JOURNAL OF MATERIALS SCIENCE 17 (1982) 1036–1040

On the equilibrium distribution of the impurity atoms in real crystals

J. N. JAGODZINSKI, Y. V. KORNYUSHIN
Institute of Metal Physics, Academy of Sciences of the Ukranian SSR, Kiev, USSR

This work discusses the equilibrium distribution of impurity atoms among different sinks and the matrix of a real crystal. A simple formula, interpolating the McLean formula is obtained. Impurity segregation in crystals, containing two types of sinks (e.g. grain boundaries and dislocations) is investigated. Impurity concentration on a weakly-binding sink (grain boundary) as a function of the temperature, T, may be represented by a curve, the shape of which depends on the ratio of the average impurity concentration and the relative volume of a strongly-binding sink (dislocation) and on the ratio of the binding energies of an impurity atom on different sinks. There are four possible shapes of the curve. Three of them are not monotonic and show a maximum at $T = T_{\max}$. One of these three also exhibits a minimum at $T = T_{\min} < T_{\max}$. This may be used to diminish the content of a "harmful" impurity on the grain boundaries.

1. Introduction

The impurity atoms in a real crystal are distributed inhomogeneously. They segregate on different sinks which may be grain and subgrain boundaries, dislocations, stacking faults, etc. This influences different physical (in particular, mechanical) properties. The first theory to consider the distribution of the impurity atoms among the bulk and the boundary area was performed by McLean [1]. McLean and further authors used the following assumptions: (a) a sink (e.g. boundary) has a definite number of positions which may be occupied by the impurity atoms; (b) the free energy of an impurity atom in a sink differs from that in the matrix and both energies are independent of the concentration of the impurity; (c) the interaction energy of the impurity atoms (both in a sink and the matrix) is neglected.

Notwithstanding the simplicity of this model, it takes into account the main features of the problem, so it was used as the basis of a series of works on the influence of the equilibrium segregation upon the condition of grain boundaries in one- and two-phased solid solutions, e.g., a competitive grain boundary segregation of two impurities was investigated on the basis of the McLean's model [2]. An equilibrium segregation of an impurity on a series of sinks simultaneously in a crystal, a competitive segregation of a series of impurities on a sink of a fixed volume and a segregation in two-phased systems were also considered, in [3]. It was shown that an equilibrium concentration of different impurities on the grain boundaries as a function of the temperature is not monotonic if: (i) there are dislocations in a crystal and the binding of an impurity atom to a dislocation is stronger than that to a grain boundary; (ii) there is another impurity, which is bound to a grain boundary more strongly than that of the considered impurity and (iii) a system is a two-phased one. Another result obtained is that the temperature of disintegration and the content of an impurity in the grain boundaries depends essentially on the size of a grain if the solubility of the impurity is rather small.

In the present work an equilibrium distribution of the impurity atoms between two types of sinks is more completely investigated on the basis of the McLean approximation.

An equilibrium distribution of the impurity atoms may be achieved if the atomic mobility is considerable. For the more usual heavy impurities this is so only if the temperature is high enough, and equilibration may take place during e.g. an

0022–2461/82/041036–05$03.10/0 © *1982 Chapman and Hall Ltd.*

annealing. As for the very light impurities, their atomic mobility is high enough down to very low temperatures, leading to the rapid equilibration of the system.

2. Modification of the McLean relation

An equilibrium segregation of the impurity atoms on one sink (for example, a grain boundary), having a binding energy per impurity atom, F, may be described by the McLean formula,

$$C_1 = \frac{C_m \exp(F/kT)}{1 + C_m[\exp(F/kT) - 1]}, \qquad (1)$$

where C_1 and C_m are the impurity atomic concentration on a sink and in the matrix respectively, and kT is the temperature in units of energy. Usually the value of an average concentration of the impurity atoms in a sample C_0 is known. Therefore it is convenient to express C_1 as a function of C_0 (instead of C_m). For the case when both in the sink and in the matrix the numbers of the positions which may be occupied by impurity atoms (per unit volume) are equal, one may write

