RADIATION-ENHANCED DIFFUSION IN METALS AND ALLOYS

By

Ngai Q. Lam and Steven J. Rothman

Prepared for Presentation

ASM Materials Science Seminar:
Radiation Damage in Metals
Cincinnati, Ohio
November 9-10, 1975
The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U.S. Energy Research and Development Administration, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona  Kansas State University  The Ohio State University
Carnegie-Mellon University  The University of Kansas  Ohio University
Case Western Reserve University  Loyola University  The Pennsylvania State University
The University of Chicago  Marquette University  Purdue University
University of Cincinnati  Michigan State University  Saint Louis University
Illinois Institute of Technology  The University of Michigan  Southern Illinois University
University of Illinois  University of Minnesota  The University of Texas at Austin
Indiana University  University of Missouri  Washington University
Iowa State University  Northwestern University  Wayne State University
The University of Iowa  University of Notre Dame  The University of Wisconsin

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or 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. Mention of commercial products, their manufacturers, or their suppliers in this publication does not imply or connote approval or disapproval of the product by Argonne National Laboratory or the U.S. Energy Research and Development Administration.
INTRODUCTION

Diffusion during the high-temperature service of alloys is a well-known phenomenon. The alteration of the diffusional behavior of alloys by radiation is a new development, which can be encountered when materials are subjected to irradiation. Some of the technically important phenomena that involve diffusion during irradiation are fission-product redistribution in reactor fuels, defect clustering in CTR first-wall or fast-reactor cladding, the smearing-out of concentration gradients in ion-implanted semiconductors, and development of microstructures in a high-voltage electron microscope. A study of radiation-enhanced diffusion, henceforth abbreviated as RED, can aid in the understanding of all these phenomena, as well as offering insight into the basic behavior of radiation-produced point defects. The present review concentrates on the study of the basics of RED.

In the absence of irradiation, diffusion in metals and alloys takes place via the thermally activated motion of equilibrium lattice vacancies (1). The self-diffusion coefficient of the material under these conditions is given by

\[ D_{\text{th}} = C_v^0 D_v, \]

where \( C_v^0 \) is the equilibrium concentration of vacancies, and \( D_v \) is their diffusion coefficient (2). The contribution of interstitials is thought to be negligible. Radiation can enhance diffusion by increasing the concentration of vacancies and interstitials, accelerating their motion, or introducing completely new mechanisms.

*Work supported by the U.S. Energy Research and Development Administration.
Energetic radiation can displace atoms, thus increasing the concentration of vacancies and interstitials. If the temperature is sufficiently high for these radiation-induced point defects to be mobile, but low enough so that the concentration of excess vacancies is much larger than \( C_0 \), radiation-enhanced diffusion will be dominant. The exact temperature obviously depends on the irradiation conditions, but 0.6 \( T_M \) seems to be the upper limit for conventionally attainable particle fluxes (3). At low temperatures, where interstitials are still mobile, irradiation can enhance diffusion by many orders of magnitude, even though the values of the radiation-enhanced diffusion coefficient, \( D_{\text{rad}} \), expected in this temperature range are small (\( D_{\text{rad}} < 10^{-14} \text{ cm}^2/\text{s} \)).

Radiation can also accelerate diffusion by increasing the jump frequency of the point defects (4). The radiation must impart only a few electron volts of energy to an atom to permit a jump into a neighboring vacancy or an exchange with a neighboring interstitial.

In addition to interstitial-vacancy pairs (Frenkel defects), radiation can also produce large collision cascades (displacement spikes) and, especially in insulators, short-lived regions of quite high temperature (thermal spikes). The atoms inside the collision cascades can undergo mixing during the formation of the cascades, and this can induce some atomic motion at 0 K. Similarly, the rapid diffusion inside the thermal spike can cause increased mixing; this is thought to be of particular importance in reactor-irradiated UO₂ (5).

RED was first considered in the early days of the Manhattan project (6), demonstrated experimentally in 1952 (7), and the basic equations were solved by Lither in 1954 (8). The subject was most recently reviewed by Adda et al. (9), who presented complete tables of experimental results on which we have drawn extensively.

The emphasis of the present paper is on diffusion by radiation-induced point defects. In the next sections, we present the theory of this process and review the experimental work on metals and alloys, concentrating on quantitative measurements of radiation-enhanced diffusion. Rather than comment on every paper in the field, we treat a few topics critically.
KINETICS OF DIFFUSION BY RADIATION-INDUCED POINT DEFECTS

The Simple Model

We consider a model in which diffusion occurs as a result of motion of vacancies and interstitials only, that is

\[ D_{\text{rad}} = D_v C_v + D_i C_i, \]  

where \( C_v \) and \( D_i \) are the concentration and diffusion coefficient of interstitials. We assume that we know \( D \) and \( D_v \) a priori, e.g., from low-temperature irradiations (10). To know \( D_{\text{rad}} \), we calculate \( C_v \) and \( C_i \) as follows.

A monatomic solid is irradiated so as to produce Frenkel pairs (interstitials and vacancies) at a rate of \( K \) atomic fraction per second. Since the concentrations of the vacancies and interstitials are larger than their equilibrium concentrations, the free energy of the solid will be lowered by their disappearance. Thus, if the point defects are mobile, they will tend to annihilate, either by mutual recombination or at sinks such as surfaces, grain boundaries, dislocations, and voids. The change in the average concentration of vacancies, \( C_v \), or interstitials, \( C_i \), with time is then given by (3,11,12):

\[ \frac{3C_v}{3t} = K_v - K_{iv} C_i C_v - K_{sv} C_{sv} (C_v - C_v^0) + D_v \dot{C}_v^2 \]  

(3a) and

\[ \frac{3C_i}{3t} = K_i - K_{iv} C_i C_v - K_{si} C_{si} C_i + D_i \dot{C}_i^2 \]  

(3b)

Here \( K_{iv} \), \( K_{sv} \), and \( K_{vi} \) are the rate constants for mutual recombination and the annihilation at sinks of vacancies and interstitials, respectively, \( C_{sv} \), \( C_{sv} \), \( D_v \), and \( D_i \) are the atomic fractions of sinks and diffusion coefficients for interstitials and vacancies, respectively. For simplicity, the equilibrium concentration of vacancies, \( C_v^0 \), will be neglected. Since \( D_{\text{rad}} \) is a bulk property, we are interested in the average \( C_v \) and \( C_i \) in the sample. Before solving Eq. (3), we consider each of the terms on the right-hand side.

Defect Production. RED reflects a different aspect of point-defect behavior than electrical resistivity or transmission-electron microscopy; hence, the defect-production rate \( K \) must be calculated (13) taking these differences into account. For RED, \( K \) refers to point defects that are free to migrate and thus contribute to diffusion. Both the
vacancies trapped in the core of a collision cascade (13) and close-pair Frenkel defects (10) contribute to the resistivity of the irradiated sample but not to RED. Close-pair recombination does not contribute to diffusion because all the displaced atoms return to their original sites, and cascades and other defect clusters may actually decrease RED by acting as sinks for the mobile defects. Corrections for these effects increase the uncertainty of a calculated $K_0$ to about a factor of two.

An additional assumption implicit in Eq. (3) is that the defect-production rate, usually assumed to be proportional to the flux $\phi$, is independent of space and time. Care is required to assure that this assumption is fulfilled especially in the case of bombardment by low-energy heavy ions that have short ranges in solids.

Mutual Recombination. The model for mutual recombination envisages that the vacancies and interstitials diffuse by random walk, the latter much faster than the former (10). Annihilation occurs instantaneously when the interstitial is sufficiently close to the vacancy to be in a volume centered on the vacancy, which is called the recombination volume. A rigorous treatment of this case (14) gives, for the rate constant $K_{iv}$

$$K_{iv} = 4\pi r_{iv} (D_i + D_v)/\Omega \approx 4\pi r_{iv} D_1/\Omega \approx 6 \times 10^{16} \times D_1 \text{s}^{-1}$$

where $r_{iv}$ is the radius of the recombination volume, $\Omega$ is the atomic volume, and the numerical value comes from the experimental fact that the recombination volume is $\approx 125$ atomic volumes (15).

