Ion-Irradiation Studies of Cascade Damage in Metals[*]

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ABSTRACT

Ion-irradiation studies of the fundamental aspects of cascade damage in metals, which have been performed at Argonne National Laboratory, are reviewed. The emphasis of these studies has been the determination of the primary state of damage (i.e. the arrangement of atoms in the cascade region prior to thermal migration of defects). Progress has been made towards understanding the damage function (i.e. the number of Frenkel pairs produced as a function of primary recoil atom energy), the spatial configuration of vacancies and interstitials in the cascade and the cascade-induced mixing of atoms. It is concluded for these studies that the agitation of the lattice in the vicinity of energetic displacement cascades stimulates the defect motion and that such thermal spike motion induces recombination and clustering of Frenkel defects.

1. Introduction

Defect production in energetic displacement cascades, has long been of interest in the field of radiation effects in metals because of its direct bearing on the design of fission and fusion reactors. More recently the realization that ion irradiations can be employed for materials—modification applications[1] has provided new motivation to understand cascade damage in materials. Yet, the fundamental aspects of defect production in energetic displacement cascades, despite years of study, remain a controversal problem.[2] Significant progress towards understanding some aspects of defect production in cascades has, however, been achieved both theoretically and experimentally. Computer simulations which employ the approximation of binary collisions (e.g. MARLOWE[3]), have proven valuable for describing the high energy phase of the cascade development (atom energies $\gtrsim$ 100 eV), yielding reliable information regarding the spatial dimensions of the cascade damage zone and the local concentrations of defects within the cascade region. Complementary experimental work employing FIM[4] TEM[5] and diffuse x-ray scattering[6] techniques have also provided reliable information regarding these aspects of the cascade. At end of the energetic displacement process, many of the atoms are situated in unstable configurations. In addition, the cascade region contains considerable kinetic energy, corresponding to some 10^4 K. Hence following the displacement phase of the cascade development, the lattice begins to relax; the relaxation process, however, is complex. One aspect of the relaxation is spontaneous clustering and recombination of Frenkel-pair defects (FP's), i.e. vacancies and self-interstitial atoms (SIA's); it results from the interactions between very close defects. Relaxation can also occur by defect diffusion that is stimulated by the residual agitation of the lattice. This latter motion, which is referred to

here as "thermal-spike"[7] motion has been the subject of considerable debate
in regard to its magnitude and to its analogy with equilibrium thermal
motion.[2] This analogy is appealing, however, as it provides a convenient
basis for analytical theories of cascade effects.[8,9] A more atomistic
understanding of relaxation processes in cascades has been obtained from
molecular-dynamic computer simulations as these calculations include the
residual agitation of the lattice. Recently, these simulations have been
extended to cascade energies of 10 keV.[10] The results of such calculations
are described in Section 4. Some experimental progress has also been achieved
toward understanding relaxation effects in cascades. In this paper we
summarize the contributions from our lab to these experimental studies.

    We have studied relaxation effects associated with energetic displacement
cascades by investigating the influence of cascade energy and energy
density[11] on various radiation effects. These effects include radiation
annealing, stage I recovery, defect production, defect clustering and
radiation-induced diffusion. Ion irradiations are particularly useful for
such studies as the primary-recoil spectrum of the irradiation can be
systematically varied. For example, 15-keV proton irradiation produces FP's
in low-energy recoils; most of the FP's result from recoils which produce just
one or two FP's. High-energy self-ion irradiations, on the other hand,
produce FP's in energetic cascades which may contain some thousands of FP's.
In this regard it is useful to characterize the recoil collision parameters
for various ion irradiations. Typically an irradiation is characterized by
its primary-recoil spectrum, however, for studying defects, it is more
enlightening to weight the probability for the occurrence of a particular
recoil by the number of FP's produced by the recoil. We therefore define a
function which yields the fraction of FP's produced in cascades that are

initiated by recoils with energies less than T. The function is defined by relation[12]

$$W(T) = 1/\nu^t \int_0^E dE/S(E) \int_0^T dT' \frac{d\sigma(E,T')}{dT'} \nu(T') .$$ (1)

Here $d\sigma(E,T')/dT'$ is the appropriate cross section for a particle of energy E to produce a recoil of energy T'; $\nu(T')$ is the number of FP's produced by a recoil of energy T'; and the integral over recoil energy extends up to energy T. The integral over projectile energy E is generally necessary for ion irradiations since the projectile loses considerable energy while moving through in the material; S(E) is the stopping power, dE/dx; it describes the slowing down process. The quantity ν^t is the total number of FP's produced by the projectile. Figure 1 illustrates the function W(T) for a few ion irradiations, and for comparison, for 1 MeV electrons and a moderated fission-neutron spectrum.[13] It is apparent that by the appropriate selection of ion masses and energies, the predominant cascade energies of an irradiation can be varied from tens of eV's to hundreds of keV's. It is also apparent in regards to neutron-simulation experiments, that defect production for energetic self-ions is quite similar to that for fast neutrons. A convenient parameter to characterize the irradiations is the energy $T_{1/2}$, the energy for which W(T) = 0.5. Half of the FP's are produced in recoils with energy lower than $T_{1/2}$ and half in recoils with energy higher than $T_{1/2}$.

