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NEUTRON IRRADIATION OF PURE METALS AND ALUMINUM-ZINC ALLOYS

by

James A. Horak

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James A. Horak

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NEUTRON IRRADIATION OF PURE METALS AND ALUMINUM-ZINC ALLOYS

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J. A. Horak

ABSTRACT

To determine the source of the initial electrical-resistivity rise during neutron irradiation of metals near 4°K and the induced resistivity produced by a fission-neutron spectrum, the metals Al, Cu, Ag, Au, Pt, Pd, Fe, and Ni were irradiated at about 4.5°K in the Argonne CP-5 VT-53 cryogenic facility. The initial resistivity increase that occurs in low-temperature neutron irradiation of metals is thermal in nature and appears to be due to gamma-ray heating. The irradiation-induced resistivity, ρ_i , as a function of time, t , at about 4.5°K, obeys the equation $\rho_i = A(1 - e^{-\alpha t}) + B(1 - e^{-\beta t})$, where A , B , α , and β are experimentally determined parameters for each metal. The first term is attributed to the production of displacement cascades, and the second to stable defect clusters or dislocation loops produced by the interaction of the cascades. The irradiation effects in this facility are due to fission neutrons, the damage rate being 13 times that of the ORNL Hole 12 facility and one-fifth that of the Munich FRM facility. In addition, aluminum and the alloys Al-1.70, Al-3.41, and 5.27a/oZn in the quenched state and in the reverted state have been irradiated and isochronally annealed to study the effects of irradiation-induced lattice defects on the formation of Guinier-Preston (G.P.) zones. The damage rate for the aluminum and the alloys was the same, indicating that no G.P. zones formed during irradiation. The defects that are mobile below 77°K do not appear to affect G.P. zone formation in these alloys. The formation of G.P. zones began at the same temperature as the start of Stage III in aluminum, suggesting that the same defect, the vacancy, is responsible for both processes. Recovery was complete in aluminum at 260°K, but continued up to 400°K in the alloys. This indicates that there is an interaction between vacancies and zinc atoms that gives the vacancies a much longer lifetime in the alloy than in the aluminum.

Irradiation greatly enhanced zone formation, especially in the reverted case, and the temperature of the start of zone formation and of the resistivity maximum was a function of defect concentration. These results suggest that the formation and growth of the G.P. zones in aluminum-zinc alloys are controlled by the point-defect concentration.

I. INTRODUCTION

A. The Preprecipitation Process

The decomposition of supersaturated solid solutions of aluminum-base alloys has been studied rather extensively for the past three decades. The submicroscopic work began with the independent discovery in the late 1930's (by Guinier in France and Preston in England) that the precipitation that was observable in the optical microscope was preceded by a definite structural change in the alloy.¹ The structures produced during these preprecipitation stages consisted of regions rich in solute atoms and were subsequently named Guinier-Preston (G.P.) zones in honor of these two men. Since that time, there have been many investigations of these structural changes in Al-Cu, Al-Ag, and Al-Zn alloys.²

In these alloy systems, the preprecipitation process at room temperature occurs at a rate about ten million times more rapid than the rate that is calculated from extrapolation of the diffusion coefficients of these solutes in aluminum from high temperature to room temperature. For example, in an Al-1.7a/oCu alloy, clustering of the solute atoms to form G.P. zones is half completed in 3 hr at room temperature.³ Extrapolation of the high-temperature diffusion data for copper in aluminum of Bückle to 27°C indicates that, in 3 hr copper atoms on the average will move about 10^{-9} cm, which is a small fraction of the interatomic distance, which is 2.9×10^{-8} cm (Ref. 3). On this basis, it would require 2,000 years, which is a factor of about 10^7 longer than observed, for the zone-forming process to be half-complete. In 1952, Seitz suggested that the rapid kinetics of the room-temperature aging in aluminum alloys could be due to an anomalous density of vacancies in the lattice that would result in a high rate of diffusion in the alloys.⁴ To test this hypothesis, several experiments have been conducted in the past decade.⁵⁻¹⁵ The general results of these experiments are in agreement that excess lattice vacancies can give rise to the type of enhanced diffusion required to explain the rapid kinetics of preprecipitation in aluminum-base alloys. For example, consider an alloy of approximately Al-5a/oZn, where preprecipitation has been readily observed.^{5,6,9,14,15} By utilizing the standard equation for the equilibrium concentration of lattice vacancies as a function of temperature, we have¹⁶

$$C_{V_T} = e^{S_F/k} e^{-E_F/kT}, \quad (1)$$

where

C_{V_T} = the equilibrium vacancy concentration at temperature T,

S_F = entropy of formation of a vacancy,

k = Boltzmann constant (0.86×10^{-4} eV/°K),

E_F = formation energy of a vacancy,

and

T = temperature (°K).

If we consider an annealing temperature of 640°K, which is well within the solid-solution region for this alloy, and use the information of Simmons and Balluffi¹⁷ that $S_F/k = 2.4$ and $E_F = 0.77$ eV for pure aluminum, we calculate that the vacancy concentration at this temperature is 10^{-5} atom fraction.* This is a factor of 10^7 more vacancies than are in thermodynamic equilibrium at room temperature ($\approx 300^\circ\text{K}$). This value is of the correct order of magnitude to account for the extrapolated low-temperature diffusion coefficients, being a factor of 10^7 too small. When the alloy is quenched to room temperature, it is thought that most, or at least many, of these vacancies are retained. Hence, at room temperature the system contains a supersaturation of vacancies in addition to a supersaturation of solute atoms. This excess concentration of vacancies greatly enhances diffusion of the zinc and aluminum.

Recall that diffusion in face-centered-cubic metals and alloys is by a vacancy mechanism. The activation energy for bulk diffusion, Q , is the energy of formation, E_F , of the vacancy plus the energy of motion, E_m , of the vacancy. Since the vacancies are already present after quenching to room temperature, only the energy of motion, E_m , of the vacancy is required. In fact, the observed activation energy for preprecipitation in aluminum-zinc alloys is even slightly lower than the energy of motion of a single vacancy in pure aluminum.^{6,7,9,14,15,18}

An important property of vacancies in aluminum and aluminum-base alloys that is different from vacancies in the noble face-centered-cubic metals is that there appears to be an expansion of slightly greater than one atomic volume for a lattice vacancy in aluminum.^{19,20} Hence, the presence of an undersized solute atom (such as zinc, which is 7% smaller than the aluminum atom) as a near neighbor to a vacancy can relax some of the strains upon the other near-neighbor atoms of the vacancy by absorbing some of this excess atomic volume. For this reason there is thought to be an attractive force between undersized solute atoms and vacancies in aluminum-base alloys.

*The values of S_F/k and E_F for aluminum are used since values with equivalent accuracy have not been obtained for aluminum-zinc alloys. This should not affect the above calculations too much, and the values obtained by this method should serve as at least a good first approximation. For example, if we use the value of $E_F = 0.70$ eV for the formation energy of vacancies in an Al-4.4a/oZn alloy, as given by Panseri and Fedèrighi,⁶ the equilibrium vacancy concentration at 640°K is 3×10^{-5} atom fraction. This is not very different from the above value of 1×10^{-5} atom fraction obtained using the experimental parameters for aluminum.

It is postulated that the presence of the zinc atom-vacancy complex perturbs the vibration frequency of the atoms in the vicinity of the complex to the extent that the zinc atoms are moved by vacancies with an activation energy lower than that for single vacancy. This situation is somewhat analogous to the case of vacancies and divacancies, where the divacancies are thought to require a lower energy for motion than single vacancies.

In addition, the zinc-vacancy interaction could allow more vacancies to be retained in the alloy on quenching than are retained in pure aluminum; and the zinc-vacancy complex would have a longer lifetime in the alloy than a vacancy in pure aluminum. This longer lifetime could account in part for the preprecipitation reaction continuing long after the simple vacancies have been eliminated in pure aluminum. However, vacancies are probably trapped in the zones and become available as small zones dissolve in the coarsening process. Some experimental evidence, which supports the concept that quenched-in vacancies play an important role in the preprecipitation process in aluminum-zinc alloys, is as follows:

Graf observed that in Al-4.4a/oZn the kinetics of G.P. zone formation at room temperature (as measured by Brinell Hardness) are more rapid the higher the homogenization and quenching temperature in the range of 200-460°C (Ref. 5). This is consistent with the idea that at higher temperatures more vacancies are in thermodynamic equilibrium; hence, more are retained in the alloy on quenching and are available to participate in zone formation. Quenching from above 460°C decreases the reaction kinetics. We must consider that the reaction kinetics are most rapid immediately after quenching and then decrease with increasing time of aging; zones actually begin forming during the quench. Because of this, quenching from very high temperatures allows more volume of zones to form during the quench. Therefore, for the same interval of time after quenching, material quenched from 460 to 615°C would be further along in the aging process than material quenched from within the range of 300-460°C. For material quenched from above 460°C, the kinetics at a given time after quenching would therefore be slower.

Many of the investigators of G.P. zone formation in aluminum-base alloys have used electrical resistivity as the parameters to follow the zone-forming process. At the beginning of aging, the resistivity increases as the zones are formed and begin to grow. As the spherical zones grow to about 9 Å in size in aluminum-zinc alloys, the resistivity goes through a maximum.¹⁵ This maximum is thought to be due to the resonant scattering of conduction electrons, since at 9 Å the size of the zones is the same as the wavelength of the conduction electrons in aluminum. Following the maximum, the resistivity decreases gradually. The zones are now growing and on the average are larger in size than the wavelength of the conduction electrons, and resonance scattering of the electrons by the zones does not occur. In addition, diffusion of zinc atoms to the zones removes electronic

scattering centers from the matrix. For long aging times, the resistivity eventually decreases to a value that is less than the as-quenched value; this is attributed to the removal of the zinc-scattering centers from the aluminum matrix. The initial resistivity increase and the maximum, which is followed by the subsequent decrease, make the electrical resistivity a convenient and simple parameter to follow the course of G.P. zone formation in aluminum-base alloys.

Panseri and Federighi used electrical resistivity to study the effects of quenching temperature and aging temperature on zone formation in Al-4.4a/oZn (Ref. 6). The work of Panseri and Federighi indicates the following:

1. The higher the quenching temperature:

- a. The greater the amount of zone formation during the quench. This helps to explain the slower kinetics of zone formation observed by Graf after quenching from high temperatures as previously mentioned.

- b. The lower the temperature at which rapid aging occurs. This supports the quenched-in excess-vacancy hypothesis.

- c. The shorter the aging time at room temperature to reach the resistance maximum for increased quenching temperatures in the range of 219-339°C. This could be attributed to the enhanced diffusion due to the additional vacancies retained upon quenching from increased temperatures. However, there is evidence to indicate that G.P. zones may be a defect structure and that vacancies are an integral part of zones. It may be that the vacancy concentration affects zone formation in two ways. Increasing the vacancy concentration provides more diffusion and provides more vacancies that become a part of zones.

2. The lower the aging temperature:

- a. The higher the resistivity maximum. This is thought to be due to the presence of more zones, since the solubility limit is less at lower temperatures and the critical size for a nucleus to become stable and grow is also smaller at lower temperatures.

- b. The longer the time to the resistance maximum (lower temperature, hence less diffusion). Recall that the resistance maximum in aluminum-zinc alloys occurs when the zones are about 9 Å in size; hence, at lower temperatures it takes longer for the zones to grow to about 9 Å in size.

In addition to the vacancies enhancing diffusion, there is evidence that they are an integral part of G.P. zones.^{9-15,21,22} If a specimen that is aged near room temperature to form zones is heated for a few minutes at about 400°K, the zones are dissolved; this process is called reversion.^{5,6,21} The reversion temperature is well within the two-phase region of the temperature-composition phase diagram; therefore, if any atomic motion can occur, further clustering will take place in order to lower the overall free energy of the system. However, the vacancy concentration at the reversion temperature (for reversion at 420°K) is about 10^{-8} atom fraction. This is 10^3 less than is in equilibrium at a solid-solution temperature of 640°K. After the alloys are cooled to room temperature and isothermally reaged, zone formation occurs at a much slower rate than after quenching from the solid-solution temperature, even though clustering already exists after reversion. In addition, when the alloys are reaged near room temperature after reversion at 150°C, the resistivity does not go through a maximum; and only a very slight maximum is observed for reaging after reversion at 180°C (Ref. 21). This indicates that the zones grow to only a small size (about 9 Å) during reaging and then stop growing. Both of these observations suggest that the lower vacancy concentration, which exists after reversion, results in limited diffusion and reduced zone growth.

Recently Cohen *et al.* observed by electron microscopy the formation of what appear to be vacancy loops after reversion.²² This suggests that during reversion, vacancies are released from the G.P. zones, and that for long reversion times, these vacancies form the observed dislocation loops. Hence vacancies may do more than just provide diffusion; they appear to be trapped at zones and/or are an integral part of zones. This seems reasonable since during a 2- or 5-min reversion treatment the zinc atoms cannot move more than one atomic distance from a cluster and, as mentioned previously, thermodynamic considerations require more clustering at the reversion temperature than exists at the solid-solution temperature. However, the time is sufficient for a simple rearrangement of vacancies either within a cluster or in the vicinity of a cluster. When the alloys are reaged, the slow kinetics and limited zone growth could also be due to the fact that the vacancies within or near zones must undergo rearrangement to the prereversion configuration in addition to providing diffusion. After reversion, there appears to be an insufficient concentration of vacancies to provide all that is required for the structural rearrangement and the diffusion necessary for the zones to grow rapidly and large.

With this information obtained on the influence of lattice vacancies after quenching and reversion, we are led to consider the two other methods for producing nonequilibrium concentrations of point defects in metals, namely, plastic deformation and energetic-particle irradiation. This report is concerned with the latter.

B. Irradiation of Aluminum-Zinc Alloys

There have been two studies of the effects of irradiation on the aging process in aluminum-zinc alloys. In the first of these, Ceresara, Federighi, and Pieragostini irradiated aluminum (99.995%) and the Al-4.4a/oZn alloy at 77°K with reactor neutrons with a fast-neutron dose of $2.9 \times 10^{17} \text{ n/cm}^2$ of $E > 1.0 \text{ MeV}$ (Ref. 23). They studied the alloy in the following three thermodynamic states:

1. Quenched.
2. Quenched and aged at 293°K to the resistivity maximum.
3. Quenched and aged at 293°K well past the resistivity maximum.

They observed that the irradiation-induced resistivity rate of the alloy was about twice that of the aluminum. This same ratio of damage rates had been previously observed by them in an Al-0.1a/oZn alloy where zone formation does not occur. Hence, they concluded that the higher dose rate in the alloy was not due to G.P. zone formation during irradiation.

During the isochronal annealing of the specimens, the resistivity maximum occurred 50° lower in temperature in the quenched and irradiated samples than in the quenched samples. Also, the maximum was 30% higher for the lower-temperature aging, which is consistent with the earlier work of Panseri and Federighi, which indicated the lower the aging temperature the higher the maximum.

The beginning of zone formation occurred at the same temperature as the start of Stage III in aluminum. This occurrence suggests that the same defect is moving in both the alloy and the aluminum. However, when Stage III is complete in aluminum, the alloy is at the resistivity maximum. Ceresara et al. suggest that all the defects must be gone in the alloy since they are gone in the aluminum; hence the maximum observed is not the true maximum associated with 9 Å zones, but is due to the stopping of zone growth due to the elimination of all the defects in the lattice. They suggest that the subsequent resistivity decrease is due to the dissolving of zones as the temperature is increased.

For isothermal aging at 230 and 250°K, Ceresara et al. observed that, during early aging times, irradiation enhances zone formation. However, for long aging times, zone formation became slower in the quenched-irradiated specimens than in the quenched specimens. They suggest that the irradiation-induced vacancies are rapidly eliminated and that for long aging times the supersaturation of vacancies in the quenched-irradiated material became lower than in the quenched alloy.

For the samples aged to the resistivity maximum before irradiation, they observed another small resistivity increase during the postirradiation isochronal annealing. This additional resistivity increase is shifted to a few degrees lower in temperature than the original peak. This is probably due to the formation of more zones in the irradiated alloy. This is again consistent with the previous results obtained on quenching; i.e., aging at lower temperatures results in a higher resistivity maximum.

For the material preirradiation aged for a long time beyond the resistivity maximum, Ceresara et al. observed only a resistivity decrease during isochronal annealing after irradiation. This suggests that the only process taking place was the recovery of the irradiation-induced lattice defects.

The second irradiation study of aluminum-zinc alloys was by Herman, who irradiated the Al-5.3a/oZn alloy in both the as-quenched state and in the reverted state at 77°K to 10^{15} - 10^{16} deuterons/cm of 10.5-MeV energy.²⁴ Upon isochronal annealing, the resistivity maximum occurred 20° lower in reverted-irradiated material than in reverted material, with a slight increase in the height of the maximum for the irradiated material over that in the unirradiated material. For the quenched sample, no effect of irradiation was observed on isothermal annealing at 290°K. With the reverted samples, on isothermal aging at 290°K, there appeared to be slightly faster kinetics at early times for the irradiated sample. Little or no difference between irradiated and unirradiated samples was observed for later aging times, which agrees with the observations of Ceresara et al. For material reverted and reaged for 10,000 min at 290°K before irradiation with 10^{15} deuterons/cm², no further preprecipitation was observed upon postirradiation aging at 290°K, again agreeing with Ceresara et al.

