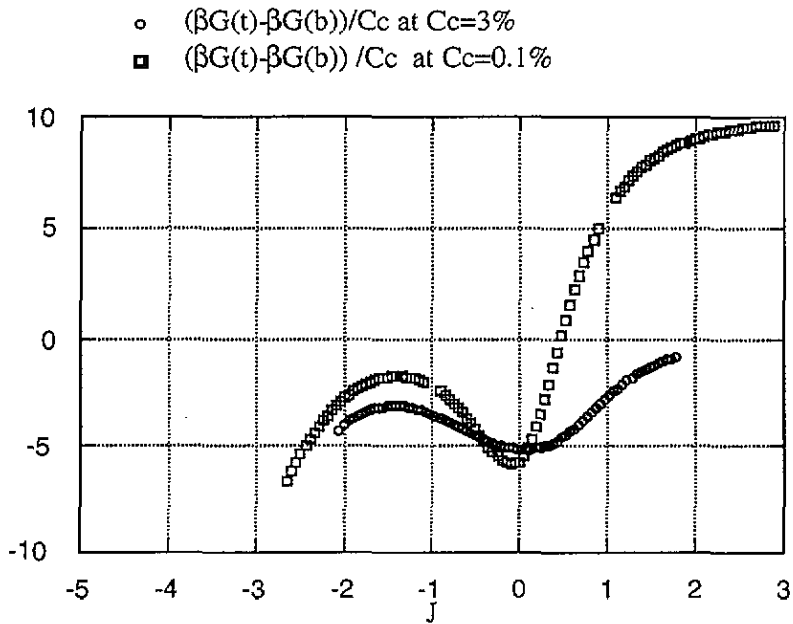


Figure 10. Variation of the APB excess free energy $(\beta G(t) - \beta G(b)) / C_c$ against J for two concentrations $C_c = 0.1\%$ and $C_c = 3\%$.

4. Discussion

So far, we have shown that the behaviour of the added element and the effect of the addition could be determined by considering an equilibrium between the ordered and disordered phases. This conclusion is all the more valid as the temperature is close enough to the transition temperature and the APB thus consists of two IPB. One question then arises: does the behaviour of the added element considerably vary at low temperatures, where the equilibrium between the two phases no longer exists (i.e. below the spinodal temperature T_s)? This question is of some interest, for if T_s is low for the T-CVM, it rises to $1.8J_{AB}$ for the TO-CVM and more for further cluster expansions of the CVM. If indeed the domain where the equilibrium between the two phases can be considered is very small, then the scope of our study could be considerably restricted and valid only very near to T_0 .

However, calculations show that the behaviour of the added element does not change below T_s . If Γ_c is close to zero, it may change sign with a decrease of the temperature, but this variation may happen above or below T_s and is not due to the spinodal itself. When Γ_c is well determined (i.e. its absolute value is well above zero), the behaviour of the added element does not change when crossing T_s . In fact, the tetrahedron of the APB is disordered because it lowers the energy of the defect and thus exists at much lower temperatures than T_s . There is no physical reason why the behaviour of the added element should change below T_s .

However, the location of T_s has an influence on the morphology of the APB. Below T_s , the chemical profile remains sharp. When the temperature comes close to T_0 , the width of the APB diverges. This phenomenon is all the more intense as T_s is close to T_0 . The fact that T_s comes nearer to T_0 when expanding the cluster approximations of the CVM means that the width of the APB will remain small until a few degrees below T_0 where the width