Much of the work described in this paper is based on the use of electrical-resistivity measurements to determine radiation-induced defect concentrations. It is assumed for these measurements that the defect concentration is given by

$$c = \Delta\rho/\rho_f \qquad (2)$$

where ρ_f is the Frenkel-pair resistivity and $\Delta\rho$ is the measured change in electrical resistivity. Thus the number of FP's produced per incident-ion/cm², ν^e, is determined from the relation,

$$\nu^e = \frac{N_o t}{\rho_f} \cdot \frac{d\Delta\rho}{d\phi} \qquad (3)$$

.where $d\Delta\rho/d\phi$ is the change of elecrical resistivity per incident ion/cm², N_o is the atomic density, and t is the specimen thickness. The determination of the absolute concentration of FP's relies on the value of ρ_f, which is unknown for most metals. There are, however, semi-empirical rules for ρ_f which seem reasonably reliable.[14,15] In many cases the absolute number of FP's produced by an irradiation is not of as much interest as is the relative numbers of FP's produced by irradiations having different cascade parameters. The important question for these studies is whether ρ_f is the same for isolated Frenkel pairs as for clustered Frenkel pairs. This question has been discussed extensively in references (12,16,17), and will not be discussed in detail here. The results of two experiments, however, are briefly noted. First Ehrhart et al.[16] have found using combined diffuse x-ray scattering, lattice-parameter and electrical-resistivity measurements on electron irradiated copper, that ρ_f changes only ∼ 20% upon annealing from 4K through stage II, even though the average SIA-cluster size at the end of the anneal had grown to ∼ 100. Second, it was found that the ratio of the relative change in lattice parameter to electrical resistivity does not change upon annealing through stage II for electron[18] or fast neutron[19] irradiated copper, and that the ratio is nearly the same for the two types of

irradiation. These results suggests that ρ_F is rather insensitive to the detailed configuration of the defects. Thus, for the experiments described here, which were all carried out near 4K so that no large defect clusters or dislocation loops were expected, the assumption that $\Delta\rho$ is proportional to the defect concentration seems reasonable. Finally we note regarding the experimental technique, that because of the relatively short range of ions in metals, thin-film specimens (typically 300 nm) were employed. The use of electrical-resistivity measurements on such film is more complicated than on bulk specimens and special procedures were necessary. We do not discuss these procedures here but again refer those interested to ref. [12].

2. Evidence for Thermal-Spike Motion

Rather direct evidence for thermal-spike motion of defects in energetic displacement cascades has been obtained from the following radiation annealing experiment.[20] First a copper specimen was doped with isolated Frenkel-pair defects by irradiating it with 150-keV protons at 6 K. Proton irradiations produce defects predominantly in low-energy recoil events ($T_{1/2}$ = 335 eV) and hence minimize cascade effects. The left side of fig. 2 shows the increase of defect concentration as a function of dose during the doping irradiation. The FP concentration is observed to increase monotonically with dose, although the rate of defect production decreases nearly proportionately to the defect concentration. The decrease in the rate of defect production results from the increasing probability that a newly produced FP recombines with one produced earlier in the irradiation. This phenomenon is the 'normal' radiation-annealing effect.[21] After a high concentration of FP's had been introduced into the specimen, the proton irradiation was terminated, and without warming, an energetic self-ion irradiation begun. The results of this subsequent irradiation are shown on the right side of fig. 2. Initially the FP

concentration decreases with dose. This decrease has been interpreted as evidence that many close SIA-vacancy pairs (close pairs)[22] recombine due to the agitation of the lattice in the vicinity of an energetic cascade. To demonstrate that this 'anomalous' radiation-annealing effect could be associated with the recombination of close pairs, the experiment was repeated but with the proton doping irradiation performed above stage I. This doping treatment is similar to the 6K irradiation except that all close pairs thermally anneal during the irradiation. The subsequent self-ion irradiation for this case did not show the anomalous annealing effect but only normal radiation annealing.[20] Similar results were obtained for silver, and to a lesser extent for gold.