Annealing to Sinks. The third term of Eq. (3) implies only one type of sink is present for each defect, and the sinks are inexhaustible, immobile, and uniformly distributed in the solid. For this model, the rate constants are given by (14)

$$K_{sv,i} = 4\pi r_{sv,i} D_v,i/\Omega,$$

where $r_{sv}$ and $r_{si}$ are the effective capture radii of sinks for vacancies or interstitials, respectively. The value of $4\pi r_{sv,i}/\Omega$ depends on the type of sink. For microvoids, $4\pi r_{sv,i}/\Omega \approx 4\pi r_0 N_0$, where $r_0$ is the void radius, and $N_0$ is the number of voids/cm$^3$ (16). For dislocations, $4\pi r_{sv,i}/\Omega \approx \rho_d$ where $\rho_d$ is the number of dislocations per cm$^2$ (17). A sink efficiency factor should be included.
it is known, for instance, that interstitials are absorbed more efficiently than vacancies by dislocations. In real materials, several different sinks are present simultaneously, and the sink terms should rigorously be a sum over the different types of sinks.

The assumption of time-independent sink density is questionable for many irradiation conditions. For example, the collision cascades and defect clusters formed during bombardment by heavy ions or fast neutrons are likely to become the dominant sinks.

Diffusion to Extended Sinks. In the region near a surface or a grain boundary, the diffusion of defects to the sink must be taken into account. Hence, an explicit diffusion term is included in Eqs. (3a) and (3b), and the boundary condition \( C_v = C_i = 0 \) at the sink must be added.

Time-Dependent Solutions of Eqs. (3a) and (3b)

Equations (3a) and (3b) are not solvable analytically because of the nonlinear mutual recombination terms. Special techniques (17,18) are needed for the numerical solution because the equations are very "stiff", i.e., \( K_{iv} \) and \( K_{si} > K_{sv} \). The equations are solvable for the steady state (8,12), nevertheless, as emphasized by many authors (17,19-22), steady state is not attained in many experiments on radiation-enhanced diffusion. The time-dependent solutions are thus quite important. The details of these solutions depend on the relative values of \( D_v \) and \( C_S \) and on the temperature \( T \) through its influence on \( D_v \). We shall assume that the sinks are unbiased, \( C_{si} = C_{sv} \), and \( D_i >> D_v \).

Low Sink Densities and Low Temperatures (Vacancies Immobile). Both \( C_v \) and \( C_i \) increase linearly until recombination starts; (Fig. 1a) the \( C_v \), \( C_i \) versus \( t \) curves begin to level off at \( \sim 1/2 (K_0 K_{iv})^{1/2} \) (19). In this regime \( C_v = C_i \), and, since \( D_i >> D_v \), interstitials will dominate the mass transport (19,20,22). If interstitials move with Stage I activation energies, \( D_i \) near room temperature is sufficiently large so that the \( C_v = C_i \) condition is not observed. Even when the interstitials are assumed to move with Stage III activation energies, the existence of the \( C_v = C_i \) regime is short (e.g., 160 s for an equivalent sink density of \( 10^8 \) cm\(^{-2} \) and \( D_i = 1.8 \times 10^{-10} \) cm\(^2\)/s)(11). The radiation-enhanced diffusion coefficient in this region is given by (19)

\[
D_{rad} = D_i \left( \frac{K_0 K_{iv}}{2} \right)^{1/2}.
\]
The condition $C_V = C_i$ persists until $\sim 1/K_{sv} C_s$, when the interstitials begin to go to sinks in significant numbers. Then $C_i$ begins to decrease with time ($C_i \approx t^{-1}$), $C_V$ increases ($C_V \approx t^{1/2}$, i.e., $C_i \propto C_V = \text{constant}$), and (17,20,22)

$$D_{rad} = D_i \left( \frac{K_o}{2K_{iv} K_{sv} C_s} \right)^{1/4} t^{-1/2}.$$  

Note that $D_{rad}$ in Eq. (7) depends on time not temperature.

The time to attain $C_V = (1 - 1/e) \times$ the steady-state value (8)

$$\theta = 1/2 K_{sv} C_s.$$  

For low $C_s$ and low $T$, $\theta$ can be large, e.g., $\sim 10^8$ s for silver containing $10^6$ dislocations/cm$^2$ near room temperature. For intermediate $C_s$ and $T$, the defect buildup is the same as for low $C_s$ and $T$, except that the $C_V = C_i$ regime is negligible.

High Sink Penalties and High Temperatures (Vacancies Mobile). The interstitials are annihilated at sinks from the beginning of the irradiation. $C_i$ remains constant near its peak value after a time $\sim (K_{sv} C_s)^{-1}$, $C_V$ increases linearly with time (Fig. 1b), and (8)

$$\theta = 1/K_{sv} C_s.$$  

will be small. Thus the steady-state solutions, discussed in the next section, can be applied to this case.
Steady-state Solutions of Eqs. (3a) and (3b)

At steady state,

\[ D_i C_i = D_v C_v. \]  

(10)

Thus at steady state, the contributions of vacancies and interstitials to radiation-enhanced diffusion are equal. The form of \( D \) in this regime again depends on the relative values of \( T, C_s, \) and \( K_Q. \)

At low \( T \) and \( C_s \) or high \( K_Q \) (Fig. 2, curve 1), mutual recombination is the dominant mechanism of defect annihilation, and (3,12)

\[ D_{rad} = 2 \left( K_O V D_i / K_{V_i} \right) \frac{1}{2}. \]  

(11)

This would be the dominant mechanism for a well-annealed crystal, even at high \( T. \) For high \( T \) and \( C_s (> 10^{-4}) \), annealing at sinks is the dominant mode of defect annihilation (Fig. 2, curve 2), and

\[ D_{rad} = \frac{2 D K}{K_{V_i} C_s} \]  

(12)

The complete solution to Eqs. (3a) and (3b) must be used when the two annihilation mechanisms make roughly equal contributions. This occurs at a temperature given by (17)

\[ T_C (°K) = H^m_V/k\ln(C_s/K_Q)+36.8, \]  

(13)

where \( H^m_V \) is the vacancy migration energy (eV), and \( k \) is Boltzmann's constant (8.625 x 10^{-5} eV/°K).

The characteristics of all the regimes discussed are given in Table I. A comparison of Table I with the experimentally measured values of the \( T \) and \( K_Q \) dependence of \( D_{rad} \) enables one to identify the dominant regime.
Table 1. Characteristics of Radiation-enhanced Diffusion

<table>
<thead>
<tr>
<th>Regime</th>
<th>Conditions</th>
<th>T-dependence of $D_{rad}$</th>
<th>$K_0$-dependence of $D_{rad}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quasi-steady state</td>
<td>Low $T$, $C_s \leq 0$</td>
<td>$\frac{H}{2}$</td>
<td>$\alpha \sqrt{K_0} $</td>
</tr>
<tr>
<td>Nonsteady state</td>
<td>Low $T$, low $C_s$</td>
<td>Independent</td>
<td>$K_0$</td>
</tr>
<tr>
<td>Steady-state mutual</td>
<td>Low $T$, low $C_s$,</td>
<td>$\frac{H}{2}$</td>
<td>$\alpha \sqrt{K_0}$</td>
</tr>
<tr>
<td>recombination</td>
<td>high $K_0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steady-state recombination</td>
<td>Intermediate $T$ and</td>
<td>Complex</td>
<td>Complex</td>
</tr>
<tr>
<td>+ fixed sinks</td>
<td>$C_s$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steady-state annealing to</td>
<td>High $T$, high $C_s$</td>
<td>Independent</td>
<td>$K_0$</td>
</tr>
<tr>
<td>fixed sinks</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Deficiencies of the Simple Model

Contribution of Divacancies: The simple model ignores defect-defect interactions other than mutual recombination. The formation of divacancies is neglected, even though the number of single vacancies participating in the formation of divacancies is of the same order as lost by mutual recombination. Inclusion of divacancy and defect-cluster terms makes an analytical solution of Eqs. (3a) and (3b) impossible even for the steady state. Numerical solutions (23) show that the value and the temperature and flux dependences of $D_{rad}$ are changed by the inclusion of these terms; the simple relationships shown in Table I do not hold for the complex case.