$$C_1 q_1 + C_m(1 - q_1) = C_0, \qquad (2)$$

where $q_1 = V_1/V$ is the ratio of the volume of a sink, V_1, to the total volume of a sample, V. The two equations given may be used to determine $C_1 = C_1(T, C_0)$. This was done for the general case in [3]. However, the general formula is rather complicated. Now we have noticed that for the rather general case of $q_1 \ll 1$ a simple convenient interpolation formula may be used:

$$C_1 = \frac{C_0 \exp(F/kT)}{1 + (C_0 + q_1)[\exp(F/kT) - 1]}. \qquad (3)$$

This expression satisfactorily describes the dependence of C_1 on T and C_0 for all values of the parameters save $C_0 \approx q_1$ at $\exp(F/kT) \gg 1$ (low temperatures).

3. One impurity and two sinks

The spatial distribution of the impurity atoms in an inhomogeneous crystal is generally given by the formula [4]

$$C(\mathbf{r}) = \frac{C_m \exp[F(\mathbf{r})/kT]}{1 + C_m\{\exp[F(\mathbf{r})/kT] - 1\}}, \qquad (4)$$

where $C(\mathbf{r})$ is an atomic concentration of the impurity atoms, and the binding energy per one impurity atom $F(\mathbf{r})$ is generally a function of $C(\mathbf{r})$. The constant C_m is determined by the condition

$$\int_{(V)} C(\mathbf{r})\,\mathrm{d}V = C_0 V. \qquad (5)$$

The number of positions per unit volume for the impurity atoms in the sinks will be regarded as equal to that of the matrix as before.

Let us consider a crystal, containing two sinks of a fixed volume having binding energies for an impurity atom of F_1 and F_2 respectively (where 1 refers to grain boundaries and 2 refers to dislocations). Let the impurity concentration on the first sink be $C_1 \ll 1$, and C_2 be arbitrary. This may be realised if $F_2 > F_1$ at not too low temperatures and $C_0 \ll 1$, or if $F_2 > F_1$ and $q_1 \gg C_0$ at arbitrary T and C_0. An equilibrium segregation in this case according to the McLean's model is described by the following equations

$$C_1 = C_m A_1, \qquad (6)$$

$$C_2 = C_m A_2/[1 + C_m(A_2 - 1)], \qquad (7)$$

and

$$q_1 C_1 + q_2 C_2 + (1 - q_1 - q_2)C_m = C_0, \qquad (8)$$

where $A_i = \exp(F_i/kT)$, $i = 1$ or 2. Equations 6 to 8 yield

$$\begin{aligned} C_2 = {} & (1 + (C_0 + q_2)(A_2 - 1) + q_1(A_1 - 1) \\ & - \{[1 + (C_0 + q_2)(A_2 - 1) \\ & + q_1(A_1 - 1)]^2 - 4C_0 q_2 A_2 \\ & \times (A_2 - 1)\}^{1/2})[2q_2(A_2 - 1)]^{-1}, \end{aligned} \qquad (9)$$

and

$$\begin{aligned} C_1 = {} & A_1((C_0 - q_2)(A_2 - 1) - q_1(A_1 - 1) \\ & - 1 + \{[1 + [1 + (C_0 + q_2)(A_2 - 1) \\ & + q_1(A_1 - 1)]^2 - 4C_0 q_2 A_2 \\ & \times (A_2 - 1)\}^{1/2})\{2(A_2 - 1) \\ & \times [1 - q_2 + q_1(A_1 - 1)]\}^{-1}. \end{aligned} \qquad (10)$$

Analysis of the Equation 9 yields the monotonic decrease in C_2 as T increases, C_0 being the asymptotic limit for C_2 at $T \to \infty$. At $T \to 0$

$$C_2 \to (C_0 + q_2 - |C_0 - q_2|)/2q_2. \qquad (11)$$

Using Equation 11, it can quite easily be seen that $C_2 \to 1$ if $C_0 \geqslant q_2$ and $C_2 \to (C_0/q_2) < 1$ at $C_0 < q_2$ as $T \to 0$.

