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Point-Defect Migration and Binding in Metals*

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The kinetics of decay of an excess defect concentration in metals is examined with special attention to the initial stages of decay. A particular case, excess vacancy migration to sinks in a slightly impure metal, is treated in detail; analog computer plots of isothermal and constant-tempering-rate recovery studies are presented and analyzed. Initial recovery is determined by the migration energy only; final recovery is determined by an energy generally less than the sum of the migration plus vacancy-impurity binding energy but more than the migration energy alone. Initial and final recovery are easily resolved into two annealing stages. The intermediate recovery range may actually give rise to a resistivity increase.

INTRODUCTION

A CENTRAL problem in the field of lattice defects in metals is the experimental determination of the various activation energies which determine the concentration and mobility of particular defects. Attention in this article is focused on the determination of the migration energy, E_m, of a point defect in a pure metal and the binding energy, B, of this defect to an impurity atom in the otherwise pure metal. This general problem has been considered recently by Damask and Dienes[1] (hereafter referred to as DD). To facilitate the discussion, the same specific problem considered by DD will be investigated, using the same notation. The conclusions arrived at agree with DD for long annealing times but differ in an important manner at short times. Following the discussion of this specific problem, consideration is given to the more general problem of point-defect migration.

VACANCY ANNEALING IN SLIGHTLY IMPURE METALS

A. Short Time Behavior

Consider a metal which has been quenched from elevated temperatures. As a result of this quench, an initial concentration of vacancies, v_Q, given by

$$v_Q=\exp(-E_f/kT_q), \tag{1}$$

is produced in the lattice. E_f, the formation energy is taken, with DD, as 1.0 ev. Only the case of the quench temperature, T_q, equal to 600°C is considered here. With these assumed values of E_f and T_q, we have $v_Q=1.74\times10^{-6}$ (atomic fraction). The conclusions concerning annealing at short times or low temperatures are, however, independent of the initial conditions if multiple vacancies and other similar complicating factors are neglected.

We now consider the annealing of vacancies to sinks in the presence of impurities to which they can be bound. In the model in which this annealing is considered to proceed as a chemical rate process, the pertinent reactions are

$$v+I \underset{K_2}{\overset{K_1}{\rightleftharpoons}} c, \tag{2}$$

and

$$v \xrightarrow{K_3} \text{sinks}, \tag{3}$$

where v, I, and c are concentrations (atomic fractions) of free vacancies, unassociated impurities, and vacancy-impurity complexes, respectively, and the rate constants are given by the expressions

$$K_1=42\nu\exp(-E_m/kT), \tag{4}$$

$$K_2=7\nu\exp[-(E_m+B)/kT], \tag{5}$$

$$K_3=\alpha\nu\lambda^2\exp(-E_m/kT), \tag{6}$$

as stated by DD. In these latter expressions, ν, the vibration frequency is taken as 10^{13} sec^{-1}; λ^2 is taken as 10^{-15} cm^2; and α, the vacancy sink concentration, is taken as 10^{10} cm^{-2}. [The numerical factor in Eq. (4) should be 84 instead of 42. Since the actual value is of no essential consequence in the development given below, the factor of 42 was retained.] We let the total impurity concentration be $I_0=I+c$. The differential equations for these reactions are

$$dc/dt=K_1I_0v-K_1cv-K_2c \tag{7}$$

$$dv/dt=-K_1I_0v+K_1cv+K_2c-K_3v. \tag{8}$$

Consider first the behavior of the vacancy concentration at short times. Since at short times $c\approx0$, we may initially neglect terms containing c. Equation (8) can then be written as

$$d(\ln v)/dt=-K_1I_0-K_3, \tag{9}$$

with solution

$$v=v_Q\exp[-(K_1I_0+K_3)t]. \tag{10}$$

Thus, we have immediately our first important result: The initial slope of a plot of ln$v$ vs t curve is determined by the rate constants K_1 and K_3, both of which have in common an $\exp(-E_m/kT)$ term. That this should be the case is physically obvious: The *initial* free vacancy decay is determined only by the jump rate of vacancies

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* This research was supported by the U. S. Atomic Energy Commission.