A second interesting aspect of the results shown in fig. 2 is that the thermal-spike annealing effect saturates at a low self-ion dose relative to that required for defect saturation. This result suggests that the annealing volume is large compared to the damage volume. From the saturation behavior of the annealing it is possible to estimate the volume V_a, asociated with each cascade in which annealing is effective. For this purpose it is assumed that during the cascade event all close pairs within V_a anneal; then the annealing rate is given by the relation

$$\frac{d\Delta\rho}{d\phi}\bigg|_{anneal} = \frac{\rho_f C_p V_a}{t} (1 - V_A/V) \qquad . \qquad (4)$$

Here C_p is the initial concentration of close pairs in the doped specimen,

       t is the specimen thickness,

       V is the specimen volume,

and V_A is the fraction of the specimen volume that has been annealed

       during the heavy-ion irradiation.

The second term on the right is the probability that the annealing volume associated with a newly produced cascade overlaps with a region previously annealed. In addition to annealing preexisting damage, the self-ion irradiation produces new damage. This is apparent in fig. 2 at doses above which the thermal-spike annealing has saturated. The damage rate for the self-ion damage has the form,[21,23]

$$d\Delta\rho/d\phi|_n = A(1 - B\Delta\rho) . \tag{5}$$

Thus using the relation for the measured damage rate, $d\Delta\rho/d\phi|_m$

$$d\Delta\rho/d\phi|_m = d\Delta\rho/d\phi|_n - d\Delta\rho/d\phi|_{anneal} \tag{6}$$

with eqns. (4) and (5), the quantities C_p and V_a can be estimated. The results for a few irradiations are shown in Table I. The first point to consider is the ratio of the annealing volume to the damage volume, V_a/V_t. The value of V_t used in the table was calculated from the relation[24]

$$V_t = 4/3\pi\{\delta\cdot(\langle\Delta x^2\rangle + 2\langle Y^2\rangle)\}^{3/2}. \tag{7}$$

Here, $\langle\Delta x^2\rangle$ and $\langle Y^2\rangle$ are the longitudinal and transverse straggling, respectively, and δ is a contraction factor which relates the average cascade volume of a single cascade to the average volume of an ensemble of cascades (for which $\langle\Delta x^2\rangle$ and $\langle Y^2\rangle$ are calculated). The values of δ were taken from ref. 24, and the values of the moments from tables complied by Winterbon.[25] For copper the annealing volumes are somewhat less than V_t, contrary to our conclusion that the annealing volume is greater than the

damage volume. This apparent discrepancy arises from the pronounced subcascade structures which are typical of the irradiations used here. The damage for such cases consists of localized regions of high defect density which are dispersed in a large cascade volume.[26] The result that $V_a \sim V_t$, is in fact evidence that V_a is greater than the actual volume that is damaged.

The second aspect of the table which is of interest is the dependence of the ratio V_a/V_t on cascade energy density. To calculate the energy density, θ_D, we have used the formulation due to Sigmund,[9] although as noted in reference (11), the concept of energy density is difficult to quantify. For the three types of irradiation of copper, the ratio V_a/V_t increases with increasing energy density. We note also that for the same type of irradiation, θ_D and V_a/V_t are both larger in silver than in copper, although differences between cascades in copper and silver other than the energy density may influence this comparison. We conclude, therefore, that V_a/V_t increases with increasing energy density. This result can be partially attributed to the method with which V_t is calculated. For cascades of lower energy density, subcascade structure is more extensive and V_t has a greater tendency to overestimate the true damage volume.[26] A second reason for the observed dependence of V_a/V_t on energy density is that those close pairs which recombine outside the displacement zone, V_t, require energy which emanates from within the damage zone. The greater the energy within the damage zone, the further away can recombinations be effected.

Finally we remark on the fraction of defects which anneal during the heavy-ion irradiation, i.e. $\Delta\rho/\Delta\rho_d$. The highest annealing fraction observed is ~ 0.25. This fraction compares with ~ 0.4 for stage I recovery of a similarly doped copper specimen.[27] Hence thermal-spike annealing is less effective than stage I annealing of proton damage. This result is not surprising since

during thermal annealing, SIA's migrate until they are trapped or recombine
with vacancies, whereas during thermal-spike annealing SIA's can trap,
recombine or interact with the newly produced defects in the cascade. If they
undergo the last interaction, they are included as normal radiation annealing
and not subthreshold annealing. We note that the ratio $\Delta\rho_a/\Delta\rho_d$ increases
strongly with $\Delta\rho_d$ for both copper and silver. This suggests that as the
distance between defects becomes less, the probability for them to interact
with each other increases relative to that for interacting with the defects
produced in the cascade. In cascades the defects have a high spatial
correlation, unlike the proton irradiation used here for doping. Therefore
the reduction of defect production in cascades due to thermal-spike annealing
effects may be considerably higher than that observed for the annealing of
proton damage.

Table I. Results for thermal-spike annealing volumes V_a, and fractional
thermal-spike annealing, $\Delta\rho_a/\Delta\rho_d$. Here E is the projectile energy, $\Delta\rho_d$ is the
defect resistivity induced by the doping proton irradiation, $\Delta\rho_a$ is the
resistivity annealed by heavy-ion irradiation, θ_D is the energy density and V_t
is the calculated damage volume of the cascade.