Effects of Correlation and Binding. The neglect of correlation causes an error of 20% for tracer self-diffusion. For solute diffusion, solute-defect binding and correlation can affect $D_{rad}$ profoundly (24,25).

Radiation-induced Migration of Point Defects. The assumption that radiation affects only the concentration and not the migration of point defects, implicit in the above model, has not been universally accepted. Direct activation of defect motion by subthreshold collisions is as well as other
mechanisms can give rise to defect motion (4). The effectiveness of these mechanisms has not been calculated, and additional experimental confirmation appears to be desirable.

The Motion of Intercalals. The lowest energy form of the self-interstitial is the dumbbell, which lies in the <100> direction in a face-centered-cubic lattice. This defect moves by a nearest-neighbor 90° rotation step (25,26), and its motion is limited by crystallographic considerations. This is especially true if the interstitial is bound to an impurity. Impurities can trap interstitials so strongly that the vacancies become mobile before the interstitials detrap. If the components of an alloy differ greatly in size, interstitials of the smaller species may exchange only with the same type of atom because of steric hindrance. In a concentrated alloy, paths of small atoms will exist so that defects can anneal out, but their motion will not cause atomic ordering or disordering.

EXPERIMENTAL TECHNIQUES, RESULTS, AND DISCUSSION

The characteristic that most affects the measurement of RED is the smallness of $D_{\text{rad}}$. Modifications of conventional techniques or special techniques must be used to measure the $D$'s in this range. We group the techniques into two categories: direct and indirect. The direct techniques yield values of $D$ through Fick's laws, although not without complications. These techniques are analogs of methods used to measure conventional diffusion coefficients (27); one constructs a sample to match the chosen initial and boundary conditions, measures the concentration of the diffusing species, or some quantity that is uniquely related to the concentration, and obtains $D$ from a fit of the measured concentration profile to the appropriate solution of the diffusion equation. The indirect techniques involve the measurement, as a function of time, of some physical property that changes strongly as a result of a few atomic jumps; resistivity change due to ordering or clustering is a frequently used example. This technique usually yields a relaxation time, $\tau$, and it is assumed that $D_{\text{rad}} = \lambda^2 / 6 \tau$ where $\lambda$ is the jump distance. Such measurements can be obtained only on alloys, and their interpretation can be cloudy. Both direct and indirect measurements are difficult and a detailed understanding of the method is needed to evaluate the results.

Self-diffusion: Techniques

The usual technique for measuring self-diffusion is the so-called thin-layer sectioning method, in which a thin layer of tracer, usually radioactive, is deposited on the surface
of the sample, diffusion is allowed to occur, the sample is sectioned, and the removed sections are counted to determine the penetration plot. The concentration of tracer $C$ depends on $X$, the distance from the surface, according to (28)

$$C = \frac{M}{\sqrt{\pi} \sqrt{4Dt}} \exp \left(-\frac{X^2}{4Dt}\right),$$

(14)

i.e., the penetration plot is Gaussian. ($M$ is the amount of isotope deposited.) Since $D_{rad}$ is small, the sections are thin, $\sim \sqrt{Dt}/3$ or $10^{-7}$ to $10^{-5}$ cm, and electrochemical (27, 29-33) or sputtering techniques (34-37) must be used. The uncertainties involved in taking such thin sections are discussed in Ref. 38. The thin-layer sectioning method is attractive because self-diffusion can be measured, and self-diffusion measurements best reflect the behavior of the point defects without the complication of defect-impurity interactions.

Unfortunately, in the case of diffusion under irradiation, the very surface on which the isotope is deposited is a powerful sink for defects. The concentration of defects and therefore, by Eq. (2), $D_{rad}$ are thus zero at the surface and increase with $X$. As $D_{rad}$ depends on $X$, the penetration plot is not Gaussian along its entire length but rather becomes Gaussian with slope $1/4 D_{rad} t$ at large $X$ (Fig. 3). Here diffusion of defects to the surface is negligible, and $D_{rad}$ can, in principle, be determined from Eq. (14). However, this procedure is not universally valid because similar tails, thought to be artifacts of surface preparation, have been observed for diffusion without irradiation (38).

Near the surface at small $X$ (Fig. 3), the defect concentrations increase linearly with $X$ (11), i.e., $D_{rad}(x) = D_x X$. The solution of the diffusion equation for the isotope is then (39)

$$C = \frac{M}{D_x t} \exp \left(-\frac{X}{D_x t}\right),$$

(15)

i.e., the penetration plot is exponential; this has been observed experimentally (40). The problem is to relate the experimentally determined $D_x$ to $D_{rad}$ in the bulk, and this can be done only for steady state (40,41),

$$D_{rad} = D_x^{2/2} K_0.$$

(16)

For the nonsteady state case, the value of $D_x$ must be calculated numerically from Eqs. (3a) and (3b) and compared with the experimental value.
Other techniques for measuring self-diffusion utilize the absorption of radiation from the diffusing isotope. In the alpha-recoil technique, the radioactive daughters that recoil from α-decay of the diffusing isotope are collected. Recoil atoms from precursors that have diffused into the solid deeper than the relatively short recoil range are not collected, and $D_{\text{rad}}$ is obtained from the time-dependent daughter activity. The decrease of surface activity technique, used with radioisotopes that emit weak β or α radiation, is similar, in principle, to the alpha-recoil technique. The last two methods are inferior to the sectioning technique, because the concentration profile is not measured.

Surface smoothing is another kinetic process that involves diffusion over small distances and is affected by irradiation (42). Although this phenomenon has been used to measure conventional volume and surface diffusion (43), it is not suitable for the irradiation case because the surface acts as a sink for defects and the equations become too complicated for solution (42).

Self-diffusion: Results and Discussion

Less than a dozen measurements of self-diffusion during irradiation have been obtained compared with hundreds of measurements of ordinary diffusion. Furthermore, a number of results were obtained by techniques that measure the concentration of the diffusing isotope at or near the surface, without taking into account the sink properties of the surface. Some of the results obtained by the sectioning technique are also suspect because of the possible presence of artifacts. The results that appear valid either agree with the simple theory or give values $D_{\text{rad}}$ several orders of magnitude higher.

![Diagram](image-url)
Self-diffusion in Ag and Au. Studies of self-diffusion in Ag during proton (44) or electron (45) irradiation at temperatures above 555°C show no evidence of enhancement because $D_{\text{th}} \gg D_{\text{rad}}$ under these conditions. Also, no enhancement is found during electron irradiation (46) for $T \geq 350°C$; below this temperature, what enhancement may exist is at least partially concealed by an artifact of the sectioning technique, and thus could not be evaluated (46). The same type of artifact may invalidate the measurement of self-diffusion in Au under α-irradiation (41) and may also affect the data on self-diffusion in Ag during proton irradiation (40).

The data on self-diffusion in Au during neutron irradiation ($E > 1 \text{ MeV}$, $\phi = 6 \times 10^{12}/\text{cm}^2 \text{s}$, $K_0 = 4 \times 10^{-9}$ dpa/s, and $144 < T < 421°C$) (47) have not been published, so a detailed analysis is not possible. The diffusion enhancement is small above 260°C, and below this temperature, an activation energy of 0.51 eV is obtained. This value is close to $H_{\text{r}}/2$, indicating that mutual recombination is dominant. However, the measured value of $D_{\text{rad}}$ (e.g., $2.4 \times 10^{-16} \text{ cm}^2/\text{s}$ at 144°C) is more than two orders of magnitude higher than the value calculated from Eq. (11) ($10^{-18} \text{ cm}^2/\text{s}$). The fact that $D_{\text{rad}}$ (experimental) $\gg D_{\text{rad}}$ (calculated) cannot be attributed to the sinks formed during neutron irradiation because sinks decrease $D_{\text{rad}}$.

