Energy Release in Reactor-Irradiated Copper. II. 600° to 700°K Release

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The energy release associated with the recovery peak occurring between 600 and 700°K in neutron-irradiated copper was measured utilizing a new technique, that of nuclear heating. Following a bombardment at 40°C of 1.7×10^{20} fast neutrons of a $1/E$ distribution which raised the critical shear stress to 12.8 kg/mm^2 at 4.2°K (5.2 kg/mm^2 at 300°K), a release of 7.7 cal/mole was measured. Using this measured value of the energy release it is possible to estimate the number of defects annihilated if it is assumed that the annealing is the result of the migration and subsequent annihilation of a single defect. In this way the number of interstitials, vacancies, interstitial-vacancy pairs, and dislocation lines required to account for the measured energy release were estimated. The values were, respectively, 5×10^{19} per mole, 2×10^{20} per mole, 4×10^{19} per mole, and 1×10^{12} cm per mole.

INTRODUCTION

THE fast-neutron bombardment of metals results in the formation of lattice defects which substantially affect some properties of metals.[1] While there is insufficient experimental evidence at this time to completely understand the exact nature of these defects, it does seem reasonably clear that vacant lattice sites and interstitial atoms play an important role. On the other hand, the postulate that only these defect types are formed by the irradiation makes it difficult to understand the observation of a greatly enhanced hardness in irradiated metals.[2]

Annealing experiments following low-temperature bombardment (ranging from 4 to 20°K) have played an important role in the determination and possible identification of the radiation-induced defects.[1,3,4] These experiments, utilizing the electrical resistivity contributed from the defect formation, show that defect recovery occurs in series of stages for many metals. In the case of copper there are pronounced annealing peaks at 35 to 45°K and at 600 to 700°K, with about 30% recovery occurring at the former peak and 5% recovery at the latter peak with the balance of the resistivity dribbling out without the appearance of discrete peaks. This latter phenomenon accounts for about 7% of the resistivity decrease in the range between 7° and 35°K and the remaining 58% between 45° and 600°K. This annealing spectrum is illustrated in Fig. 1.

While other property changes, for example the change in density, recover with a one-to-one correspondence to the electrical resistivity,[4] it has been established that the yield stress, which is extremely sensitive to neutron bombardment, does not recover in the same manner.[2] There is, for example, only slight recovery of the yield stress in the temperature region below 250°K in copper with the majority of the recovery occurring at 600° to 700°K where only a small portion of the radiation-induced resistivity recovers. Figure 1 illustrates this striking difference in the recovery of yield stress and electrical resistivity. This difference in annealing behavior is one of the factors which suggests that a different defect is associated with radiation hardness than is associated with the radiation-induced resistivity. An important criterion in establishing the nature of the defects involved in each case is the energy associated with them. The energy associated with the recovery of the electrical resistivity in the 35° to 45°K region has been measured. It is the purpose of the research described here to measure the amount of energy associated with the recovery occurring in the 600° to 700°K ranges where the majority of the radiation hardness is observed to recover.

EXPERIMENTAL TECHNIQUES

The measurement of the stored energy associated with the recovery of radiation damage in the 600° to 700°K region represents a rather difficult problem as a comparatively small amount of energy is released over a relatively large temperature interval. Furthermore, in this instance the specific heat is relatively high and the radiation losses are quite substantial, compared to the energy release even when radiation shields of relatively low emissivity are used. Classically this basic problem is solved by measuring the difference in specific heat between a standard or "dummy" sample and the sample containing the stored energy. In the Sykes[5] method

* Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

[1] T. H. Blewitt, R. R. Coltman, D. K. Holmes, and T. S. Noggle, *Creep and Recovery* (American Society of Metals, Cleveland, Ohio, 1957), p. 84.

[2] T. H. Blewitt, R. R. Coltman, and J. K. Redman, J. Nuclear Materials (to be published).

[3] T. H. Blewitt, R. R. Coltman, and C. E. Klabunde, Australian J. Phys. (to be published).

[4] T. H. Blewitt, R. R. Coltman, and C. E. Klabunde (to be published).