Target	Ion	E(keV)	$\Delta\rho_d(\Omega\text{-cm})$	$\Delta\rho_a/\Delta\rho_d$	$V_d(cm^3)$	$\theta_D(ev/atom)$	V_a/V_t
Cu	Ar	400	2.2×10^{-7}	.04	4.4×10^{-17}	3.2×10^{-3}	.082
Cu	Ar	400	4.7×10^{-7}	.26	2.7×10^{-17}	3.2×10^{-3}	.050
Cu	Cu	400	4.4×10^{-7}	.22	4.1×10^{-17}	1.4×10^{-2}	0.24
Cu	Au	870	4.1×10^{-7}	.16	1.6×10^{-16}	3.8×10^{-2}	0.94
Ag	Ag	500	1.6×10^{-7}	.02	5.1×10^{-16}	6.2×10^{-2}	4.7
Ag	Ag	500	3.9×10^{-7}	.07	3.9×10^{-16}	6.2×10^{-2}	3.6

3. Isochronal Annealing in Stage I

The anomalous annealing effect described in the preceeding section
suggests that close Frenkel pairs are unstable in the vicinity of energetic
displacement cascades. As stage I annealing is attributed to the migration of
SIA's to vacancies, it is expected that thermal spike annealing in cascades

should suppress this annealing. It has long been known that stage I recovery after electron irradiation is significantly greater than after fast neutron irradiation. This result was attributed to an enhanced probability for SIA's to cluster in cascades with high defect densities rather than to the elimination of many close pairs by thermal spike annealing. Indeed, stage I recovery decreases with increasing defect concentration for electron irradiation.[28] We have employed ion irradiations to systemmatically investigate the effect of energy density on stage I annealing.[29] Figure 3 shows the fractional recovery in stage I of Cu specimens after low-dose ion irradiations. The reduction in recovery with increasing energy density is apparent; recovery decreases from 60% for 150-keV proton irradiation to 15% for 400-keV Bi irradiation. It is also observed that the close-pair substages, I_A-I_C, (T < 32 K) are almost completely suppressed for the Bi irradiation. This latter result is noteworthy in view of the fact that recovery in these close-pair substages for electron-irradiated copper is essentially independent of defect concentration;[29] it suggests therefore, that the high defect concentration in the cascade region is not totally responsible for the suppression of stage I recovery after fast-neutron or heavy-ion irradiations. To further investigate the influence of defect concentration and thermal-spike annealing on stage I annealing, a similar set of recovery data were obtained after high-dose irradiations. These data are shown in fig. 4. The defect concentration for the proton-irradiated specimen is nearly equal to the maximum concentration of defects that can be introduced by irradiations which produce cascade damage.[23] Stage I recovery of the proton damage in this case is ~45%, which is nearly three times greater than the recovery after the low-dose Bi irradiation, and nearly ten times greater than that after the high-dose Bi irradiation. This demonstrates that even

when the average defect concentration produced by proton irradiation is equal to the highest possible concentration of defects in a cascade, stage I recovery is far greater for proton damage than for cascade damage. Hence the high defect concentrations in cascades cannot in itself sufficiently explain the small amount of recovery in stage I after cascade-producing irradiations. It is interesting that for the high-dose Bi irradiation, when the cascades have overlapped several times, stage I recovery is nearly totally suppressed, <5%, in copper. Similar results were obtained for silver. We conclude, therefore, that due to the high density of defects in cascades, coupled with thermal-spike stimulated diffusion of defects, many of the SIA's initially produced in cascades, either find vacancies or form immobile clusters during the lifetime of the cascade.

4. The Damage Function

The number of FP's produced in a metal as a function of host-atom recoil energy T, or damage function $\nu(T)$, is of fundamental importance in the field of radiation effects as it is the basis for all defect-production calculations. This can be seen from the relation,

$$\nu^t(E) = \int dE'/S(E') \int dT \frac{d\sigma(E'T)}{dT} \nu(T) . \tag{8}$$

which yields the number of FP's produced by a projectile of energy E. Here $\frac{d\sigma(E'T)}{dT}$ is the relevant cross section for a particle with energy E' to produce a host-atom recoil of energy T, and $\nu(T)$ is the damage function. For ions, as noted for eq. (1), the irradiation particles generally lose appreciable energy in the material and an integral over particle energy is necessary. S(E') is the stopping power for the particle in the material. The significance of $\nu(T)$ is that it is a property of the material and does not

depend on the type of irradiation.