The information obtained from the quenching experiments and the irradiations at 77°K indicated that fast-neutron irradiation near 4°K, where almost all thermally induced atomic motion is absent, would provide valuable information in the following areas:

1. Whether the dose rate for dilute aluminum-zinc alloys is much larger than for pure aluminum, or that the results obtained by Ceresara et al. were the result of thermally activated atomic motion during irradiation.

2. Whether the defects that are mobile during Stage I annealing and during the portion of Stage II annealing below 77°K have an effect on G.P. zone formation in aluminum-zinc alloys.

3. The annealing stage in which zones form in the alloy. A comparison of the recovery stages in the pure aluminum and the stage in which zone formation occurs in the alloy would provide information on the defects responsible for the observed annealing stages in pure aluminum. For example, there is considerable controversy as to whether vacancies or interstitials are responsible for Stage III annealing in aluminum.^{23,25-28}

4. The role of irradiation-induced lattice defects in the zone-forming process in aluminum-zinc alloys, especially in reverted samples, where the initial defect concentration is small.

C. Irradiation of Pure Metals

For most of the cryogenic irradiation experiments conducted on metals and alloys, electrical resistivity has been the experimental parameter used to study the effects of the irradiation. For neutron irradiation, there is a large anomalous curvature at the origin of the curve of the irradiation-induced resistivity, ρ_i , vs neutron dose. The interpretation of this curvature is extremely important in irradiation-damage theory. Recently Schilling and co-workers have interpreted this anomalous curvature as evidence for long-range focusing events.²⁹⁻³¹ These focusing events, which are suggested to be more than 1000 atom distances in magnitude, are proposed to give rise to a type of "radiation annealing" that gives the large curvature in the curve of resistivity vs dose. This suggestion, when combined with the earlier observations of the same phenomenon by Blewitt and co-workers at Oak Ridge,³² indicated that further work was required to ascertain the source of the initial anomalous resistivity increase.

The Argonne CP-5 VT-53 cryogenic facility has a pure fission neutron spectrum; the fast-neutron flux is 6×10^{11} n/cm²-sec of $E > 1.0$ MeV, with a thermal-neutron flux of only 2×10^8 n/cm²-sec of $E < 0.144$ eV. Therefore, we can study the effects of a pure fission spectrum on metals and alloys and separate the radiation-damage effects due to thermal neutrons from those due to fast neutrons. Hence, a study of the saturation value of ρ_i , if such a value exists, would provide valuable information on the number of lattice atoms affected and the size of the displacement cascades produced by each primary neutron event for a pure fission spectrum. This study would also provide information on the portion of the observed damage in a reactor neutron spectrum that is due to thermal neutrons.

The specific information desired at this time is:

1. An explanation of the anomalous resistivity rise observed during the beginning of neutron irradiation.
2. The change in the residual electrical resistivity as a function of neutron dose in a pure fission spectrum.

II. EXPERIMENTAL PROCEDURE

A. Electrical Resistivity Measurements

As mentioned previously, electrical resistivity has been the parameter most often used to study the effects of irradiation at cryogenic temperatures and the subsequent isochronal annealing. Electrical resistivity was the parameter utilized in this investigation; the specimens were in the form of polycrystalline wires approximately 10 cm long (7 cm between potential probes) and about 0.7 mm in diameter. All the resistivity measurements made during irradiation were made at a temperature near 4.2°K. For the in situ isochronal annealing, the resistivity was measured at 4.2°K; then the specimens were pulsed to the desired annealing temperature and subsequently rapidly cooled to 4.2°K again for resistivity measurement. For the annealing performed out of pile, the resistivity measurements were made at 77°K. A schematic diagram of the resistivity-measuring circuit is shown in Fig. 1. The sensitivity of the measurements was from 2×10^{-12} to $5 \times 10^{-13} \Omega\text{-cm}$.

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Fig. 1. Schematic Diagram of Resistivity-measuring Circuit

B. Metals and Alloys Utilized

The pure metals utilized were of the purity shown in Table I and were obtained from the suppliers indicated. The aluminum-zinc alloys were supplied by the Aluminum Corporation of America as 0.5-in.-diam rods and were cold-drawn down to 0.07500-mm diam along with the pure aluminum and received the same etching and washing between reductions. Chemical analyses of the alloys after the final drawing operation indicated the composition shown in Table II. Three samples of each wire were analyzed; the samples were taken from widely separated portions of the wire as a check on the homogeneity of the alloy. The zinc concentration was determined by wet chemistry, the rest of the analyses were by mass spectrophotograph.

TABLE I. Chemical Analysis of Pure Metals Irradiated

Metal	Manufacturer Stated Purity, %	Supplier
Copper	99.999+	American Smelting & Refining Corp., So. Plainfield, New Jersey
Silver	99.999+	Materials Research Corp. Orangeburg, New York
Gold	99.999+	Materials Research Corp. Orangeburg, New York
Platinum	99.999+	Materials Research Corp. Orangeburg, New York
Palladium*	99.995+	Materials Research Corp. Orangeburg, New York
Iron*	99.998+	Materials Research Corp. Orangeburg, New York
Nickel*	99.997+	Materials Research Corp. Orangeburg, New York
Aluminum**	99.9999	A.I.A.G. Metals, New York, New York

*The impurities given for these elements were O₂, N₂, H₂, and C, with these plus the substitutional impurities totaling 50 ppm for palladium, 20 ppm for iron, and 30 ppm for nickel.

**The aluminum was obtained in ingot form and was etched in a 10w/o NaOH-distilled H₂O solution (at 313°K), H₂O washed (297°K), rinsed in 50v/o HNO₃-distilled H₂O (297°K) and washed again (297°K), between each rolling and drawing operation. After being rolled to a bar shape, the aluminum was cold-drawn to wire of 0.7500-mm diam.

TABLE II. Chemical Analysis of Aluminum-Zinc Alloys Irradiated

Element	Nominal Al-4w/o-Zn, w/o	Nominal Al-8w/o-Zn, w/o	Nominal Al-12w/o-Zn, w/o
Ag	<0.001	<0.001	<0.001
As	<0.1	<0.1	<0.1
B	<0.01	<0.01	<0.01
Ba	<0.01	<0.01	<0.01
Be	<0.01	<0.01	<0.01
Bi	<0.01	<0.01	<0.01
Ca	<0.01	<0.01	<0.01
Co	<0.01	<0.01	<0.01
Cr	<0.001	<0.01	<0.01
Cu	<0.01	<0.01	<0.01
Fe	<0.01	<0.01	<0.01
Hg	<0.01	<0.01	<0.01
K	<0.1	<0.1	<0.1
Li	<0.01	<0.01	<0.01
Cd	<0.01	<0.01	<0.01
Mg	<0.01	<0.01	<0.01
Mn	<0.001	<0.001	<0.001
Mo	<0.001	<0.001	<0.001
Na	<0.01	<0.01	<0.01
Ni	<0.001	<0.01	<0.01
P	<0.1	<0.1	<0.1
Pb	<0.01	<0.01	<0.01
Sb	<0.01	<0.01	<0.01
Si	<0.01	<0.001	<0.01
Sn	<0.01	<0.01	<0.01
Sr	<0.1	<0.1	<0.1
Ti	<0.01	<0.01	<0.01
V	<0.01	<0.01	<0.01
Zn	4.03 (1.70 a/o)	7.88 (3.41 a/o)	11.88 (5.27 a/o)
Zr	<0.01	<0.01	<0.01

A measure of the purity and perfection of pure metals is the ratio of the room-temperature resistivity to the liquid-helium resistivity. While a large ratio is not an absolute guarantee of specimen purity and freedom from defects, it is a criterion that is satisfied by high-purity metals containing only a small concentration of lattice defects. For the aluminum, the resistivity ratio of room temperature to helium was 3290, the highest known value for this metal.

The specimens were irradiated in five separate groups, which will be designated Irradiation Experiments I through V. These will be referred

to as Irradiation I, Irradiation II, etc., in this text. Since specimen history is vitally important to the interpretation of the experimental results, reference will be made to specimen size, heat treatment, residual resistivity, etc., separately for the five irradiation experiments.

Irradiation Experiments I and II were on the resistivity increase as a function of neutron dose for the pure metals listed in Tables III and IV. The specimens were individually annealed in a vacuum of 10^{-6} mm Hg with subsequent slow cooling before silver-soldering the copper potential-lead wires to the specimens. The specimens were connected in series; hence the current paths between specimens were made by soldering the ends of the specimens together. After final assembly and installation in the reactor, the specimens received a final preirradiational anneal at 820°K for 2 hr in an atmosphere of 38.1 mm of helium that remained after evacuating the helium liquid from the specimen chamber. The specimens were cooled from the annealing temperature to room temperature over a period of 4 hr and then cooled to 4.2°K and irradiated. (See Tables III and IV.)

Irradiations III, IV, and V were on the aluminum-zinc alloys with specimens of aluminum and copper included in each run to provide a comparison between the pure metals and the alloys. (See Tables V, VI, and VII.)

TABLE III. Description of Materials in Irradiation I

Specimen	Individual Preirradiation Treatment	Specimen Dimensions	$\rho_{0.2^\circ\text{K}}$, n Ω -cm*
1. Copper	Annealed for 8 hr at 1273°K at 10^{-6} mm Hg and cooled to room temperature over 16 hr.	Physical measurements not obtained. AL was calculated by measuring the resistance at 293°K and using the resistivity values at 293°K given in the American Institute of Physics Handbook, Sec. 5, p. 204 (1957).	2.41
2. Silver	Annealed for 8 hr at 1173°K at 10^{-6} mm Hg and cooled to room temperature over 16 hr.		7.04
3. Gold	Same as for copper.		35.67
4. Platinum	Annealed in air for 8 hr at 1473°K and cooled to room temperature over 16 hr.		2992.25
5. Iron	Annealed for 8 hr at 1473°K at 10^{-6} mm Hg and cooled to room temperature over 16 hr. Also used as neutron dosimeter.		44.37
6. Nickel	Same as for iron.		130.80
7. Palladium	Same heat treatment as for iron.		709.52
8. Cu ₃ Au	Annealed for 14 hr at 523°K at 1 atm of helium and slowly cooled to room temperature.		-
9. Al-0.12w/oCo	Neutron dosimeter.		-
10. Al-0.12w/oCo (Cd covered)	Neutron dosimeter.		-

*n = nano = 10^{-9} .

TABLE IV. Description of Materials in Irradiation II

Specimen	Individual Preirradiation Treatment	Specimen Dimensions	$\rho_{0.2^\circ\text{K}}$, $\text{n}\Omega\text{-cm}$
1. Copper (0.074-mm diam)	Annealed for 10-hr at 1253°K at $<10^{-6}$ mm Hg and cooled to room temperature over 14 hr.		1.61
2. Copper (0.046-mm diam)	Same as for Specimen 1.		1.96
3. Copper (0.028-mm diam)	Same as for Specimen 1.		3.51
4. Silver	Annealed for 8 hr at 1173°K at $<10^{-6}$ mm Hg and cooled to room temperature over 16 hr.		8.66
5. Gold	Same as for copper.		38.80
6. Platinum	Annealed for 10 hr in air at $\approx 1523^\circ\text{K}$ and cooled to room temperature over 18 hr.		2844.53
7. Platinum	Same as for Specimen 6.		2863.00
8. Palladium	Annealed for 8 hr at 1373°K in a static Vycor capsule evacuated to $\approx 10^{-7}$ mm Hg and cooled to room temperature over 12 hr.	Physical measurements not obtained. A/ℓ was calculated by measuring the resistance at 293°K and using the resistivity values at 293°K given in the American Institute of Physics Handbook, Sec. 5, p. 204 (1957).	2297.62
9. Iron	Annealed for 10 hr in $<10^{-6}$ mm Hg at 1473°K and cooled to room temperature over 15 hr.		43.15
10. Nickel	Same as for palladium.		226.09

TABLE V. Description of Materials in Irradiation III*

Specimen	Specimen Dimensions		$\rho_{0.2^\circ\text{K}}$, $\text{n}\Omega\text{-cm}$
	Length, cm (± 0.001 cm) (between potential probes)	Diam, mm	
1. Copper	6.826	0.707 ± 0.001	1.72
2. Aluminum	6.904	$0.722 \pm 0.002^{**}$	$0.92^\dagger$
3. Al-5.27a/oZn	6.838	0.721 ± 0.002	1052.47
4. Al-5.27a/oZn	6.734	0.722 ± 0.001	1038.91
5. Al-3.41a/oZn	6.400	0.712 ± 0.005	680.81
6. Al-1.70a/oZn	6.382	0.721 ± 0.002	328.76
7. Al-5.27a/oZn	6.124	0.727 ± 0.001	1039.61
8. Al-5.27a/oZn	5.888	0.721 ± 0.001	1010.43
9. Aluminum	6.282	0.717 ± 0.004	0.81
10. Al-3.41a/oZn	6.548	0.717 ± 0.003	668.68

*Heat treatment of entire group of specimens in text.

**All readings larger than ± 0.001 mm are a measure of the ellipticity of the wire specimens and are probably due to the etching and cleaning process. $^\dagger \rho_0$ for Specimen 2 not measured but calculated from all other data obtained on Specimens 2 and 9 and normalized to Specimen 9.

TABLE VI. Description of Materials in Irradiation IV*

Specimen	Specimen Dimensions		$\rho_{0.2^\circ\text{K}}$, $\text{n}\Omega\text{-cm}$
	Length, cm (± 0.001 cm) (between potential probes)	Diam, mm	
1. Copper	6.826	0.707 ± 0.001	6.99
2. Aluminum	6.904	$0.722 \pm 0.002^{**}$	0.92
3. Al-5.27a/oZn	6.838	0.721 ± 0.002	1148.76
4. Al-5.27a/oZn	6.734	0.722 ± 0.001	1121.30
5. Al-3.41a/oZn	6.400	0.712 ± 0.005	730.55
6. Al-1.70a/oZn	6.382	0.721 ± 0.002	340.86
7. Al-3.41a/oZn	6.124	0.727 ± 0.001	1126.19
8. Al-3.41a/oZn	5.888	0.721 ± 0.001	1119.42
9. Aluminum	6.282	0.717 ± 0.004	0.91
10. Al-3.41a/oZn	6.548	0.717 ± 0.003	726.77

*Heat treatment of entire group of specimens described in text.

**All readings larger than ± 0.001 mm are a measure of the ellipticity of the wire specimens and are probably due to the etching and cleaning process.

TABLE VII. Description of Materials in Irradiation V*

Specimen	Specimen Dimensions		$\rho_{0.2^\circ\text{K}}$, $\text{n}\Omega\text{-cm}$
	Length, cm (± 0.001 cm) (between potential probes)	Diam, mm	
1. Aluminum	6.300	$0.722 \pm 0.002^{\dagger\dagger}$	0.89
2. Al-1.70a/oZn	6.536	0.719 ± 0.001	334.17
3. Al-3.41a/oZn	6.120	0.709 ± 0.005	652.92
4. Al-5.27a/oZn	6.284	0.710 ± 0.002	1027.06
5. Al-5.27a/oZn	6.736	0.707 ± 0.002	1065.34
6. Al-3.41a/oZn	6.490	0.703 ± 0.006	698.01
7. Al-1.70a/oZn	6.904	0.714 ± 0.004	310.72
8. Copper	†		2.01
9. Tantalum** $T_c = 4.38^\circ\text{K}$			
10. Niobium** $T_c = 9.22^\circ\text{K}$			

*Heat treatment of entire group of specimens described in text.

**Included as superconductors to provide temperature information during irradiation and isochronal annealing.

† For copper, ℓ and d were not measured since the specimen was inserted after the specimen holder was attached to the irradiation assembly. The A/ℓ value was obtained by measuring the resistance at 293°K and dividing it into the 293°K value of the resistivity of $1.662 \mu\Omega\text{-cm}$ given in the American Institute of Physics Handbook, Sec. 5, p. 204 (1957).

†† All readings larger than ± 0.001 mm are a measure of the ellipticity of the wire specimens and are probably due to the etching and cleaning process.

For the aluminum and aluminum-zinc alloys, a solder composed of 92.85w/oPb, 4.86w/oIn, and 2.38w/oAg secured the potential leads to the specimens and the specimens to each other. Isothermal aging at 295°K of the Al-5.27a/oZn alloy after quenching from 555°K indicated no difference in aging characteristics between the alloy with the soldered joint and that with a spot-welded joint. It is reasonable to assume that the solder had no effect on the aging characteristics observed in this experiment.