Self-diffusion in Ni during Electron Irradiation (48). The values of $D_{\text{rad}}$ (48), measured on Ni single crystals irradiated by 2-MeV electrons ($\phi = 1.25 - 13.8 \times 10^{13}/\text{cm}^2 \text{s}$, $K_0 = 3 - 32 \times 10^{-9}$ dpa/s, and $145 < T < 567°C$) are shown in Fig. 4. These data appear to be of good quality; the values of $D_{\text{th}}$ are in good agreement with the data collected in other laboratories. The sputtering technique used for sectioning is reliable, although some problems may be associated with atomic mixing during the removal of material. The loss of defects to the surface seems to have been greatly decreased by covering the active layer with $\approx 150 \text{ Å}$ of inactive Ni. The artifact noted in Ref. 46.

Fig. 4. Temperature Dependence of $D_{\text{rad}}$ for Self-diffusion in Ni during 2-MeV Electron Irradiation. $D_{\text{th}}$ was also measured (48).
is present, but is small compared with the total penetration.

The activation energy for $D_{\text{rad}}$ is 0.50 eV, which is half of $Q_{\text{III}}$, the Stage-III activation energy for Ni [1.03 eV (49)], and $D_{\text{rad}}$ is proportional to the square root of the electron flux. These conditions fit both the $C_v = C_i$ regime [recombination only with interstitials dominant Eq. (6)](48) and the steady state regime with dominant mutual recombination [Eq. (11)]. In the first regime, $Q_{\text{III}} = H^M$ and vacancies become mobile in Stage IV, whereas in the second, $Q_{\text{III}} = H^M$, and interstitials become mobile in a lower temperature stage, usually thought to be IR (50). One cannot distinguish between these two regimes on the basis of the activation energy and the flux dependence alone. A decision can be made from a comparison of the diffusion length of the Stage III defects ($\lambda = \sqrt{D_{\text{III}}t}$, where $D_{\text{III}}$ is the diffusion coefficient of the Stage III defects, $\nu 10^{-2} \exp (-Q_{\text{III}}/kT)$ cm$^2$/s, and $t$ is the time of the experiment) with the intersink spacing $d$. If $\lambda > d$, Stage III defects are being lost to sinks and $C_i < C_v$. If $d > \lambda$, then $C_v = C_i$. In the present case, $d$ is the distance from the center of the diffusion zone to the surface ($\approx 300$ Å) so that $\lambda >> d$, and the steady state regime obtains. This leads to the conclusion that vacancies move in Stage III. The values of $D_{\text{rad}}$ are in excellent agreement with those calculated from Eq. (11).

**Self-diffusion in Pb during a-Irradiation.** These data (51,52), obtained by the $\alpha$-recoil technique, are uncertain because the range of the recoil particle is not known accurately and the values of $D$ obtained by this technique depend strongly on surface preparation (53). A more serious error is that the data were analyzed incorrectly because a Gaussian concentration profile was assumed instead of a profile that develops from the space and time-dependent value of $D_{\text{rad}}$. The incorrect analysis yields a low value of $D_{\text{rad}}$, but how low depends on the details.

The preliminary data of Ref. 51 will not be discussed. The work of Frenzel (52) on self-diffusion in Pb during $\alpha$-irradiation ($\phi = 3 \times 10^{10}$/cm$^2$; $\Phi_0 = 1.2 \times 10^{-8}$ dpa/s, and $20 < T < 80^\circ$C) indicates an enhancement of about a factor of 100 in single crystals at 30°C. Below this temperature, $D_{\text{rad}}$ stays constant, whereas above 30°C, $D_{\text{rad}}$ increases with an activation energy of $\approx 0.30$ eV; thus, the temperature dependence of $D_{\text{rad}}$ does not fit the theory. Another unusual result in Ref. 52 is that $D_{\text{rad}}$ is higher in samples with a high $C_s$, introduced by cold working, than in single crystals. This indicates that diffusion along short-circuiting paths is being measured in both types of samples as additional sinks decrease $D_{\text{rad}}$. 
Impurity Diffusion: Techniques

Since the impurity is chemically different from the host material, its concentration can be determined by a number of methods or instruments that do not require radioactive isotopes. One such instrument is the ion microprobe in which the concentration profile is determined by on-line mass spectroscopic analysis of material sputtered from the sample and ionized in a plasma. The total amount of material removed by sputtering is measured with an interference microscope, but the instantaneous rate of material removal is monitored via the host element's line in the mass spectrometer. Material is sputtered from a relatively large area, but only the material from an \( \sim 1 \text{–} \text{mm}^2 \) area of the center is used in the analysis. The analyzed area is kept small so that flaws from surface preparation and the resultant artifacts may be avoided. This method is only applicable to diffusion zones > 1000 Å in thickness (54). Details of this technique are given in a series of papers by Beyeler and coworkers (24, 55–57).

Rutherford backscattering is also suitable for measuring the concentration profiles generated by RED. The sample surface is bombarded with a small, well-focused beam of light ions of known energy, and the energy spectrum of particles backscattered from binary collisions with the target atoms is determined. The analysis of this spectrum yields the distribution of atomic masses as a function of depth (58) and hence the concentration profile. This technique can be used only if the impurity is significantly heavier than the host atoms; for heavy impurities in a low-mass matrix, the sensitivity is \( \approx 10^{18} \) atoms/cm\(^3\) (59), and the depth resolution is 100 Å. Diffusion zones up to 2 μm in thickness can be studied by this technique.

Impurity Diffusion: Results and Discussion

Measurements of heterodiffusion during irradiation are not numerous. The interpretation is more complicated than for self-diffusion because of defect–impurity binding and correlation.

Diffusion of Cu and Au in Al during Neutron Irradiation. The measurements of \( D_{\text{rad}} \) were made for \( \phi = 0.6 - 4.5 \times 10^{13} \) cm\(^2\) s, \( K_{\text{d}} = 1.3 - 9 \times 10^{-8} \) dpa/s, and 35 \( < T < 220 \)°C. The authors used the ion microprobe to determine concentrations and have deduced \( D_{\text{rad}} \), from the Gaussian portion of the penetration plot [X large, see Eq. (14)] (24). The artifacts appear to have been avoided (54), and the work seems, in general, to be free of experimental error.
The observed temperature dependence of $D_{\text{rad}}$ for Au in Al (Fig. 5) indicates that mutual recombination is the dominant mechanism of defect annihilation at low temperatures, (with $\theta = 0.31$ eV) and annihilation at sinks predominates at higher temperatures. However, the values of $D_{\text{rad}}$ are several orders of magnitude higher than expected; $\sim 5 \times 10^{-19} \text{ cm}^2/\text{s}$ is calculated for self-diffusion in aluminum at 35°C from Eq. (11) compared with $9.7 \times 10^{-15} \text{ cm}^2/\text{s}$ measured for the diffusion of Cu in Al at the same temperature. The authors propose that the difference is due to a rapid diffusion of the impurity via the interstitial mechanism. That is, one should include the factors for correlation and defect-impurity binding in Eq. (2).

$$D_{\text{rad}} = \alpha C_v D_v + \beta C_i D_i .$$

The factor $\alpha$ is of order unity for impurities in Al (60), but $\beta$ can be large. In fact, recent electron microscope work (61) and theoretical calculations (25) have indicated the existence of strong impurity segregation due to the interaction of radiation-induced point defects, especially interstitials, with impurities. The presence of similar interactions in Al alloys would explain the large values of $D_{\text{rad}}$ for heterodiffusion in Al.