[5] F. W. Jones and C. Sykes, Proc. Roy. Soc. (London) **A157**, 213 (1936).

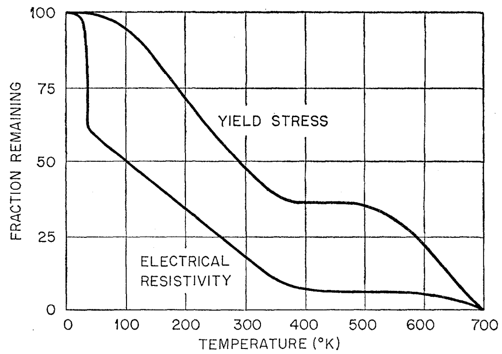

FIG. 1. Recovery in irradiated copper crystals. Pulse annealing curves of resistivity and the cube of the critical shear stress are shown after a low-temperature pile irradiation. The cube of the critical shear is plotted against temperature since the radiation-induced hardening has been experimentally determined to be proportional to the cube root of the bombarding flux.

both samples are placed in the same temperature environment (to reduce radiation effects), and the temperature of the environment and of each of the samples is raised at the same rate by electrical heat. The energy release is determined from the difference in heat input of the two samples.[6]

The method used in this experiment is a unique one insofar as the temperature range is concerned. Heating by γ rays supplied by the Oak Ridge National Laboratory Research Reactor is substituted for the electrical heating used in the Sykes method. This has several advantages. First, it permits a high heat input which is absorbed homogeneously in the sample so that equilibrium conditions always exist. In this experiment the γ-ray heating amounted to 0.7 watt/g and in the case of copper a heating rate of about 100°C/min. Secondly, the construction of radiation shields is relatively simple as the γ rays are also absorbed uniformly in the radiation shield, heating them at the same rate as the sample (providing they are made of the same material). It is thus possible to keep the samples in a temperature environment which has the same characteristics as the sample. These two advantages make it possible to determine the stored energy by measuring the difference in temperature between a sample and a dummy sample.

It should be noted that considerable experimental difficulty was experienced in the construction of a suitable differential thermocouple. The major difficulty arose from spurious emf's apparently arising from inhomogeneities in the thermocouple as the temperature gradient changed during the heating (Thomson emf). Careful selection of standard thermocouple wire did not correct this difficulty. Good results were obtained when statistical wire[7] was used as both legs of the differential thermocouple.

The details of the experimental facility are shown in Fig. 2. The sample assembly, consisting of an irradiated sample (3.5×10^{19} fast neutrons/cm^2)[8] and a dummy sample in a polished copper radiation shield, was thermally isolated from the reactor pool in an evacuated aluminum tube. This sample assembly was suspended in this tube by the thermocouple wires. Two thermocouples were used. A copper-constantan thermocouple was held in a well on the top of the upper (the dummy or unirradiated sample) sample along with an additional copper lead which formed one leg of a differential thermocouple. The lower sample was suspended from the upper sample by a constantan wire of about one-half inch in length. The junction of these wires formed the hot and cold junction of the differential thermocouple. A copper lead was held in a well at the bottom of the lower specimen. The thermocouple wires were brought out of the evacuated chamber by moulding them into a plastic cap which was clamped to a flange (an "O" ring seal being used) on the end of a $\frac{1}{4}$-in. o.d. stainless steel tube four feet long. This tube in turn passed through a Wilson seal so that the sample assembly could be moved four feet from the center of the flux field by withdrawing the rod. This distance proved sufficient to reduce the γ field (and the neutron field) to negligible proportions.