[1] A. C. Damask and G. J. Dienes, Phys. Rev. **120**, 99 (1960).

and, therefore, only by the migration energy, not the binding energy.

However, the extent to which the decay is governed solely by the migration energy, within the precision of measurement, depends on the value of B with respect to E_m. The situation is clarified in the figures presented subsequently. (We are assuming, of course, that the impurity concentrations are always sufficiently dilute so that the migration energy is unaltered in magnitude from its value in a pure metal.)

The important question is, then, whether the migration energy can be feasibly measured by experiment. It is obviously necessary that the capture of a free vacancy by an impurity atom forming a cluster results in a physical property change which is measurable. Since electrical resistivity, ρ, is the predominant property used in such measurement, we shall only consider it. We have

$$\rho=\rho_v v+\rho_c c+\rho_I I, \tag{11}$$

where ρ_v, ρ_c, and ρ_I are resistivities per unit concentration of vacancies, clusters, and impurities, respectively. DD assumed, for convenience, that $\rho_c=\rho_I+\rho_v$.

There are a number of techniques which may be used to determine the migration energy. The most straightforward, in principle, is to monitor ρ during isothermal recovery and fit ρ to the appropriate solutions of Eqs. (7) and (8). As our discussion suggests and DD have shown, there is little point in fitting such a solution, even if available, at anything but short times since the recovery is determined in a complex manner by both E_m and B. Furthermore, a knowledge of ρ_v and ρ_c is required and is rarely available.

The obvious approach is to analyze the resistivity behavior at short times only. This is best done by recovering at low temperatures where the time scale is expanded. However, the effect of recovering at lower temperature is not merely to expand the time scale. This will be discussed later.

Before proceeding further, it is pertinent to consider the manner in which the resistivity recovers in the early time region. From Eq. (11), whenever vacancy sinks are not involved,

$$d\rho=(\rho_v+\rho_I-\rho_c)dv, \tag{12}$$

and, thus, at short times, a plot of $\ln\rho$ vs t is linear. In the model leading to Eq. (10), the slope of this line gives the rate constant, $K_1I_0+K_3$. If the pre-exponential factors are accurately known, which is rarely true, a single measurement of slope yields E_m. A more practical approach is to measure the slopes following recoveries at two different temperatures, T_1 and T_2. The ratio of these slopes is

$$r=\exp\left[(E_m/k)\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right], \tag{13}$$

allowing a direct computation of E_m.

Other methods of determining E_m may be applied. We would especially recommend the method devised by Brinkman[2] which utilizes data obtained from comparison of isochronal and isothermal annealing treatments. We shall not go into details of the method here except to point out that consideration of isochronal recovery data allows one to easily select a convenient temperature for isothermal recovery. Furthermore, this method allows a determination of activation energies quite generally without any specific knowledge of the annealing characteristics as well as providing a critical test of the extent to which a unique activation energy applies. Finally, an isochronal recovery curve is probably the most informative qualitative display of recovery characteristics. This is demonstrated in the next section.

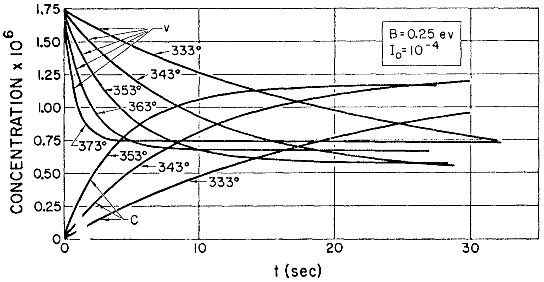

FIG. 1. Isothermal decay of vacancy concentration, v, and buildup of cluster concentration, c (in atomic fractions). The temperature (°K) of each isothermal curve is indicated.

B. Analog Computer Results

To pursue the detailed recovery behavior further, we have graphically solved the problem described by Eqs. (4) through (8) under a range of the parameters I_0, K_3, and B on the Electronic Associates, Inc. analog computer, model 231R. The migration energy has been maintained equal to 0.8 ev. Figure 1 displays the behaviors of v and c for the parameters shown. The numbers near each curve are the value of temperature (°K) at which the annealing proceeds. Three observations are noteworthy.