**Diffusion of Zn in Al under Ne$^+$ Bombardment.** Zinc ions were implanted in single-crystal Al at room temperature, and its diffusion was studied at 130°C during bombardment by 80-keV Ne$^+$ ($\phi = 1.4 - 70 \times 10^{13}/\text{cm}^2 \cdot \text{s}$ and $K_o = 2 \times 10^{-4} - 10^{-2} \text{ dpa/s}$) (62). The concentration profile of Zn in Al was readily determined by Rutherford backscattering, but an accurate value of $D_{\text{rad}}$ could not be obtained from the concentration profile because of the spatial dependence of both the defect-production rate and the defect concentrations. The "effective" enhanced diffusivity $D_{\text{rad}}^*$ was linearly proportional to the Ne$^+$ flux ($D_{\text{rad}} = 7.27 \times 10^{-18} \text{ ions/cm}^2 \cdot \text{s}$),
which indicates that the defects were annihilated at sinks. The sinks were produced by both the implantation of Zn and the Ne+ bombardment. These estimates of $D^\times$ are of the same order of magnitude as $D_{\text{rad}}$ for diffusion of Au and Cu in Al (24) at a defect-production rate about five orders of magnitude lower, probably as a result of large $C_s$ introduced by Ne+ bombardment.

Diffusion of Ni in Cu and Cu in Al during Ion Implantation. In Ref. 57 the diffusing material was implanted at 500 keV ($\phi = 6.9 \times 10^{11}/\text{cm}^2 \text{s}$, and $K_0 \simeq 10^{-3} \text{dpa/s}$) continuously during the experiment, and the damage caused by the implantation process gave rise to RED. The implantations were carried out at room temperature, 200°C (Cu in Al), or 350°C (Ni in Cu). The profiles of the room-temperature implants were in good agreement with the ion-distribution theory of Lindhard et al. (63), except for a small peak near the surface and a tail deep inside. Annealing of a sample implanted at room temperature produced a larger tail than expected from theory. The concentration profiles obtained via the ion microprobe from the samples implanted at high temperatures agreed with the damage-distribution theory (64), except that the tails deep inside the sample were higher. However, effects such as channeling and diffusion of interstitials, which would result in higher tails, were neglected in the analysis. Diffusion enhancements were $\sim 1.5 \times 10^3$ for Ni in Cu and $\sim 10^2$ for Cu in Al, which correspond to $D_{\text{rad}} = 1.2 \times 10^{-14} \text{cm}^2/\text{s}$ for Ni in Cu and $3.6 \times 10^{-13} \text{cm}^2/\text{s}$ for Cu in Al. The calculated $D_{\text{rad}}$ is $\sim 4 \times 10^{-15} \text{cm}^2/\text{s}$ for both systems, if the heavy-ion bombardment produces a large number of sinks ($\sim 10^{12} \text{cm}^{-2}$). If, on the other hand, mutual recombination is dominant because of the large production rate, $D_{\text{rad}} \% 7 \times 10^{-15} \text{cm}^2/\text{s}$ for Ni in Cu and $3 \times 10^{-14} \text{cm}^2/\text{s}$ for Cu in Al, which are also lower than the measured values.

These studies bear closely on the technologically important problem of ion implantation. They also have the advantage of very high defect-production rates, which give rise to high values of $D_{\text{rad}}$ that may predominate over the artifacts. On the other hand, the inhomogenous tracer and damage distributions, as well as the changes in microstructure due to bombardment, make the results more difficult to interpret.

Diffusion of $^{63}\text{Ni}$ in Cu during $\alpha$-Irradiation. The values of $D_{\text{rad}}$ were measured for $\phi = 8 \times 10^9/\text{cm}^2 \text{s}$, $K_0 = 6 \times 10^{-9} \text{dpa/s}$, and $210 < T < 285^\circ\text{C}$ using the surface-activity technique (65) and incorrect boundary conditions that led to low values of $D_{\text{rad}}$. The zero activation energy suggests annealing to sinks, and one calculates a $C_s$ of $\sim 10^9$ to $10^{10} \text{cm}^{-2}$ from the given values of $D_{\text{rad}}$. The true $C_s$ would thus be lower and therefore reasonable for an annealed polycrystal. The
value of $D_{rad}$ reported in Ref. 65 is close to the prediction of the simple theory.

The data on diffusion of $^{212}$Pb in Ag during α-irradiation (66), obtained by the alpha-recoil technique, were seriously affected by tarnishing of the samples (67) and will not be discussed.

Chemical Diffusion: Techniques

In this type of experiment, a finite concentration gradient is set up either by bringing two or more layers of different compositions into contact or by exposing an alloy that has a volatile component to a vacuum. The concentration profiles can be analyzed in different ways.

A multilayer sandwich couple can be prepared by evaporation of the two components from separate boats through a rotating slit (68). A square-wave concentration profile is obtained with wavelengths as low as 7-40 Å. The decay of the concentration profile, followed by X-ray diffraction or electrical resistivity (69), yields $D_{rad}$, the chemical diffusion coefficient averaged over the composition range. One problem with the method is that the structure of the evaporated layers which make up the sandwich can be highly imperfect (69-70) with microtwins, stacking faults, etc., acting as sinks for point defects.

The out-diffusion of a volatile element from an alloy can be studied using optical reflectivity. The relationship between the reflection coefficient and the concentration is calibrated, the reflection coefficient of the diffusion sample is measured as a function of time, and $D_{rad}$ is deduced from a comparison of the experimentally obtained and calculated concentration profile.

Interdiffusion of Ag and Au during Electron Irradiation. $D_{rad}$ was measured in the Au-Ag system during 2-MeV electron irradiation ($\phi = 1.25 \times 10^{13}/\text{cm}^2 \text{s}$ and $K_0 = 1.2 \times 10^{-10} \text{ dpa/s}$) (69). The decay of a sinusoidal concentration profile (wave length 10-20 Å) was obtained from x-ray measurements (the change in the intensities of satellites of higher order Bragg peaks) or from the change of the electrical resistivity. The dependence of the resistivity change on the amplitude of the initial concentration distribution indicated that the resistivity change was due to composition changes and not the accumulation of defects. Measurements were made during irradiation at -196°C and during warm-up to room temperature. The values of $D_{rad}$ obtained in these two stages were roughly equal,
1.2 \times 10^{-22} \text{ to } 3.0 \times 10^{-22} \text{ cm}^2/\text{s}; \text{ the range is an indication of the uncertainty.}

The diffusion during irradiation is clearly due to the motion of interstitials, as vacancies in Au-Ag alloys are immobile at -196°C. The diffusion during warm-up, which occurred in one stage at 200-263 K, was due to annealing out of vacancies. During irradiation, the interstitials were probably annihilated mostly at sinks as the production rate was quite low and the samples had a large concentration of stacking faults and twin boundaries. Using Eq. (12), we obtain \( \approx 10^{12} \text{ cm}^{-2} \) for \( K_{\text{Si}} C_g/D_i \), which is not unreasonable for evaporated films, and is much larger than the number of vacancies accumulated. The interstitials may well have reached a quasi-steady state in less than the irradiation time (\( \approx 10^5 \text{s} \)). Also \( D_\text{rad} \) increased with electron energy, and these results appear to be valid.

**Interdiffusion of Al and Mg during Neutron Irradiation.**

In these experiments, massive Al-Mg couples were irradiated in a reactor (\( E > 1 \text{ MeV}, \phi = 3.6 \times 10^{12}/\text{cm}^2 \text{ s}, K_0 = 7 \times 10^{-9} \text{ dpa/s}, \text{ and } 180 < T < 444^\circ \text{C} \)) for long times (hundreds of hours), and \( D_\text{rad} \) was obtained from a concentration profile measured with an electron microprobe (71). The average \( D_\text{rad} \) at infinite dilution were determined as a function of \( T \) for the solid solution of Mg in Al; one value of \( D_\text{rad} \) was obtained for the Mg-base solid solution. The values of \( D_\text{th} \) at infinite dilution without irradiation agreed well with data for tracer diffusion of Mg in Al (72). Thus, the comparison of \( D_\text{rad} \) at infinite dilution with \( D_\text{rad} \) for tracers is justified.

