THEORY OF ADSORPTION AT ANTIPHASE BOUNDARIES IN TERNARY FCC ORDERED ALLOYS

V. P. Fadin, V. V. Prushinskii,
V. E. Panin, S. F. Kiseleva,
and L. A. Prushinskaya

UDC 548.4.01

The adsorption of alloying elements at (111) antiphase boundaries (APB's) in ternary fcc ordered alloys is analyzed. The atomic segregation at the APB's and the long-range order parameters at the APB's and within domains are studied as functions of the temperature and the concentration of alloying elements. The results are compared with experimental data for ternary bcc alloys.

1. The alloying of a binary ordered alloy with a third element can cause significant changes in the effects and kinetics of ordering. In several studies the effect of the third element has been attributed to its adsorption at antiphase boundaries (APB's) [1-6]. The effect of adsorption at APB's has been shown to depend on the nature of the binary alloy and the nature of the alloying element.

The adsorption of a third alloying element in binary bcc alloys was treated theoretically in [6, 7]; the calculated results were found to be in satisfactory qualitative agreement with experimental results [2-6] for fcc alloys. It thus seemed worthwhile to carry out a similar calculation for fcc alloys; below we analyze theoretically the adsorption of alloying elements at APB's in ternary fcc ordered alloys.

2. We will first give the condition derived for the formation of a segregation of atoms of species D at a (111) APB in a ternary fcc alloy by the procedure used in [6, 7] for a plane square grid and for bcc alloys. For the case \( V_{BB} = V_{DD} \) (where \( V_{BB} \) and \( V_{DD} \) are (minus) the binary-interaction energies corresponding to B–B and D–D interactions, respectively) this condition is

\[
L_1 = 3w_{BD} + w_{AB} - w_{AD} > 0.
\]

where \( w_{XY} = 2V_{XX} - V_{XX} - V_{YY} \) (X, Y = A, B, or D) is the ordering energy for the X–Y binary alloy. When condition (1) holds, the third element, D, can be adsorbed at a (111) APB, since this adsorption would reduce the energy of the ternary alloy. When condition (1) does not hold, it is energetically unfavorable for element D to concentrate near APB's.

Condition (1) was derived on the basis of a model for the ternary alloy which includes two types of lattice positions (in general, it is better to include three [8, 9] or four [10] types of positions). If a ternary superstructure does not form in the alloy, the treatment can be restricted to two types of positions. As in [7], therefore, we will use the theory of [11] for the calculation, considering ordering in a ternary alloy with two types of lattice positions. As in [12], we neglect the "smearing" of the APB's; only a small error is involved.

3. We consider an ordered solid solution A–B–D with an fcc lattice in which there are APB's parallel to (111) planes. The configurational energy per unit volume of such an alloy can be written in the following form in the approximation in which only nearest-neighbor interactions are taken into account:

\[
E = - \left[ \frac{z}{2} (N - 4N_s Q) + N^2 Q (z_1 + z_2) \right] (p_{AA}V_{AA} + p_{BB}V_{BB})
\]

\[
+ p_{DD}V_{DD} + p_{AB}V_{AB} + p_{AD}V_{AD} + p_{BD}V_{BD} + N Q z_1 (p_{AA}V_{AA})
\]

where \( N \) is the total number of atoms per unit volume of the alloy; \( z \) is the coordination number; \( z_1 \) is the number of nearest neighbors which an atom in the (111) plane has in that plane; \( z_2 \) is the number of nearest neighbors which an atom in the (111) plane has in the neighboring plane; \( Q \) is the APB area; \( N_q \) is the number of atoms per unit APB area; and \( p_{XYi} \) are the probabilities for X–Y bonds within an antiphase domain (\( i = 0 \)), in the plane of an APB (\( i = 1 \)), between APB planes (\( i = 2 \)), and between an APB and a neighboring matrix plane (\( i = 3 \)).

The configurational part of the entropy in the case of an fcc ternary alloy containing two types of lattice positions and APB’s can be written as

\[
S = \kappa \cdot \ln (L \cdot q),
\]

where

\[
L = \left( \frac{1}{4} (1 - \eta) N \right)! \left( \frac{3}{4} (1 - \eta) N \right)! \left( \frac{1}{4} \eta N \right)! \left( \frac{3}{4} \eta N \right)! .
\]

\[
q = \left( \frac{1}{N(\beta)^{(1)}} \right)! \left( \frac{1}{N(\beta)^{(2)}} \right)! \left( \frac{1}{N(\beta)^{(3)}} \right)! .
\]

In Eqs. (3)–(5), \( N_{L(\beta)}^{(\beta)} \) is the number of positions of type \( \beta \) (\( \beta = 1, 2 \)) within antiphase domains; \( N_q^{(\beta)} \) is the number of \( \beta \) positions in planes forming APB’s; \( N_X^{(\beta)} \) and \( N_X^{(\beta)} \) are the corresponding numbers of atoms of species X at \( \beta \) positions; \( \eta = 2N_qQ/N \) is the relative number of positions in planes forming APB’s; and \( \kappa \) is the Boltzmann constant.

The long-range order parameter for this model can be written, according to [11], as

\[
S = \frac{P_{ADL} - c_{ADL}}{1 - \nu} .
\]

Then the long-range order parameter for planes forming APB’s can be found from

\[
S_q = \frac{P_{ADQ} - c_{ADQ}}{1 - \nu} .
\]

In Eqs. (6) and (7), \( p_{ADL}^{(i)} \) is the probability that a given position of the first type within an antiphase domain is occupied by an atom of species A or D; \( p_{ADQ}^{(i)} \) is the same probability, for the planes forming APB’s; \( c_{ADL} = c_A + c_D \); \( c_{ADQ} = c_A + c_D \); \( c_A \), and \( c_D \) are the concentrations of atoms of species A and D within domains; \( c_A \) and \( c_D \) are the same, for the planes forming APB’s; and \( \nu \) is the concentration of positions of the first type.

Using (6), (7), and the results of [11], we find

\[
p_{AAB} = c_A \left[ 1 - \frac{s^2}{16 (c_A + c_D)^2} \right] ; \quad p_{AAB} = c_A \left[ 2c_B + \frac{s^2}{8 (c_A + c_D)^2} \right] ;
\]

\[
p_{ABB} = c_B \left[ 1 - \frac{s^2}{16 (c_A + c_D)^2} \right] ; \quad p_{ABB} = c_D \left[ 2c_B + \frac{s^2}{8 (c_A + c_D)^2} \right] ;
\]

\[
p_{AD0} = c_B \left[ 1 - \frac{s^2}{16 (c_A + c_D)^2} \right] ; \quad p_{AD0} = c_A \left[ 2c_B + \frac{s^2}{8 (c_A + c_D)^2} \right] ;
\]

\[
p_{ADD} = c_B \left[ 1 - \frac{s^2}{16 (c_A + c_D)^2} \right] ; \quad p_{ADD} = c_D \left[ 2c_B + \frac{s^2}{8 (c_A + c_D)^2} \right] ;
\]

\[
p_{AAB} = c_A \left[ 1 - \frac{s^2}{16 (c_A + c_D)^2} \right] ; \quad p_{AAB} = c_A \left[ 2c_B + \frac{s^2}{8 (c_A + c_D)^2} \right] ;
\]

\[
p_{ABB} = c_B \left[ 1 - \frac{s^2}{16 (c_A + c_D)^2} \right] ; \quad p_{ABB} = c_D \left[ 2c_B + \frac{s^2}{8 (c_A + c_D)^2} \right] ;
\]