

Theory of Vacancy Annealing in Impure Metals*

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 (Received May 18, 1960)

The general equations for the annealing of vacancies in metals containing impurities to which the vacancies can be attached have been solved on an analog computer for a wide variety of parameters. The computer results show that some simplifying assumptions may be made which permit the general equations to be solved analytically. It is shown that for many physically interesting cases of vacancy migration the decay curve is exponential, and the decay constant is related to, but not equal to, the rate constant for vacancy migration. It is further shown that only experiments performed on zone-refined metals can give the correct vacancy migration energy, and that impurity contents as low as 10^{-5} can seriously affect the results. Experimental methods and calculations are discussed which can be used to measure the binding energy of vacancies to impurities in metals prepared by controlled doping.

INTRODUCTION

THE annealing of vacancies in quenched, cold-worked, and irradiated metals is now a rather standard method for the measurement of the activation energy for their mobility. It is well established that vacancies can become bound to some impurity atoms, but no theoretical analysis has been made of the effect of this binding on the annealing kinetics. For instance, the purity of the metal required to yield accurate data is not known, but the investigators feel that the metal should be quite pure. Several annealing curves have shown deviations from exponential, and it is not known if this can be caused by impurity binding.

Modern theories of impurity diffusion in metals require that vacancies be bound to the impurities to form a "Johnson molecule." Calculations have been made of this binding energy¹⁻⁴ and the results have been checked against measured diffusion coefficients. Agreement has been rather poor in many cases casting some doubt on the calculations. However, there are other factors, in addition to vacancy-impurity binding, which can affect the diffusion of impurities,^{2,5} and the existence of these possibilities implies that diffusion measurements are not a fair test of the validity of binding energy calculations. One of the natural results of a theory of vacancy annealing in the presence of impurities will be the suggestion of a more direct type of experiment by which the binding energy of impurities to vacancies can be determined.

The problem of vacancy-impurity interaction is treated in the most simple form by solving the corre-

sponding differential equations on the analog computer (Electronic Associates, Incorporated, Type 31R) at Brookhaven National Laboratory. It is realized that divacancies⁶ can form which can alter the kinetics and that the formation of trivacancies⁷ and larger clusters probably supply an increased number of sinks for the removal of the vacancies. This general problem, which is obviously much more complex, is currently being studied, and the results will be published in a later paper. However, it is believed that as long as the vacancy concentration is low, clusters of vacancies can be ignored. This is indicated by experiments which show that significant deviations from exponential decay usually occur for high-temperature quenches where the initial concentration of vacancies is high.

It will be shown that, regardless of the impurity concentration, an exponential decay almost always occurs. However, the rate constant of this decay is only partly related to the activation energy of vacancy mobility. Even metals of 10^{-5} impurity content can yield false values for vacancy migration energy, and only zone-refined metals of purity of at least 10^{-7} can guarantee a true value. This requirement of extremely high purity has been anticipated in the experiments on aluminum by DeSorbo and Turnbull.⁸

THEORY

The two reactions in the annealing of vacancies to sinks in the presence of impurities to which they can be bound are:

$$v + I \xrightleftharpoons[K_2]{K_1} C, \quad (1)$$

$$v \xrightarrow{K_3} \text{sinks}, \quad (2)$$

where v , I , and C are the concentration (atomic fraction) of vacancies, unbound impurities and vacancy-

⁶ J. S. Koehler, F. Seitz, and J. E. Bauerle, *Phys. Rev.* **107**, 1499 (1957).

⁷ A. C. Damask, G. J. Dienes, and V. G. Weizer, *Phys. Rev.* **113**, 781 (1959).

⁸ W. DeSorbo and D. Turnbull, *Phys. Rev.* **115**, 560 (1959).

* This work was supported in part by the U. S. Atomic Energy Commission.

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¹ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958), p. 88.

² D. Lazarus, *Phys. Rev.* **93**, 973 (1954).

³ F. J. Blatt, *Phys. Rev.* **99**, 600 (1955).