The remarkable features of the results, which differ from the theory and from other experimental results (24), are: (a) the enhancement is measurable at the unexpectedly high temperature of 300°C (Acker et al. (24) observed no enhancement at 218°C); (b) the magnitude of the enhancement is immense, \( D_\text{rad} - D_\text{th} = 3 \times 10^{-12} \text{ cm}^2/\text{s} \) at 300°C; and (c) the ratio \( D_\text{rad}/D_\text{th} \) changes only slightly from 1.5 at 350°C to 3.5 at 250°C, whereas Acker et al. found it changes from 3 at 180°C to 10^6 at 35°C; and (d) the activation energy for \( D_\text{rad} \) is 1.07 eV as opposed to 1.35 eV for \( D_\text{th} \), 0.30 eV for the diffusion of Au in Al under neutron irradiation (24). Thus the activation energy is \( > 1 \text{ eV} \). The values of \( D_\text{rad} \) (Mg-Al) (1.4 \times 10^{-14} \text{ cm}^2/\text{s}) and \( D_\text{rad} \) (Au-Al) (1.6 \times 10^{-14} \text{ cm}^2/\text{s}) are in excellent agreement at 180°C, the temperature where the two sets of measurements overlap. The data on \( D_\text{rad} \) in the Al-Mg system above this temperature could, at first glance, be explained by an error in the measurement of the in-reactor temperature. However, the care exercised in measuring \( T \) makes this explanation unlikely.
Chemical Diffusion in a Cu-Zn Solid Solutions during Ne⁺ Bombardment. This pioneer experiment on diffusion under very large $K_0 (\phi = 1.8 \times 10^{13}/\text{cm}^2 \text{s} \text{ and } K_0 = 4.5 \times 10^{-2} \text{ dpa/s})$ was used to study out-diffusion of Zn from 10% Zn-90% Cu by monitoring the optical reflection coefficient of the surface during irradiation (73). The composition of the 300-Å-thick layer at the surface determines the reflection coefficient, so $D_{\text{rad}}$ is an average over that region, which also corresponds to the 270 Å range for 30-keV Ne⁺ in Cu.

The results of measurements without bombardment lay three orders of magnitude above the values extrapolated from high temperature. Bombardment increased $D_{\text{th}}$ by an additional order of magnitude at 243°C and by 50% at 316°C.

The values of $D_{\text{rad}}$ obtained from this experiment are incorrect because the dependence of $D_{\text{rad}}$ on $x$ due to the surface sink was neglected. Different concentration profiles for bombarded and unbombarded samples are indeed indicated by the reflection coefficient versus time curves. The difference between the $D$'s for unbombarded samples and the extrapolations from high temperature also cast doubt on the validity of $D_{\text{rad}}$. Possible complications such as Ne bubble formation were also neglected in the investigation.

Ordering and Clustering: Techniques

Because clustering and ordering can produce large changes in physical properties for a small number of atomic jumps, these phenomena have often been used to measure $D_{\text{rad}}$, although actual values of $D_{\text{rad}}$ are seldom obtained. In these experiments, the alloy is quenched to retain a high-temperature random state, and the atomic rearrangement during irradiation is observed via the changes in electrical resistivity $\rho$, which is measured in situ (74). $D_{\text{rad}}$ is obtained from these data as follows. It is assumed that $\rho$ follows a chemical reaction equation (75)

$$\frac{d\rho}{dt} = -(\Delta\rho)^\gamma/\tau,$$

where $\gamma$ is the order of the reaction, $\tau$ the relaxation time, and $\Delta\rho = \rho - \rho_\infty$ ($\rho_\infty$ is the equilibrium $\rho$ for the irradiation temperature). First, $\gamma$ is obtained from a plot of log $(d\rho/dt)$ versus log $(\Delta\rho)$, Eq. (18) is solved using that value of $\gamma$, and $\tau$ is obtained from a linearized form of the solution,

$$\ln(\Delta\rho/\Delta\rho_\infty) = -t/\tau$$

(19)
for first order kinetics, and

$$\frac{\Delta \rho}{\Delta \rho_0} - 1 = \left(\frac{\Delta \rho_0}{R}\right)t/\tau$$  \hspace{1cm} (20)

for second order. Here $\Delta \rho = \rho - \rho_0$, where $\rho_0$ is the quenched-in resistivity and $R$ is the difference in resistivity between a completely disordered and a completely ordered (or clustered) alloy. The value of $D_{\text{rad}}$ for an fcc metal is given by

$$D_{\text{rad}} = \frac{a_o^2}{12\tau},$$  \hspace{1cm} (21)

where $a_o$ is the lattice parameter. We emphasize that the order of reaction refers to $\rho$ and not to the order of the defect reaction responsible for the annihilation of defects. Also, changes in $\rho$ caused by ordering or clustering are much larger than changes due to the introduction of defects, although during fast-neutron bombardment, disordering by cascades eventually becomes dominant (7).

The measurement of resistivity is a relatively simple experimental technique, but obtaining $D_{\text{rad}}$ from $\rho(t)$ is sometimes difficult. Equation (18) appears to be empirical and not obtainable from any simple quasi-chemical model (76). Also, the determination of $\gamma$ can be ambiguous; different workers obtain $\gamma = 1$ or 2 from the same set of data (19,75-77).

The magnetic property usually measured is the temperature and time-dependence of the magnetization (78). The change in the average composition of an alloy, $\overline{c}$, is measured via the magnetization, and a fit of $\overline{c}(t)$ to the solution of the appropriate diffusion equation can yield a value of $D_{\text{rad}}$. This method again averages over concentrations; it has not yet been used for a quantitative measurement of $D_{\text{rad}}$.

The Zener relaxation method consists of elastically loading and unloading the sample during irradiation and measuring the resultant anelastic strain. This strain is then analyzed by the methods described by Nowick and Berry (79) to determine $\tau$ and $D_{\text{rad}}$ [Eq. (21)].

A method quite similar in principle to Zener relaxation is the magnetic after-effect, which is manifested as a decrease in the permeability of a ferromagnetic material owing to the anchoring of Bloch walls by impurities or defects (80,81).
Ordering and Clustering: Results and Discussion

Our discussion will be limited to Ag- and Cu-base alloys because more data are available for these systems.

Electron Irradiation of Ag-8.75 at. X Zn Alloys. Annealed (75) and 95% cold-rolled (82) alloys were irradiated by 2.3-MeV electrons \( \phi = 9.35 \times 10^{12} \) to \( 4.66 \times 10^{13}/\text{cm}^{2}\) and \( K = 1.2-6.0 \times 10^{-9} \) dpa/s). The irradiation temperature varied from -20 to 190°C for the annealed alloys, and from 10 to 35°C for the cold-rolled alloys.

The most important feature of the results is that steady state (no change in \( T \) over 5 h) is found for the annealed alloys (structure nearly single crystal), whereas in the 95% cold-rolled alloys, \( x \) increases as \( t^{1/2} \) after a short incubation time. According to Eq. (7), this time dependence of \( T \) \( (D_{\text{rad}} \propto t^{-1/2}) \) indicates that the dominant mechanism of ordering is interstitial motion. If a nonsteady state defect distribution obtains in the samples with high sink density, the steady state in the annealed samples must correspond to the \( C_1 = C_N \) (quasi-steady state) regime (Eq. 6), in agreement with the observed \( T \propto f^{-1/2} \) dependence. However, the observed activation energy, 0.41 eV, deduced from the temperature dependence of \( T \) shown in Fig. 6, would then be \( H_f^2/2 \), i.e., \( H_f^2 = 0.82 \) eV, a surprisingly high energy for interstitial motion in this alloy.