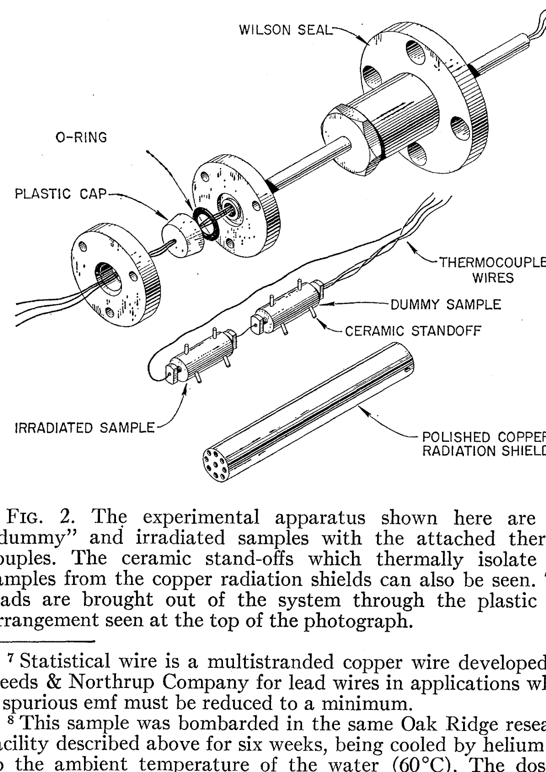

FIG. 2. The experimental apparatus shown here are the "dummy" and irradiated samples with the attached thermocouples. The ceramic stand-offs which thermally isolate the samples from the copper radiation shields can also be seen. The leads are brought out of the system through the plastic cap arrangement seen at the top of the photograph.

[6] The work of Clarebrough and Hargreaves [L. M. Clarebrough, M. E. Hargreaves, D. Mitchell, and G. W. West, Proc. Roy. Soc. (London) **A232**, 252 (1955)] is an outstanding example of the application of the Sykes method to measure the energy release in solid state process.

[7] Statistical wire is a multistranded copper wire developed by Leeds & Northrup Company for lead wires in applications where a spurious emf must be reduced to a minimum.

[8] This sample was bombarded in the same Oak Ridge research facility described above for six weeks, being cooled by helium gas to the ambient temperature of the water (60°C). The dose is equivalent to 1.7×10^{20} neutrons/cm^2 whose energy is distributed between 1 ev and 2 Mev in a $1/E$ distribution.

The experimental procedure was then as follows. The sample assembly was held in the upper position by withdrawing the stainless steel rod, and the aluminum tube was then evacuated to 2×10^{-4} mm Hg (two hours being required for the evacuation). The stainless steel tube was then pushed in causing the sample assembly to be on the center line of the reactor flux field. A time-temperature curve for the upper sample was then determined by recording the output of the copper constantant hermocouple. The output of the differential thermocouple was also recorded.

RESULTS

The time-temperature curve obtained from the copper constantan thermocouple can be used to estimate the heat losses during the warmup as well as to monitor the absolute temperature.

To a good first approximation the specific heat of copper, C_p, is given as

$$C_p=5.39+1.5\times10^{-3}T \text{ cal/mole},$$

in the temperature range from 0° to 600°C.[9] During the heat input we have

$$\int_{336°\text{K}}^{T} C_p dT=\int_0^t \gamma dt,$$

where γ=the gamma-ray heating (cal/mole/sec), t=time in seconds, and T=the absolute temperature. Then

$$\int_{336°\text{K}}^{T} (5.39+1.5\times10^{-3}T)dT=\gamma t,$$

or

$$\gamma=(5.39T-1.895\times10^3+7.5\times10^{-4}T^2)/t.$$

During the experiment, which lasts about six minutes, it is safe to assume that γ is a constant and any deviation in γ is a result of heat losses. Figure 3 shows the plot of γ as a function of temperature as determined from the experimental time-temperature curve and the above equation. It can be seen that only about six

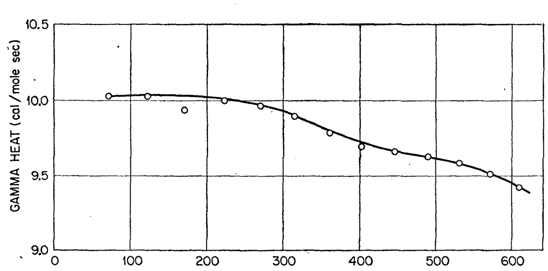

FIG. 3. Effective nuclear heating rate plotted against sample temperature. The deviation from a horizontal line represents the heat losses of the sample to the radiation shield.