At $C_0 \geqslant q_2$ the number of the impurity atoms equals or exceeds the number of the positions for them on the strongly binding second sink. So, according to the McLean model all positions will be occupied when $T \to 0$. At $C_0 < q_2$ on the contrary, the number of positions for the impurity atoms exceeds their number. Hence the concentration of the impurity atoms on the second sink remains less than 1 even if all impurity atoms are gathered on the strongly-binding sink.

Equation 10 represents the impurity atomic concentration on the weakly-binding sink as a function of temperature. The limit of the small C_0 has been treated in [3]. There, it was shown that C_1 was not a monotonic function of T as it had a maximum. This may be easily understood. At high temperature the impurity atomic concentration on the sinks and the matrix tends to C_0; C_1 and C_2 remain $> C_0$. At low temperatures and $C_0 \ll q_2$ all the impurity atoms occupy the strongly-binding sink, i.e., $C_1 \to 0$ at $T \to 0$. Hence $C_1(T)$ has a maximum. In the case when $C_0 < q_2$, apparently also (as in a case when $C_0 \ll q_2$) $C_1(T) \to 0$ if $T \to 0$ and has a maximum at $T = T_{\max}$ (see Equation 20).

To analytically investigate C_1 as a function of T let us use the approximation $A_1, A_2 \gg 1$ and $q_1, q_2 \ll 1$. The second inequalities are always satisfied. The first ones are usually fulfilled. So, for example, for carbon impurities in polycrystalline molybdenum containing dislocations ($F_1 \doteq 0.44\,\text{eV}$, $F_2 = 1.2\,\text{eV}$) at $T = 2000\,\text{K}$ we have $A_1 \doteq 12.85$, $A_2 = 1057$. A_1 and A_2 steeply increase as the temperature decreases.

4. Relatively low temperatures

Let us begin with an investigation of $C_1(T)$ in the low temperature range, restricted by the following inequality.

$$|C_0 - q_2| A_2 \gg 1 + q_1 A_1. \qquad (12)$$

Using this approximation one may get:

$$C_1 = \frac{A_1}{2(1+q_1A_1)}\left(C_0 - q_2 + |C_0 - q_2| + \frac{C_0 + q_2 - |C_0 - q_2|}{|C_0 - q_2|} \times \frac{1 + q_1A_1}{A_2}\right). \qquad (13)$$

The two cases $C_0 < q_2$ and $C_0 > q_2$ should be regarded separately as before. For $C_0 < q_2$ we have

$$C_1 = \frac{(A_1/A_2)C_0}{(q_2 - C_0)}. \qquad (14)$$

This formula yields $C_1 = 0$ at $T = 0$ and a monotonic increase in C_1 along with that in T. For $C_0 > q_2$ Equation 13 yields

$$C_1 \doteq \frac{A_1(C_0 - q_2)}{(1 + q_1A_1)} + \frac{(A_1/A_2)q_2}{(C_0 - q_2)}. \qquad (15)$$

At $T \to 0$ the impurity atoms occupy all available positions on the strongly-binding sink and the surplus impurity atoms go to the weakly-binding sink. Accordingly, at $T = 0$, Equation 15 yields $C_1 = (C_0 - q_2)/q_1$. As the temperature rises, some of the impurity atoms leave the weakly-binding sink for the matrix. This amount is determined by the factor $A_1 = \exp(F_1/kT)$. Simultaneously some of the impurity atoms leave the strongly-binding sink for the weakly-binding one. This amount is determined by the factor $(A_2/A_1) = \exp[(F_2 - F_1)/kT]$. The concentration of the impurity atoms in the matrix at a finite (though small) temperature is determined by the factors A_1 and A_2. Bearing this in mind it may easily be found that at $F_2 \geqslant 2F_1$, C_1 decreases with the increase in T when T is small. On the other hand at high T the concentrations of the impurity atoms on the sinks tend towards C_0 from above. Hence the function $C_1(T)$ at $C_0 > q_2$ and $F_2 \geqslant 2F_1$ has first a minimum and then a maximum as T rises. At $F_1 < F_2 < 2F_1$ the amount of impurity atoms falling onto weakly-binding sinks from the strongly-binding ones exceeds the amount of the impurity atoms leaving the weakly-binding sinks for the matrix. That is why $C_1(T)$ increases with increasing T from $T = 0$, attains a maximum value at $T = T_{\max}$ and tends to C_0 from above as $T \to \infty$. Analysis of Equation 15 accordingly yields $(\partial C_1/\partial T) < 0$ for small $T > 0$ (at $T \to 0$) only if $F_2 \geqslant 2F_1$. Using Equation 15 one may get an equation which determines the position of the minimum of the function $C_1(T)$