On the other hand, these data can be perhaps better interpreted in terms of vacancy motion in Stage III (83). Because of the symmetry of Eqs. (3a) and (3b), vacancies and interstitials are not distinguished until one assumes that \( D_i \gg D_v \), that is, \( D_{\text{rad}} \propto t^{-1/2} \) indicates that the faster moving species is responsible for the transport. This species is usually considered to be the interstitial; however, recent work of Platov et al. (84) has indicated that interstitials are trapped in concentrated Ag-Zn alloys and are retained in the traps until Stage III, making vacancies the more mobile species. Under this interpretation \( Q = 0.41 \) eV = \( H_f^2/2 \). This value is somewhat higher than the activation energy of 0.33 eV obtained from preliminary measurements of Zener relaxation in neutron-irradiated Ag-30% Zn alloys (85) as expected from high temperature diffusion measurements.
Table 2. Experiments on Ordering and Clustering in Cu-base Alloys during Irradiation

<table>
<thead>
<tr>
<th>Alloy System</th>
<th>Irradiation Conditions</th>
<th>Temperature (°C)</th>
<th>Observation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-36% Zn</td>
<td>Neutrons</td>
<td>46 to 145</td>
<td>See Fig. 7. Q = 0.35 eV and ( \tau^{-1} \approx 0.5 ) for fresh samples. Q ( \approx 0 ) and ( \tau^{-1} \approx 0 ) for previously irradiated samples (second run effect). Reaction is of order ( \approx 1.75 ) in resistivity.</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Fast: 1.1-55x10^10/cm^2/( s )</td>
<td>Thermal: 6.6x10^11-10^13/cm^2/( s )</td>
<td>5.5-87x10^{-11} dpa/s</td>
<td></td>
</tr>
<tr>
<td>Cu-30% Zn</td>
<td>Neutrons</td>
<td>0 to 300</td>
<td>See Fig. 7. First-order reaction in resistivity. Q = 0, D = 10^{-20} cm^2/s.</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Fast: 1.2x10^{12}/cm^2/( s )</td>
<td>Thermal: 1.1x10^{12}/cm^2/( s )</td>
<td>10^{-10} dpa/s</td>
<td></td>
</tr>
<tr>
<td>Cu-30% Zn</td>
<td>Neutrons</td>
<td>50 to 125</td>
<td>Linear flux dependence</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>Flux not given</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-30% Zn</td>
<td>2-MeV electrons</td>
<td>50</td>
<td>Resistivity vs time curve same as curve for 50°C, 10^{12} fast + 4 x 10^{12} thermal n/cm^2/( s )</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>2.6x10^{14}/cm^2/( s )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-30% Zn</td>
<td>1-MeV ( \gamma )-rays</td>
<td>0 to 127</td>
<td>Temperature-dependence complex. Flux dependence roughly linear. Cold work increases ( \tau ). Fits no simple model.</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>1.7-47x10^5 R/h</td>
<td>4.2x10^{-13} dpa/s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Experiments on Ordering and Clustering in Cu-base Alloys during Irradiation (Contd)

<table>
<thead>
<tr>
<th>Alloy System</th>
<th>Irradiation Conditions</th>
<th>Temperature (°C)</th>
<th>Observation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-30% Zn cold worked, annealed at 300-600°C</td>
<td>Fast neutrons 10^{11}/cm²s</td>
<td>35</td>
<td>The higher the annealing temperature (fewer dislocations remaining) the lower</td>
<td>89</td>
</tr>
<tr>
<td>Cu-15% Al</td>
<td>Fast neutrons 5x10^{-12} - 10^{-10} dpa/s, 0.3-2.0-MeV electrons 2x10^{10} to 1.4x10^{13}/cm²s and γ photons 2-3.7x10^{12}/cm²s</td>
<td>35 to 250</td>
<td>See Fig. 7. Q = 0.41-0.50 eV for fresh samples, (\phi)-dependence over entire range neutrons through γ-rays</td>
<td>77</td>
</tr>
<tr>
<td>Cu-15% Al</td>
<td>Fast neutrons 5x10^{-12} to 10^{-10} dpa/s</td>
<td>30 to 150</td>
<td>See Fig. 7. Second run effect, Q decreases to 0.15 eV and (t)-dependence approaches linear</td>
<td>90</td>
</tr>
<tr>
<td>Cu-55% Ni</td>
<td>Neutrons Fast: 1.7x10^{11}/cm²s Thermal: 10^{13}/cm²s</td>
<td>80 to 150</td>
<td>Q = 0.56 eV for fresh samples; Q = 0 after (\sim 4 \times 10^{15} \text{nvt(fast)} )</td>
<td>86</td>
</tr>
<tr>
<td>Cu-59% Ni</td>
<td>3-MeV electrons 1-2x10^{14}/cm²s</td>
<td>-153 to 347</td>
<td>(t^{-1}) varies as (t^{-\frac{1}{2}}) and increases as temperature increases</td>
<td>91</td>
</tr>
</tbody>
</table>
Radiation-enhanced Ordering and Clustering in Cu-Zn, Cu-Al, and Cu-Ni Alloys. RED in Cu alloys (19,22,77,86-91) has been controversial because the results (Table II, Fig. 7) have, at first glance, not been in agreement, and their interpretation has become involved in the Stage III controversy (50).

The disagreement among the data is the following. For fresh samples of Cu-36% Zn (22) Cu-15% Al (77,90) and Cu-55% Ni (86) a temperature-dependent $\tau$ is obtained, with $Q = 0.35-0.56$ eV depending on the alloy. For the first two alloys, $\tau \propto \gamma$ with a proportionality factor $\gamma$ over a range of $10^5$ in production rate (gamma-ray, electron, and neutron irradiation) for Cu-15% Al (77). The temperature and flux dependences for these alloys are characteristic of mutual recombination. A "second run effect," an increase of $\tau$ accompanied by a decrease of $Q$ after one or several irradiations, is found for Cu-36% Zn (22), and Cu-15% Al (90) (Table II). However, other studies on a similar alloy, Cu-30% Zn, have yielded different behavior in that $Q = 0$ (19) and $\tau^{-1}$ is linear in flux (87), indicating predominant annealing to sinks. A somewhat similar temperature dependence of $D_{\text{rad}}$ is observed in neutron-irradiated Fe-3% Si (92).

We believe that the disagreement is due to different pre-irradiation heat treatments of the samples. The Cu-36% Zn, Cu-15% Al, and Cu-55% Ni alloys were annealed at relatively high temperatures (560°C, 750°C, and 700°C, respectively) but the Cu-30% Zn at only 350°C. The dislocations left in the Cu-30% Zn alloy may cause annealing to sinks to be the dominant regime. This concept is supported by the factor of ~5 increase in $\tau$ observed for a decrease in preirradiation annealing temperature from 300 to 600°C (89).

The "second run effect" observed on Cu-36% Zn and Cu-15% Al is probably due to the formation of defect clusters during the first irradiation, which act as sinks during the subsequent
irradiation. Such clusters are indeed shown by electron microscopy (22).

The activation energy for $\tau$ in Cu-Al differs little from that in Cu-36% Zn (Fig. 7) because the defect properties of the two alloys are similar. The "second run" $\tau$'s for these alloys are perhaps not the same because the radiation-induced sink structures vary as a result of differences in alloy composition and in reactor spectra (93).

Only data on ordering in Cu-30% Zn under $\gamma$ irradiation do not fit this scheme (89). Here $\tau^{-1}$ is temperature dependent, although the preannealing temperature and the defect production rate are low. The authors' interpretation of their data, that the temperature dependence is due to close pair recombination, is disputed (94,95).

The temperature and flux dependences of $\tau$ for Cu-36% Zn and Cu-15% Al again lead to the Stage-III controversy, as discussed above for self-diffusion in nickel. One can, in the present instance, choose between these two cases by carrying out the irradiation at a temperature below Stage III, as was done for a Cu-59% Ni alloy (91). A finite rate of clustering was observed down to 120 K, the lowest temperature investigated, indicating that some defect was diffusing freely at a temperature below Stage III. This defect can be assumed to be the interstitial. The relation $\tau^{-1} = \tau^{-2}$ observed in Ref. 91 indicates that the interstitials are annihilated at sinks and through recombination. The sinks in this instance are, according to the authors, impurities that trap the interstitials; the temperature dependence of $\tau$, not expected from the simple model (Eq. 7), is then due to the temperature-dependence of the trap radii (96).