[9] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), pp. 4–42.

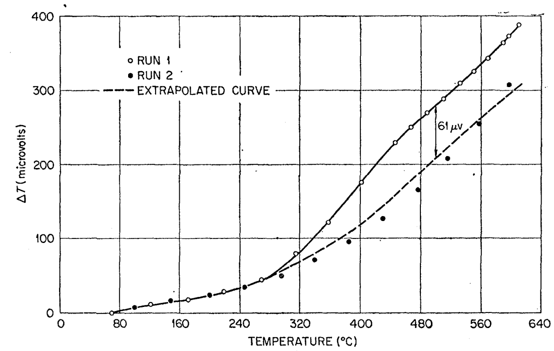

FIG. 4. Energy release at high temperatures in irradiated copper. The differential thermocouple voltage as measured between the "dummy" and irradiated sample is plotted as a function of temperature. In run I the sample contains the energy associated with 3.5×10^{19} fast neutrons/cm^2, and in run II the sample is annealed. The difference between run I and run II is the result of released energy.

percent of the heat input is lost, even at 600°C. The addition of a second radiation shield would reduce this loss still further.

In Fig. 4 the output of the differential thermocouple is plotted as a function of temperature. This graph represents the difference in temperature between the dummy sample and the irradiated sample as a function of temperature. The bump in the curve of the first run between 290° and 420°C arises from the release of the energy associated with the removal of defects introduced by the bombardment, whereas the second run shows a smooth curve between 70° and 600°C. The differences between the two curves presumably arise as a result of the energy release. This corresponds to 91 μv or 1.50°C at 460°C. It would appear, however, that some difficulty arises from spurious Thomson emf's, as in the region from 460° to 600°C Curve 2 is not parallel to Curve 1. It would seem then that an extrapolation of Curve 1 in the region from 280° to 600°C, making the portion in the region from 460° to 600°C parallel to the experimentally determined curve, might more accurately fit the picture.[10] In doing this it can be seen that the 73 μv difference appears which corresponds to a 1.2°C rise in temperature in the irradiated sample. If we use this latter figure, the stored energy in the sample amounts to 7.7 cal/mole after a bombardment of 1.7×10^{20} fast neutrons/cm^2 ($1/E$ distribution).

Samples suitable for resistivity and tensile measurements were simultaneously bombarded with the stored energy sample. It was found that the resolved critical shear stress for plastic flow was increased from 0.2 kg/mm^2 to 12.8 kg/mm^2 at 4.2°K (5.2 kg/mm^2 at 300°K). The electrical resistivity had increased 3.35 $\times10^{-2}$ μohm cm following the bombardment. These samples were annealed for ten minutes at 250°C. This

[10] It is assumed that the small increase in C_p with temperature will be just about compensated by the increase in thermoelectric power of the thermocouple. In any event, the correction will be small.

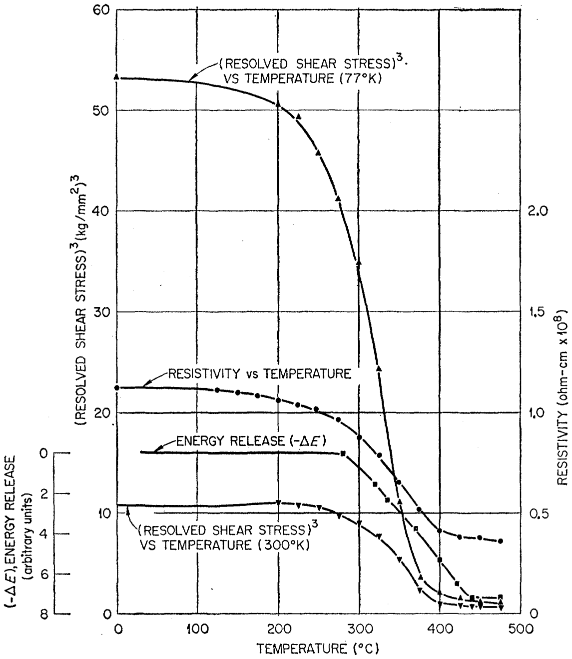

FIG. 5. Comparison of the annealing characteristics of neutron radiation-induced resistivity (at 4.2°K) and the cube of the shear stress measured at 77°K and 300°K. These data were obtained by annealing for a period at successively higher temperatures and examining these properties at a reference temperature after each anneal.

