EVAPORATION OF UNIFORMLY STRAINED SUBSTITUTIONAL-
INTERSTITIAL SOLID SOLUTIONS

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The equilibrium vapor pressures and evaporation heat of substitutional-interstitial solid solution components are calculated. The effect of uniform strain on the foregoing characteristics is discussed.

Keywords: evaporation, substitutional-interstitial solutions, evaporation heat, strain.

Many properties of solids are directly determined by interatomic interaction forces. Among these, in particular, is crystal evaporation. There exists a comprehensive theory of crystal evaporation taking into account the effective transformation of interatomic forces due to changes in the composition, development of long-range and short-range orders, magnetic ordering, etc. [1]. One such way of changing the interatomic interaction force in crystals is strain resulting in a change in the bond radius which, in turn, leads to a change in the interaction force between the atoms. It is evident that the foregoing effect would cause changes in the pressure of natural vapor above the crystals.

In this work, we calculated equilibrium vapor pressure above a bcc solid $A-B-(C)$ solution subject to a uniform strain specified by a diagonal strain tensor with the $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$ components. Since it is the high-temperature evaporation which is of interest, no allowance for possibility of emergence of short- and long-range orders in the alloy was made. For simplicity, no account was taken of the dependence of the lattice constant on the composition. It is assumed that the vapor above crystals consists of monatomic molecules of the $A$, $B$, and $C$ components.

The impurity interstitial atoms will be considered to occupy octahedral interstitial sites. Due to strain, they are splitted into interstitial sites of three types [2] with the following energies:

$$U_1^{(0)} = U_0 + \Delta U_1, \quad U_2^{(0)} = U_0 + \Delta U_2, \quad U_3^{(0)} = U_0 + \Delta U_3,$$

where $U_0$ is the energy of the $C$ atom at the octahedral interstitial site in the unstrained state, $\Delta U_1$, $\Delta U_2$, and $\Delta U_3$ are the displacements of the energy level $U_0$ due to strain. For simplicity, use will be made of a model of noninteracting interstitial atoms [3].

The free energy of the crystal + gaseous system is written as

$$F = F_{\text{conf}} + F_{\text{ph}} + F_{\text{gas}}.$$ 

Here $F_{\text{conf}}$ is the configuration energy of the $A-B-(C)$ solution.
\[ F_{\text{conf}} = -\frac{z}{2(N_A + N_B)} \left( N_A^2 V_{AA} + N_B^2 V_{BB} + 2N_A N_B V_{AB} \right) + U_0 N_C + \Delta U_1 N_C^{(1)} + \Delta U_2 N_C^{(2)} + \Delta U_3 N_C^{(3)} - kT \left\{ 4(N_A + N_B) \ln(N_A + N_B) - N_A \ln(N_A) - N_B \ln(N_B) \right\} \]

\[ -N_A \ln(N_A - N_B) - N_B \ln(N_B - N_C) - N_C^{(1)} \ln(N_A + N_B - N_C^{(1)}) \ln(N_A + N_B + N_C^{(1)}) \]

\[ -N_C^{(2)} \ln(N_C^{(2)}) - (N_A + N_B - N_C^{(2)}) \ln(N_A + N_B - N_C^{(2)}) - N_C^{(3)} \ln(N_C^{(3)}) \]

\[ - \left( N_A + N_B - N_C^{(3)} \right) \ln(N_A + N_B - N_C^{(3)}) \],

where \( N_A \) and \( N_B \) are the numbers of the A and B atoms in the solution, \( N_C \) is the total number of the C atoms at the interstitial sites, \( N_C^{(i)} \) \( i = 1, 2, 3 \) are the numbers of the C atoms at the \( i \)-th interstitial sites, \( V_{\alpha\beta} \) \( (\alpha, \beta = A, B) \) is the interaction energy of the nearest neighbors \( \alpha - \beta \) taken with a “minus” sign, and \( z \) is the coordination number.

\[ F_{\text{ph}} = 3kT \left( N_A + N_B + N_C \right) \left[ \ln \left( 2\sinh \frac{h\omega}{2kT} \right) \right] g(\omega) d\omega, \]

where \( g(\omega) \) is the density of natural oscillation frequencies normalized with respect to unity in the \( A-B-(C) \) solution.

\[ F_{\text{gas}} = \sum_{i=A,B,C} N_{i}^{\text{gas}} kT \ln \left( \frac{2\pi \hbar^2}{M_i kT} \right)^{\frac{3}{2}} \frac{N_{i}^{\text{gas}}}{V}, \]

where \( N_{i}^{\text{gas}} \) is the number of \( i \)-particles in the gaseous phase, \( M_i \) is the mass of an \( i \)-atom, and \( V \) is the gas volume.

The variables, through which the free energy (2) is written, fulfill the following conditions:

\[ N_A + N_A^0 = N_A^0; \quad N_B + N_B^0 = N_B^0; \quad N_C + N_C^0 = N_C^0; \]

\[ N_C^{(1)} + N_B^0 + N_C^{(3)} = N_C. \]

Here \( N_A^0 \), \( N_B^0 \), \( N_C^0 \) are the total numbers of the A, B, and C atoms in the system.

Let us write the energies of interatomic bonds \( V_{\alpha\beta} \) \( (\alpha, \beta = A, B) \) involved in \( F \) as expansions in terms of strain-tensor components, and we have

\[ V_{\alpha\beta} = V_{\alpha\beta}^0 + \frac{\gamma_{\alpha\beta}}{12} (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)^2, \]

where \( V_{\alpha\beta}^0 \) are the corresponding values for an unstrained state, \( \alpha \) is the lattice constant, and \( \gamma_{\alpha\beta} > 0 \).

The equilibrium conditions are as follows:

\[ \frac{\partial F}{\partial N_{C}^{(3)}} = 0, \quad \frac{\partial F}{\partial N_{C}^{(2)}} = 0, \quad \frac{\partial F}{\partial N_{C}^{(1)}} = 0, \]

\[ \frac{\partial F}{\partial N_A^{\text{gas}}} = 0, \quad \frac{\partial F}{\partial N_B^{\text{gas}}} = 0, \quad \frac{\partial F}{\partial N_C^{\text{gas}}} = 0. \]