C. Thermal History of Aluminum and Aluminum-Zinc Alloys

1. Thermal History for Irradiations III and IV

a. The specimens were solution-annealed at 555°K for 1 hr and quenched in distilled water at 273°K, held at 273°K for 10 sec, transferred to a bath of petroleum ether at 193°K for 10 sec, and then into liquid nitrogen at 77°K.

b. The specimens were cooled to 4.2°K and irradiated (Irradiation III) to 2.4×10^{17} n/cm² of $E > 1.0$ MeV.

c. The specimens were isochronally annealed in situ (5-min pulses) to a reversion temperature of 400°K. This was done by evacuating the specimen chamber until only 38 mm of helium gas remained in it. This gas served as a heat-transfer medium between the heater and specimens, but limited the thermal transfer between the irradiation chamber and the cryostat chamber. The cold helium around the specimen chamber was pumped out before each annealing pulse and then dumped back in at the end of each annealing pulse.

d. The specimens were cooled from reversion temperature to 4.2°K and irradiated (Irradiation IV) to a dose of 1.7×10^{17} n/cm²/sec. At this dose, operating difficulties arose in the helium liquefier system, and the specimen irradiation assembly was removed from the reactor and quickly inserted into liquid nitrogen. This decision was made since no effects on the preprecipitation reaction were observed upon annealing the quenched and irradiated state until about 160°K was reached; hence warming to and storing at 77°K should have no effect on the process being studied.

e. Isochronal annealing from 77 to 465°K was performed as follows: Isochronal annealing from 77 to 260°K was performed by leaving part of the specimen chamber immersed in liquid nitrogen and turning the heater on. The pulse to 265°K was made by withdrawing the specimen chamber from the liquid nitrogen and inserting it into a bath of dry ice and acetone at 233°K; the heater was then turned on to bring the temperature within the chamber to 265°K. At the end of the 5-min annealing pulse, the specimen chamber was rinsed with acetone to remove the water and then reinserted into the liquid-nitrogen bath. The pulses from 273 to 373°K were

made in stirred and heated (where necessary) distilled H₂O held just below the desired annealing temperature. The final few degrees were obtained by using the heater. From 383 to 465°K the annealing bath was Dow Corning No. 703 Silicone oil. After 95% of the elapsed annealing pulse, the specimen chamber was dipped in a rinse bath of Freon-11 before being returned to the liquid nitrogen.

2. Thermal History for Irradiation V

a. The specimens were solution-annealed at 555°K for 1 hr and quenched into liquid nitrogen. The quenching into liquid nitrogen was prompted by the following facts: For the samples quenched into H₂O followed by petroleum ether at 153°K, some type of solid (either solid H₂O or solid petroleum ether) was observed on the specimen holder. This resulted in several small explosions during the irradiation due to the decomposition of the ether or due to ozone formation from the solid H₂O. These explosions can be very serious; hence, all attempts were made to avoid them in future runs. Also, since we were going to study the reverted state, the cooling rate was not so important as when we were studying the as-quenched state, since the material is aged before reversion. In addition, the resistivity values after quenching the specimens into water at 273°K followed by petroleum ether at 190°K and into liquid nitrogen were approximately the same as those obtained on quenching the specimens directly into the liquid nitrogen.

b. The specimens were isothermally aged at 290°K for 650 min and inserted into reactor at 298°K.

c. After being inserted into the reactor at 298°K, the specimens underwent reversion at 440°K for 5 min and was cooled to 4.5°K after reversion.

d. The specimens were irradiated at 4.2°K to a dose of 2.0×10^{17} n/cm² of energy greater than 1 MeV.

e. The specimens were isochronally annealed in situ to 85°K, removed from the pile, and put into liquid nitrogen at 77°K.

f. The copper irradiation can was removed from the specimens for better heat control during subsequent isochronal annealing.

g. Isochronal annealing from 113 to 243°K was performed by placing the specimen holder in a bath of Freon-12 cooled to the temperature of interest. From 250 to 297°K, Freon-11 was used as the bath, and from 308 to 468°K, Dow Corning No. 703 Silicone oil was used. After 95% of the elapsed annealing pulse (4.75 min), the specimen holder was dipped in a rinse bath of Freon-11 before being returned to the liquid-nitrogen reservoir.

3. Thermal History of Unirradiated Materials

The thermal history of the unirradiated materials was identical to that of the irradiated materials wherever possible for the two cases studied, namely, (a) As-quenched and, (b) As-quenched, aged, and reverted.

a. For the as-quenched condition the treatment was: The specimens were solution-annealed for 1 hr at 555°K and quenched in distilled H₂O at 273°K, held at 273°K for 10 sec, and transferred to a bath of petroleum ether at 193°K for 10 sec and then into liquid nitrogen at 77°K. This was followed by isochronal annealing from 77 to 420°K. This was performed by withdrawing the specimen holder from the liquid nitrogen and placing it in a bath that was held at the desired temperature of the pulse. This was followed by rapid reinsertion of the specimen holder into the liquid nitrogen. Freon-12 was used as the bath from 119 to 243°K. Freon-11 was used from 250 to 297°K. From 313 to 420°K, Dow Corning No. 703 oil was used as the bath with the same postannealing rinses employed as described earlier.

b. For the as-quenched, aged, and reverted material the treatment was: The specimens were solution-annealed at 555°K for 1 hr and quenched into liquid nitrogen. They were then isothermally aged at 290°K for 650 min, followed by reversion at 440°K for 5 min, and cooled to 77°K. The cooling rate from the reversion temperature was the same for the irradiated and unirradiated materials. Reversion was followed by isochronal annealing from 116 to 528°K in the identical manner as the reverted and irradiated material was annealed from 113°K and up. To obtain more information about thermal effects on the initial resistivity increase during irradiation, the temperature coefficient of resistivity from 4.2 to 12.1°K was measured for copper, aluminum, Al-1.70a/oZn, Al-3.41a/oZn, and Al-5.27a/oZn. This was performed with the reactor off and the irradiation assembly in place within the cryostat. The temperature was controlled by varying the flow of helium through the Joule-Thompson throttle valve for the range of 4.2 to 4.8°K. From 5.6 to 12.1°K, the Nichrome heater was used and the flow through the throttle valve was controlled to obtain the desired temperature.

D. Irradiation Assembly

The general experimental techniques will now be described. The specimens in the form of polycrystalline wires were placed symmetrically about the longitudinal axis of the holder as shown in Fig. 2. The specimens were always loaded into the specimen holder before receiving the preirradiation heat treatment. This was to prevent possible plastic deformation of the specimens. In fact, for all but one of the irradiations (the as-quenched state), the final preirradiation heat treatment was performed with the irradiation assembly in its irradiation position in the reactor.

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Fig. 2. Specimen Holder for Resistivity Measurements in the Reactor

the specimens near the periphery of the discs and the aluminum rod that held the discs in place. The heater was centered about the aluminum rod, and information obtained during the isochronal postirradiation annealing of Irradiation IV indicated that the heat was traveling up the center rod by conduction, and the temperature near the rod was much higher than that at the specimens. The two carbon resistors were employed to determine whether there was a vertical temperature gradient within the irradiation capsule due to stratification of the helium liquid.

Because of the stresses imposed upon the specimen holder during quenching and the desire to have a material with little nuclear heating, oxidized Type 1100 aluminum was used for all the components of the specimen holder.

Below the specimens was a heater in the shape of a helix of 0.018-mm-diam Nichrome wire, which had a total resistance of 15-18 ohms. Adjacent to the aluminum rod of the holder at the longitudinal midplane of the specimens was a copper-constantan thermocouple for thermometry above 77°K, and a carbon resistor (Allen-Bradley Type TS, 1/8 watt, hermetically sealed) for thermometry below 77°K. In Irradiation V, two thermocouples and two carbon resistors were employed. One thermocouple was adjacent to the aluminum rod at the center of the specimen holder, and one adjacent to the aluminum specimen; this was done to determine whether there was a temperature gradient between

An electrical tough-pitch copper can with a wall thickness of 0.011 in. and a 0.011-in.-thick, stainless-steel upper portion was placed over the specimen holder and heliarc-welded to the 3.3-meter long, stainless-steel (Type 304 0.020-in. wall thickness) tube that served as an umbilical attachment between the experimental chamber and the top of the reactor. The top of the copper can was made of stainless steel so that it could be heliarc-welded to the stainless-steel tube. The low heat generation (compared to silver soldering) of heliarc welding, low thermal conductivity of stainless steel, together with the lower 90% of the capsule being immersed in liquid nitrogen during the welding, prevented the specimen temperature from

rising above 77°K during the welding. Hence no structural changes, such as G.P. zone formation in the aluminum-zinc alloys, took place during this operation. As a check of this, the thermocouple output of Irradiation V was recorded during the welding operation; it showed no deviation from 77°K.

At the top of the reactor a bolted flange secured the irradiation assembly to the cryostat. The 32 lead wires from the specimen holder were passed through a hole in the flange, and the assembly made vacuum-tight by an epoxy resin seal between the flange and the wires. Attached to the flange was a vacuum valve and piping. Through the valve and piping, helium gas was added to the specimen chamber to be condensed to liquid for irradiation, or the chamber could be evacuated for annealing without affecting the cryostat.

Figure 3 shows the specimen holder with all components in place; adjacent to the specimen holder is the copper can that separates the specimen chamber from the cryostat. As shown in Fig. 4, the environment within the irradiation assembly was completely separated from the cryostat proper.

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Fig. 3. Irradiation Specimen Holder with All Components in Place (A) and Copper Specimen Chamber (B)

The cryostat and liquid helium generating system are described in detail by Blewitt,³³ and its operation during these experiments is described by Klank *et al.*³⁴

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Fig. 4. Irradiation Assembly for Cryogenic Irradiations

III. RESULTS

A. Irradiation-induced Resistivity as a Function of Irradiation Time for Pure Metals

The resistivity increase as a function of irradiation time for the copper, silver, and gold of Irradiation I are shown in Fig. 5; Fig. 6 shows the corresponding data for palladium, nickel, and iron. In all cases there is a large initial increase in the resistivity during the first 100 min, followed by an apparent linear region until the reactor shutdown at 1400 min of irradiation time. The resistivity increase rates for the first 1400 min, the second 2200 min, and the irradiation are shown in Table VIII, together with the magnitude of the initial resistivity increase and the total irradiation-induced resistivity for Irradiation I. Figure 7 shows the initial resistivity jump of 0.2 nΩ-cm obtained for copper when the plot of induced resistivity vs irradiation time is extrapolated to zero time.

43898

Fig. 5. Irradiation-induced Resistivity as a Function of Irradiation Time for Copper, Silver, and Gold for Irradiation I

43899

Fig. 6. Irradiation-induced Resistivity as a Function of Irradiation Time for Iron, Nickel, and Palladium for Irradiation I

TABLE VIII. Resistivity Increase Rate, Total Induced Resistivity, and Magnitude of Initial Jump for Irradiation I

Specimen	$\frac{d\rho}{dt}$, $10^{-12} \Omega\text{-cm}/\text{min}$			Total Induced Resistivity, $\text{n}\Omega\text{-cm}$	Magnitude of Initial Jump, $\text{n}\Omega\text{-cm}$
	0-3600 min	0-1400 min	1400-3600 min		
1. Copper	5.27	5.58	5.04	18.92	0.2
2. Silver	4.20	5.24	3.55	15.04	1.9
3. Gold	4.77	5.98	4.08	17.04	1.73
4. Platinum	4.97	-	-	17.76	*
5. Iron	39.78	41.56	38.40	142.66	3.31
6. Nickel	16.37	18.84	14.71	58.72	3.20
7. Palladium	12.60	16.22	10.72	45.29	2.93

*Thermal effects made the early irradiation time values erratic.

Fig. 7
Portion of Induced Resistivity as a
Function of Irradiation Time for
Copper, Indicating Magnitude of
Initial Resistivity Jump

106-8213 Rev. 1

The resistivity increase as a function of irradiation time for the materials contained in Irradiation II is shown in Figs. 8, 9, and 10.

For the longer irradiation time of Irradiation II, the curves depart from linearity with an apparent tendency toward saturation. This is also shown in Table IX, which contains the resistivity increase rates, the total amount of induced resistivity, and the magnitude of the initial jump for Irradiation II.

Figure 11 shows a portion of the induced-resistivity plot as a function of irradiation time for copper specimens of three different diameters contained in Irradiation II. The insert shows some details of the resistivity decrease as a function of the specimen diameter on reactor shutdown, and the transient that exists on subsequent reactor startup.

Further indication of the thermal effects associated with resistivity measurements in copper and aluminum taken with the reactor on are shown in Figs. 12 and 13. The data for copper with the reactor on are above those with the reactor off; in addition, the resistivity values obtained with the reactor on are a direction function of the reactor power level. As shown in Fig. 13, the resistivity values for aluminum are the same with the reactor on or off.

B. Irradiation-induced Resistivity as a Function of Irradiation Time for Aluminum and Aluminum-Zinc Alloys

During Irradiations III, IV, and V, the resistivity change as a function of irradiation time was the same for the pure aluminum and for the three alloy compositions in both the as-quenched state and in the reverted state. Figures 14, 15, and 16 show the resistivity increase as a function of irradiation time for Irradiations III, IV, and V, respectively.

106-8730

Fig. 8. Irradiation-induced Resistivity as a Function of Irradiation Time for Copper, Gold, and Silver for Irradiation II

106-8729

Fig. 9. Irradiation-induced Resistivity as a Function of Irradiation Time for Palladium and Platinum for Irradiation II

106-8728 Rev. 1

Fig. 10. Irradiation-induced Resistivity as a Function of Irradiation Time for Iron and Nickel for Irradiation II

TABLE IX. Resistivity Increase Rate, Total Induced Resistivity, and Magnitude of Initial Jump for Irradiation II

Specimen	$\frac{d\rho}{dt}$, 10^{-12} Ω -cm/min				Total Induced Resistivity, $n\Omega$ -cm	Magnitude of Initial Jump, $n\Omega$ -cm
	0-5,000 min	5,000-10,000 min	10,000-15,000 min	15,000-20,000 min		
1. Cu ₁	5.29	4.79	4.40	4.04	92.06	*
2. Cu ₂	5.54	4.98	4.56	4.18	95.91	0.09
3. Cu ₃	5.65	5.08	4.65	4.25	97.58	0.02
4. Silver	4.14	3.74	3.44	3.22	72.33	0.02
5. Gold	5.29	4.71	4.34	4.31	93.98	*
6. Platinum	8.65	8.00	7.54	7.30	162.23	3.54
7. Platinum	8.54	7.79	7.36	7.13	157.74	1.44
8. Palladium	10.69	9.82	9.11	8.52	193.56	1.24
9. Nickel	14.16	13.36	12.68	11.96	261.05	0.76
10. Iron	41.01	41.17	39.95	38.71	796.15	0.25

*Thermal effects made the early time values erratic.

43900

Fig. 11. Portion of Irradiation-induced Resistivity as a Function of Irradiation Time for Copper Specimens of Three Different Diameters

106-8726

Fig. 12. Portion of Irradiation-induced Resistivity as a Function of Irradiation Time for Copper, Showing the Difference between Reactor-on and Reactor-off Values

106-8727

Fig. 13. Portion of Irradiation-induced Resistivity as a Function of Irradiation Time for Aluminum, Showing the Similarity between Reactor-on and Reactor-off Values

44070

Fig. 14. Irradiation-induced Resistivity as a Function of Irradiation Time for Irradiation III

44068

Fig. 15. Irradiation-induced Resistivity as a Function of Irradiation Time for Irradiation IV

43902

Fig. 16. Irradiation-induced Resistivity as a Function of Irradiation Time for Irradiation V

For each case, we immediately note the discontinuities in the damage-rate curves. In Fig. 14 the first discontinuity is at reactor start-up, which is accompanied by a large resistivity increase in the alloys. No early time data were obtained for aluminum since the thermal emf's were about as large as the small value of the residual resistivity. At 2450 min, the reactor was shut down with an accompanying decrease in the resistivity of all the specimens as shown. After this discontinuity there are seven additional discontinuities during the irradiation. These were all due to temperature pulses within the irradiation cryostat. These pulses, which momentarily brought the temperature within the specimen chamber (as indicated by the recorded output of the thermocouple) to a maximum of 77°K, are attributed to the irradiation-induced decomposition of either solid acetone or solid water (ice), which froze on the outer walls of the specimen chamber when the irradiation assembly was lifted from the liquid nitrogen and wiped with acetone (to remove frost) prior to insertion of the assembly into the cold cryostat. This decomposition was accompanied by an exothermic release of gas, which was indicated by a pressure rise on the manometer attached to the cryostat chamber. This gas may have been ozone, whose presence in a radiation environment is very dangerous because of its explosive characteristics upon decomposition. In addition, there may have been ice or solid petroleum ether within the specimen chamber as a result of the quenching operations. For this reason, the subsequent quenches were directly into liquid nitrogen.

During these temperature pulses, Stage I annealing was taking place in the materials; the amount of annealing was a function of the maximum temperature reached during the peak since all the peaks were of the same time duration. Although fairly large amounts of annealing occurred in the pure aluminum during the pulses, very little annealing occurred in the alloys until late in the irradiation. Table X lists the resistivity increase per minute for the times between the discontinuities, the total induced resistivity, and the magnitude of the initial jump for Irradiation III.