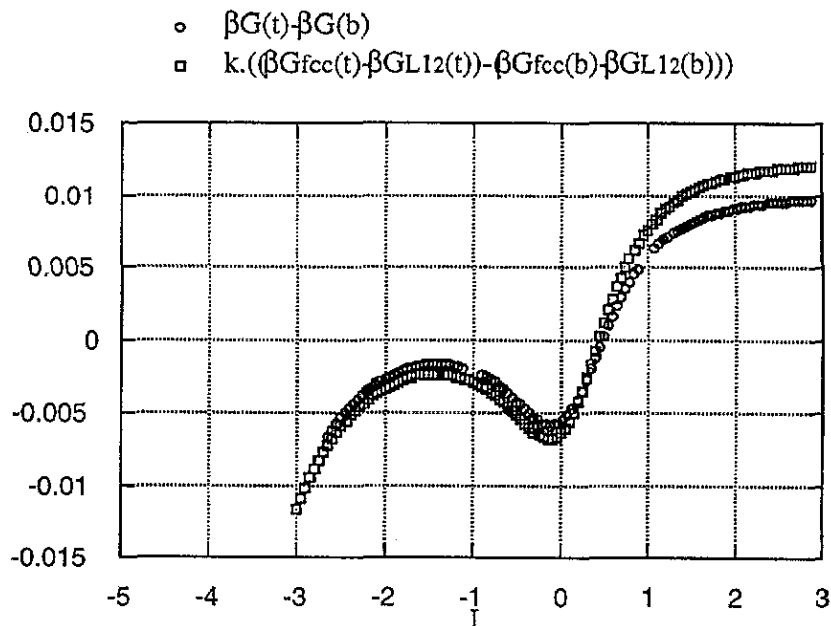


Figure 11. Variation of the APB excess free energy $\beta G(t) - \beta G(b)$ and corresponding homogeneous ordered and disordered phases free energy variation $k\{[\beta G_{FCC}(t) - \beta G_{L12}(t)] - [\beta G_{FCC}(b) - \beta G_{L12}(b)]\}$ against J .

greatly increases. This phenomenon has been (among other studies) studied by Ricolleau *et al* (1992).

Another interesting point is the comparison of this study with the one carried out by Wu *et al* (1989) on (111) APB. These authors show that for $A_{3+x}B_{1-x}$ alloys the segregation is governed by its substitutional behaviour. The excess element (i.e. A if $x > 0$, B if $x < 0$) will segregate at the APB for all temperatures so that the ordered phase tends towards the stoichiometric composition. If the added element C substitutes on A sites (B sites) it will segregate like A (B). If the final composition of the alloy is $A_{3-x}B_{1-y}C_{x+y}$ with $x > 0$ and $y > 0$, then the site preference of the ternary addition plays an important role on the segregation of the host elements. If C substitutes on A sites (B sites) the alloy has to be considered as an $(A,C)_{3+y}B_{1-y}$ alloy ($A_{3-x}(B,C)_{1+x}$), and A (B) segregates to the APB. A maximum of segregation of C at the APB is found for a random distribution of C on A and B sites.

From our point of view, since the behaviour of the added element is governed by an equilibrium between the ordered and disordered phases, this behaviour should be identical when comparing (100) APB and (111) APB. Although Wu *et al* (1989) chose the substitutional behaviour of the ternary element as a parameter for their study, the effects of the ternary addition on (111) APB described are identical to those presented in this paper. This demonstrates that the chemical properties of these APB are induced by the equilibrium between the stable ordered phase and the metastable disordered phase. There is no reason why this conclusion should not be extended to APB of any direction. Furthermore, this implies that the variations of the chemical and thermodynamic properties of APB upon addition are all dictated by this equilibrium and tend towards the same direction. The geometry of the APB can, however, have a 'second-order' influence on these quantities

(for example, every APB will be stabilized by the same addition, some APB can be more stabilized than others owing to their orientations). However, looking at the tie-lines of the phase diagram and carrying out simple simulations of the two homogeneous phases, we can predict the effect of the addition on the APB.

5. Conclusion

Considering a configuration expansion of the CVM, we have defined a pertinent parameter J in order to study the behaviour with respect to an APB of an element C added in small quantity to a $L1_2$ ordered A_3B alloy. The study of the APB has shown that the disordered phase appearing at the defect was indeed the disordered FCC phase. Moreover, it has been assessed that, at temperatures for which the disordering occurs for at least a few planes at the boundary, every characteristic of the APB (i.e. chemical and energy) was due to an equilibrium between the stable $L1_2$ ordered phase and the metastable disordered FCC phase, the existence of which is made possible by the presence of the APB. As was stated by Kikuchi and Cahn (1979), the APB then truly consists of two IPB between the ordered phase and the metastable disordered phase. The variation of the APB chemical description and excess free energy upon adding the ternary element is then directed by the variation of the concentration and free energy of these two phases. If the temperature at which the APB is considered is not too low, then the behaviour of the added element (segregation at the APB or rejection in the bulk) can be known directly from the phase diagram. If there is more (less) ternary element in the disordered FCC phase at the transition temperature than in the ordered phase, then the added element will segregate at the APB (be rejected in the bulk).

