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THERMODYNAMICS OF STACKING FAULTS IN BINARY ALLOYS

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Thermodynamics of Stacking Faults in Binary Alloys

John E. Dorn

Whereas the thermodynamics of stacking faults has already been discussed by Suzuki[1-3] and Flinn,[4, 5] several simplifying approximations were introduced into their analyses: Suzuki abandoned his original formulation[1, 2] of treating stacking faults as a separate phase in his third paper,[3] where he employed the concept of a surface phenomenon to describe the behavior of the stacking fault; he nevertheless retained the regular solution approximations. Flinn correctly used the concept of surface phenomenon, but he retained the approximation of regular solutions, introduced the simplifying assumption, which is not necessarily always correct, that the compositions of the stacking fault differs only slightly from that of the stable phase, and retained the quantity pertaining to the change in stacking fault energy with the composition of the stacking fault, a quantity that is not directly measurable experimentally, in his final equations. It is the purpose of this article to derive the general conditions for equilibrium between a stacking fault and a phase for any binary solid solution alloy. The procedure is merely a generalization of that used originally by Flinn.[5]

The free energy, F, of the stable phase, consisting of n_A

and n_B atoms of types A and B respectively is

$$F = n_A \frac{F_A\{T\}}{N} + n_B \frac{F_B\{T\}}{N} + (n_A + n_B) \frac{\Delta F\{m_B, T\}}{N} \tag{1}$$

where N is Avogadro's number, F_A and F_B are the free energies per mole of pure A and pure B, T is the temperature, and $\Delta F\{m_B, T\}$ is the free energy of mixing one mole of the alloy which has a composition of n_B mole fraction of B atoms. Designating the variables pertaining to the faulted region by the prescripts f, we have

$$^fF = {^fn_A}\, F_A\{T\} + {^fn_B}\, F_B\{T\} + ({^fn_A} + {^fn_B}) \frac{\Delta F\{^fm_B, T\}}{N} + ({^fn_A} + {^fn_B}) \frac{V}{Nt} \gamma\{^fm_B, T\} \tag{2}$$

where V and t are the molar volume and thickness respectively of the faulted region and $\gamma\{^fm_B, T\}$ is the free energy per unit area of the fault. In effect, Equation 2 merely defines $\gamma\{^fm_B, T\}$ as the excess free-surface energy of the faulted region above that of a solution of the stable phase of the same composition as the fault. All extraneous effects, such as strain energy, etc., are, of course, incorporated in $\gamma\{^fm_B, T\}$.

At high temperatures where diffusion is sufficiently rapid, equilibrium will be established. As shown by Cottrell,[6] when the stacking fault ribbon is due to the decomposition of dislocations into their Shockley partials, the partials will acquire a greater separation during this stage due to a decrease in the stacking fault energy. We assume here that equilibrium has been so established and consider now an infintesimal virtual transfer of atoms, holding the stacking fault volume and the total number of A and B atoms in the system constant. For such a virtual change at equilibrium $\delta F = 0$. We let $\delta n_A = -\delta n$, $\delta {}^f n_A = \delta n$, $\delta n_B = \delta n$ and $\delta {}^f n_B = -\delta n$, where δn is the number of A atoms transferred from the stable phase to the faulted region.

Therefore,

$$\delta F = \frac{\partial F}{\partial n_A}(-\delta n) + \frac{\partial F}{\partial n_B}(\delta n) + \frac{\partial\, {}^f F}{\partial\, {}^f n_A}(\delta n) + \frac{\partial\, {}^f F}{\partial\, {}^f n_B}(-\delta n)$$

and consequently the equilibrium condition is given by

$$-\frac{\partial F}{\partial n_A} + \frac{\partial F}{\partial n_B} + \frac{\partial\, {}^f F}{\partial\, {}^f n_A} - \frac{\partial\, {}^f F}{\partial\, {}^f n_B} = 0 \qquad (3)$$