$$(C_0 - q_2)\left(\frac{q_2^{-1}F_1}{F_2 - F_1}\right)^{1/2} = (1 + q_1A_1)A_1^{-F_2/2F_1}. \qquad (16)$$

This equation has exact solutions for $F_2 = 2nF_1$ ($n = 1, 2, 3, 4$). When $q_1A_1 \gg 1$, unity, in the brackets of the right-hand part of the last equation, may be neglected and so the approximate solution of the equation may be also found. Not all the solutions will be given but consideration will be restricted to the most urgent cases of $q_1A_1 \ll 1$. In this case we have

$$T_{\min} = \frac{F_2}{k}\ln^{-1}\left[\frac{q_2}{F_1}\frac{F_2 - F_1}{(C_0 - q_2)^2}\right]. \qquad (17)$$

For example, for carbon impurities in molybdenum $(F_2/k) = 13\,913\,\text{K}$. Therefore, reasonable values of $T_{\min}$ in such cases may be only found in the narrow range of C_0 and q_2 near $C_0 = q_2$. That is why at $F_2 \gtrsim 1\,\text{eV}$ the considered peculiarities are actual only at $C_1 \approx q_2$. At $F_2 \lesssim 0.1\,\text{eV}$ the minimum of $C_1(T)$ may be observed in a more wide range of the parameters C_0 and q_2.

When C_0 increases, the content of the impurity on the weakly-binding sink also increases at $T \to 0$; the position of the minimum, moving to higher temperatures, catches up with the position of the maximum when C_0 assumes some critical value C_0^*. This critical value may be estimated as

$$C_0^* \approx q_1 + q_1 q_2^{1/2}(F_2 - F_1)/F_1. \qquad (18)$$

At $C_0 > C_0^*$, $C_1(T)$ decreases monotonically with increasing the temperature from $T = 0$.

5. Relatively high temperatures

Let us consider a temperature range which is determined by the reverse inequality to Inequality 12. In this range

$$C_1 = \frac{C_0 A_1}{1 - q_2 + q_1(A_1 - 1)} \times \left[1 - \frac{q_2 A_2}{1 + (C_0 + q_2)(A_2 - 1) + q_1(A_1 - 1)}\right]. \qquad (19)$$

At high enough temperatures, when $q_i A_i \ll 1$, i.e., at $T > \max(F_i/k \times \ln^{-1} q_i^{-1})$ Formula 19 yields the Boltzmann equation, $C_1 = C_0 A_1$. Using Equation 19 one may also obtain:

$$T_{\max} = \frac{F_2}{k} \ln^{-1} \frac{F_1}{(C_0 + q_2)(F_2 - F_1)}. \qquad (20)$$

6. Conclusions

It has been shown that at different values of $C_0 \gtreqless q_2$ and F_2/F_1 there are four types of the curves that represent C_1 as a function of T. They are all given on Fig. 1. All possible functions, $C_1(T)$, are such that $(\partial C_1/\partial T) = 0$ at $T = 0$. Three out of the four curves represent functions which are not monotonic. They exhibit a maximum at $T = T_{\max}$. One of them has also a minimum at $T = T_{\min} < T_{\max}$. This may be used to decrease the content of a "harmful" impurity on the grain boundaries by the means of special mechanical and thermal treatment. Mechanical treatment is necessary to achieve a favourable relationship of q_1 and q_2 to C_0. The size of the grain boundaries determines the value of q_1. The density of dislocations determines the value of q_2.

