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Observations of Fission Fragment Damage in Some Crystals

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Electron microscopic observations were carried out on fission fragment-irradiated crystals such as molybdenum oxide, germanium, copper-aluminium alloy and aluminium-copper-uranium alloy.

Tracks of fission fragments were observed in molybdenum oxide but none in the other crystals. A number of small defect regions were observed as dark spots in germanium and as dark and light spots or sometimes loops in copper-aluminium alloy. The densities of these defect regions increased with increasing dose of fission fragments passing through the crystals. None of them was observed in aluminium-copper-uranium alloy. It was concluded that the track registrations in molybdenum oxide are a result of the evaporation due to the energy dissipated in electron excitations by fission fragments and that small defect regions in germanium and copper-aluminium alloy are displacement spikes due to the nuclear collisions. Separations of these defect regions were discussed in terms of the calculated mean free path for Rutherford collisions. The natures of displacement spikes were also discussed.

I. Introduction

Recently, experimental evidences for large size of lattice defects which are produced by fission fragment irradiation, were given by several workers using a transmission electron microscope in some crystals.

For example, mica[1),2)] and evaporated films of uranium oxide[3),4)] showed the linear tracks of fission fragments, revealing the vaporization or melting of the material due to thermal spike effect of fission fragments. Graphite[5)] and molybdenite[6)] crystals which have layer structures showed not only linear tracks but relatively large concentric fringe patterns which indicate the large lattice distortion of lenticular shape presumably produced by a number of atomic displacements due to spike effect. Direct resolution of the lattices in platinum phthalocyanine[7)] showed the molecular disarray around a fission fragment track. Platinum foils[8)] relatively thick showed no linear track but small dots or loops which seemed clusters of vacancies formed by displacement cascades of primary knock-ons, however, very thin evaporated films[9)] ($\sim$25Å) of platinum were found to show linear track registration.

As were reported, there existed remarkable varieties in the aspects of fission fragment damage to crystals, depending upon the nature and the structure of the crystals.

Systematic studies on various kinds of crystals are, therefore, desired to make clear the basic processes in the fission fragment damage to solids.

In this work, the nature and the origin of lattice defects produced by fission fragment irradiation were investigated in some crystals such as molybdenum oxide, germanium, copper-aluminium alloy and aluminium-copper-uranium alloy by means of electron microscopy.

II. Experimental Procedure

The specimens were prepared and treated in the following ways prior to irradiation.

(A) Thin flakes of molybdenum oxide were made by combustion of molybdenum metal in air.
(B) Germanium was cut from a block and chemically thinned in CP-4 etching solution.
(C) Copper-aluminium (95.5-4.5%) alloy foils containing stacking faults were thinned by electropolishing technique in a bath of phosphoric acid saturated with chromium trioxide.
(D) Aluminium-copper-uranium (95.7-4-0.3%) alloy foils containing G. P. zones were thinned by electropolishing in a phosphoric-chromic acid bath.

For fission fragment irradiation, these crystals (except (D)) were brought in contact with uranium foils (thickness, 250Å, 500Å,

100μ) and they were exposed to the thermal neutrons to the total dose of the order of $10^{16} \sim 10^{17}$n/cm^2 in the JRR-1 and JRR-2 reactors at the temperature below 50°C. Aluminium-copper-uranium alloy was irradiated without contact of uranium foil.

Electron microscopic observations were carried out with Hitachi electron microscope of HU-10 type operating at 75KV.

III. Observations

The tracks of fission fragments in molybdenum oxide appeared notably as shown in Fig. 1, increasing the number with increasing dose of fission fragments. The image contrasts are due to the vaporization of the material within the narrow regions along the tracks of fission fragments. Such track registrations were so clear and accurate that they were used as standards for estimating the densities of fission fragments in this experiment by putting them in the reactor together with other specimens at the same time.

On the other hand, no linear track was observed in germanium and copper-aluminium alloy, but small spots appeared dispersed randomly as shown in Figs. 2, 3 and 4. The densities of spots increased with increasing dose of fission fragments passing through the crystals. The spot sizes in germanium were about 40Å~100Å and their images appeared always dark and seem to be insensitive to the variation of the Bragg diffraction condition in the crystal as shown in Fig. 2, where no predominant change in image contrasts is seen between spots which appeared in the extinction contour bands and those in the other places. This observation seems to suggest that these spots represent defect regions which are in almost amorphous state. Some of the spots took linear arrangements as shown by arrows in Fig. 3.

