

Lawrence Berkeley National Laboratory

Recent Work

Title

THERMODYNAMICS OF STACKING FAULTS IN BINARY ALLOYS

Permalink

<https://escholarship.org/uc/item/77s8j3c2>

Author

Dorn, John E.

Publication Date

1962-09-30

University of California
Ernest O. Lawrence
Radiation Laboratory

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

THERMODYNAMICS OF STACKING FAULTS
IN BINARY ALLOYS

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to Acta Metallurgica as
Letter to the Editor

UCRL-10487

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
Contract No. W-7405-eng-48

**THERMODYNAMICS OF STACKING FAULTS
IN BINARY ALLOYS**

John E. Dorn¹

September 30, 1962

¹Miller Professor of Materials Science in the Department of Mineral Technology and Research Metallurgist of the Inorganic Materials Research Division of the Lawrence Radiation Laboratory, University of California, Berkeley, California.

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

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

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

$$\begin{aligned} {}^f F = & {}^f n_A F_A\{T\} + {}^f n_B F_B\{T\} + ({}^f n_A + {}^f n_B) \frac{\Delta F\{{}^f m_B, T\}}{N} \\ & + ({}^f n_A + {}^f n_B) \frac{V}{Nt} \gamma^f\{{}^f m_B, T\} \end{aligned} \quad (2)$$

where V and t are the molar volume and thickness respectively of the faulted region and $\gamma^f\{{}^f m_B, T\}$ is the free energy per unit area of the fault. In effect, Equation 2 merely defines $\gamma^f\{{}^f m_B, T\}$ 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 $\gamma^f\{{}^f m_B, T\}$.

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 infinitesimal 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

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

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

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

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

$$\begin{aligned} \frac{\partial f F}{\partial f n_A} &= \frac{F_A\{T\}}{N} + \frac{\Delta F\{f_{m_B}, T\}}{N} + \frac{(f_{n_A}+f_{n_B})}{N} \frac{\partial \Delta F\{f_{m_B}, T\}}{\partial f_{m_B}} \frac{\partial f_{m_B}}{\partial f n_A} \\ &+ \frac{V}{Nt} \gamma\{f_{m_B}, T\} + \frac{(f_{n_A}+f_{n_B})}{N} \frac{V}{t} \frac{\partial \gamma\{f_{m_B}, T\}}{\partial f_{m_B}} \frac{\partial f_{m_B}}{\partial f n_A} \quad (4c) \end{aligned}$$

$$\begin{aligned} -\frac{\partial f F}{\partial f n_B} &= -\frac{F_B\{T\}}{N} - \frac{\Delta F\{f_{m_B}, T\}}{N} - \frac{(f_{n_A}+f_{n_B})}{N} \frac{\partial \Delta F\{f_{m_B}, T\}}{\partial f_{m_B}} \frac{\partial f_{m_B}}{\partial f n_B} \\ &- \frac{V}{Nt} \gamma\{f_{m_B}, T\} - \frac{(f_{n_A}+f_{n_B})}{N} \frac{V}{t} \frac{\partial \gamma\{f_{m_B}, T\}}{\partial f_{m_B}} \frac{\partial f_{m_B}}{\partial f n_B} \quad (4d) \end{aligned}$$

Adding Equations 4, equating to zero, and introducing the fact that

$$\frac{\partial m_B}{\partial n_B} - \frac{\partial m_B}{\partial n_A} = \frac{1}{(n_A + n_B)} \quad \text{gives}$$

the equilibrium condition that

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

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

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

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

$$\left(\frac{\partial \Delta F \{m_B, T\}}{\partial m_B} \right)_{m_B} - \left(\frac{\partial \Delta F \{m_B, T\}}{\partial m_B} \right)_{k m_B} \quad (7)$$

$$= \frac{V}{t} \left(\frac{\partial \gamma^2}{\partial m_B} \right)_{m_B} \left(\frac{1}{k + m_B \frac{\partial k}{\partial m_B}} \right)$$

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.

ACKNOWLEDGEMENTS

The author expresses his appreciation to the Faculty of the University of California for the grant of a Miller Research Professorship (1962-63) and to the Inorganic Materials Research Division of the Lawrence Radiation Laboratory, sponsored by the United States Atomic Energy Commission, for their continuing support of his research.

BIBLIOGRAPHY

1. H. Suzuki, Sci. Repts. Res. Inst., Tohoku University, A 4 (1952) 455.
2. H. Suzuki, Dislocations and Mechanical Properties of Crystals, John Wiley and Sons, (1953) 351.
3. H. Suzuki, J. Phys. Soc. Japan 17 No. 2 (1962) 322.
4. P. A. Flinn, Acta Met 6 (1958) 631.
5. P. A. Flinn, Strengthening Mechanisms in Solids. A. S. M. (1960) 17.
6. A. H. Cottrell, Relation of Properties to Microstructure, A. S. M. (1953) 191.
7. A. H. Cottrell, Dislocations and Plastic Flow in Crystals. Oxford (1953).
8. M. J. Whelan, Proc. Roy. Soc., A 249 (1957) 114.

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