anneal did little to the critical shear stress but reduced the resistivity 4.5×10^{-3} μohm cm. This anneal was followed by an anneal similar to that in the stored energy anneal by the use of γ-ray heating. This latter anneal reduced the resistivity 2.9×10^{-2} μohm cm and the critical shear stress to 0.7 kg/mm^2 at 4.2°K and to 0.5 kg/mm^2 at 300°K. It can thus be concluded that a release of 7.7 cal/mole is accompanied by a recovery of 2.9×10^{-2} μohm cm and 11.8 kg/mm^2 critical shear stress at 4.2°K (4.7 kg/mm^2 at 300°K).

DISCUSSION

It seems reasonably safe to assume that the 7.7 cal/mole released in this experiment is associated with the annihilation of the defects causing the radiation hardness. This conclusion is based on the fact that release of energy occurs during the same temperature interval in which the hardness is observed to recover.

Figure 5 illustrates the fact that the resistivity, the radiation hardening, and the energy all recover in the same temperature interval. In this figure the cube of the critical shear stress is plotted, as it has been experimentally determined that the critical shear stress is proportional to the cube root of the dose. Presumably, the number of defects present will then be proportional to the cube of the flow stress.

It is interesting to compare the ratio of the resistivity to the stored energy with that found at the lower temperature. In the case of the low-temperature stored energy release, it was found that 0.56 cal/mole was associated with a change in resistivity of 3.8×10^{-3} μohm cm so that 148 (cal/mole)/μohm cm are released in this region.[11] The present experiments show an energy release of 7.7 cal/mole for a change in resistivity of 2.9×10^{-2} μohm cm or 264 (cal/mole)/μohm cm which is about 70% greater than the low-temperature results. The great difficulty in making stored energy measurements, however, makes it questionable as to whether this factor lies outside of experimental error. At this time, therefore, it is premature to evaluate this apparent discrepancy.[12]

While the defect responsible for the hardness cannot be identified, it is worthwhile to speculate on the number of defects formed using different models. Consider the cases where this high-temperature annealing is assumed to be either vacancy, interstitial, or vacancy-interstitial annihilation. If it is assumed that 4 ev is the formation energy of an interstitial, and 1 ev is the formation energy of a vacancy,[13] then the 7.7 cal/mole (2×10^{20} ev) release would be accounted for the annihilation of 2×10^{20} vacancies/mole, 5×10^{19} interstitial/mole, or 4×10^{19} interstitial-vacancy pairs/mole. It has been shown that the electrical resistivity varies linearly with the dose, and hence it can be expected that the stored energy would vary in the same way so that a decrease in dose would reduce the number of defects proportionally. On the other hand, the critical resolved shear stress depends on the cube root of the dose so that a substantial reduction in the number of defects would still leave an appreciable increase in the critical resolved shear stress. This is illustrated in Table I. It can be seen that an extremely small number of defects, if indeed these cause the hardness, can cause appreciable hardness.

It has also been suggested that small dislocation loops are formed during the radiation from either a thermal stress[14] or from the migration, coagulation, and collapse of vacancies.[15] While the latter suggestion can hardly bear on the hardness since the critical shear stress is observed to increase at 25°K much below the migration temperature of vacancies, it is nevertheless worthwhile to estimate the number of loops from the

[11] T. H. Blewitt, R. R. Coltman, and C. E. Klabunde, Phys. Rev. Letters 3, 132 (1959).

[12] It should be noted, however, that a room-temperature bombardment may not be equivalent to low-temperature bombardment followed by a room-temperature anneal; and in fact, there is experimental evidence indicative of differences in the two cases. This is due to a difference in concentration of the radiation-induced defects. In the case of the low-temperature bombardment, a high concentration of defects will exist as the annealing occurs so that self-annihilation has a high degree of probability. On the other hand, during room-temperature bombardment the concentration of defects will be relatively small so that there is a greater probability for the defects to be trapped in existing defects rather than by self-annihilation.