TABLE X. Resistivity Increase Rate, Total Induced Resistivity, and Magnitude of Initial Jump for Irradiation III

Specimen	$\frac{d\rho}{dt}$, 10^{-11} Ω -cm/min							Total Induced Resistivity, $n\Omega$ -cm	Magnitude of Initial Jump, $\Delta\rho$, $n\Omega$ -cm
	0-160 min	160-2410 min	3020-3780 min	4190-5070 min	5180-5710 min	5780-6930 min	7070-8070 min		
1. Copper	**	0.13	0.47	0.81	0.14	0.84	0.85	22.51	**
2. Aluminum	0.58	0.90	1.73	1.76	1.84	1.78	1.83	49.83	≈ 0
3. Al-5.27a/oZn	*	1.98	1.86	1.31	1.48	1.53	1.58	139.43	46
4. Al-5.27a/oZn	*	2.17	1.73	1.13	1.68	1.39	2.17	137.19	32
5. Al-3.41a/oZn	*	1.94	1.78	1.26	1.46	1.49	1.54	131.31	23
6. Al-1.70a/oZn	*	1.87	1.72	1.36	1.51	1.50	1.54	105.05	7
7. Al-5.27a/oZn	*	1.91	1.68	1.26	1.70	1.41	1.37	138.55	34
8. Al-5.27a/oZn	*	1.99	1.73	1.25	1.72	1.39	1.33	146.35	53
9. Aluminum	0.60	1.13	1.69	1.69	2.10	1.73	1.78	51.50	≈ 0
10. Al-3.41a/oZn	*	2.03	1.85	1.40	1.88	1.58	1.51	141.93	33
Average Values									
Aluminum	0.60	1.06	1.71	1.73	1.97	1.76	1.81	50.66	
Al-1.70a/oZn	-	1.87	1.72	1.36	1.51	1.50	1.54	105.05	
Al-3.41a/oZn	-	1.98	1.82	1.33	1.67	1.53	1.53	136.62	
Al-5.27a/oZn	-	2.01	1.73	1.22	1.64	1.42	1.60	140.38	
Copper	**	0.13	0.47	0.81	0.14	0.84	0.85	22.51	

*Early irradiation time values were not obtained because of the anomalous initial jump in resistivity.

**Early irradiation time values were not obtained because of a broken lead wire that was later repaired.

For Irradiation IV, Fig. 15 shows there are two discontinuities besides the initial startup and shutdown. These were due to a warming in the refrigeration system. This warming led to the eventual termination of the irradiation. The irradiation assembly was removed from the reactor and placed in liquid nitrogen. The amount of annealing that occurred during the warming of the refrigerator system and the transfer from the reactor are also shown in Fig. 15. Table XI lists the total induced resistivity, the resistivity increase rate for the periods between the discontinuities during Irradiation IV, and the magnitude of the initial jump.

TABLE XI. Resistivity Increase Rate, Total Induced Resistivity, and Magnitude of Initial Jump for Irradiation IV

Specimen	$\frac{d\rho}{dt}$, 10^{-11} Ω -cm/min				Total Induced Resistivity at 4.2°K, $n\Omega$ -cm	Magnitude of Initial Jump, $\Delta\rho$, $n\Omega$ -cm
	0-60 min	60-235 min	2710-3190 min	4260-5700 min		
1. Copper	0.76	0.61	0.47	0.81	17.78	0.02
2. Aluminum	2.22	1.69	1.79	1.78	35.78	≈ 0
3. Al-5.27a/oZn	**	1.90	1.54	2.02	96.89	20
4. Al-5.27a/oZn	**	1.89	1.49	2.15	89.81	14
5. Al-3.41a/oZn	**	1.85	1.47	2.04	78.39	4
6. Al-1.70a/oZn	**	1.75	1.47	1.95	81.11	12
7. Al-5.27a/oZn	**	1.72	1.28	2.01	76.55	1
8. Al-5.27a/oZn	**	1.77	1.24	2.06	87.92	20
9. Aluminum	2.12	1.64	1.63	1.67	33.94	≈ 0
10. Al-3.41a/oZn	**	1.82	1.41	2.09	85.64	12
Average Values						
Aluminum	2.17	1.67	1.71	1.72	34.86	
Al-1.70a/oZn	-	1.75	1.47	1.95	81.11	
Al-3.41a/oZn	-	1.84	1.44	2.06	82.01	
Al-5.27a/oZn	-	1.82	1.39	2.06	87.79	
Copper	0.76	0.61	0.47	0.81	17.78	

*This is the induced resistivity remaining after the specimens had been removed from the pile, stored in liquid nitrogen, and remeasured at 4.2°K.

**Early irradiation-time values were not obtained because of the anomalous initial jump in resistivity.

Figure 16 shows the resistivity vs irradiation time for Irradiation V. There are several discontinuities in the alloy data, but only one for the pure aluminum and copper. The initial jump at reactor startup was very large for the alloys. The alloy curves exhibit several small changes, because of changes in the operating power of the reactor. There were 24 changes in power level after the reactor initially came to power, the major changes being indicated at the top of Fig. 16. Two large decreases in resistivity occurred when the pile was shut off at 700 min and at 1300 min. With the reactor off, the irradiation-induced resistivity increase in the alloys is about the same as that in the pure aluminum. At about 1700 min, an increase in the reactor power to 4.6 MW led to a temporary warming of the cryogenic system. During the warming, the temperature reached a brief maximum of 61°K, during which annealing of Stage I was occurring in the specimens, especially in the pure copper and aluminum. The warmup was halted, the system was stabilized again at about 4.5°K, and the remainder of the irradiation proceeded without interruption. Table XII shows the total induced resistivity, the induced resistivity remaining after storage at 77°K, the resistivity increase rate for the uninterrupted portions of the irradiation, and the magnitude of the initial jump for Irradiation V.

TABLE XII. Resistivity Increase Rate, Total Induced Resistivity, and Magnitude of Initial Jump for Irradiation V

Specimen	$\frac{d\rho}{dt}$, 10^{-11} Ω -cm/min		Total Induced Resistivity at 4.2°K, n Ω -cm	Induced Resistivity at 4.2°K,** n Ω -cm	Magnitude of Initial Jump, $\Delta\rho$, n Ω -cm
	170-1500 min	2050-5050 min*			
1. Aluminum	1.93	1.86	83.90	32.38	≈ 0
2. Al-1.70a/oZn	1.90	1.86	102.83	64.87	27
3. Al-3.41a/oZn	1.60	1.88	121.26	64.56	90
4. Al-5.27a/oZn	1.68	1.62	85.68	63.56	65
5. Al-5.27a/oZn	1.79	1.76	86.81	65.98	25
6. Al-3.41a/oZn	1.65	1.92	120.18	71.17	52
7. Al-1.70a/oZn	1.98	1.88	103.46	62.96	36
8. Copper	0.551	0.510	24.72	13.89	0.2
Average Values					
Aluminum	1.93	1.86	83.90	32.38	
Al-1.70a/oZn	1.94	1.87	103.14	63.41	
Al-3.41a/oZn	1.63	1.90	120.72	67.87	
Al-5.27a/oZn	1.74	1.69	86.24	64.77	
Copper	0.551	0.510	24.72	13.89	

*These are best values since they were all taken at one power level.

**This is the induced resistivity remaining after the specimens were isochronally annealed to 85°K, subsequently removed from the reactor, stored in liquid nitrogen, and remeasured at 4.2°K.

C. Resistivity Change as a Function of Isochronal Annealing Temperature for Quenched and Quenched-Irradiated Aluminum and Aluminum-Zinc Alloys

Figure 17 shows the isochronal annealing data from 4 to 85°K for the materials in Irradiation V; also shown is the total recovery observed after the assembly was stored in liquid nitrogen after the isochronal annealing to 85°K.

44065

Fig. 17. Stage I Recovery in Copper, Aluminum, and Aluminum-Zinc Alloys after Irradiation V

The information obtained on isochronal annealing above 77°K of the alloys in the quenched state and the quenched-irradiated state are shown in Figs. 18-20. Since many specimens of each alloy were studied, the

Fig. 18
Resistivity Change as a Function of Isochronal Annealing Temperature for Quenched and Quenched-Irradiated Al-1.70a/oZn and Aluminum

43903

43904

Fig. 19. Resistivity Change as a Function of Isochronal Annealing Temperature for Quenched and Quenched-Irradiated Al-3.41a/oZn and Aluminum

43905

Fig. 20. Resistivity Change as a Function of Isochronal Annealing Temperature for Quenched and Quenched-Irradiated Al-5.27a/oZn and Aluminum

values plotted are those for representative specimens. The values for each specimen were in very good agreement, as shown in Table XIII. In all the isochronal annealing plots, the resistivity change of the aluminum is also shown to indicate the resistivity recovery associated with only the annihilation of the irradiation-induced lattice defects.

TABLE XIII. Isochronal Annealing Behavior of Quenched and Quenched-Irradiated Aluminum-Zinc Alloys

Specimen	Treatment	Start of Aging, °K	$T_{\max}$, °K	$\Delta\rho_{\max}$, $n\Omega\text{-cm}$
Al-1.70a/oZn				
RAL-3-7	Quenched from 555°K	220	200	10.04
RAL-2-6	Quenched from 555°K and irradiated	220	240	4.38
Al-3.41a/oZn				
RAL-3-3	Quenched from 555°K	220	280	115.70
RAL-3-6	Quenched from 555°K	220	283	113.76
RAL-2-5	Quenched from 555°K and irradiated	170	250	115.95
RAL-2-10	Quenched from 555°K and irradiated	170	260	114.67
Al-5.27a/oZn				
RAL-3-4	Quenched from 555°K	220	277	176.70
RAL-3-5	Quenched from 555°K	220	277	185.91
RAL-2-3	Quenched from 555°K and irradiated	180	255	246.08
RAL-2-4	Quenched from 555°K and irradiated	170	255	250.14
RAL-2-7	Quenched from 555°K and irradiated	170	255	246.78
RAL-2-8	Quenched from 555°K and irradiated	180	255	244.75

For the quenched alloys, irradiation shifted the start of zone formation by 50° from 220 to 170°K, the peak being shifted by 25° from 280 to 255°K in the two alloys having higher zinc content. In the Al-1.70a/oZn alloy, the peak was shifted by 40° from 280 to 240°K.

D. Resistivity Change as a Function of Isochronal Annealing Temperature for Reverted and Reverted-Irradiated Aluminum and Aluminum-Zinc Alloys

The isochronal annealing behavior of the reverted and the reverted-irradiated aluminum-zinc alloys, together with the aluminum (Irradiation V) are shown in Figs. 21-23. Again, the agreement among specimens is good, as indicated in Table XIV.

For the reverted samples, zone formation began at 240°K. The peak was at 314°K in the two more concentrated alloys and at 296°K in the Al-1.70a/oZn. Recall that in the quenched samples the temperature shift of the start of zone formation was the same in all three alloys. In the reverted samples, the shift increased with increasing zinc content. The shift was 20, 50, and 75°, respectively. The maximum was at 245°K (50° shift) for the Al-1.70a/oZn, and at 253°K for the two other alloys (60° shift).

43906

Fig. 21. Resistivity Change as a Function of Isochronal Annealing Temperature for Reverted and Reverted-Irradiated Al-1.70a/oZn and Aluminum

43907

Fig. 22. Resistivity Change as a Function of Isochronal Annealing Temperature for Reverted and Reverted-Irradiated Al-3.41a/oZn and Aluminum

Fig. 23
Resistivity Change as a Function of
Isochronal Annealing Temperature
for Reverted and Reverted-Irradiated
Al-5.27a/oZn and Aluminum

TABLE XIV. Isochronal Annealing Behavior of Reverted
and Reverted-Irradiated Aluminum-Zinc Alloys

Irradiation No.	Specimen	Treatment	Start of Aging, °K	T _{max} , °K	Δρ _{max} , nΩ-cm
Al-1.70a/oZn					
IV	6	Reverted at 400°K and irradiated*	230	250	2.05
V	2	Reverted at 440°K	240	296	5.35
V	2	Reverted at 440°K and irradiated	218	244	6.44
V	7	Reverted at 440°K	240	296	5.18
V	7	Reverted at 440°K and irradiated	218	243	5.73
Al-3.41a/oZn					
IV	5	Reverted at 400°K and irradiated	170	265	88.50
V	3	Reverted at 440°K and irradiated	190	253	115.98
V	3	Reverted at 440°K	240	314	36.87
V	6	Reverted at 440°K and irradiated	190	253	113.35
V	6	Reverted at 440°K	240	314	30.61
Al-5.27a/oZn					
IV	3	Reverted at 400°K and irradiated	140	273	172.15
IV	4	Reverted at 400°K and irradiated	140	273	190.16
IV	7	Reverted at 400°K and irradiated	160	265	197.06
IV	8	Reverted at 400°K and irradiated	160	265	176.83
V	4	Reverted at 440°K	240	314	105.10
V	4	Reverted at 440°K and irradiated	164	253	216.27
V	5	Reverted at 440°K	240	314	117.02
V	5	Reverted at 440°K and irradiated	164	253	212.71

*The isochronal annealing data for Irradiation IV have not been plotted owing to temperature-control difficulties during the annealing (as mentioned in the text), and apparently reversion at 400°K did not eliminate all the irradiation-induced resistivity. The data are shown here since there was good temperature control in the temperature range of the peak, and the peak temperature and height are valid. The data show that irradiation after 400°K reversion enhances zone formation and growth.

IV. DISCUSSION

A. Pure Metals

1. Initial Jump in Resistivity

As shown in Figs. 5-12, there is a large initial rise in resistivity upon reactor startup. The magnitude of this initial increase for the pure metals varied from Irradiation I to Irradiation II, the values for Irradiation II being less than those for Irradiation I. This is probably due to the manner in which the reactor was brought to the full operating power of 4.6 MW in the two cases. In Irradiation I, the reactor was brought to power quite rapidly. This resulted in large thermal effects in our resistivity measurements, and we did not get reproducible stable resistivity measurements until after about an hour of irradiation time. Extrapolation of the induced-resistivity vs irradiation-time curve from 100 to 1400 min to zero time resulted in the "initial jump" listed in Table VIII

After experiencing this difficulty in Irradiation I, we requested that the reactor be brought to power more slowly for Irradiation II. For Irradiation II, the reactor was brought to 1 MW and held there for about an hour, then brought to 2 MW and held for about an hour. This process was continued until the full power level of 4.6 MW was attained. By this method, we obtained much more early-time data and were able to extrapolate to zero irradiation time more accurately, which resulted in smaller initial jump values for Irradiation II.

In addition, if the curve of irradiation-induced resistivity as a function of irradiation-time is examined on an expanded scale (such as the portion of the curve for the three copper specimens of different diameters shown in Fig. 11), we see that for the seven reactor shutdowns and subsequent startups during Irradiation II the magnitude of the initial jump is always the same. This suggests that the jump is due to the same mechanism in all seven instances.

Further, as shown in Fig. 11, the smaller the specimen diameter the shorter the initial transient that is responsible for the initial jump. Figure 11 shows that the duration of the transient is significantly longer for the 0.029-in.-diam copper wire than for the 0.011-in.-diam copper wire, the duration for the 0.018-in.-diam copper wire being between these two.

The size effect indicates that the initial jump is thermal in nature since a larger-diameter copper wire would take longer to establish thermal equilibrium with its surroundings than a smaller-diameter copper wire. It is impossible to comprehend how a long-range focusing mechanism could give rise to the observed size effect and how the focusing-mechanism

contribution to the resistivity could be the same over the wide range of defect concentrations associated with the seven reactor shutdowns and startups during Irradiation II. It is equally difficult to comprehend how the focusing mechanism can explain the observed resistivity decrease on reactor shutdown that is of the same magnitude as the jump on subsequent startup.

The above information strongly indicates that a thermal effect gives rise to the resistivity anomaly observed in neutron irradiation. The data to be discussed at this time clearly show that the anomaly is completely removed when precautions are taken to eliminate the heating. Figure 12 shows the early-time-induced resistivity in copper as a function of irradiation time. The open circles are data taken with the reactor on, and the solid circles are data obtained with the reactor off. The resistivity undergoes an anomalous increase each time the reactor is turned on, and the resistivity values obtained with the reactor on are proportional to the reactor power level. Each time the reactor is turned off, the resistivity decreases to the values shown. For the reactor-off data a straight line can be drawn that joins all the points and goes exactly through the origin. In addition, the reactor-on data have a slope that is discernibly greater than that of the reactor-off data. This suggests that thermal equilibrium has not yet been obtained after 7 hr of reactor operating time.

Figure 13 shows that for aluminum there is essentially no difference between the reactor-on data and reactor-off data. This is in complete agreement with the work of Schilling, which also indicates no anomalous curvature in the resistivity-vs-dose data for aluminum. Therefore, it appears that the interpretation that the anomalous resistivity jump is due to long-range focusing events is incorrect.

Two possible suggestions for the source of the initial jump are (1) gamma-ray heating inside the cryostat from the fission events in the fuel and the converter surrounding the cryostat, and (2) heating due to the gamma-ray emission from the fission-product buildup in the fuel.

Gamma-ray heating is proportional to the mass absorption coefficient of the elements and is directly related to the densities of the elements. The second column of Table XV contains the observed initial jump for the specimens of Irradiation II. The third and fourth columns contain the mass density and thermal conductivity at 4.2°K for each element. These are then normalized to copper as shown in columns five and six to give an effective density and thermal conductivity. For gamma-ray heating, the heating (with respect to copper) should be proportional to the density and inversely proportional to the thermal conductivity as suggested in column seven. Finally, column eight shows the magnitude of the initial jump in each element, normalized to the initial jump in copper. There is apparent agreement between the suggested effective heating rate and the initial jump for all the metals except iron.