If the interstitials are indeed mobile in Stage I, the higher temperature irradiations discussed above cannot possibly be in the $C_v = C_i$ regime because $D_i$ is large so a significant number of interstitials is lost at dislocations, grain boundaries, and sample surfaces. We conclude therefore that the behavior of the Cu-36% Zn, Cu-15% Al, and Cu-55% Ni alloys represents a steady state with dominant mutual recombination and the observed $Q = h_{\nu N_0}/2$.

The low-temperature irradiation of the Cu-Ni alloy is the first proven case of atomic mixing (or demixing) due to the motion of interstitials. We note that the size difference of Cu and Ni is small; if one adds Ni to Cu, the lattice parameter decreases only by 0.035% per atomic percent Ni. If
the size difference is larger than this, interstitials apparently will not cause atomic mixing. For instance, annealing of a neutron-irradiated Cu-12.9% Zn (97) or Cu-15% Al (98) alloy indicates that motion of the interstitial does not cause ordering, even though the size differences are only 0.053% or 0.072% on the above scale. In this connection, it would be worthwhile to ascertain if Cu-Zn alloys order during irradiation in Stage II.

High-voltage Electron Microscopy

Although it is difficult to use high-voltage electron microscopy (HVEM) to measure $D_{\text{rad}}$ directly, the evolution of the defect structure during in-situ electron irradiation can be followed and the kinetics of the migration and annihilation of radiation-induced point defects can be studied.

In general, the formation of visible defects in a metal specimen in a HVEM consists of two successive stages: nucleation of defect clusters and their growth. If the temperature dependences of the density and the growth rate of dislocation loops formed by clustering of interstitial atoms are measured, the migration energies of the interstitial and vacancy can be deduced (99-103).

Interstitial Clustering in Al, Au, and Fe. The concentration $C_L$ of interstitial dislocation loops produced during irradiation is given by (100)

$$C_L = a_0 Z (K_0/D_t)^{1/2}. \quad (22)$$

This relation and the numerical factor $Z$ are obtained by considering the possible defect reactions and assuming that di-interstitials are the nuclei of dislocation loops. The $K_0^{1/2}$ dependence of the loop density predicted by Eq. (22) has been observed for Au and Fe irradiated at room temperature (100,101). The loop density increased exponentially with temperature for Al, Au, and Fe (102) with $H^m_1$ equal to 0.19 eV for Au and 0.26 eV for Fe. Although these values are slightly higher than the Stage I migration energies, probably because of trapping of interstitials by impurities, these data give strong evidence for interstitials migrating at elevated temperatures with a small (Stage I) activation energy. An accurate evaluation of $H^m_1$ for Al is not possible from Eq. (22) because the vacancy mobility in Al is too high. Straight-line plots of $\log C_L$ versus $1/T$ also indicate that $Z$ is independent of temperature (102).

Vacancy Mobility in Cu. The growth of interstitial dislocation loops during constant irradiation at low temperatures is governed by a $t^{1/3}$ law (100,104,105), if the vacancies
are immobile. At higher temperatures, however, where the vacancies are mobile and control the growth of the interstitial loops, the growth rate, L, is independent of time and proportional to \( (K_0D_V)^{1/2} \) \(^{(103)}\).

The \( K_0^{1/2} \) dependence of \( L \) has been observed experimentally \(^{(103)}\), and \( H_m \) has been deduced from the temperature dependence of \( L \) (Fig. 8) \(^{(103)}\). The value of \( H_m \) obtained from the thick part of the foil and at low temperature was 0.60 eV, which is slightly less than the accepted value \( \gamma_{\text{III}} \) in Cu \(^{(49)}\). The loop growth rate in the thin part of the foil, and in all parts of the foil at high temperatures was independent of the temperature. In this case, annealing of defects at surfaces is the dominant mode of defect annihilation, since in thin foils the equivalent internal-sink concentration is high and vacancies move to the surfaces in significant numbers at high temperatures. On the other hand, in thick foils, annihilation of point defects at the surfaces is negligible and mutual recombination becomes the dominant mechanism.

**CONCLUSIONS**

The present status of radiation-enhanced diffusion is somewhat the same as the status of diffusion in the 1940's. Few measurements exist, some of which appear to be questionable. The simple theory appears to be upheld by the data in a number of cases (self-diffusion in Ni, ordering in Cu-base alloys) but not in others (self-diffusion in gold, heterodiffusion in Al, ordering in Cu-Zn during gamma irradiation).

Much work remains to be done. First, some of the measurements should be repeated to increase the credibility of the experimental data. Next, measurements should be expanded to cover other systems. The experiments must be carried out with
extreme care, and control experiments should be run, since
the expected effect is so small that any artifact can conceal
it and give rise to a spuriously high $D_{\text{rad}}$. The microstruc-
ture and composition of the samples must be accurately spec-
ified. Clean experiments, e.g., the measurement of self-
diffusion under low fluxes of particles that create separate
Frenkel defects should be run, keeping in mind that the effects
of such low $K_0$'s may be too small to measure. Experiments
under very high defect production rates e.g., heavy-ion
bombardments should be run, and changes of the sink structure
during the experiment should be followed by electron micros-
copy. Additional work should include studies of the depend-
ence of $D_{\text{rad}}$ on flux and type of irradiating particles, as
well as on the microstructure.

The interpretation of experiments on radiation-enhanced
diffusion ties in well with other experiments on radiation
effects. It appears to us that evidence obtained from the
diffusion experiments strongly favors the migration of va-
cancies in Stage III, but this view is not universally
accepted.

ACKNOWLEDGMENTS

This work was begun in collaboration with Prof. R.
Sizmann, whom we thank for useful discussions. Thanks are
also due Drs. M. Beyeler, T. H. Blewitt, J. R. Cost, G. J.
Dienes, V. Levy, R. Poerschke, W. Schüle, R. W. Siegel, and
H. Wollenberger for helpful discussion and correspondence.

REFERENCES

1. N. L. Peterson in "Solid State Physics" (F. Seitz, D.
   Turnbull, and H. Ehrenreich, eds) Academic Press, New
   York, 22, 409 (1968).
2. This $D$ is the self-diffusion coefficient, which must be
   multiplied by the correlation factor $f_v$ to obtain the
   tracer self-diffusion coefficient. We shall neglect
   correlation effects in most of this review.
3. For instance, if a single crystal of silver were kept at
   room temperature in a fast reactor, the radiation-enhanced
   self-diffusion coefficient would equal the equilibrium $D$,
   $6 \times 10^{-16}$ cm$^2$/s for about 370°C or 0.52 Tm.
5. D. Bruchlacher, W. Dienst, and F. Thummler in "Ceramic
   Nuclear Fuels" (O. L. Kruger and A. I. Kaznoff, eds.),
   American Ceramic Society, Columbus, Ohio, 1969, p. 100.
10. F. W. Young, Jr., this volume.
25. R. A. Johnson and Nghi Q. Lam, unpublished work.
41. U. Ermert, W. Rupp, and R. Sizmann, in "Int. Conf. on Vacancies and Interstitials in Metals" V. 2, KFA, Jülich, Germany, 1968, p. 30.
47. D. Acker, M. Beyeler, G. Brébec, and M. Sapin, unpublished work, quoted in ref. 9.
50. The controversy concerning which defects move in Stage III is best summarized in the papers of W. Schilling and of A. Seeger, Int. Conf. on Fundamental Aspects of Radiation Damage in Metals, Gatlinburg, Tenn. 1975.
54. M. Beyeler (private communication).
67. T. S. Lundy (private communication).
74. The resistance is usually measured at liquid Helium or Nitrogen temperature to reduce the thermal component.
76. R. Sizmann, Nghi Q. Lam, and S. J. Rothman, unpublished work.
83. S. J. Rothman and Nghi Q. Lam, unpublished work.
93. The Cu-36% Zn alloys were irradiated in a D_2O moderated reactor and the Cu-15% Al ones in a graphite moderated one. The latter has a harder spectrum.