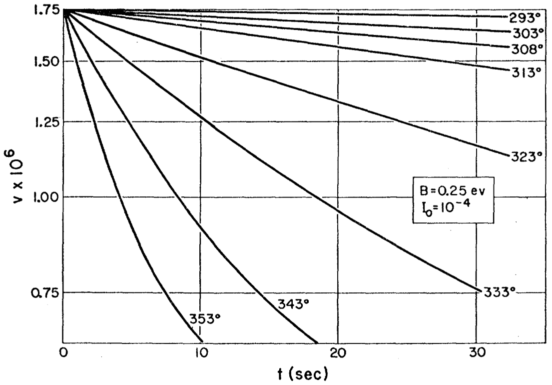

FIG. 2. Logarithm of vacancy concentration vs t at indicated temperatures (°K) at short times.

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[2] J. A. Brinkman, Phys. Rev. **100**, 1807(A) (1955); C. J. Meechan and J. A. Brinkman, Phys. Rev. **103**, 1193 (1956).

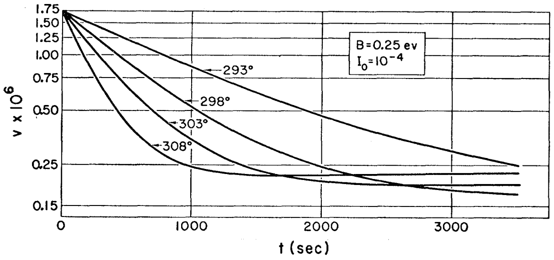

FIG. 3. Logarithm of vacancy concentration vs t at indicated temperatures (°K) at times longer than in Fig. 2.

(1) $c+v$ is almost identically equal to v_Q. This is due to the fact that vacancy sinks play no essential role at the short times shown here. Only at long time as DD show do both v and c decay due to the presence of sinks.

(2) The curves of the decay of v (and c) at different temperatures cross. Physically, this is a reflection of the greater relative mobility of free vacancies at lower temperatures with respect to the rate of cluster break up and is discussed further below.

(3) The behavior of v (and c) at very short times, referred to as a transient by DD, actually accounts for over half of the free vacancy concentration. This "transient" is the important section of decay for the determination of E_m, as shown in the above section.

The temperatures shown in Fig. 1 are too high for use in the determination of E_m. This is demonstrated in Figs. 2 and 3 where $\ln v$ is plotted vs time. It appears that temperatures well below 313°K are desirable for application of the analysis using Eq. (13). The behavior of $\ln v$ at the same temperatures was found to be fundamentally the same for $I_0=10^{-5}$, 10^{-4}, and 10^{-3} (the initial slopes are, of course, proportional to I_0). Application of Eq. (13) to these curves gives $E_m=0.8$ ev. A very simple direct demonstration of this was achieved by plotting the data as shown, then plotting on the same graph with $K_2=0$. The curves superpose very closely at early times, deviating only where nonlinearity begins to become noticeable. Obviously, a process described by $K_2=0$ proceeds with $E_m=0.8$ ev.

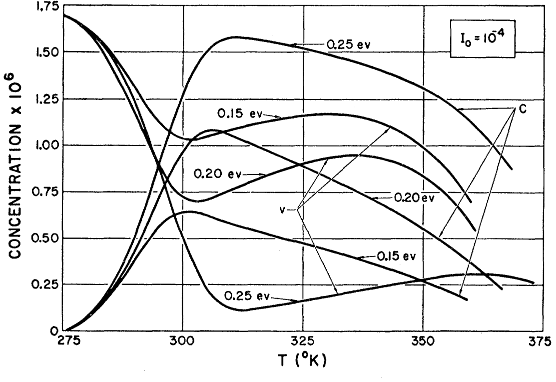

FIG. 4. Constant-tempering-rate (1°K/minute) recovery plots for $I_0=10^{-4}$ and indicated binding energies.