TABLE XV. Parameters for Evaluating Heating due to Fission Gamma Rays in Metals Studied

Element	Initial Jump, m Ω -cm	Density, ρ , g/cc at 20°C	Thermal Conductivity, K, Watts cm-sec at 4.2°K	$PIP_{Cu} =$ ρ_{eff}	$K/K_{Cu} =$ K_{eff}	Heating in Metal Heating in Copper $\alpha \frac{\rho_{eff}}{K_{eff}}$	Initial Jump in Element Initial Jump in Copper
Copper	0.05	8.9	72	1	1	1	1
Silver	0.02	10.5	144	1.3	2	0.6	0.5
Gold	1.73 Irr. I	19.3	18	2.2	0.25	8.7	8.5
Platinum	2.5	21.4	9	2.4	0.12	20	50
Palladium	1.2	12.2	8	1.4	0.11	14	24
Iron	0.25	7.9	1	0.9	0.01	64	5
Nickel	0.76	8.9	2	1	0.03	27	15
Aluminum	≈ 0	2.7	32**	0.3	0.44	0.7	≈ 0.1
Aluminum	≈ 0	2.7		0.3	1	0.3	≈ 0.1

*American Institute of Physics Handbook (1957).

**Recent data by the NBS indicate that the thermal conductivity of high-purity aluminum is much greater than that for the 1100 aluminum given in the table.

Even with the apparent agreement between the calculated heating due to gamma rays and the observed initial jump, it is difficult to explain how such an effect could account for a transient that exists for such long times. In addition, the thermal conductivities of metals are large enough so that equilibrium should be established in a matter of seconds. Furthermore, the same type of jump can be observed when the reactor is off and the heater is turned on. In this case, the heat source is not in the samples but in the liquid helium below the specimens. The heat must be transferred through the liquid helium into the specimens, which means that the helium liquid is at the same temperature as the specimens. It is difficult to comprehend how the liquid helium could be heated more than a few tenths of a degree or so without a tremendous increase in the vapor pressure over the liquid helium.

A possible contribution to the long duration of the transient could be the time required for the gamma-ray-emitting fission products to build up to an equilibrium concentration in the fuel. In the CP-5 reactor, the time required for this is a few hours. The energy release due to the gamma rays from radioactive decay of the fission products is 6 MeV per fission event, and that due to the instantaneous gamma rays from the fission process is 5 MeV per fission event.³⁶ Hence the two processes give rise to about the same amount of heating. This could at least partially account for the long duration of the observed transient on reactor startup.

Additional information that confirms the thermal origin of the anomalous resistivity rise was obtained from Irradiation V and the measurement of the temperature coefficient of the aluminum, copper and aluminum-zinc alloys between 4.2 and 12.1°K.

As mentioned previously, the aluminum-zinc alloys exhibited a large anomalous resistivity jump at reactor startup and a decrease at reactor shutdown. To determine the nature of this anomaly, the temperature coefficients of the electrical resistivities of the materials in Irradiation V were measured from 4.2 to 12.1°K.

From 4.2 to 4.8°K, the resistivity change is essentially zero. From 5.6 to 7.4°K, the resistivity jumps rapidly to a value that ranges from 5 to 10% higher than the residual resistivity of each specimen, as shown in Fig. 24. Table XVI shows the resistivity at each measurement temperature from 4.2 to 12.1°K, together with the thermal jumps observed for these specimens during Irradiation V.

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Fig. 24. Resistivity Changes in Aluminum, Copper, and Aluminum-Zinc Alloys, as a Function of Temperature in the Range of 4.2 to 12.1°K

TABLE XVI. Resistivity Changes in Aluminum, Copper, and Aluminum-Zinc Alloys in Temperature Range of 4.2 to 12.1°K.

Specimen	Temperature, °K						Magnitude of Jumps during Irradiation V			
	4.2	4.4	4.8	5.6	7.4	12.1	$\Delta \rho$, n Ω -cm			
	$\Delta \rho$ Values, from 4.2°K Value, n Ω -cm						Reactor Startup	700 min	1300 min	End of Run
1. Aluminum	0	-0.02	0.00	0.04	0.11	0.39	≈ 0	0.17	≈ 0	1.6
2. Al-1.70a/oZn	0	-0.02	0.00	23.51	34.53	35.36	27	23	25	13
3. Al-3.41a/oZn	0	0.03	-0.02	55	55.33	56.35	90	83	86	33
4. Al-5.27a/oZn	0	-1.22	-0.53	54.15	67.13	68.40	65	63	65	13
5. Al-5.27a/oZn	0	-0.04	0.09	22.86	74.82	75.95	25	21	23	49
6. Al-3.41a/oZn	0	-0.01	0.08	48	67.89	68.74	52	43	45	30
7. Al-1.70a/oZn	0	-0.04	-0.02	32.11	44.67	45.40	36	36	35	22
8. Copper	0	0.01	0.01	0.11	0.13	0.30	0.2	0.1	0.1	0.86

The source of the large increase in resistivity of the aluminum-zinc alloys between 4.8 and 5.6°K is attributed to the transition of the solder used to attach the potential leads to the specimens from the superconducting state to the ordinary state. Since the low-temperature electrical resistivity of the solder is much greater than that of the aluminum and aluminum-zinc alloys, the effective length, ℓ , between the potential leads is the measured ℓ value between the lead wires when the solder is in the normal state. When the solder undergoes the transition to the superconducting state, the effective ℓ is decreased to the distance between the innermost edges of the solder. This difference for the specimens of Irradiation V is between 2 and 4 mm.

The solder used for the aluminum and aluminum-zinc alloys was 92.85w/oPb-4.76w/oIn-2.38w/oAg. The superconducting transition temperature, T_c , for lead is 7.22°K, and for indium is 3.37°K. The transition temperature for an alloy, Pb_yIn_x , ranges from 3.37 to 7.22°K, depending on the prior heat treatment, impurity concentration, degree of strain, and segregation.³⁷ Shoenberg pointed out that T_c for an alloy can usually be estimated by using a linear relation between the transition temperature and composition for the two component metals.³⁸ With this as a basis, T_c is calculated to be 6.82°K. As the data indicate, we do not have a strain-free, homogeneous, high-purity solder since the transition is spread out over a broad range. This range appears to be from just less than 5.6°K to under 7.4°K. This is consistent with the observations of both Roberts and Shoenberg that alloys usually do not exhibit a unique transition temperature but the transition is usually spread out over a temperature range. In fact, only high-purity, strain-free, homogeneous metals exhibit a unique T_c .

When the reactor is off, the specimen temperature is about 4.2°K and the solder is superconducting. When the reactor is brought to

power, the specimen is heated by gamma rays, which cause the specimen temperature to increase to between 5.6 and 7.4°K, and the solder loses its superconductivity. The effective path length has now been increased by between 5 and 10%, and the resistivity increases by between 5 and 10%, which causes the large anomalous resistivity jump observed in the alloys on reactor startup.

This behavior enables us to estimate the average specimen temperature during the irradiation. Recall that two superconductors, tantalum and niobium, were included in Irradiation V for this exact purpose. However, a short circuit that developed in their circuitry just before the assembly was inserted into the reactor prevented us from obtaining any information from these specimens. The data in Table XVI indicate that specimens 2, 5, 6, 7, and 8 were at about 5.6°K when the reactor was at power. Specimen 4 apparently was at about 7.4°K. Specimen 3 appears to be completely anomalous as far as the initial jump is concerned. Specimen 1, which is pure aluminum, appears to have been at the lower end of the temperature range (<5.6°K) during most of the irradiation; however, the resistivity decrease observed when the pile was shut down at the end of the irradiation was 1.6 nΩ-cm. The cause of this is not known at this time. The drop for copper at the end of the irradiation is 0.86 nΩ-cm, which is almost an order of magnitude more than the jump observed during the early part of the irradiation.

2. Irradiation-induced Resistivity as a Function of Irradiation Time

To obtain a physical significance of the resistivity increase as a function of irradiation time, least-squares analyses of the data were performed on the Control Data Corp. 3600 Computer. Since the curves in Irradiation II indicated a tendency toward saturation, a fit of the data was attempted to the following exponential expression:

$$\rho_i = A(1 - e^{-\alpha t}), \quad (2)$$

where A and α are experimentally determined parameters for each element.

However, for Eq. 2 the data points did not exhibit a random or oscillating distribution of plus and minus to the curve, which is a final measure of the agreement between the data and the curve. The data were above the curve for the first half of Irradiation II and below the curve for the last half. This, combined with the fact that for the fission-product irradiation-damage experiments performed by Blewitt and co-workers at Oak Ridge there appeared to be a linear term in addition to the exponential term,³⁹ suggested the addition of a linear term to Eq. 2. The linear term was

multiplied by an exponential function to provide for eventual saturation of the linear term and to maintain convergency as the irradiation time becomes very large as shown in the following equation:

$$\rho_i = A(1 - e^{-\alpha t}) + B(1 - e^{-\beta t}). \quad (3)$$

Equation 3 gives an oscillating distribution of data above and below the curve and a small root-mean-square error between the data points and the curve for the noble metals and aluminum. The parameters obtained for Eq. 3 for the elements studied are given in Table XVII. Parameters were not obtained for the alloys because of the large anomalous resistivity increase in startup and the temperature pulses that occurred during irradiation of the alloys.

TABLE XVII. Experimentally Determined Parameters for Eq. 3

Element	A, $10^{-8} \Omega\text{-cm}$	B, $10^{-6} \Omega\text{-cm/min}$	α , $10^{-5}/\text{min}^*$	β , $10^{-7}/\text{min}$	$\Sigma(e)^2 \times 10^{18}$
Aluminum	50.0	4.52	3.17	8.44	1.50
Copper	7.83	9.94	3.93	2.51	0.22
Silver	3.12	11.8	5.00	2.07	0.18
Gold	0.88	16.4	11.1	2.15	1.41
Platinum	0.91	13.4	20.1	7.25	11.5
Palladium	2.51	28.6	15.6	2.96	50.0
Iron	20.7	1.12	0.38	38.3	829
Nickel	0.37	1.57	3.99	95.8	31.0

$\Sigma(e)^2$ = the summation of the square of the difference between each data point and the least-squares curve. The smaller this value the more accurately the curve defines the data.

*The appendix contains calculations of the number of Frenkel pairs, the diameter in Å, and the atomic volume affected per neutron event and an attempt to relate these values to the parameters of Eq. 3.

The physical interpretation of Eq. 3 is as follows: The term $A(1 - e^{-\alpha t})$ represents the production of the highly concentrated regions of damage that are believed to occur in fast-neutron irradiation of metals. This displacement cascade is pictured as a vacancy-rich core surrounded by an interstitial-rich shell within a far lesser-disturbed matrix.⁴⁰ The exponential modification explains the fact that no new vacancy-interstitial pairs are created when the defect cascades overlap. The second term is thought to be due to stable defect clusters or dislocation loops that are produced by the interactions of the displacement cascades. As mentioned, the exponential modification of this term allows for an eventual saturation of this process also.

Holmes has calculated that for a dose of 1×10^{17} neutrons/cm² (of pure fission spectrum) the induced residual resistivity in copper should be $0.38 \times 10^{-7} \Omega\text{-cm}$.⁴⁰ For this dose, we observe a value of $0.16 \times 10^{-7} \Omega\text{-cm}$. Hence, the observed value is only a factor of 2.4 times less

than the theoretical value; for neutron irradiation, this is the best agreement obtained to date between theory and experiment. For the most recent previous data, the observed resistivity increase was a factor of 4.5 smaller than that calculated from theory.⁴⁰ Our agreement is at least in part due to the neutron spectrum in VT-53 being an almost pure fission spectrum.

3. Observed Damage Rates at ANL, ORNL, and Munich

The resistivity-increase rate in silver (see Fig. 8) was about 20% less than that of copper, whereas Blewitt, using the Hole 12 cryostat of the Oak Ridge Graphite Reactor, observed that the resistivity increase rate in silver was more than twice that in copper.³⁹ This observation prompted a comparison with the resistivity-increase rates at the Oak Ridge and Munich fast-neutron, cryogenic irradiation facilities.

Blewitt observed that the damage rates were in the descending order: silver, gold, and copper, silver having a damage rate more than twice that of copper.³⁹ Schilling's results indicate the order to be copper, silver, and gold, all three damage rates being within 7% of each other.³⁰ For our data, the order is copper, gold, and silver, the gold damage rate being 5% less than in copper and the silver damage rate being almost 20% less than in copper.

Coltman and co-workers, using the Oak Ridge Graphite Reactor, have been studying low-temperature thermal-neutron damage in metals.⁴¹ Many of the gamma rays that are emitted after a neutron capture event have sufficient energy to displace one or more atoms in a metallic lattice. Since silver has an (n, γ) cross section 16 times that of copper, it seemed feasible to see if there is any correlation between Coltman's thermal-neutron damage rates and our observed damage rates.

Coltman and co-workers found that, in their facility, thermal-neutron damage could account for as much as 20% of the observed damage in copper, 40% in platinum, and 60% in both silver and gold. This is probably the reason why our observed damage rate in silver is 20% less than that in copper. A simple analysis without a detailed knowledge of the neutron energy spectrum is impossible because of the very large resonance peak for the (n, γ) reaction in both gold and platinum. The existence of these resonances in the eV energy range is probably why our gold data and platinum data do not show the same degree of thermal-neutron contribution as the silver data. However, we can still obtain some general information on the neutron energy spectra in these three facilities.

The investigations at all three sites have included the study of the damage rate in aluminum. It was suggested earlier in this report that there is essentially no thermal-neutron-induced damage in aluminum.

This has been proven by Coltman and co-workers. Hence, a comparison of the damage rates in aluminum for the three facilities is the best measure of the fast-neutron damage rate only. As shown in Table XVIII, which summarizes the damage-rate information for the three facilities, our fast-neutron damage rate is 13 times that of the Oak Ridge Hole 12 facility and only one-fifth that of the Munich facility. This result is useful since it helps to explain why our damage rates for the other elements studied were less than one-fifth of the Munich values. The Munich facility has a thermal-neutron flux of 2×10^{12} n/cm²/sec, with a fast-neutron flux of 1×10^{13} n/cm²/sec, whereas our thermal-neutron flux is only 2×10^8 n/cm²/sec, the fast-neutron flux being 6×10^{11} n/cm²/sec. The higher damage rates for copper, silver, gold, and platinum are due to the large thermal-neutron flux in the Munich facility. As mentioned earlier in this section, the large resonance peaks in the electron-volt energy regions make it hard to arrive at a one-to-one correspondence for gold and platinum.

TABLE XVIII. Damage-rate ($d\rho/dt$) Information for Argonne CP-5 VT-53, ORNL Hole 12, and Munich FRM Cryogenic Facilities

Element	$d\rho/dt, 10^{-12} \Omega\text{-cm/min}$ Damage-rate Ratios									
	ANL	ORNL ^{1*}	Munich ^{**}	ORNL _{Total} [†]	ORNL _{Fast} [†]	ANL ORNL ₁	Munich ANL	ANL ORNL _{Total}	ANL ORNL _{Fast}	$\frac{\sigma(n,\gamma)}{\sigma(n,\gamma)_{\text{Cu}}}$
Aluminum	18.60	1.40	97.3	1.45	1.45	13	5	13	13	0.05
Copper	5.02	0.41	30.2	0.49	0.40	12	6	10	13	1
Silver	4.20	0.86	29.5	0.81	0.32	5	7	5	13	16.4
Gold	4.77	0.50	27.8	0.73	0.28	10	6	6	17	2.4
Platinum	8.20	1.10	78.7	1.47	0.92	7	10	6	9	2.7
Palladium	12.60	-	-	-	-	-	-	-	-	-
Iron	39.78	2.67	-	-	-	15	-	-	-	0.7
Nickel	16.37	2.21	86.0	-	-	7	5	-	-	1.1

*From Ref. 33.

**Calculated from Figs. 1 and 2 of Ref. 30.

†From Ref. 41.

B. Aluminum and Aluminum-Zinc Alloys

1. Irradiation-induced Resistivity as a Function of Irradiation Time

Since the resistivity increase rate (i.e., $d\rho_i/dt$) was the same for aluminum and the three aluminum-zinc alloys in both the as-quenched state and the reverted state, the same damage mechanism seems operative in aluminum and aluminum-zinc alloys. Hence, zinc atoms did not cluster during the irradiation. If clustering were taking place, $d\rho_i/dt$ in the alloys would be higher than in the aluminum because of the anomalous resistivity increase that occurs during the early growth of the clusters to about 9 Å in size.

This is in contrast to the results of Ceresara *et al.*, who observed that the resistivity increase rate in the Al-4.4a/oZn alloy was twice that of the aluminum during irradiation at 77°K.²³ Considerable atomic motion, which is rather well agreed to be due to the mobility of interstitial atoms at this temperature, occurs during irradiation at 77°K. It therefore

appears as though some interstitial-solute atom reactions or clustering of interstitials occurs during 77°K irradiation. It does not seem possible that zone formation is responsible for the larger resistivity increase since the same ratio of resistivity increase rate is observed for an Al-0.1a/oZn alloy irradiated at 77°K with fast neutrons. In addition, Sosin and Rachel²⁸ observed the resistivity increase rate to be four times as much for the Al-0.1a/oZn alloy as for aluminum irradiated at 77°K with 1.1-MeV electrons. In this very dilute alloy, there are too few zinc atoms for any zone formation to take place. The experiments by Sosin and Rachel and by Ceresara *et al.* involving irradiation at 77°K further show the need for performing these experiments at temperatures sufficiently low so that no thermally activated atomic motion occurs during the irradiation.