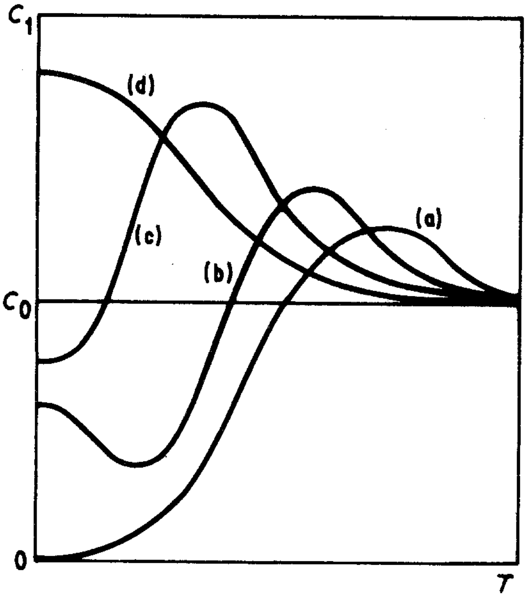

Figure 1 Equilibrium concentratin of the impurity atoms on the weakly-binding sink, as a function of temperature at (a) $C_0 < q_2$, (b) $q_2 < C_0 < C_0^*;\ F_2 \geqslant 2F_1$, (c) $q_2 < C_0 < C_0^*, F_1 < F_2 < 2F_1$ and (d) $C_0 > C_0^* > q_2$.

7. Numerical evaluations

Let us consider a metal, containing a relatively high density of dislocations, i.e., about 10^{10} to $10^{11}\,\text{cm}^{-2}$. This corresponds to a value of $q_2 = 10^{-4}$. Let every thousandth crystal atom belong to the grain boundary (fine-grained material). This corresponds to a value of $q_1 = 10^{-3}$. Let $C_0 = 1.05 \times 10^{-4}$, $F_2 = 1\,\text{eV}$ (11605 K) and $F_1 = 0.2\,\text{eV}$ (2321 K). Such values of the parameters are characteristic for the light impurities in molybdenum. For $(F_2 - F_1)/F_1 = 4$, Equation 17 yields $T_{\min} = 700\,\text{K}$. At $T = 700\,\text{K}, A_1 = 27.5$, $A_2 = 1.58 \times 10^7$, $(C_0 - q_2)A_2 = 79.2$, $1 + q_1 A_1 = 1.028$. All the criteria used to obtain Equation 17 are satisfied. Equation 17 yields $C_1(T_{\min}) = 1.69 \times 10^{-4}$. At $T = 0$ $C_1(0) = 5 \times 10^{-3}$. The critical value $C_0^* = 1.4 \times 10^{-4}$. Equation 20 yields $T_{\max} = 1633\,\text{K}$. At $T = 1633\,\text{K}$, $A_1 = 4.14$, $A_2 = 1220$, $(C_0 - q_2)A_2 = 6.1 \times 10^{-3}$, $1 + q_1 A_1 = 1.004$. All criteria used to obtain Equation 20 are satisfied. Equation 20 yields $C_1(T_{\max}) = 4.1 \times 10^{-4}$.

Therefore in the considered examples the equilibrium impurity content in the grain boundaries is varying essentially in the temperature range where the mobility of the impurity atoms is high enough.

Acknowledgement

This paper is published by kind permission of the Institute of Metal Physics, The Academy of Sciences of the Ukranian SSR.

References

1. D. McLEAN, Grain boundaries in Metals. (Clarendon Press, Oxford, 1957). p. 432.
2. E. E. GLIKMAN, R. E. BRUVER and K. Y. SARYCHEV, *Dokl. Akad. Nauk. SSSR* **200** (1971) 1055.
3. Y. V. KORNYUSHIN, A. N. KUDRYAVTSEV and S. A. FIRSTOV, *Fiz. Met. Metalloved.* **50** (1980) 151.
4. J. P. HIRTH and J. LOTHE, "Theory of dislocations" (McGraw-Hill Book Company, New York, 1968). p. 600.

Received 29 April
and accepted September 1981