⁴ L. C. R. Alfred and N. H. March, *Phys. Rev.* **103**, 877 (1956); *Phil Mag.* **46**, 759 (1955).

⁵ A. Ascoli and A. C. Damask, *Bull. Am. Phys. Soc.* **5**, 182 (1960).

impurity complexes, respectively, and the K 's are the corresponding rate constants. The physical meaning of Eq. (2) is that vacancies disappear by migration to a fixed number of sinks (for example, dislocations). The differential equations for these reactions can be written as (after the substitution $I = I_0 - C$)

$$dC/dt = K_1 I_0 v - K_1 C v - K_2 C, \quad (3)$$

$$dv/dt = -K_1 I_0 v + K_1 C v + K_2 C - K_3 v, \quad (4)$$

where I_0 is the total impurity concentration, which is a constant for any given experiment. Experimentally, for example by resistivity methods,⁹ the total vacancy concentration, i.e., the sum of C plus v , is the measured quantity. Thus the pertinent quantity to be calculated is $N = C + v$, which from Eqs. (3) and (4) is described by the differential equation

$$dN/dt = d(C + v)/dt = -K_3 v. \quad (5)$$

Equations (3) and (4) form a set of nonlinear coupled differential equations which when solved will describe the complete annealing behavior of the system. The equilibrium concentration of vacancies at the annealing temperature is negligibly small, and hence v and C approach zero as time approaches infinity. (The equilibrium concentration is easily included, if desired, by a simple change in variables.)

These equations were solved on the analog computer for a wide variety of parameters (initial vacancy concentration, impurity concentration, and binding energy) and the details of these calculations will be discussed in the next section. The first general result of interest from the machine calculation was the finding that the number of complexes, C , increased very rapidly during the early stage of the annealing. During this same transient period the concentration of free vacancies decreased rapidly. After these fast transients, C and v decayed steadily. The physical basis for this behavior is as follows: The equilibrium concentration of complexes at the annealing temperature is much larger than that at the quench temperature. The fast transient is therefore the establishment of the new equilibrium and is largely governed by the jump rate of the vacancies (see Appendix I). The rapid elimination of these transient conditions suggested that an analytic approximation could be used for the bulk of the decay curve. Equilibrium for the first reaction, Eq. (1), implies that

$$\frac{C}{v(I_0 - C)} = \frac{K_1}{K_2} \equiv K, \quad (6)$$

or

$$C = \frac{K I_0 v}{1 + K v}. \quad (7)$$

⁹ It is assumed throughout that the electrical resistivity of a bound vacancy is the same as a free one.

Substitution into Eq. (5) gives

$$\left(\frac{1}{v} + \frac{K I_0}{v(1 + K v)^2} \right) dv = -K_3 dt. \quad (8)$$

Integration gives

$$\ln v + \frac{K I_0}{1 + K v} - K I_0 \ln \left(\frac{1 + K v}{v} \right) + A = -K_3 t, \quad (9)$$

where A is the constant of integration. Equation (9) gives v as a function of time. The value of C corresponding to any value of v can be calculated from Eq. (7) and thereby $C + v$ can be determined as a function of time.

Equations (7) and (9) were found to fit all of the curves obtained in the machine calculations. Somewhat surprisingly, however, many of the decay curves (the change of N with time) were found to be simply exponential in time which implies that the ratio of C to v remained constant. This constancy of C/v arises from a further approximation in Eq. (6), namely $C \ll I_0$. This latter approximation is valid over a wide range of the physically interesting parameters. Substitution of