2. Stage I Recovery in Aluminum and Aluminum-Zinc Alloys

In addition, as mentioned in Section III-C, there appears to have been no clustering of zinc atoms to form G.P. zones during Stage I annealing. The recovery during Stage I annealing is shown in Fig. 17 and Table XIX, and the differential recovery curve for Fig. 17 is shown in Fig. 25. For the aluminum-zinc alloys, the resistivity exhibits a continual decrease during Stage I that is similar to the Stage I recovery of copper containing small concentrations of gold.⁴²

TABLE XIX. Stage I Recovery in Copper, Aluminum, and Aluminum-Zinc Alloys after Irradiation V

Material	Recovery, %/°K				Stored at 77°K
	Annealing Temperature, °K				
	33	45	63	85	
Copper	6.1	26.6	29.4	32.0	43.8
Aluminum	8.9	36.6	41.5	49.6	61.2
Al-1.70a/oZn	5.6	12.4	14.3	31.7	36.7
Al-1.70a/oZn	6.1	12.2	14.5	No data	39.5
Al-3.41a/oZn	4.3	7.5	10.1	41.0	46.8
Al-3.41a/oZn	5.5	9.0	29.8	35.4	40.8
Al-5.27a/oZn	5.9	10.3	12.5	18.4	25.8
Al-5.27a/oZn	5.4	8.7	10.7	17.5	24.2
Average Values					
Al-1.70a/oZn	5.9	12.3	14.4	31.7	38.1
Al-3.41a/oZn	4.9	8.3	20.0	38.2	43.8
Al-5.27a/oZn	5.7	9.5	11.6	18.0	25.0

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Fig. 25. Differential Recovery of Stage I Annealing in Copper, Aluminum and Aluminum-Zinc Alloys after Irradiation V

interstitial is annihilated or trapped. In addition, zinc atoms are smaller than aluminum atoms; hence, the interchange between a zinc atom in an interstitial position and an aluminum atom on a lattice site would be energetically unfavorable and would probably not occur. These two factors suggest that interstitial motion could not provide the long-range diffusion required for the formation and growth of zones. Furthermore, the resistivity continues to decrease up to 160-170°K (see Figs. 18-23), which is the beginning of Stage III annealing in aluminum and these alloys.

The reason for the larger Stage I recovery in the Al-3.41a/oZn alloy than in the Al-1.70a/oZn alloy may be that a portion of the Stage I annealing had already occurred in the Al-1.70a/oZn alloy during the temperature pulse to 61°K, that occurred about one-third of the way through the irradiation.

As shown in Fig. 16, 39% of the induced resistivity in aluminum was recovered during the temperature pulse to 61°K. The resistivity jumps for the alloys due to the temperature rise within the irradiation assembly vary from specimen to specimen; however, at least a small amount of annealing has occurred in even the Al-5.27a/oZn alloy and the Al-3.41a/oZn alloy. It is reasonable to assume that at least as much or more annealing occurred in the Al-1.70a/oZn alloy, since the amount of Stage I recovery observed in alloys is usually inversely proportional to alloy content. As shown in Fig. 16, the recovery during the temperature rise in the Al-3.41a/oZn samples was greater than in the Al-5.27a/oZn samples. The smaller than expected resistivity jump (based on Table XVI and Fig. 24) for the Al-3.41a/oZn alloy may be due to some annealing that occurred during the temperature rise. This would seem, qualitatively at least, to explain the larger amount of Stage I recovery in the Al-3.41a/oZn alloy than in the Al-1.70a/oZn during postirradiation isochronal annealing.

It might be suggested that the smaller amount of recovery to 77°K in the alloys is due to zone formation that superimposes a resistivity increase upon the decrease due to the recovery of lattice defects. However, the lattice defect that is responsible for zone formation is the vacancy. Interstitial motion during Stage I annealing in face-centered-cubic metals and alloys is limited to only a few atomic distances before the

3. Isochronal Annealing of Quenched and Quenched-Irradiated State

Since the purpose of this portion of the investigation was to study the role of irradiation-induced defects on G.P. zone formation, it would seem feasible to discuss the point-defect concentration as a function of isochronal annealing temperature for pure aluminum before proceeding to the alloys. In the pure aluminum the only change in resistivity observed is the decrease associated with the recovery of lattice defects, whereas, in the alloys the resistivity decrease due to the recovery of lattice defects is complicated by the resistivity increase due to G.P. zone formation and growth. For the alloys, at temperatures below that where zone formation and growth begins, the point-defect concentration can be estimated by the remaining irradiation-induced resistivity; for temperatures above this, it is assumed that at a given temperature the point-defect concentration is equal to or greater than that in the aluminum due to the trapping of defects by the solute atoms.

Consider first the aluminum, and use the information by Simmons and Balluffi that the resistivity of lattice vacancies in aluminum is $3 \times 10^{-4} \Omega\text{-cm}$ per atom fraction.¹⁷ A reasonable assumption then would be to assign a value of $6 \times 10^{-4} \Omega\text{-cm}$ per atom fraction (a.f.) of Frenkel pairs in aluminum. We then divide the induced resistivity remaining by this value to obtain the concentration of Frenkel pairs.* For example, the irradiation-induced resistivity remaining in the aluminum of Irradiation III at the end of the irradiation was $50.06 \times 10^{-9} \Omega\text{-cm}$. Thus we have

$$C_{\text{F.P.}} = \frac{\text{Resistivity Remaining}}{6 \times 10^{-4} \Omega\text{-cm}} \quad (4)$$

and for aluminum,

$$C_{\text{F.P.}} = \frac{50.06 \times 10^{-9}}{6 \times 10^{-4}} = 8.3 \times 10^{-5} \text{ a.f.}$$

Although the calculation of defect concentration by this method is only an approximation of the absolute values, there should be sufficient internal consistency among the values calculated by this method to allow comparisons to be made. At temperatures above 77°K, it may be more meaningful to speak in terms of point defects or lattice defects, since considerable atomic rearrangement of the initial irradiated state has taken place, and in fact, the initial irradiated state does not contain Frenkel pairs but clusters of defects. The point-defect concentrations as a function of isochronal annealing temperature for the specimens in Irradiation III are contained in Table XX.

*Even though the defects are thought to exist in clusters after fast-neutron irradiation, recent calculations by Alfred⁴³ indicate that the resistivity per defect is essentially the same for the defects when they are separated as when they are clustered.

TABLE XX. Point-defect Concentrations as a Function of Isochronal Annealing Temperature for Specimens in Irradiation III

T, °K	Atom-Fraction of Point Defects			
	Aluminum	Al-1.70a/oZn	Al-3.41a/oZn	Al-5.27a/oZn
4.2	8.3×10^{-5}	1.8×10^{-4}	2.2×10^{-4}	2.3×10^{-4}
40	8.3×10^{-5}	1.6×10^{-4}	2.2×10^{-4}	2.1×10^{-4}
55	8.3×10^{-5}	1.5×10^{-4}	2.1×10^{-4}	1.9×10^{-4}
75	8.3×10^{-5}	1.5×10^{-4}	2.1×10^{-4}	1.9×10^{-4}
100	6.9×10^{-5}	1.4×10^{-4}	1.9×10^{-4}	1.8×10^{-4}
110	6.7×10^{-5}	1.3×10^{-4}	1.7×10^{-4}	1.7×10^{-4}
130	6.5×10^{-5}	1.2×10^{-4}	1.6×10^{-4}	1.6×10^{-4}
163	6.4×10^{-5}	1.0×10^{-4}	1.6×10^{-4}	1.5×10^{-4}
180	5.9×10^{-5}	9.2×10^{-5}	Aging began*	Aging began*
190	5.3×10^{-5}	7.9×10^{-5}		
200	4.4×10^{-5}	2.1×10^{-5}		
210	3.4×10^{-5}	6.5×10^{-5}		
220	1.8×10^{-5}	Aging began*		
230	7.3×10^{-6}			
240	2.5×10^{-6}			
250	5.7×10^{-7}			
260	-			
320	-			
400	-			

*When aging begins, the resistivity increase associated with zone formation and growth makes it impossible to calculate the point-defect concentration by this method. At this temperature and above, it is reasonable to assume that the point-defect concentration in the alloys is at least as large as that in the aluminum.

Stage III in the aluminum samples began at about 165°K and was complete at 270°K. Above 270°K, the resistivity undergoes no further changes to the end of the annealing at 400°K.

For the quenched Al-1.70a/oZn alloy, the slight resistivity maximum shown in Fig. 18 indicates the formation of G.P. zones.* The height of the maximum may be very low because there are two effects on the resistivity during zone formation. The resistivity increases because the electrons are scattered by zones; at the same time, the resistivity decreases because the number of solute atoms in the matrix reduces.

*The assumption made in the interpretation of the alloy data is the same as that made by previous investigators,^{6,23,24} namely that the resistivity maximum obtained during isochronal annealing is associated with zones of about 9 Å in size.

For this low zinc concentration, the decrease may offset the increase, resulting in only a small maximum. Eventually, as the temperature is increased, the zones grow to larger than 9 Å, and continued growth leads to the observed decrease at the higher annealing temperatures.

For the quenched-irradiated state, the induced resistivity was 105 nΩ-cm. If we assume the same resistivity per Frenkel pair as in aluminum, without specifying the spatial distribution of the vacancies and interstitials at this time, we have

$$C_{F.P.} = \frac{105 \times 10^{-9} \Omega\text{-cm}}{6 \times 10^{-4} \frac{\Omega\text{-cm}}{\text{a.f.}}} = 1.8 \times 10^{-4} \text{ a.f.}$$

During isochronal annealing from 4.2 to 160°K, there is a gradual decrease in resistivity, the major portion of the recovery occurring between 75 and 130°K. For this temperature range, the resistivity decrease rate in the alloy is greater than that in the aluminum. This additional recovery in the alloy is the "smearing out" of Stage I annealing to include the temperature range of Stages I and II.

As has been observed previously, the addition of small concentrations of substitutional solute atoms smears out the discrete annealing stages observed in pure metals.⁴² This occurs in the Al-1.70a/oZn alloy. Table XXI shows the percent recovery of Stage I annealing that resulted

TABLE XXI. Annealing in Copper, Aluminum, and Aluminum-Zinc Alloys due to Temperature Pulses during Irradiation III

Specimen	Pulse Number					
	1	2	3	4	5	6
	Percent Annealing due to the Pulse					
1. Copper	3	6	12	15	11	15
2. Aluminum	28	24	27	14	30	25
3. Al-5.27a/oZn	<1	<1	1	<1	3	17
4. Al-5.27a/oZn	<1	<1	<1	<1	3	12
5. Al-3.41a/oZn	<1	2	1	4	<1	8
6. Al-1.70a/oZn	<1	<1	3	<1	5	14
7. Al-5.27a/oZn	<1	<1	2	<1	2	8
8. Al-5.27a/oZn	<1	1	15	1	3	20
9. Aluminum	21	14	49	11	25	21
10. Al-3.41a/oZn	<1	No data	16	<1	3	12

from the brief temperature pulses during the irradiation. As can be seen, while a large amount of recovery was taking place in the aluminum, only a small amount occurred in the Al-1.70a/oZn alloy. The recovery that did not occur during Stage I in the alloy is that which is smeared out over Stage II annealing. This results in more rapid recovery in the latter part of the recovery curve for the alloy than in the pure metal.

An explanation for the smearing out of the recovery is that the irradiation-induced defects are trapped by the solute atoms, the traps being of a variety of strengths. Hence, during recovery, the defects in the weakest traps are released earliest and are annealed first. This process continues over the very wide temperature range corresponding to the range of trapping strengths of the solute atom-point defect interactions, the most strongly bound defects being released at the higher temperatures of the annealing.

Further evidence on the ability of solute atoms to trap point defects is given in Table X. The total induced resistivity is inversely proportional to the alloy content. Since the damage rates were the same, the differences among the final induced resistivities are the amount that annealed during the temperature pulses for Irradiation III. The more zinc atoms present, the more trapping sites for defects; hence, less annealing occurs during a temperature pulse, which has just been indicated in another way by the data in Table XXI.

In the range of 160-210°K, the recovery curves for the aluminum and the alloy are of roughly the same form. This suggests that the defect that is annealing in the aluminum is the same defect that is annealing in the alloy. The induced resistivity remaining in the alloy at 160°K is 63.19 nΩ-cm, which is 60% of that induced and represents 1.0×10^{-4} atom fraction of point defects.

If half the defects are vacancies, this corresponds to a factor of 50 more vacancies than existed after quenching. At 210°K, which is just past the center of the temperature range of Stage III in aluminum, there is a slight increase in the resistivity of the alloy. The resistivity exhibits a slight maximum at about 240°K, indicating that the resistivity increase due to zone growth overshadows the resistivity decrease due to the recovery of lattice defects, which is also occurring over this same temperature range.

The large resistivity decrease on the high-temperature side of the "peak" is probably due to zone growth and the recovery of irradiation-induced lattice defects.

An important finding is that zone growth takes place for temperatures well above that in which all the irradiation-induced defects have been annihilated in the aluminum. This strongly suggests that there is an attractive interaction between the zinc atoms and vacancies, which gives the vacancies a much longer lifetime in the alloy than in the pure aluminum; this conclusion was also reached on quenching.⁶

For the Al-3.41a/oZn alloy (see Fig. 19), doubling the solute atom content from 1.7a/oZn resulted in a distinct aging peak. In this case, the peak is sharp and the resistivity on the high-temperature side of the peak falls below the quenched value as the zones grow beyond the size for critical scattering of conduction electrons.

For the quenched-irradiated samples, the recovery of lattice defects during smeared-out Stage II annealing reduces the induced resistivity to a value of $98.54 \text{ n}\Omega\text{-cm}$ at 180°K . Using the value of $6 \times 10^{-4} \text{ }\Omega\text{-cm}$ per atom fraction of vacancy and interstitial type defects gives a concentration of 1.6×10^{-4} atom fraction of point defects. This is more than twice the concentration remaining in the aluminum and more than that remaining in the Al-1.70a/oZn alloy at this temperature. This is probably due to the increased trapping of defects by additional solute atoms.

In this case, aging begins about 50° lower than in the unirradiated alloy and occurs just after the beginning of Stage III annealing in aluminum. The maximum in the resistivity occurs at the end of Stage III in aluminum, and zone formation and growth continue up to 350°K , indicating that Stage III in the alloy is smeared out over a large temperature range.

At 400°K , the resistivity has not returned to the quenched value. At this time, considerable zone growth has occurred, as shown by the resistivity curves for the unirradiated samples. Apparently part of the irradiation-induced defects remained in this alloy at 400°K . This gives further evidence of some type of attractive interaction between vacancies and zinc atoms in aluminum, since all the vacancies in pure aluminum have been eliminated at 260°K .

The fact that Stage III began in aluminum and in the alloy at about the same temperature (165°K ; see Figs. 18-23) strongly suggests that the defect responsible for Stage III recovery in aluminum is the defect responsible for G.P. zone formation in the alloy. It is now rather well accepted that the defect responsible for the enhanced formation of zones after quenching is the lattice vacancy. Hence, it appears that vacancies are the defects mobile during Stage III annealing in aluminum and aluminum-zinc alloys.

An attempt was made to determine an activation energy for the Stage III annealing in both the aluminum and aluminum-zinc alloys. This was unsuccessful. However, as suggested by Ono and Meshii,⁴⁴ Stage III annealing in aluminum probably is not uniquely activated, but is a superposition of several processes of different activation energies. The width of our Stage III annealing in the high-purity aluminum is about 100° wide and much wider in the alloys. This, combined with the recent observation of dose-dependent asymmetry in Stage III for fast-neutron irradiated aluminum by Ceresara *et al.*,⁴⁵ gives additional credence to the suggestion that Stage III is probably not uniquely activated.

Returning to the Al-3.41a/oZn alloy, the height of the resistivity maximum in the irradiated alloys (measured from the minimum at 180°K) is the same as that in the unirradiated samples. This is not as expected, since the maximum in the irradiated case occurs about 25° lower than in the quenched case. Panseri and Federighi observed that the lower the aging temperature the higher the resistivity maximum.⁶ For a peak shift of 25°, they observed that the height of the maximum increased by approximately 10%. The resistivity decrease associated with the recovery of lattice defects during Stage III annealing may have suppressed the peak by about 10%. However, not too much emphasis can be placed on the absolute heights of the resistivity maximum since the height of the maximum is not an accurate measure of the number of zones present.

For the quenched Al-5.27a/oZn alloy, a sharp high maximum occurs at about 278°K. The maximum is 55% higher than in the Al-3.41a/oZn and extends over a significantly narrower temperature range. The Al-5.27a/oZn alloy contains 55% more zinc atoms than the Al-3.41a/oZn. Investigators in this field often make two assumptions related to the shape and height of the maximum: (1) The height of the maximum is proportional to the number of G.P. zones present; (2) the slope of the curve on both sides of the resistivity maximum is a measure of the rate of zone growth. The greater the slope the greater the rate of zone formation and/or growth. The higher the peak the more zones present. However, the correspondence among peak heights and number of zones present is usually not one to one, especially for alloys with different solute atom content. For the Al-5.27a/oZn, the high maximum and the large slope on both sides of the maximum indicate that zones form and grow very rapidly in this alloy.

Aging in the irradiated samples began at 160°K and continued up to 400°K, which was the reversion temperature for Irradiation IV. At this temperature, the resistivity had not decreased to the preirradiation values as in the Al-3.41a/oZn alloy, and the interpretation is the same as for that alloy, as given in Fig. 25 on page 57.

In contrast to the 3.41a/oZn alloy, irradiation has increased the peak height by 40%, which is appreciably greater than the increase observed by Panseri and Federighi for a 25° shift in this same temperature range (i.e., ≈280-255°K).