Figures 1 through 3 are isothermal plots of recovery. In Figs. 4 through 7, tempering plots of recovery were traced out on the computer. A heating rate of one degree per minute, typical of most annealing experiments, was assumed for these figures. The starting temperature was 275°K; the initial concentration was approximately the same as in the isothermal studies. In Figs. 4, 5, and 6, K_3 was maintained at its value given by Eq. (6) with the values previously used. In Fig. 7, K_3 was varied in magnitude and $B=0.20$ ev was assumed.

Recovery in a metal with $I_0=10^{-4}$ is displayed in Fig. 4. The vacancy concentration decreases rapidly at first, then increases to a maximum, and finally decays toward zero (only the excess vacancy concentration is considered). The cluster concentration increases to a maximum, then decreases toward zero. The magnitude and temperature positions of the maxima and minima depend on B, as shown. The behavior of v and c is easily understood. Initially, v decays and c builds up due to clustering with almost no effect due to sinks. In the middle temperature range, v increases and c decreases due to the increase in the relative number of free vacancies which are in equilibrium with clusters in the absence of sinks encountered previously. Finally, the effect of the sink concentration takes over and v and c go to zero. As DD have shown, this final decrease in v and c at sufficiently high temperatures (above those in Fig. 4) follows in a quasi-equilibrium manner; that is,

$$c \simeq KI_0v/(1+Kv), \tag{14}$$

where $K \equiv K_1/K_2$.

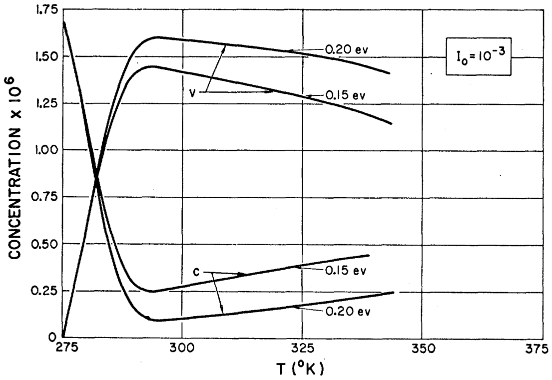

FIG. 5. Constant-tempering-rate (1°K/minute) plots for $I_0=10^{-3}$ and indicated binding energies.

In Fig. 4, B has been set alternately equal to 0.15, 0.20, and 0.25 ev. The behavior for B outside this range was difficult for the computer to handle on this same plot; features of this behavior can be easily inferred from the plot however. In Fig. 5, $I_0=10^{-3}$. This relatively large concentration of impurities quickly depletes the free vacancy concentration and only reluctantly yields vacancies to traps at high temperatures even with $B=0.15$ ev. In Fig. 6, $I_0=10^{-5}$. This is a typical range of impurities for so called "pure" metal. The effect of trapping is reduced from that shown in Fig. 4 but still clearly discernible, particularly for larger values of B.

In Fig. 7, the effect of varying sink density is shown. Only the case of $I_0 = 10^{-4}$ and $B = 0.20$ ev is considered. The curves labelled $\alpha = 10^{10}$ cm^{-2} are plotted with the sink density used previously. The sink density is increased by factors of 10 and 100 for other curves, as indicated. As expected, an increased sink concentration results in earlier removal of vacancies.

Also included in Fig. 7 is the case of $\alpha = 0$. This is the case in which there are no sinks in the metal. Note that v increases at higher temperatures, the best demonstration that the equilibrium concentration of free vacancies with respect to clusters increases at higher temperatures. It is simple to show that when $K_3 = 0$,

$$v = \left(\frac{K_2}{K_1 I_0 + K_2}\right) v_Q \tag{15}$$

in equilibrium.

Since K_2 increases more rapidly than $K_1 I_0$ at increasing temperatures, we see that the value at which the free vacancy concentration reaches a quasi-equilibrium in Fig. 1 decreases with decreasing temperature. The rise in free vacancy concentrations in Figs. 4, 5, and 6 also closely follow Eq. (15). Finally, v formally approaches asymptotically to its initial value, v_Q, at high temperatures.