$$\frac{C}{v} = \frac{K_1}{K_2} I_0, \quad (10)$$

into Eq. (5) and integration gives

$$C + v = N = B \left(1 + \frac{K_1}{K_2} I_0 \right) e^{-K_e t}, \quad (11)$$

where

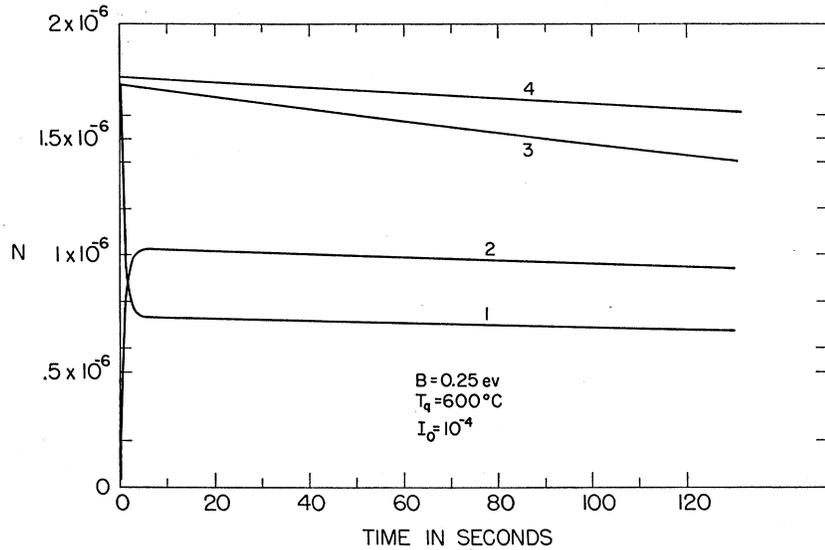
$$K_e = K_3 / \left(1 + \frac{K_1}{K_2} I_0 \right). \quad (12)$$

Equations (11) and (12) can also be derived from Eq. (9) with the approximation that $K v < 1$ and $v < 10^{-3}$. (This latter approximation allows one to neglect $K I_0$ with respect to $|K I_0 \ln v|$.)

Two things are immediately evident from Eq. (12). First, K_e is a composite of all the rate constants and the impurity concentration and will therefore, in general, not obey a simple Arrhenius equation even though the decay curves are purely exponential. Secondly, the pre-exponential term contains two of the rate constants and is therefore temperature dependent. It is therefore obvious that the determination of activation energy by a change of annealing temperature and calculation of the slope ratio is an unsatisfactory method.

It is also clear from Eq. (12) that the effective rate constant decreases with increasing impurity concentration. The physical basis for this behavior may be described as follows. The vacancies, in their random migration toward sinks, encounter impurity atoms at which they become trapped temporarily, i.e., the complexes must dissociate to furnish free vacancies for

FIG. 1. Computer-produced curves of Eqs. (3), (4), and (5) with $B=0.25$ ev, $T_q=600^\circ\text{C}$ and $I_0=10^{-4}$. Curve 1—concentration of free vacancies; curve 2—concentration of complexes; curve 4—concentration of $N=C+v$; curve 3— v (and N) vs time for pure metal, i.e., $I_0=0$.



further annealing. Thus, the whole annealing process is slowed down.

DETAILS OF CALCULATIONS AND RESULTS

A wide range of physically interesting parameters were selected for the machine solution of the general coupled nonlinear Eqs. (3) and (4). The pertinent parameters, which determine the rate constants and the initial conditions, are the annealing temperature, the vacancy migration energy, the effective sink concentration, α , the vacancy formation energy, the quench temperature, the impurity concentration and the vacancy impurity binding energy. The following parameters were held constant throughout the calculation: the annealing temperature, 100°C ; the vacancy migration energy, E_M , 0.8 ev; the vacancy sink concentration α , 10^{+10} , (see Dienes and Vineyard,¹⁰ and Dienes and Damask¹¹),¹² and the vacancy formation energy, 1.0 ev. The variable parameters were the quench temperature, 600, 800, 1000°C ; the impurity concentration, 10^{-5} , 10^{-4} , 10^{-3} ; and the vacancy-impurity binding energy, B , 0.20, 0.25, 0.35 ev.