For the convenience of the reader we give, in detail, the chemical potentials involved in Equation 3 as follows:

$$-\frac{\partial F}{\partial n_A} = -\frac{F_A\{T\}}{N} - \frac{\Delta F\{m_B, T\}}{N} - \frac{(n_A + n_B)}{N} \frac{\partial \Delta F\{m_B, T\}}{\partial m_B} \frac{\partial m_B}{\partial n_A} \tag{4a}$$

$$\frac{\partial F}{\partial n_B} = \frac{F_B\{T\}}{N} + \frac{\Delta F\{m_B, T\}}{N} + \frac{(n_A + n_B)}{N} \frac{\partial \Delta F\{m_B, T\}}{\partial m_B} \frac{\partial m_B}{\partial n_B} \tag{4b}$$

$$\begin{aligned} \frac{\partial\, {}^fF}{\partial\, {}^fn_A} = {} & \frac{F_A\{T\}}{N} + \frac{\Delta F\{{}^fm_B, T\}}{N} + \frac{({}^fn_A + {}^fn_B)}{N} \frac{\partial \Delta F\{{}^fm_B, T\}}{\partial\, {}^fm_B} \frac{\partial\, {}^fm_B}{\partial n_A} \\ & + \frac{V}{Nt} \gamma\{{}^fm_B, T\} + \frac{({}^fn_A + {}^fn_B)}{N} \frac{V}{t} \frac{\partial \gamma\{{}^fm_B, T\}}{\partial\, {}^fm_B} \frac{\partial\, {}^fm_B}{\partial\, {}^fn_A} \end{aligned} \tag{4c}$$

$$\begin{aligned} -\frac{\partial\, {}^fF}{\partial\, {}^fn_B} = {} & -\frac{F_B\{T\}}{N} - \frac{\Delta F\{{}^fm_B, T\}}{N} - \frac{({}^fn_A + {}^fn_B)}{N} \frac{\partial \Delta F\{{}^fm_B, T\}}{\partial\, {}^fm_B} \frac{\partial\, {}^fm_B}{\partial\, {}^fn_B} \\ & - \frac{V}{Nt} \gamma\{{}^fm_B, T\} - \frac{({}^fn_A + {}^fn_B)}{N} \frac{V}{t} \frac{\partial \gamma\{{}^fm_B, T\}}{\partial\, {}^fm_B} \frac{\partial\, {}^fm_B}{\partial\, {}^fn_B} \end{aligned} \tag{4d}$$

Adding Equations 4, equating to zero, and introducing the fact that $\partial m_B / \partial n_B - \partial m_B / \partial n_A = 1/(n_A + n_B)$ gives the equilibrium condition that

$$\left(\frac{\partial \Delta F\{m_B, T\}}{\partial m_B}\right)_{at\, m_B} - \left(\frac{\partial \Delta F\{m_B, T\}}{\partial m_B}\right)_{at\, {}^f m_B} = \frac{V}{t} \frac{\partial \gamma\{{}^f m_B, T\}}{\partial\, {}^f m_B} \qquad (5)$$

This equation reduces to that derived by Flinn when his simplifying conditions are introduced. It permits the evaluation of the equilibrium composition of the stacking fault ${}^f m_B \equiv {}^f m_B\{m_B, T\}$ when $\Delta F\{m_B, T\}$ and $\gamma\{{}^f m_B, T\}$ are known. Whereas $\Delta F\{m_B, T\}$ can be obtained from standard thermodynamic data on alloy systems, $\gamma\{{}^f m_B, T\}$ is not directly obtainable from experiments, under the necessary conditions for equilibrium. When γ is determined at sufficiently high temperatures to assure equilibrium, either by measuring the separation of the partial dislocations[7] or by employing Whelan's[8] nodal technique, γ is measured as a function of the alloy composition m_B and the temperature T. We, therefore, must express Equation 5 in terms of measurable quantities, namely

$$\left(\frac{\partial \Delta F\{m_B, T\}}{\partial m_B}\right)_{at\, m_B} - \left(\frac{\partial \Delta F\{m_B, T\}}{\partial m_B}\right)_{at\, {}^f m_B} = \frac{V}{t} \frac{\partial \gamma}{\partial m_B}\{m_B \text{ in alloy}, T\} \frac{\partial m_B}{\partial\, {}^f m_B} \qquad (6)$$

It is now possible to determine ${}^{f}m_B$ under equilibrium conditions as a function of m_B and T. To illustrate, we let the distribution coefficient be given by $k = {}^{f}m_B / m_B$ but admit that k is not a constant. Then

$$\left(\frac{\partial \Delta F\{m_B, T\}}{\partial m_B}\right)_{m_B} - \left(\frac{\partial \Delta F\{m_B, T\}}{\partial m_B}\right)_{km_B} = \frac{V}{t}\left(\frac{\partial \gamma}{\partial m_B}\right)_{m_B}\left(\frac{1}{k + m_B \frac{\partial k}{\partial m_B}}\right) \quad (7)$$

The appropriate equilibrium value of k, which can be determined graphically, is that which satisfies Equation 7, all other quantities having been determined experimentally. Equation 7 is not restricted to stacking faults only; it is generally valid for all surface phenomena.

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