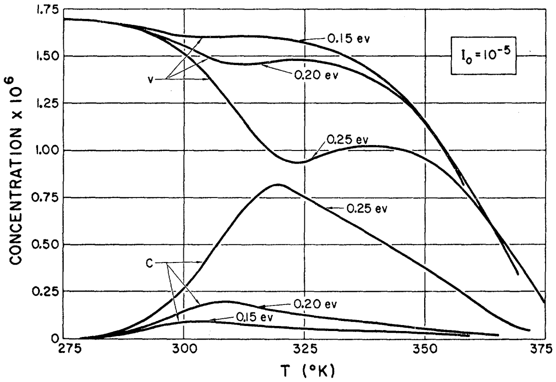

FIG. 6. Constant-tempering-rate (1°K/minute) plots for $I_0 = 10^{-5}$ and indicated binding energies.

There is one important conclusion to be drawn from these tempering curves: The decay of vacancy concentration in an impure lattice occurs, for a realistic range of physical parameters, in two reasonably distinct and resolvable stages. The first stage is dominated by an inherent property of the vacancies, namely, by E_m, regardless of the magnitudes of I_0 and B. E_m may be unambiguously determined, in principle. The second stage is a complex process adequately discussed by DD. The main conclusion of DD regarding this second stage annealing is that the measurable activation energy may range between E_m and $E_m + B$ depending on the magnitude of I_0 and B. Only prudent or fortuitous selection of material will permit a true determination of B.

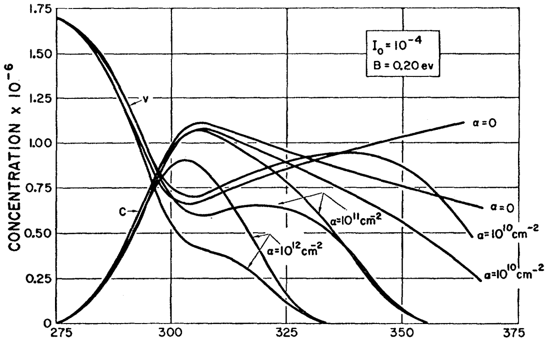

FIG. 7. Constant-tempering-rate (1°K/minute) plots with indicated sink concentration, α.

The nature of the sinks has not been stated. An obvious choice of sinks in metals is dislocations. A value of $\alpha = 10^{10}$ cm^{-2} probably is most typical of an annealed metal with a dislocation density of 10^7 to 10^8 cm^{-2}, if one assumes a "trapping region" around each dislocation of 10 to 30 atoms radius. A more sophisticated approach[3] to the problem of defect annihilation at dislocations starting from the diffusion equation shows that, except at short times, the defect decay proceeds in a manner equivalent to a first-order process. It is likely, in fact, that the actual mechanism of annihilation at dislocations is further complicated by the strain-energy interaction between dislocations and point defects, the role of jogs as sinks, and the influence of stacking-fault width. These complications are beyond the scope of the present work. However, these effects probably will be relatively unimportant in determining the qualitative features of the recovery behavior since the emission of defects from traps and the free migration after emission and before encountering sinks are also rate-determining features of recovery.

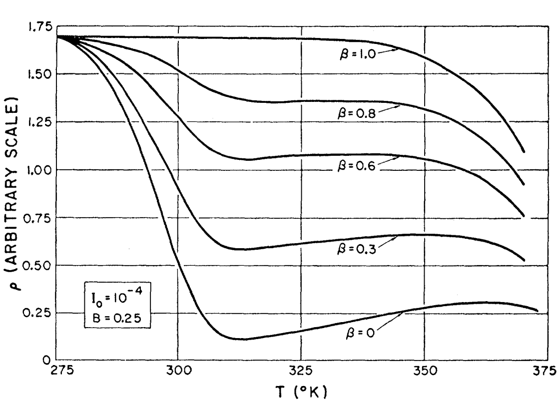

FIG. 8. Constant-tempering-rate (1°K/minute) plots of resistivity recovery for indicated values of β, the parameter which effectively measures the relative electrical resistivity contribution due to free and bound vacancies.

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[3] P. Penning, Phillips Research Rept. 14, 337 (1957).