The initial concentration of free vacancies was assumed to be the equilibrium concentration at the quench temperature and therefore calculated from the relation

$$v_0 = e^{-E_F/kT},$$

¹⁰ G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957), p. 143.

¹¹ G. J. Dienes and A. C. Damask, *J. Appl. Phys.* **29**, 1713 (1958); see p. 1716.

¹² The quantity frequently measured experimentally is the mean number of jumps a vacancy makes before annihilation which, from a random walk approximation, is roughly the reciprocal of the atomic fraction of sinks, α , from reference 10, is given as $\alpha = 2\pi N_0 / \ln(r_1/r_0) \sim N_0$ where N_0 is the number of dislocation lines per cm^2 . Therefore the concentration of sinks is $N_0 \times$ number of lattice sites per cm of line, and the atomic fraction of sinks $= N_0 \times (\text{number of lattice sites/cc})^{-1}$ if it is assumed that

$$(\text{sites/cm of line})^3 = \text{lattice sites/cc.}$$

where E_F is the energy of formation. This assumes that the number of free vacancies is independent of the number of bound vacancies. This assumption is valid up to a concentration of about 10^{-3} impurity atom; at this concentration the error is about 1% (because 13 I_0 lattice sites are not accessible to the free vacancies). The initial concentration of complexes was calculated from Eq. (6) using the above values for v_0 . The K 's are written as follows:

$$K_1 = 42\nu \exp(-E_M/kT),$$

$$K_2 = 7\nu \exp[-(E_M+B)/kT],$$

$$K_3 = \alpha\nu\lambda^2 \exp(-E_M/kT),$$

where 42 and 7 are the appropriate combinatory numbers for association and dissociation of complexes, respectively, and the values assigned to the other constants are $\nu = 10^{13}$ and $\lambda^2 = 10^{-15}$.

A typical solution for the early stages of the annealing is shown in Fig. 1. The rapid build up of the complexes and the associated decay of the free vacancies are clearly observable. The transients obviously disappear very fast with respect to the decay of N . For comparison the annealing of vacancies in the absence of impurities is also shown.

Figure 2 shows some selected curves which have been plotted semilogarithmically. For these curves the binding energy is 0.2 ev. The lower four curves represent runs at the same quench temperature but different impurity concentrations. The upper curve has the same parameters except for a different quench temperature. It is seen to be parallel to the curve at equivalent impurity concentration but of lower quench temperature. All of these curves are straight which indicates that each has a single decay constant. It is also seen that the decay constant is the K_0 of Eqs. (11) and (12), and K_0 calculated by these equations is exactly the same

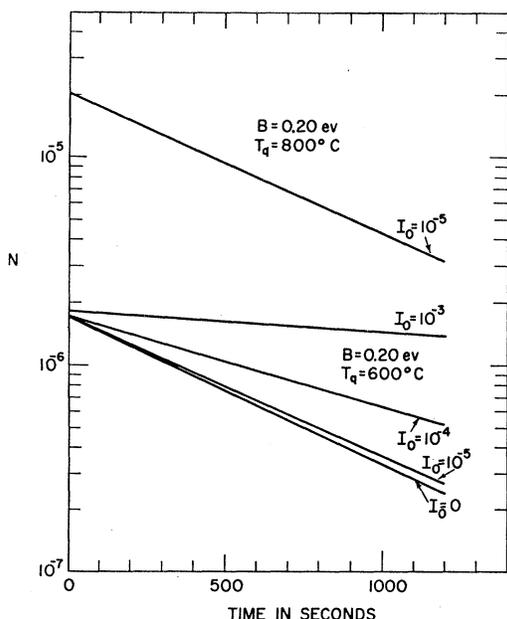


FIG. 2. Semilogarithmic plots of curves of the type shown in Fig. 1 for the decrease of N with time. All curves in this figure are straight lines.

as read from these curves. The important point demonstrated is that a good exponential plot of vacancy annealing data does not mean that the activation energy thereby determined is the activation energy of motion of the vacancy.