Until recently, modified Kinchin-Pease expressions similar to the form

$$
\nu^{KP}(T) = \begin{cases}
= 0 & T_d > T \\
= 1 & T_d < T < 2.5 \ T_d \\
= \dfrac{0.8 \ E_D(T)}{2T_d} & T < 2.5 \ T_d
\end{cases}
\qquad (9)
$$

have been employed for defect calculations; here, T_d is the average threshold energy for displacements, and $E_D(T)$, the damage energy, is the portion of the recoil energy T available for producing displacements.[30] Both computer simulation employing binary collisions[3] and linear transport theory[31] are in good agreement with eq. (9). These theories, however, do not include the effects of lattice agitation, i.e. thermal spike, on the stability of Frenkel pairs, whereas the radiation-annealing and stage I-annealing experiments described above suggest that this effect can reduce defect production in cascades. We have studied the damage function in three fcc metals over a wide range of energies in order to evaluate the importance of relaxation effects in cascades on defect production.[12,32]

The difficulty associated with an experimental determination of the damage function is evident upon inspection of eq. (8) which shows that the calculated quantity, ν^t, is an integral quantity containing $\nu(T)$. The most direct way to obtain $\nu(T)$ would be to irradiate a material with self-ions over a wide range of energies and measure ν^e; however, there are presently no techniques available to measure ν^e over such a range. The method we have employed has been to use a wide variety of ion masses and energies for irradiation. This procedure weights the different regions of the function $\nu(T)$ through the scattering cross section $d\sigma(E,T)/dT$, (cf Fig. 1). For

example, irradiation with 20-keV protons produces FP's which result mostly
from recoils whose energies are between the threshold energy and $\sim$ 100 eV,
whereas for 500-keV self-ion irradiation, the defects are produced by recoils
between 5 keV and 100 keV.

Figure 5 illustrates the results for defect production in copper. It
show the ratio of the experimentally deduced number of defects ν^e, (eq. (3)),
to the theoretically deduced number, ν^t (eq. (8)), as a function of the
quantity $T_{1/2}$ for several ion irradiations. The modified Kinchin-Pease
expression, eq. (9), was employed to calculate ν^t. The ratio ν^e/ν^t, is
denoted as the defect production efficiency, ξ, as it is the ratio of the
number of defects that are observed to be produced in a cascade to the number
which theoretically would have been produced were it not for cascade
effects. A plot of ξ vs. $T_{1/2}$, therefore, illustrates at what energies the
simple cascade theory is inadequate. (We point out that $T_{1/2}$ is not a unique
recoil energy of an irradiation so that the function $\xi(T_{1/2})$ does not yield
the damage function directly.) For copper, the efficiency is observed to
decrease monotonically with energy up to a value of $T_{1/2}$ near 10 keV. Above
10 keV, ξ has the value $\sim$ 0.35 and is independent of energy. Also shown are
the efficiencies for defect production for fast-neutron (in the VT-53
facility)[13] and fission-fragment irradiations.[33] These two data are in
excellent agreement with the ion damage work. The result that the efficiency
becomes constant at $T_{1/2} \sim$ 10 keV, indicates that the transition from high to
low efficiency occurs considerably below that energy as 50% of the defects are
produced in recoils below $T_{1/2}$. A similar study (12) for silver revealed that
the data could be best fit by an efficiency function which had a transition
from high to low values at recoil energies between 1 and 3 keV and which had a
constant efficiency of $\sim$ 0.4 at high energies.

We have also investigated defect production in aluminum. This study was of interest since aluminum is a relatively light metal and thermal-spike annealing would be expected on the basis of the energy density in the cascades, to be less important. However, the results of this work, shown in fig. 6, illustrate that $\xi(T_{1/2})$ for aluminum has the same general behavior as it does for copper and silver. Again, agreement is excellent with fast-neutron irradiations at the CP-5 reactor.[13]

We have attempted to construct the damage function for aluminum from the experimental results. The damage function was cast in the form,

$$\nu(T) = \nu^{KP}(T) \cdot \xi(T) \tag{10}$$

in order to show explicitly at what recoil energies cascade effects influence defect production. Using the hypothetical efficiency functions shown in the inset of fig. 6, defect production for the various irradiations was calculated. The ratios of these values to those calculated using $\nu^{KP}(T)$ as the damage function, or the theoretical efficiencies, are shown in fig. 6 for comparison with the experimental efficiencies. This comparison shows that the damage function for aluminum has an effective transition from high to low efficiency in the range 5-10 keV and a minimum efficiency of ~ 0.50. Both the transition energies and the minimum efficiency are somewhat higher in aluminum than in copper and silver but the general behavior of $\xi(T)$ for aluminum is similar to the other two metals.