Finally, we return to the behavior of the resistivity during annealing. This is shown in Fig. 8 for the case of $I_0 = 10^{-4}$ and $B = 0.25$ ev. Since the relative magnitudes of ρ_I and ρ_c are not usually available, several values of $\beta = (\rho_c - \rho_I)/\rho_v$ are assumed. It is clear that resolution of recovery into two stages is still present. A small rise in resistivity in the intermediate temperature range may or may not be measurable depending on the pertinent values of I_0, B, and β. Presumably, the simplest manner to attempt to observe such a rise would be to use a metal where $I_0 \approx 10^{-3}$ or somewhat greater.

The results presented in the previous sections are basically more general than it may first appear. A particular model has been used only to demonstrate the various features of defect recovery. Obviously, interstitial atoms may migrate and be bound in a manner formally equivalent to vacancies.

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Polarization of Co^{57} in Fe Metal*

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A study has been made of the effect of low temperatures on the resonant emission and absorption of 14.4-kev Mössbauer radiation from Fe^{57} in Fe metal. Analysis of intensity changes in the hyperfine spectrum is made in terms of the Zeeman level splittings of the ground states of Fe^{57} absorbing nuclei and of the ground states of Co^{57} parent nuclei. The theory for the temperature dependence is developed in terms of the properties of the Co^{57} decay and of the subsequent gamma transitions. Experiments were carried out with a source of Co^{57} nuclei in Fe metal at temperatures between 4.5° and 0.85°K. The experimental results, analyzed in terms of the theory, yield a value of the hyperfine magnetic field at the Co^{57} nuclei. Comparison of the result with other pertinent experimental values indicates that depolarization of the nuclei by the K-capture decay of Co^{57} is not evident in the present material.

I. INTRODUCTION

The 14.4-kev gamma rays of Fe^{57} nuclei are known to have, in suitable crystals, a high proportion f of recoil-free, or "Mössbauer" radiation.[1-4] Interest in the Fe^{57} system is enhanced by the relatively narrow linewidths characteristic of the excited state (lifetime 10^{-7} sec) and the clearly resolvable hyperfine components of the Mössbauer pattern. Experiments with Fe crystal sources and absorbers are facilitated by the large value of f even at room temperature as a consequence of the high Debye characteristic temperature ($\Theta \simeq 420$°K) and the low nuclear recoil temperature ($T_R \simeq 40$°K). A source of Co^{57} nuclei dissolved in a Fe lattice at room temperature has $f \simeq 0.7$[1]; cooling the source to 0°K increases f to 0.92. This limit is achieved to within 0.1% by 20°K, and similar "saturation" obtains for the fraction f' of recoil-free absorption by an absorber of Fe^{57} in Fe metal. Further cooling will result in a negligible increase of f and f'; cryogenic studies of the system might appear unprofitable.

At sufficiently low temperatures, however, a redistribution of the populations of the Zeeman sublevels takes place, and the nuclei become polarized.[5] This polarization can be quantitatively studied through the effect upon the hyperfine Mössbauer spectrum. While nuclear polarization in ferromagnets has been observed before,[6] the present technique offers certain advantages. In this type of experiment the magnitude and sign of the magnetic field at the Co nucleus may be determined. The effects of the nuclear polarization are the concern of this paper.

II. Fe^{57} IN Fe METAL

The ground state of Co^{57}, with a half-life of 270 days, decays by K-electron capture and neutrino emission to the second excited state of Fe^{57}. The decay is probably an allowed transition, since its value of $\log ft = 6$ lies

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[2] J. P. Schiffer and W. Marshall, Phys. Rev. Letters 3, 556 (1959).

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[4] S. S. Hanna, J. Heberle, C. Littlejohn, G. J. Perlow, R. S. Preston, and and D. H. Vincent, Phys. Rev. Letters 4, 177 (1960).

[5] J. G. Dash, R. D. Taylor, P. P. Craig, D. E. Nagle, D. R. F. Cochran, and W. E. Keller, Phys. Rev. Letters 5, 152 (1960).

[6] M. J. Steenland and H. A. Tolhoek, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1957), Vol. II, Chap. X, p. 292.