The approximation which applies in the above cases is that the number of complexes is small compared to the number of impurities. It is therefore expected that this approximation will become invalid at higher

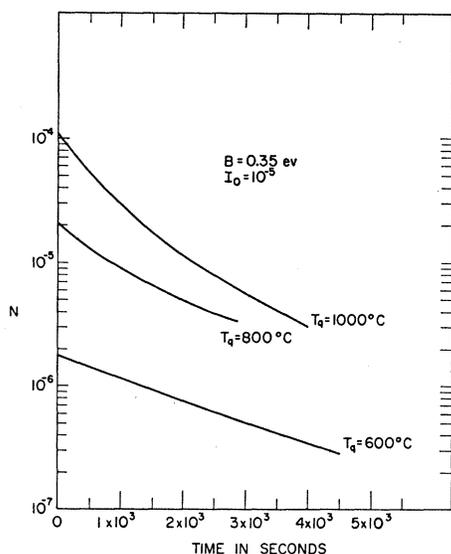


FIG. 3. Semilogarithmic plots of computer-produced curves of the same type as in Fig. 2 showing decrease of N with time in cases where exponential approximation is invalid.

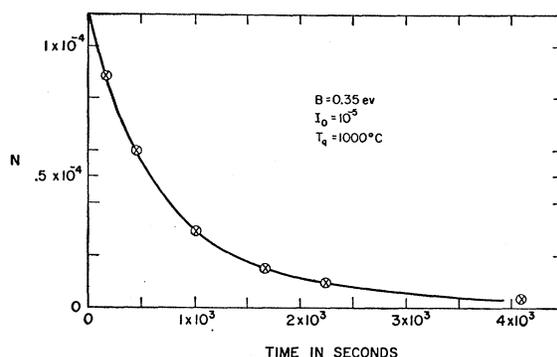


FIG. 4. Computer-produced curve for the case $B=0.35$, $I_0=10^{-5}$, and $T_q=1000^\circ\text{C}$. Circles are points calculated from Eq. (9).

vacancy concentration, i.e., higher quench temperatures, high binding energies, and low impurity concentrations. This deviation from linearity is shown by the examples of Fig. 3. These curves show how the deviation from linearity increases with quench temperature. For this high binding energy even the lowest curve, $T_q=600^\circ\text{C}$, is not quite linear. For these curves the more complete solution of Eq. (9) must be applied. An example of the validity of this analysis is shown in Fig. 4. This is the original machine drawn curve from which the upper curve of Fig. 3 was plotted. The constant A of Eq. (9) was evaluated at the first (early time) point on the curve to avoid transient effects, and the succeeding points were calculated from the same equation. It is seen that the equilibrium solution fits the general solution with excellent accuracy. The curvature of the examples of Fig. 3 diminishes with increasing time since the vacancies are being removed and the condition approaches the approximation of Eq. (10). This behavior of a rather fast early decay followed by exponential behavior has been observed experimentally in quenched samples,¹³⁻¹⁶ although divacancy formation may cause some of the early variation (Appendix II). A similar early fast decay has been observed during the annealing of copper irradiated at low temperature.¹⁷ It is possible that interstitials interact with impurities in this case; the formal theory of this interaction is identical to the vacancy-impurity interaction discussed here. According to the present theory, deviations from pure exponential behavior due to the presence of impurities are expected to be predominant for low impurity concentrations.

Even if the early parts of annealing curves are avoided, difficulties in analysis still arise. As was pre-

¹³ F. J. Bradshaw and S. Pearson, *Phil. Mag.* **1**, 812 (1956); **2**, 379 (1957).

¹⁴ G. L. Bacchella, E. Germagnoli, and S. Granata, *J. Appl. Phys.* **30**, 748, 1959.

¹⁵ G. Airoidi, G. L. Bacchella, and E. Germagnoli, *Phys. Rev. Letters* **2**, 145 (1959).

¹⁶ J. E. Bauerle and J. S. Koehler, *Phys. Rev.* **107**, 1493 (1957), see Fig. 7.