Irradiation has shifted the peaks in the 3.41 and 5.27a/oZn alloys from 280°K to about 255°K. The method of Meechan and Brinkman⁴⁶ for analyzing isochronal annealing curves indicates that an order of magnitude more vacancies are required for the resistivity maximum at 255°K compared to that at 280°K. The Meechan and Brinkman method may

be used for comparison of processes that are of the same order of reaction and have the same activation energy. This should be the case for the formation and growth of G.P. zones in the quenched samples and in the quenched-irradiated samples. Their analysis allows us to determine the center of an annealing stage as a function of the concentration of the reacting species or to determine the concentration of the reacting species if the temperature range of the annealing stage is known.

The assumption made in the analysis is that the isochronal annealing curve can be approximated by a uniform rate of temperature rise. Hence the time, t , in the chemical-rate equation is replaced by $T = AT$ where T is the temperature and A is the heating rate calculated from the experimental values of T/t , to give

$$\frac{dn}{dT} = \frac{\nu}{A} n \gamma_0^{-E/kT_A} \quad (5)$$

where

n = concentration of reacting species,

T = temperature ($^{\circ}\text{K}$),

ν = vibration frequency of the reacting species (the value used here is $1 \times 10^{13} \text{ sec}^{-1}$),

A = heating rate ($^{\circ}\text{K}/\text{min}$),

γ = order of the reaction (the value used here is 2),^{16,28}

E = activation energy for the reaction (the value used here is 0.47 eV),⁴⁷

k = Boltzmann constant ($0.86 \times 10^{-4} \text{ eV}/^{\circ}\text{K}$),

and

T_A = temperature of annealing stage.

For zone formation, we are interested in calculating the defect concentrations required for the observed temperature of the resistance maximum, T_M ; hence we replace T_A with T_M in Eq. 5. We then want to compare the values calculated by this method with the defect concentrations calculated for the quenched samples (Eq. 1) and the irradiated samples (Eq. 4) to examine the extent of agreement among the three methods for calculating the defect concentrations. Equation 5 can be solved to give

$$n = \frac{A(T_M)^{-1}}{v_e^{-E/kT_M}} \left(\frac{2}{E/kT_M} - \frac{1}{1 + E/kT_M} \right)^{-1} \quad (6)$$

With the use of T_M of 280°K for the quenched state, the resultant vacancy concentration required is 2×10^{-7} atom fraction, and for the peak at 255°K in the quenched-irradiated state, the concentration required is 1×10^{-6} atom fraction. Hence, the computed vacancy concentration of 7.5×10^{-5} atom fraction remaining at 163°K is adequate to account for the temperature shift of the resistivity peak. In fact, if these numbers are taken literally, then a portion of the point defects remaining in the lattice at the start of zone formation does not actually take part in the zone-forming process. This seems reasonable since most of the defects produced by fast-neutron irradiation are in fairly large clusters⁴⁰ and are not as homogeneously distributed throughout the volume of material as in quenched samples. Hence, in the irradiated case some of the defects apparently undergo annihilation without being effective in transporting zinc atoms to zones.

The results of the Meechan-Brinkman analysis indicate that a vacancy concentration of only 2×10^{-7} atom fraction is required for the peak to be at 280°K. The maximum vacancy concentration calculated for the quenched case, that is, at the solution temperature, was 1×10^{-6} atom fraction. The actual concentration present at the beginning of zone formation will be less than that at the solution temperature because vacancies are annihilated during the quench and/or because some of the vacancies are trapped as a structural part of a zone. The agreement between the two calculations is actually rather good since the methods of calculation are different. One calculation indicates the "maximum" vacancy concentration existing at the quenching temperature and does not require that all of these are retained upon quenching. The second calculation, by the Meechan-Brinkman analysis, gives the minimum value required for a certain temperature range of annealing since it cannot give information on those defects that do not take part in the process being analyzed. Furthermore, both calculations are "order-of-magnitude" type calculations, and the factor of five would appear to be quite acceptable, especially since some vacancies are certainly annihilated during the quench. Finally, as mentioned previously, there appears to be considerable evidence that vacancies are an integral part of G.P. zones. The number of vacancies associated with a zone is not indicated in these calculations since the binding between vacancies and zinc atoms has not been considered in the calculations.

Further support to the validity of the aforementioned results and interpretation is given by the following information: As mentioned on page 13, Panseri and Federighi studied the effect of solution temperature

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Fig. 26. Isochronal Aging Curves for Al-4.4a/oZn after Quenching from Various Temperatures⁶

on the isochronal annealing behavior of the Al-4.4a/oZn alloy.⁶ Figure 26 shows the pertinent results of their studies that are important here. Figure 26 clearly illustrates the shift toward lower temperatures of both the beginning of the zone growth and the resistivity maximum. In addition, the increasing height of the resistivity maximum as the aging occurs at lower temperature is evident. Table XXII summarizes the temperature of the resistivity maximum and the height of the maximum for each solution temperature shown in Fig. 26. In addition, the maximum vacancy concentration for each solution temperature has been calculated by Eq. 1, and the

ratio of the vacancy concentrations at the various quenching temperatures with respect to the vacancy concentration at 574°K are shown, together with the amount of peak shift with respect to the peak obtained after quenching from 574°K. The peak shift from that obtained after quenching from 574°K was chosen since it is the solution temperature nearest to that (555°K) used in this investigation. The last column of Table XXII lists the vacancy concentration for each aging peak temperature as calculated by Eq. 6. Table XXIII contains the height of the resistivity maximum as a function of aging temperature after quenching from 574°K. Table XXIV shows the percent changes in the height of the resistivity maximum for a 20° peak shift and a 60° peak shift for various aging temperatures. These temperature shifts of the aging peaks after quenching are about the same as the irradiation-induced temperature shifts of the peaks for the quenched samples and reverted samples, respectively.

TABLE XXII. Information Obtained on Isochronal Annealing of Al-4.4a/oZn Alloy (Data from Fig. 2 of Ref. 6)

Quench Temperature, °K	Peak Height, °K	Peak Height, nΩ-cm	C_V = Vacancy Concentration at T_{quench}	Peak Shift from $T_q = 574^\circ\text{K}$	$\frac{C_{VT}}{C_{V574}}$	$C_{VEq.1}$
521	311	172	4×10^{-7}	+19	1/5	7×10^{-8}
574	292	238	2×10^{-6}	0	1	3×10^{-7}
625	279	295	8×10^{-6}	-13	4	6×10^{-7}
673	254	330	2×10^{-5}	-38	10	5×10^{-6}
725	235	360	5×10^{-5}	-57	27	3×10^{-5}
773	217	360	1×10^{-4}	-75	55	3×10^{-4}
873	217	330	4×10^{-4}	-75	215	3×10^{-4}

TABLE XXIII. Height of Resistivity Maximum as a Function of Aging Temperature after Quenching from 574°K (Data from Fig. 5 of Ref. 6)

Aging Temperature, °K	Resistivity Maximum, nΩ-cm	Aging Temperature, °K	Resistivity Maximum, nΩ-cm
323	169	273	288
313	193	263	317
303	222	253	331
293	260	243	348
283	267		

TABLE XXIV. Percent Change in Height of Resistivity Maximum as a Function of 20 and 60° Peak Shifts (Data from Fig. 5 of Ref. 6)

Temperature Shift of 20° in Peaks, °K	Increase in Peak Height, %	Temperature Shift of 60° in Peaks, °K	Increase in Peak Height, %
323-303	31	323-263	88
313-293	35	313-253	72
303-283	20	303-243	57
293-273	11		
283-263	19		
273-253	15		
263-243	10		

For a temperature shift of 13°, the maximum vacancy concentrations differed by a factor of four; this is in good agreement with our order-of-magnitude difference in vacancy concentrations for a 25° shift in peak temperature. Table XXIV also indicates that a shift of 20° from 283 to 263°K, which is in the range of the temperature shift observed after irradiation (i.e., from 280 to 255°K), resulted in a 19% increase in the height of the resistivity maximum. This value is significantly less than the 40% observed after irradiation. This may imply that the vacancy fraction retained in the alloy after quenching is significantly less than the fraction in equilibrium at the quenching temperature; or it may mean that a portion of the vacancies that are in equilibrium at the solid solution temperature are tied up with zinc atoms and/or zinc atom clusters and are unavailable to aid in the diffusion of zinc atoms to these clusters for subsequent zone formation and growth. This results in less G.P. zone growth on aging than would be obtained if more of the defects were retained on quenching. In the irradiated material, the vacancy concentration seems to be adequate to account for the observed temperature shift of the peak and the increased

height of the maximum. The number of G.P. zones formed and their growth after irradiation may be what we would obtain if all or almost all the vacancies that exist at the quenching temperature are available to enhance diffusion upon quenching. The number of zones that formed after irradiation may be all that can occur in an alloy of this zinc content. Whether this is so can be established by an irradiation that produces a higher defect concentration than obtained in the present work.

The fact that zone formation begins at the same temperature for the three alloys and that the peaks are at the same temperature for the Al-3.41a/oZn samples and the Al-5.27a/oZn samples further suggests that the defect concentration controls zone formation and growth for aluminum-zinc alloys in this composition range.

4. Isochronal Annealing of Reverted and Reverted-Irradiated State

The point-defect concentration as a function of isochronal annealing temperature for the aluminum and aluminum-zinc alloys in Irradiation V is given in Table XXV.

TABLE XXV. Point-defect Concentration as a Function of Isochronal Annealing Temperature for Specimens in Irradiation V

T, °K	Atom Fraction of Point Defects			
	Aluminum	Al-1.70a/oZn	Al-3.41a/oZn	Al-5.27a/oZn
4.2	1.4×10^{-4}	1.7×10^{-4}	2.0×10^{-4}	1.4×10^{-4}
33	1.3×10^{-4}	1.6×10^{-4}	1.9×10^{-4}	1.4×10^{-4}
45	9.2×10^{-5}	1.5×10^{-4}	1.8×10^{-4}	1.3×10^{-4}
63	8.5×10^{-5}	1.5×10^{-4}	1.4×10^{-4}	1.2×10^{-4}
85	7.4×10^{-5}	1.2×10^{-4}	1.3×10^{-4}	1.1×10^{-4}
113	5.9×10^{-5}	9.6×10^{-5}	1.1×10^{-4}	9.8×10^{-5}
118	5.8×10^{-5}	9.2×10^{-5}	1.1×10^{-4}	9.6×10^{-5}
125	5.8×10^{-5}	8.6×10^{-5}	1.0×10^{-4}	9.2×10^{-5}
140	5.6×10^{-5}	7.8×10^{-5}	9.5×10^{-5}	8.8×10^{-5}
153	5.6×10^{-5}	7.3×10^{-5}	9.3×10^{-5}	Aging began**
164	5.5×10^{-5}	7.2×10^{-5}	Aging began**	
174	5.2×10^{-5}	6.8×10^{-5}		
183	4.9×10^{-5}	6.1×10^{-5}		
191	4.5×10^{-5}	5.3×10^{-5}		
204	3.5×10^{-5}	4.4×10^{-5}		
214	2.4×10^{-5}	4.1×10^{-5}		
218	1.7×10^{-5}	Aging began**		
233	5.4×10^{-6}			
243	4.3×10^{-6}			
253	1.3×10^{-6}			
262	3.5×10^{-7}			
270	0*			

* ρ remains at this level for the remainder of the annealing to 467°K.

**See footnote to Table XX.

For the Al-1.70a/oZn alloy (Fig. 21), the isochronal annealing curves after irradiation are similar to those of the as-quenched samples, and the analysis and interpretation are the same as for the quenched samples and the quenched-irradiated samples on pages 58 to 63.

For the Al-3.41a/oZn alloy, the effects of the irradiation are more dramatic for the reverted samples than for the as-quenched samples. For the reverted alloy, a small resistivity maximum of $30.61 \text{ n}\Omega\text{-cm}$ occurs at 314°K ; irradiation raises this value to $113.35 \text{ n}\Omega\text{-cm}$ (measured from the resistivity minimum at 165°K); also, the maximum is shifted from 313 to 253°K . The shifting of the beginning of zone formation by 50° and the peak by 60° gives further support of the role of lattice vacancies in the zone forming process as does the following statement. The slope of the resistivity curve on both sides of the maximum is much greater in the irradiated samples than in the unirradiated samples, indicating much more rapid zone formation and growth in the irradiated samples. For temperatures above the resistivity maximum, the irradiated samples undergo a large and rapid resistivity decrease. This is probably due to zone growth and the annihilation of the irradiation-induced defects as they are released from traps. These traps may be small G.P. zones that dissolve at the expense of the larger growing ones. Above 400°K , lack of further change in the resistivity in the reverted samples or in the reverted and irradiated samples indicates that reversion is complete in this alloy at approximately 400°K and that all of the irradiation-induced lattice defects have been annihilated in the irradiated samples.

For the peak at 314°K , the Meechan-Brinkman analysis gives a vacancy concentration of 1×10^{-8} atom fraction; for the peak at 253°K , a value of 1×10^{-6} atom fraction. Hence, the peak shift of 60° requires about two orders of magnitude more vacancies in the irradiated samples than in the unirradiated samples. The 1×10^{-6} atom fraction is well within the 9.3×10^{-5} atom fraction that existed in this alloy at the beginning of aging; as mentioned previously, it appears that a portion of the irradiation-induced defects does not take part in zone formation and growth.

The increase in peak height for a 60° shift in the temperature of the peak was larger than that observed by Panseri and Federighi after quenching of the Al-4.4a/oZn alloy. This is probably due to the ratio of the initial vacancy concentrations in the quenched and reverted states. Since a high concentration of vacancies exists after quenching, zone formation is quite rapid, and as many, or almost as many, zones form as can form and grow rapidly; hence, only small changes can be produced by creating more defects. In the reverted state, there are few vacancies and zone growth occurs more slowly; therefore, when a large number of defects are introduced into the alloy by irradiation in this state, there is a large enhancement of the number of G.P. zones formed and the rate at which they are formed.

For the reverted Al-5.27a/oZn alloy, irradiation more than doubled the height of the resistivity maximum as the maximum was shifted to 60° lower in temperature. As in the previous alloy, more zones form and grow at a much more rapid rate in the reverted and irradiated material than in the reverted material, again indicating the beneficial role of vacancies in the zone-forming process. Since this alloy contains 55% more zinc atoms than the Al-3.41a/oZn alloy, about the same amount of resistivity increase only doubles the as-reverted value since more zones existed in the reverted Al-5.27a/oZn alloy than in the Al-3.41a/oZn.

For both the reverted and the reverted-irradiated samples, the resistivity continues to decrease up to 444°K but increases slightly at 467°K. This probably indicates that reversion in this alloy is complete at about 444°K and that annealing above this temperature results in some reaging during the cooling from the annealing temperature, as observed by Panseri and Federighi for isochronal annealing.⁶

With the use of the Meechan-Brinkman analysis for the reverted material, the vacancy concentration required for the isochronal aging peak to be at 314°K is 1×10^{-8} atom fraction. The maximum concentration existing in thermodynamic equilibrium at the reversion temperature of 440°K was 3×10^{-8} atom fraction. The agreement is excellent, considering the two different methods used to calculate the defect concentrations. For the peak to be at 253°K requires a vacancy concentration of 1×10^{-6} atom fraction. This is well within the 2×10^{-5} atom fraction remaining at the onset of aging. As mentioned previously, it appears that a portion of the irradiation-induced defects does not take part in the formation and growth of zones. Table XXVI summarizes the vacancy concentrations as calculated

TABLE XXVI. Vacancy Concentrations Calculated by Eq. 1 for Unirradiated Aluminum-Zinc Alloys, and by Eq. 6 for Observed Isochronal Annealing Peaks for Unirradiated and Irradiated Aluminum-Zinc Alloys

Material	T _{Peak} , °K	C _V Eq. 6	C _V Eq. 1	C _V Irr.
Al-1.70a/oZn quenched	280	2×10^{-7}	1×10^{-6}	
Al-1.70a/oZn quenched-irradiated	240	3×10^{-6}		5×10^{-5}
Al-3.41a/oZn quenched	285	7×10^{-8}	1×10^{-6}	
Al-3.41a/oZn quenched-irradiated	250	1×10^{-6}		8×10^{-5}
Al-5.27a/oZn quenched	280	2×10^{-7}	1×10^{-6}	
Al-5.27a/oZn quenched-irradiated	255	1×10^{-6}		1×10^{-4}
Al-1.70a/oZn reverted	295	3×10^{-8}	3×10^{-8}	
Al-1.70a/oZn reverted-irradiated	243	2×10^{-6}		2×10^{-5}
Al-3.41a/oZn reverted	314	1×10^{-8}	3×10^{-8}	
Al-3.41a/oZn reverted-irradiated	253	1×10^{-6}		1×10^{-5}
Al-5.27a/oZn reverted	314	1×10^{-8}	3×10^{-8}	
Al-5.27a/oZn reverted-irradiated	253	1×10^{-6}		2×10^{-5}

by Eq. 1 for the unirradiated samples, by Eq. 4 for the irradiated samples, and by Eq. 6 for the isochronal annealing peaks in the unirradiated samples and in the irradiated samples.

The 106% increase in the height of the resistivity maximum for the peak shift of 60° is 34% larger than that observed by Panseri and Federighi for the same 60° shift after quenching from 574°K . As mentioned previously, more of an enhancement of zone formation and growth is expected upon increasing the vacancy concentration in the reverted state, where the initial vacancy concentration is much smaller than in the quenched state.