To investigate the reason for the similarities in the damage functions for aluminum, copper, and silver, defect production in these three metals was simulated using MARLOWE.[32] It was found that although the defect density in aluminum cascades was much smaller than in copper and silver, the defects

produced in the aluminum cascades tended to be concentrated in regions of
locally high defect densities. It is possible therefore that thermal-spike
effects in these local regions, for recoil energies ~ 5 keV, are sufficient to
induce close-pair recombination. We conclude from the similarities of defect
production in aluminum, copper, and silver that a transition in $\xi(T)$ from high
to low values at relatively low recoil energies, and a constant value of $\xi(T)$
at high energies is a rather general feature of defect production in metals.
More inclusive defect production data from neutron irradiations show that the
reduction in efficiency to 0.3 ~ 0.5, is in fact a common feature of many
metals.[13,34]

To further investigate the transition region at low energies we compare
the results of these experiments with the molecular-dynamic simulations of
Guinan and Kinney.[10] Fig. 7 shows the efficiency function obtained by
computer simulation using a potential derived for tungsten. The energy scale
is normalized to the minimum threshold energy. These data reveal that the
reduction in efficiency begins at energies near the threshold energy and it
continues until ~ 50 T_o. Inspection of the cascade development in the
simulation showed that the reduced efficiency was indeed a result of defect
motion stimulated by the residual agitation of the lattice, and concommitant
recombination with nearby defects.[10] It is exactly within this low-energy
region that we have experimentally observed the reduction of efficiency during
ion irradiation. (We wish to point out that electron irradiations sample
recoil energies near T_o, and fast neutrons sample mostly recoils greater than
50 T_o. Only ion irradiations can be used to examine the region where the
transition in efficiency takes place.)

At high energies, the defect production efficiency becomes independent of
recoil energy. This behavior can be understood on the basis of subcascade

formation.[35] At high energies, increasing the recoil energy leads to an increase in the number of subcascades. However, each subcascade unit contains approximately the same energy density and hence behaves essentially the same. This result has also been demonstrated by comparisons of defect production efficiencies for fission and 14-MeV neutrons.[36,37]

5. Defect Clustering

Radiation-annealing experiments at low temperatures have long been employed to investigate the interaction of point defects.[21] These studies are based on an equation of the form

$$dc/d\phi = (dc/d\phi|_o) \cdot (1 - 2CV_o) . \qquad (11)$$

Here $dc/d\phi|_o$ is the initial damage rate, C is the concentration of Frenkel pairs, and V_o is the recombination volume. V_o represents the volume around one partner of a Frenkel pair in which the other is unstable to recombination. Thus the second term in eq. (11) is the probability that a newly produced vacancy or SIA will recombine with a preexisting defect. At high defect concentrations, recombination volumes begin to overlap and higher order terms are required in eq. (11). For cascade damage, the high spatial correlation between defects causes overlap of recombination volumes even at low doses. In this case, the recombination volume in eq. (11) should be rewritten as $\bar{V}$ to indicate that it is the average recombination volume per defect. The relative value of $\bar{V}$ to V_o, therefore, is a measure of defect clustering. Measuring $\bar{V}$ however, is not as straightforward as, for example, measuring the defect production as a function of defect concentration during an ion or neutron irradiation. The problem with that procedure is that eq. (11) contains the assumption that the new defects are produced in the material without otherwise disturbing the lattice; the anomalous radiation-annealing effect described above demonstrates that such an assumption is not valid for

cascade-producing radiation. Even for electron irradiation it has been found[38] that subthreshold recoils induce recombination of preexisting damage and that eq. (11) must be modified to obtain V_o. We have used a procedure to determine $\bar{V}$ for FP's in cascades which employs superposing low-dose proton irradiations onto heavy-ion damage.[39] The proton damage rates, or proton probes, can be used directly to determine $\bar{V}$ in eq. (11) since the proton irradiations produce predominatly isolated Frenkel pairs distributed homogeneously in the material, and few cascades. Moreover, the subthreshold annealing encountered during electron irradiation does not influence the proton damage rates, since the relative concentration of proton damage is low and new proton damage predominatly with the damage that has been produced in energetic cascades. Thus by periodically interrupting a heavy ion irradiation and measuring proton-probe damage rates the average recombination volume per defect in a cascade can be determined as a function of cascade overlap.