¹⁷ T. H. Blewitt, R. R. Coltman, and G. E. Klabunde, *Bull. Am. Phys. Soc.* **4**, 135 (1959).

viously stated, Eq. (11) will not obey an Arrhenius law. It is of interest to calculate the temperature dependence of Eq. (12) for some selected parameters to show what may be expected experimentally. All variations will, of course, occur within the two limiting slopes of E_M and E_M+B . These two limits are shown in Fig. 5 by curves 1 and 5. The limiting case of E_M+B cannot be attained with a binding energy lower than 0.35 for an impurity concentration as low as 10^{-8} . Conversely, if the binding energy is 0.2 eV, 10^{-6} impurity concentration will begin to cause deviation from the E_M limiting slope in the lower temperature region. This means that if the binding energies of the impurities in a metal are not known, the measurement of vacancy migration energy cannot be guaranteed to be correct even with an impurity concentration of 10^{-7} . Although not shown in this figure, a binding energy of 0.35 will correspond to a slope larger than E_M for an impurity concentration as low as 10^{-7} . This may well be an extreme case, but the general picture given by this figure is that any measurements on metals less pure than zone-refining processes permit will contain a probable error of a considerable fraction of the unknown binding energy. An example of the nonlinearity of this Arrhenius plot is evident in curves 3 and 4. The change in slope with temperature is visually evident in curve 3 and is calculated and labeled on curve 4. It is evident from this analysis that the influence of impurities is emphasized by low-temperature annealing runs.

DISCUSSION

The requirements for the study of vacancy migration in impure metals can now be examined. In order to obtain the energy for vacancy migration, zone-refined metals must be used and caution must be exercised in the subsequent handling of the material to prevent the introduction of impurities. The guarantee of results can perhaps be established by performing the same experiment after a second zone refining to see if a change has occurred. Once the vacancy migration energy has been measured, binding energy experiments can be done. This is achieved by making the same measurements on a zone-refined specimen to which a known amount of a single impurity has been added. It was shown in Fig. 5 that in order to attain the E_M+B slope with a low binding energy, impurity concentrations considerably greater than 10^{-8} must be added. This can lead to problems in the association of impurities and also to a breakdown of the present simple theory. However, in order to obtain the value of B , the slope E_M+B need not be achieved. The binding energy can be calculated immediately from any exponential decay curve by use of Eq. (12) once E_M is accurately known.

For the purposes of computation the annealing data should be taken in the range where an exponential decay occurs. This is achieved by either low-tempera-

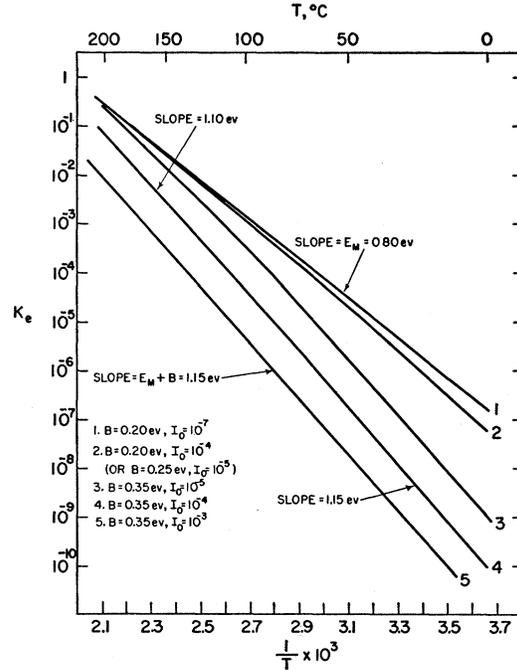


FIG. 5. Plot of calculated K_e vs $1/T$ for selected parameters.

ture quenches or analysis of only the long-time portion of the decay curve where Eq. (11) is expected to be obeyed.