[13] W. M. Lomer, *Progress in Metal Physics* (Pergamon Press, New York, 1959), Vol. 8, p. 255.

[14] F. Seitz, Phys. Rev. 98, 1530A (1955).

[15] J. Silcox and P. Hirsch, Phil. Mag. 4, 1356 (1959).

TABLE I. The number of defects associated with radiation hardening.

Dose (neutrons/cm^2)	Critical shear stress (kg/mm^2)		Number of defects/mole			
	300°K	4.2°K	Interstitials[a]	Vacancies/mole[b]	Interstitials and vacancies[c]	No. of cm of dislocation/mole[d]
3.5×10^{19}	5.5	12.4	5×10^{19}	2×10^{20}	4×10^{19}	1×10^{12}
3.5×10^{18}	2.6	5.8	5×10^{18}	2×10^{19}	4×10^{18}	1×10^{11}
3.5×10^{17}	1.2	2.7	5×10^{17}	2×10^{18}	4×10^{17}	1×10^{10}
3.5×10^{16}	0.56	1.3	5×10^{16}	2×10^{17}	4×10^{16}	1×10^{9}

[a] Based on a formation energy of 4 ev per interstitial (see reference 13).
[b] Based on a formation energy of 1 ev per vacancy (see reference 13).
[c] Based on a formation energy of 5 ev per pair (see reference 13).
[d] Based on a formation energy of 4×10^{-4} erg/cm[12].

amount of energy release. Using a formation energy of 4×10^{-4} ergs/cm of dislocation line[16,17] the energy release of 7.7 cal/mole accounts for the removal of 1×10^{12} cm of dislocation lines per mole (1.5×10^{11} cm/cm^3). This corresponds to a density found only in samples severely cold worked. The absence of line broadening in the x-ray diffraction patterns of heavily neutron-irradiated copper crystals does not, however, support the concept of a high dislocation density.[2,18]

It should be noted that Hirsch and co-workers[15] do find a dislocation density in irradiated copper which is in agreement with this number. This group, also, however, finds that line broadening occurs in irradiated foils in disagreement with the results found in bulk samples. It would seem important that this discrepancy be resolved. It should further be reported that recovery of radiation-induced expansion and radiation-induced resitivity in aluminum is exactly the same in the region from 4° to 300°K (from 0 to 99.5% recovery), implying that the same defects are recovered throughout the annealing process. This, in turn, implies that a very small fraction of the defects is associated with dislocation lines.

From the number of defects determined by the stored energy as given in Table I and the measured change in resistivity, the resistivity of the defects can be determined. Under the assumptions then that all the energy release is associated with the defect in question, the resistivity contribution is given as follows: interstitials 3.5 μohm cm per atomic percent, vacancies 0.87 μohm cm per atomic percent, interstitial-vacancy pairs 4.4 μohm cm per atomic percent, dislocations 2×10^{13} μohm per cm of dislocation line. Unfortunately, all of these values are reasonable ones, and none of the annealing models can be thrown out on this basis.

While the measurement of the stored energy cannot by itself distinguish the defect responsible for the radiation hardening, the data do show that if point defects are responsible a relatively small number will produce appreciable effects in the plastic properties of single crystals.

ACKNOWLEDGMENTS

It is a pleasure for the authors to acknowledge the assistance of Mrs. J. K. Redman in performing the experiment and the frequent discussions with R. R. Coltman, C. E. Klabunde, and F. W. Young, Jr. We would also like to thank D. S. Billington for his encouragement and support.

[16] A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Oxford University Press, New York, 1953), p. 38.

[17] This value is that given for straight dislocation lines with equal edge and screw components. Small dislocation loops undoubtedly have a smaller formation energy per cm so that the dislocation densities should be regarded as a lower limit.

[18] B. R. Warren and B. Averbach (private communication).