The results for such an experiment are shown in Fig. 8. Here the production rates in copper for: 1) 150-keV proton, 2) 500-keV Ar, and 3) proton-probes during the Ar irradiation, are all shown. Also shown are the results of the continuation of the proton irradiation after the Ar irradiation. One can see that a direct comparison of the damage rates for proton irradiation with the Ar irradiation, on the basis of eq. (11) would indicate that clustering during proton irradiation is greater than during Ar irradiation. Presumeably this result derives from an effectively large recombination volume due to lattice agitation during Ar irradiation and not from defect clustering. One could then perhaps, associate $\bar{V}$ in eq. (11) for the Ar irradiation with a dynamic recombination volume which included lattice agitation effects as well as clustering. However, the meaning of such a parameter would certainly not be clear, nor would it be especially useful

since it would depend on the type of irradiation as well as the material itself. The proton-probe damage rates superposed on the Ar damage reveal that, in fact, clustering is greater for Ar irradiation than for proton irradiation in copper. Moreover it shows that clustering effects increase strongly with dose after a defect resistivity of ~ .3 x $10^{-6}\Omega$-cm has been induced. It is interesting that at the end of the Ar irradiation, the defect concentration has nearly saturated for Ar irradiation i.e. $d\Delta\rho/d\phi) \rightarrow 0$; however, the damage rate for protons has only decreased 37% from its initial value. Also the damage-rate curve for this subsequent proton irradiation is nearly parallel to the curve for proton irradiation of a previously-undamaged specimen. These results indicate that the Ar irradiation introduces many defects that cause a resistivity change, but are sufficiently clustered that they have only a small interaction volume for the proton damage.

Similar experiments were performed on aluminum and silver. The results for all three metals have been summarized in Fig. 9. Here, the average overlap of the spontaneous recombination volume, $(V_0 - \bar{V})/V_0$, has been plotted as a function of defect concentration. Zero on the ordinate indicates no overlap and a value of one indicates complete overlap. As one would expect the tendency for defect clustering is greatest for the energetically densest cascades and the clustering increases with defect concentration. The results shown here are in qualitative agreement with results obtained for clustering during fast neutron irradiation using diffuse x-ray scattering in copper[40] and Hall-coefficient measurements in Al.[41]

6. Ion Beam Mixing (Displacement Mixing)

The experiments described to this point have illustrated the influence of cascade effects in various radiation effects. It was deduced from these measurements that thermal-spike motion of defects in the cascade is stimulated

by the residual agitation in the lattice after the displacement process has ended. In this section we describe measurements of the effective diffusion coefficient of a material under irradiation at ~ 6K. Such experiments provide a direct measure of atomic motion in cascades. The work was motivated by the observation that interdiffusion of layered materials is substantial during ion irradiation.[42] The high degree of mixing has technological significance since surface alloys can be prepared by ion beam mixing more efficiently than by ion implantation. Mixing may perhaps also effect phase stability of materials in reactor environments.[43] Mixing can be measured using two experimental geometries. The first geometry consists of a thin layer of material A deposited on a layer of material B. This diffusion couple is irradiated and the composition of the irradiated material is subsequently measured as a function of depth. Various techniques can be employed for the analysis; the required depth resolution is ~ 5.0 nm. We have used Rutherford Backscattering Spectrometry (RBS) so that both the mixing and the analysis could be performed without warming the specimen above 6 K. Using the diffusion-couple geometry, mixing of a Ni-Al diffusion couple during 250-keV Ar irradiation was studied. The experimental details involving RBS and the actual RBS spectra can be found elsewhere.[43-45] The results of these experiments, however, showed that the concentration profile after irradiation was similar to that for the interdiffusion of two semi-infinite rods joined at a common end, and for which the diffusion coefficient is independent of composition.[46] As a first approximation, therefore, it is assumed that the diffusion for the present situation is governed by the same diffusion equation. The solution is

$$C(x,t) = \frac{C'}{2}\{1 + \mathrm{erf}\,[x^2/2 \ Dt]\} \ . \tag{12}$$

Using the result that Δx between Ni concentrations of 84% and 16% is 30 nm, after a dose of $2.4 \times 10^{16}/cm^2$ (~ 25 displacements per atom (dpa)), we find from eq. 12,

$$\frac{Dt}{\phi} = 4 \text{ nm}^2/\text{dpa} . \tag{13}$$

A second geometry that we have employed is a thin marker layer of material A ($t \sim 10\text{Å}$) sandwiched between two thick layers of material B. The sandwich is irradiated and the diffusion of the marker is measured. This technique has the advantages that element A is so dilute that the mixing at 6 K is essentially determined by material B. This geometry has been employed to measure the low temperature mixing for a Si-Pt-Si system irradiated with 300-keV Kr. Here the solution to the appropriate diffusion equation is

$$C = C'\exp(-x^2/4Dt) . \tag{14}$$

Thus by measuring the standard deviation of the Pt yield into RBS spectrum for an unmixed layer, Ω_R, (which gives the resolution of the system) and the standard deviation of the Pt yield after irradiation, Ω_m, the spreading due to diffusion can be deduced from the relation,

$$\Omega_m^2 = \Omega_{diff}^2 + \Omega_R^2 . \tag{15}$$

The results show that $\Omega_{diff} = 14.0$ nm for a dose of $1.6 \times 10^{16}/cm^2$ (~ 25 dpa). It was also found that Ω_{diff} increased according to the square-root of dose dependence as predicted by eq. (14). Thus for Si-Pt-Si we again obtain the result that