ACKNOWLEDGMENTS

The authors are indebted to Cesar Sastre of Brookhaven National Laboratory who performed the computations on the analog computer. They are grateful to Dr. G. H. Vineyard and Dr. E. Germagnoli for stimulating discussions.

A portion of this work was done while one of us (A. C. Damask) was a guest of C.I.S.E. Laboratory, Milan, Italy.

APPENDIX I

The analog computer solutions have indicated that the transient is fast compared to the steady decay of the defects. Since the analog computer solutions were obtained only at one annealing temperature, we examine here the importance of the transient under more general conditions.

From Eqs. (1), (2), and (12), of the text the ratio of the transient rate, R_t , to the steady decay rate, R_s , may be written

$$\frac{R_t}{R_s} = \frac{K_1 v (I_0 - C)}{K_e (C + v)} \quad (\text{I-1})$$

This ratio, which should be large for a fast transient, is small when K_e is maximum, i.e., $K_e = K_3$ (a minimum of binding). Thus,

$$\frac{R_t}{R_s} \geq \frac{K_1 v (I_0 - C)}{K_3 (C + v)} \quad (\text{I-2})$$

At $t=0$ $C \ll v$ and $C \ll I_0$ and therefore

$$\left. \frac{R_t}{R_s} \right)_{t=0} \cong \frac{K_1 I_0}{K_3}. \quad (\text{I-3})$$

Using the values for K_1 and K_3 given in the text

$$\left. \frac{R_t}{R_s} \right)_{t=0} \sim \frac{4 \times 10^{16} I_0}{\alpha} \sim 40, \quad (\text{I-4})$$

for $\alpha = 10^{10}$ and $I_0 = 10^{-5}$ (which is again the low limit for the R_t/R_s ratio). Thus, the initial rate of approach to equilibrium is much faster than the steady decay for physically reasonable choices of the parameters, and, the equilibrium of the reaction represented by Eq. (1) is rapidly established, as already shown by typical analog computer solutions.

APPENDIX II

Experiments reported in the literature to date indicate that annealing of quenched-in defects has the following characteristics:

1. The over-all defect concentration decreases monotonically, i.e., dN/dt is always negative.

2. In most cases the second derivative, d^2N/dt^2 , is positive. For quenches from high temperature, decay curves with an inflection point have also been observed. The latter would imply a second derivative that is negative at $t=0$.

The annealing equations for the vacancy-impurity mechanism are examined for these characteristics in this Appendix.

Equation (5) of the text,

$$dN/dt = -K_3 v \quad (\text{II-1})$$

shows immediately that dN/dt is always negative as required by condition 1 above.

The second derivative is given by

$$\begin{aligned} \frac{d^2N}{dt^2} &= -K_3 \frac{dv}{dt} \\ &= -K_3 [-K_1 v (I_0 - C) + K_2 C - K_3 v]. \end{aligned} \quad (\text{II-2})$$

At $t=0$, I_0 , and C are related by the equilibrium condition at the quench temperature, i.e.,

$$\frac{C}{v(I_0 - C)} = \frac{K_1^1}{K_2^1} = 6e^{B/kT_q}. \quad (\text{II-3})$$

At $t=0$, therefore,

$$\frac{d^2N}{dt^2} = K_3 K_2 \left(\frac{K_3}{K_2} v_0 + \frac{K_1/K_2}{K_1^1/K_2^1} C_0 - C_0 \right). \quad (\text{II-4})$$

Since $T_q > T_a$, $\exp(B/kT_q) < \exp(B/kT_a)$ and, therefore, $K_1^1/K_2^1 < K_1/K_2$. Thus, $(K_1/K_2)/(K_1^1/K_2^1) > 1$ and, therefore, d^2N/dt^2 is always positive.

Thus, the vacancy-impurity mechanism cannot explain those decay curves which show an inflection point. The inflection point very probably arises from the presence of quenched in divacancies. We plan to examine the kinetics of annealing in the presence of divacancies by the techniques discussed in this paper.