As was observed for the quenched samples and the quenched-irradiated samples, zone growth started at the same temperature for the two alloys with the highest zinc content, and the resistivity maxima occurred at the same temperature.

The resistivity peak widths at half maximum were measured for the Al-3.41 and Al-5.27a/oZn alloys in both the irradiated and unirradiated conditions. For the Al-3.41a/oZn alloy, irradiation increased the width of the peak by 13% for quenched samples and by 54% for reverted samples. For the Al-5.27a/oZn alloy, irradiation increased the width of the peak by 67% in the quenched samples and by 49% in the reverted samples. The width of the peak can be related to the distribution of zone sizes that exist. A very narrow peak indicates that all the zones are about the same size at any given time and that they reach the 9 Å size at approximately the same time. A broad peak indicates that the zones are of significantly different sizes and that they reach the 9 Å size over a wide range of time.

Since this broadening is not observed after quenching, the defect distribution that exists after irradiation may be responsible for the wider peaks after irradiation. The defects thought to be present after quenching or reversion are single randomly distributed vacancies and vacancy-solute atom complexes. The interaction energy of the vacancy-solute complex is about the same for each complex, and the vacancies are distributed rather homogeneously throughout the lattice. Hence the vacancies are all released from their traps at about the same time, and they all travel about the same distance to take part in zone growth; therefore, almost all the zones are at about the same size at any given time, and a sharp maximum occurs. After irradiation, the vacancies are present in many configurations. These configurations range from single vacancies, vacancy-solute atom complexes, and even large clusters of vacancies and/or dislocation loops. The release of the vacancies from these different configurations could lead to the presence of a wide distribution of zone sizes during zone growth. The vacancies must overcome a wide variety of trapping strengths, and they must migrate over different distances to take part in zone growth. Hence, a wide variety of zone sizes exists during zone growth, and the zones do not reach 9 Å at the same time but over a range of times that gives rise to the broad maximum.

It might be suggested that the high concentration of G.P. zones in the reverted-irradiated samples compared to the reverted samples is due to irradiation-induced nucleation sites that later became G.P. zones. To test whether or not this is so requires that we compare the number of G.P. zones per unit volume in the reverted case with the number of fast-neutron events per unit volume. First, for the number of fast-neutron events for a dose of 2×10^{17} n/cm², we have

$$\begin{aligned} \frac{\text{Events}}{\text{cc}} &= (\text{neutron dose})(\text{collision cross section}) \frac{\text{atoms}}{\text{g of alloy}} \frac{\text{g of alloy}}{\text{cc}} \\ \frac{\text{Events}}{\text{cc}} &= 2 \times 10^{17} \frac{\text{events}}{\text{cm}^2} \times 4.0 \times 10^{-24} \frac{\text{cm}^2}{\text{atom}} \times \frac{6.02 \times 10^{23} \text{ atoms}}{27 \text{ g}} \\ &\times \frac{2.74 \text{ g}}{\text{cc}} = 5 \times 10^{16} \frac{\text{events}^*}{\text{cc}} \end{aligned}$$

The 5×10^{16} events/cc must be compared with the values obtained by Herman using small-angle X-ray scattering.²¹ For reverted samples of the Al-5.27a/oZn alloy, he observed values from 4×10^{19} to 5×10^{20} zones/cc at the resistivity maximum. These values range from three to four orders of magnitude larger than the number of primary events that occurred during the irradiations conducted in the current work. Hence, the primary events produced in fast-neutron irradiation apparently have not produced a detectable number of nucleation sites for the subsequent formation of G.P. zones. This hypothesis is further substantiated by the lack of more G.P. zones in the quenched-irradiated Al-1.70a/oZn alloy and the Al-3.41a/oZn alloy than in the quenched state of these alloys.

5. Discussion of the Paper of Ceresara, Federighi, and Pieragostini²³

An important observation is the large decrease in resistivity that occurs in the alloys after recovery is apparently complete in the pure aluminum. The decrease in resistivity has been attributed to both the removal of zinc atoms from the matrix as the zinc atoms diffuse to the growing zones and the growth of zones beyond the critical size for the resonant scattering of conduction electrons. For this to occur requires that vacancies or vacancy-zinc complexes exist in the alloy after the vacancies are exhausted in the aluminum. As increased thermal energy is added to the alloy, by annealing at higher temperatures, the increased energy is sufficient to impart atomic motion to the vacancy that enables it to transport a zinc neighbor to a zone. This observation suggests that the interpretation of

*See appendix for a discussion of the atomic volume affected per neutron event.

Ceresara et al. is incorrect.²³ Their interpretation was that the resistivity maximum they observed after neutron irradiation at 77°K was not the "real" maximum but was due to the cessation of zone growth due to the elimination of all of the irradiation induced resistivity (therefore defects) in aluminum. They then interpret that elimination of all the defects in the alloy occurs at the same temperature as in the aluminum; hence no further atomic motion occurs in the alloy after reaching the resistance maximum.

Ceresara et al. based their interpretation on the fact that upon isochronal annealing the resistivity maximum after quenching from 503°K and irradiation was 217 nΩ-cm. This value is appreciably lower than the maximum of 295 nΩ-cm observed upon isochronal annealing after quenching from 625°K. Since the maximum for both cases was near 273°K, they suggest that the maxima should be equal. Because the two values are not equal, they suggest that the zones have not yet reached 9 Å in size and the resistivity decrease that follows the maxima is due to the progressive dissolution of zones. As mentioned previously, the height of the peak does not give an accurate measure of the number of zones present. As indicated in Tables XXII through XXIV, Panseri and Federighi observed different peak heights for aging peaks that occurred at the same temperature for samples that were quenched from different temperatures. The criterion of the magnitude of the resistivity maximum is not sufficient to claim that no further atomic motion occurs in the alloy, as will be further discussed now.

If the interpretation of Ceresara et al. were valid, the resistivity would remain at the maximum value it had when all the defects were supposed to be eliminated. Any change in the resistivity value is associated with the transfer of zinc atoms to or from zones, both of which require atomic motion. The fact that Ceresara et al. observed a large rapid resistivity decrease after the maximum indicates that they were observing the growth of zones larger than 9 Å due to the diffusion of zinc atoms to zones; this process in face-centered-cubic metals is accomplished by the motion of lattice vacancies. The diffusion of zinc atoms from zones would result in a resistivity increase by the introduction of electronic scattering centers in the lattice.

Furthermore, if the maximum were not the true maximum because the zones had not yet grown to 9 Å, then upon continued annealing at higher temperatures the resistivity should have increased further until the zones became 9 Å and then began to decrease with continued zone growth. The fact that the resistivity decreased after the maximum indicates that the maximum observed was the real maximum associated with 9 Å zones.

Finally, some comment should be made concerning the analysis by Schüle on the irradiation of Al-4.4a/oZn at 77°K by Ceresara et al.

Schüle concluded that the defect moving during Stage III annealing in aluminum and during zone formation in the alloy was the interstitial.²⁷ He based this conclusion on his calculation that there were not enough vacancies present after irradiation to account for the peak shift of 50° observed by Ceresara *et al.* His argument goes basically as follows: He assumes a formation energy of 0.66 eV for vacancies in aluminum-zinc, which gives a concentration of 10^{-5} atom fraction after quenching from 573°K. The entropy factor of $e^{SF/k}$ is not given; however, the entropy factor is probably not as important as using the correct temperature from which Ceresara *et al.* quenched before irradiation. Their irradiated and unirradiated specimens were quenched from 503°K and not 573°K. With the use of the correct solution temperature of 503°K, together with the entropy factor and energy of formation for vacancies in aluminum obtained by Simmons and Balluffi that were given earlier, a maximum value of 3×10^{-7} atom fraction of vacancies is obtained in the quenched alloy, and not 10^{-5} as calculated by Schüle.

The resistivity remaining after irradiation at 77°K and isochronally annealing to the onset of aging at 160°K is 50 nΩ-cm (see Fig. 1 of Ref. 23). This corresponds to a point-defect concentration of $8 \times 10^{-5} \approx 1 \times 10^{-4}$ atom fraction. This is about three orders of magnitude more than the vacancy concentration that existed after quenching. We have shown that after isochronal annealing to about 160°K (the onset of G.P. zone formation), about 10^{-4} point defects are still present, and this concentration is more than adequate to account for a peak shift of at least 60°. We want to compare this value with the value calculated by Schüle for a peak shift of 50°.

After we correct the errors in Schüle's paper and use his assumption that the jump number, J , of an atom per second is given by the concentration of the point defects, C_v , times the atomic mobility, ν , of the defect, we obtain

$$J_{irr} = C_{v_{irr}} \cdot \nu_{irr},$$

$$J_{un} = C_{v_{un}} \cdot \nu_{un},$$

and

$$J_{irr})_{total} = J_{un})_{total} \text{ at the resistivity maximum,}$$

which gives

$$C_{v_{irr}} \cdot \nu_{irr} = C_{v_{un}} \cdot \nu_{un}.$$

Hence

$$\frac{C_{v_{irr}}}{C_{v_{unirr}}} = \frac{\nu_{unirr}}{\nu_{irr}}, \quad (7)$$

where

$C_{v_{irr}}$ = concentration of vacancies in the irradiated case,

$C_{v_{unirr}}$ = concentration of vacancies in the unirradiated case,

$$\nu_{unirr} = \nu_0 e^{-E_m/kT_{unirr}},$$

and

$$\nu_{irr} = \nu_0 e^{-E_m/kT_{irr}},$$

where

T_{unirr} = temperature of the resistivity maximum in the unirradiated case and is 313°K,

and

T_{irr} = temperature of the resistivity maximum in the irradiated case and is 263°K.

Use $E_m = 0.47 \text{ eV}$.⁴⁷ Hence,

$$\frac{C_{v_{irr}}}{C_{v_{unirr}}} = \frac{\nu_0 e^{-E_m/k(313^\circ\text{K})}}{\nu_0 e^{-E_m/k(263^\circ\text{K})}},$$

or

$$\frac{C_{v_{irr}}}{C_{v_{unirr}}} = 28.$$

This indicates that between one or two orders of magnitude more vacancies are required in the irradiated samples for the observed 50° shift of the resistivity maximum. This required concentration is less than the

concentration observed by Ceresara et al.²³ and is also less than the concentration determined in the present work. Furthermore, the magnitude of the temperature shift is in agreement with that observed by Panseri and Federighi⁶ upon quenching the alloy from different temperatures. These results, together with those obtained in the present work, indicate that vacancies are responsible for the observed temperature shift of the resistivity maximum and that some complex interstitial mechanism is not required.

V. CONCLUSIONS

A. Pure Metals

The initial resistivity increase that occurs in the low-temperature neutron irradiation of metals is thermal and appears to be due to gamma rays from both the fission process and fission products in the fuel. High-purity copper appears to be at a temperature of about 5.5°K during the irradiations.

The irradiation-induced resistivity, ρ_i , as a function of irradiation time, t , at about 4.5°K obeys the equation

$$\rho_i = A(1 - e^{-\alpha t}) + B(1 - e^{-\beta t}),$$

where A , B , α , and β are experimentally determined parameters for each element. The first term represents the production of the displacement cascades that are thought to be vacancy-rich regions surrounded by interstitial rich regions. The second term is thought to be due to stable defect clusters or dislocation loops that are produced by the interactions of the displacement cascades.

The irradiation effects in the VT-53 cryogenic facility are due to only the fast neutrons of a pure fission spectrum, the damage rate being 13 times that of the ORNL Hole 12 cryostat and one-fifth that of the Munich FRM facility. Of the observed irradiation damage in copper, at both the ORNL and Munich facilities, 20% is due to thermal-neutron damage. For silver, which has a much larger (n, γ) cross section, the thermal-neutron damage approaches 60% of the total damage observed for these two facilities.

B. Aluminum and Aluminum-Zinc Alloys

The residual-resistivity increase rate as a function of irradiation time near 4°K is the same for aluminum and the aluminum-zinc alloys studied. This indicates that the defect-production mechanism is the same in the pure metal and in the alloys and that zinc atoms did not cluster to form G.P. zones during the irradiation.

The defects that are mobile during Stage I annealing and during the part of Stage II annealing that occurs below 77°K do not appear to affect G.P. zone formation and growth in aluminum-zinc alloys.

The formation and growth of G.P. zones begins at the same isochronal annealing temperature as the start of Stage III recovery in pure aluminum. This suggests that the same lattice defect is responsible for both processes. Since it is rather well accepted that the defect responsible for the enhanced formation of G.P. zones after quenching is the lattice vacancy, it appears that Stage III annealing in aluminum and aluminum-zinc alloys is due to the migration of lattice vacancies.

Recovery of all of the irradiation-induced lattice defects is complete at 260°K in aluminum; however, zone growth continues in the alloy up to 400°K. This indicates that there is an interaction between vacancies and zinc atoms that allows the vacancies to have a much longer lifetime in the alloys than in aluminum.

Irradiation resulted in more zones being formed in reverted samples than in quenched samples and approximately as many zones as in quenched-irradiated samples. In addition, the temperature at which zone formation and growth began was the same for samples of different zinc content but of the same vacancy content. The temperatures of the resistivity maxima also exhibited this same dependence on vacancy concentration. These three observations suggest that the formation and growth of G.P. zones in aluminum-zinc alloys are controlled by the point-defect concentration.

APPENDIX

Calculation of the Atomic Volume Affected per Neutron Event

An analysis was made relating the saturation value of the electrical resistivity with the total number of lattice defects existing at saturation, the number of Frenkel pairs per incident neutron, the diameter of each primary event, and the atomic volume affected per event. The results of the analysis are contained in Table XXVII. Table XXVII also includes the parameters A and α from Eq. 3 to determine if there was any systematic correlation between these parameters and the volume affected by each primary event.

TABLE XXVII. Analysis of Size of Region Affected by a Fast-neutron Event in Metals

Element	σ_s	$\rho_\infty, \mu\Omega\text{-cm}$	$\rho_{FP},^* \mu\Omega\text{-cm}$	a/o FP_∞	A**	$\frac{FP}{\text{Event}}$	α^{**}	Diam, Å	$\frac{\text{Vol}}{\text{Event}}, 10^5 \text{ atoms}$
Al	4	0.21	6	0.04	50.0	282	3.17	83	0.2
Ni	3	1.24	4	0.31	0.37	370	3.99	120	1.2
Cu	3.5	0.31	2	0.15	7.83	238	3.93	135	1.6
Pd	0.7	0.43	5	0.08	2.51	850	15.6	308	11.0
Ag	6	0.26	2	0.13	3.12	104	5.00	139	0.80
Pt	6	0.41	5	0.08	0.91	84	20.1	145	1.0
Au	6	0.34	2	0.17	0.88	129	11.1	129	0.76

*Resistivity per Frenkel pair from Ref. 16.

**Parameters from Eq. 3; see Table XVII.

A typical calculation (for aluminum) is made as follows:

1. The saturation value of the resistivity, ρ_s , is obtained by assuming that the plot of $d\rho_i/dt$ vs ρ_i can be approximated by a straight line. Extrapolating this plot to $d\rho_i/dt = 0$ gives ρ_s for aluminum. This was $0.21 \times 10^6/\Omega\text{-cm}$.

2. The resistivity, ρ_s , is divided by the resistivity per Frenkel pair for aluminum, and $6 \times 10^{-6} \Omega\text{-cm/a/o}$ was used. Hence,

$$\frac{0.21 \times 10^{-6}}{6 \times 10^{-6}} = 0.04 \text{ a/o.}$$

3. The time required to reach ρ_s is calculated from Eq. 3. For aluminum, this was 1.2×10^4 min. The number of atoms in the specimen is calculated by multiplying the volume of the specimen between the potential probes ($2.579 \times 10^{-2} \text{ cm}^3$) times the number of atoms/cc:

$$\text{Atoms} = \frac{6.02 \times 10^{23} \text{ atoms}}{26.98 \text{ g}} \times \frac{2.70 \text{ g}}{\text{cc}} \times 2.579 \times 10^{-2} \text{ cc}$$

$$= 1.55 \times 10^{21} \text{ atoms};$$

$$\text{number of Frenkel pairs} = 1.55 \times 10^{21} \text{ atoms} \times 4 \times 10^{-4}$$

$$= 6.2 \times 10^{17};$$

$$\frac{\text{volume}}{\text{event}} = \frac{25.79 \times 10^{-3} \text{ cc}}{8.65 \times 10^{16}} = 3 \times 10^{-19} \text{ cc} = 3 \times 10^5 \text{ \AA}^3;$$

$$\text{diameter} = \left(\frac{6}{\pi} \times 3 \times 10^5 \text{ \AA}^3 \right)^{1/3} = 83 \text{ \AA};$$

$$\frac{\text{atoms affected}}{\text{event}} = \frac{1.55 \times 10^{21}}{8.65 \times 10^{16}} = 1.8 \times 10^4.$$

The value of 282 Frenkel pairs per event is not in bad agreement with the value of 350 Frenkel pairs per event calculated by considering the energy transfer to an aluminum atom by a fast neutron. We would expect the value calculated from ρ_s to be somewhat low since we are dealing with the region in which defect cascades overlap, and no new Frenkel pairs are created in this process.

There seems to be no simple or systematic relationship among the parameters of Eq. 3 and the values given in Table XXVII for the size of the region affected per neutron event.

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