$$Dt/\phi \sim 4 \text{ nm}^2/\text{dpa} . \tag{16}$$

These two measurements yield the diffusion per dpa and hence, the actual mixing in the cascade. In order to obtain some insight into the meaning of these numbers, a simple model of cascade diffusion is described. The model assumes that atomic motion in the cascade occurs by 'jumps' which are one interatomic distance in length. This motion describes the creation of defects by replacement-collision sequences for which the atoms along a row are displaced one atomic distance foward, leaving a vacancy at the starting point of the row and an SIA at the end point. It also describes diffusion by thermal-spike motion for which the agitation of the lattice causes vacancies and SIA's to randomly jump one atomic distance at a time. The diffusion coefficient for such a random diffusion process can be described by the relation,

$$D = 1/6 \ \nu \lambda^2 \qquad \qquad (17)$$

where ν is the replacement, or jump, frequency and λ is the interatomic distance. The product $\frac{\nu t}{\phi}$ is the total number of replacements for a given dose. Using eqns. (12), (14) and (17) our results indicate that there are $\sim$ 350 and 166 jumps per displacement in the Ni-Al and Si-Pt-Si systems respectively. Although the interpretation of these results is model dependent the measured diffusion coefficient itself is not. Therefore by varying the irradiation conditions, ion mass and energy, and target materials, the effect of different cascade mechanisms on cascade diffusion can be determined. In addition, by irradiating at higher temperatures, the diffusion length of migrating defects can be determined by this method.[47] It is of course important to realize that the results apply to highly damaged materials. Typically the saturation concentration of defects is some fraction of a

percent of Frenkel pairs, whereas the irradiation doses necessary to observe mixing are ~ 2-25 dpa. Thus, such effects as focussed replacement-collision sequences which may require defect free crystalline rows, might be suppressed. Also, diffusion mechanisms relevant only to highly damaged materials may also be a factor. Nevertheless this technique appears to be an interesting new method to study cascade effects.

Acknowledgements

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Figure Captions

Figure 1. The fraction of defects produced by various irradiations in cascades initiated by recoils of energy less than T.

Figure 2. Resistivity change vs dose in copper. The left-hand side of the curve shows $\Delta\rho$ for a 150-keV proton irradiation below 10 K. The right hand side shows $\Delta\rho$ for subsequent self-ion irradiation of the same specimen.

Figure 3. Isochronal recovery of the electrical resisitivity in copper after various ion irradiations to low dose.

Figure 4. Isochronal recovery of the electrical resistivity in copper after the same ion irradiations as in fig. 3, but to high dose.

Figure 5. Defect production efficiency ξ, in copper, as a function of the cascade parameter $T_{1/2}$.

Figure 6. Defect production efficiency, ξ, in aluminum as a function of the cascade-energy parameter $T_{1/2}$. Also shown (upper right) is an empirical efficiency function which was used to calculate theoretical efficiencies (closed symbols) using eqns. (7), (8) and (9).

Figure 7. Calculated defect-production efficiency as a function of recoil energy obtained using molecular-dynamic computer simulations. (from ref. 10).

Figure 8. Defect-production rates in copper for 500-keV Ar alone ( ) (normalized to initial 150-keV proton defect production rate); 150-keV proton alone (o); and 150-keV proton-probes during Ar irradiation ( ).

Figure 9. The average overlap of the spontaneous recombination volume as a function of defect concentration for various irradiations of copper, silver, and aluminum.

COPPER
THICKNESS 3000 Å
$\Delta\rho_{IRRAD} = 0.4 \times 10^{-7} \ \Omega\text{-cm}$
— 200 keV H$^+$
— 200 keV He$^+$
— 400 keV Ar^{++}
— 400 keV Bi^{++}

COPPER
THICKNESS = 2300 Å

H^+ $\Delta\rho_{IRRAD}$ = 4.8 x 10^{-7} Ω-cm
He^+ $\Delta\rho_{IRRAD}$ = 4.7 x 10^{-7} Ω-cm
Ar^{++} $\Delta\rho_{IRRAD}$ = 4.4 x 10^{-7} Ω-cm
Bi^{+++} $\Delta\rho_{IRRAD}$ = 3.9 x 10^{-7} Ω-cm

y-axis: $\dfrac{T}{\Delta\rho_i} \times \dfrac{d\Delta\rho}{dT}$

x-axis: TEMPERATURE (°K)

MEDIAN RECOIL ENERGY/THRESHOLD ENERGY

COPPER

$d\Delta\rho/d\phi$ (10^{-22} Ω–cm^{-3})

500 keV Ar^{++}

PROBE DAMAGE RATES

150 keV PROTONS

$\Delta\rho(10^{-6}$ Ω–cm)