One can also know if the APB will be stabilized by the ternary addition by studying the variation of the free energies of the stable ordered phase and the metastable disordered FCC phase. These energy variations are not directly accessible, but in any case their signs may be qualitatively calculated from CVM carried out on homogeneous phases. This method is much simpler (although only qualitative) than a full simulation of the APB and allows calculations using more precise CVM (tetrahedron–octahedron, second-neighbour ordering pair energies).

Appendix

Working with tetrahedron probabilities as set of variables induces a technical problem owing to the fact that these variables are redundant. However, probabilities have the advantage of being the natural basis with which thermodynamics are calculated. With the set of probabilities that have been defined, two constraints occur: the sum of the probabilities of each tetrahedron must be equal to one, and two consecutive tetrahedra overlap along the y pair probabilities. Since the probabilities of each tetrahedron subcluster can be obtained through a matrix relationship from the tetrahedron probabilities, we shall denote \mathbf{P}_1 the matrix associating the tetrahedron probabilities to the right y pair and \mathbf{P}_2 the matrix associating the tetrahedron probabilities to the left y pair. For each n th tetrahedron, the constraints defined are expressed as follows:

$$\mathbf{1} \cdot t_n = 1 \quad (\text{A1})$$

$$y_n = \mathbf{P}_1 \cdot t_n = \mathbf{P}_2 \cdot t_{n-1}. \quad (\text{A2})$$

In order to get rid of the constraint (A2), we have to build a set of probabilities based on the pair probabilities y_n and complete it with chosen tetrahedron probabilities t_n . These pair probabilities y_n are also redundant because of the normalization constraint:

$$1 \cdot y_n = 1. \quad (\text{A3})$$

If np is the dimension of y_n , then a vector of $np - 1$ probabilities will be free of the normalization constraint. This vector will be denoted y'_n . The set of variables consisting of the pair probabilities may be completed by a subset of the tetrahedron probabilities of dimension $nt - 2np + 1$, nt being the dimension of t_n . Tetrahedron probabilities belonging to the subset are denoted t_n^0 . The other probabilities will be denoted t_n^p and we have thus:

$$t_n = \begin{pmatrix} t_n^p \\ t_n^0 \end{pmatrix}. \quad (\text{A4})$$

We have now to check that every tetrahedron and its subcluster probabilities can be calculated from the set of probabilities defined. The relation (A2) can be rewritten as follows:

$$y'_n = \mathbf{P}_1^0 \cdot t_n^0 + \mathbf{P}_1^p \cdot t_n^p \quad (\text{A5})$$

$$y'_{n+1} = \mathbf{P}_2^0 \cdot t_n^0 + \mathbf{P}_2^p \cdot t_n^p. \quad (\text{A6})$$

Furthermore, we have from (A1)

$$1 = 1 \cdot t_n^0 + 1 \cdot t_n^p. \quad (\text{A7})$$

If the matrix \mathbf{R} defined as:

$$\mathbf{R} = \begin{pmatrix} \mathbf{P}_1^p \\ \mathbf{P}_2^p \\ 1 \end{pmatrix} \quad (\text{A8})$$

is regular then t_n^p can be calculated from the set of relations (A5), (A6) and (A7) from the chosen set of variables. Let us calculate the dimension of \mathbf{P}_1^p : from the definition of \mathbf{P} , this matrix has $np - 1$ rows and $nt - (nt - 2np + 1) = 2np - 1$ columns, and is thus an $np - 1$ by $2np - 1$ matrix. The dimension of \mathbf{P}_2^p is also $np - 1$ by $2np - 1$, and thus the dimension of \mathbf{R} is $2np - 1$ by $2np - 1$. The determinant of this square matrix being non-zero is in fact the criterion for choosing the tetrahedron probabilities to take into account when building the t_n^0 tetrahedron probabilities subset. The matrix \mathbf{R} then admits an inverse matrix, which makes it possible to calculate t_n^p from t_n^0 and y'_n . Probabilities of every subcluster can then be calculated from the complete tetrahedron probability. Using the set of variables (t_n^0, y'_n) thus avoids introducing Lagrange multipliers, which would reduce the efficiency of the Newton-Raphson algorithm.

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