In the copper-aluminium alloy the spot sizes distributed randomly from about 30Å to 150Å and some of the large spots were recognized as loops, as shown by A and B in Fig. 4. The image contrasts of them were reversed as the Bragg diffraction condition changed as shown in Fig. 4, where the spots which appeared in the extinction contour bands look light but those in the other places look dark. These observations seem

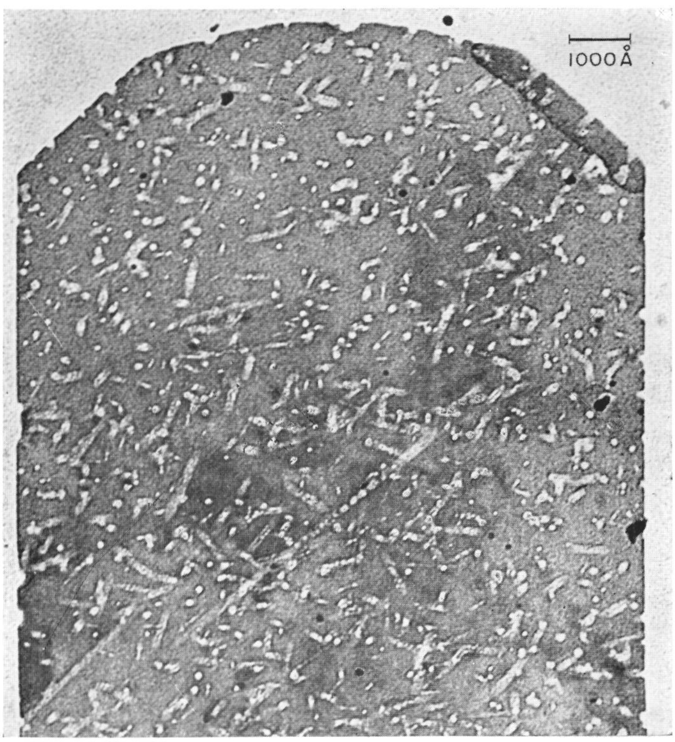

Fig. 1. Molybdenum oxide irradiated with fission fragments (dose of ~600 f.f./μ^2).

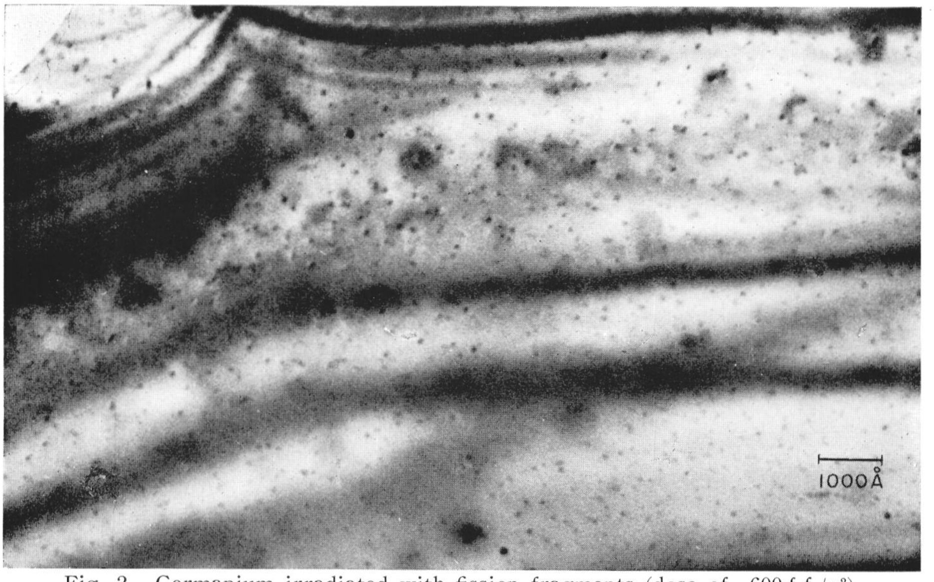

Fig. 2. Germanium irradiated with fission fragments (dose of ~600 f.f./μ^2).

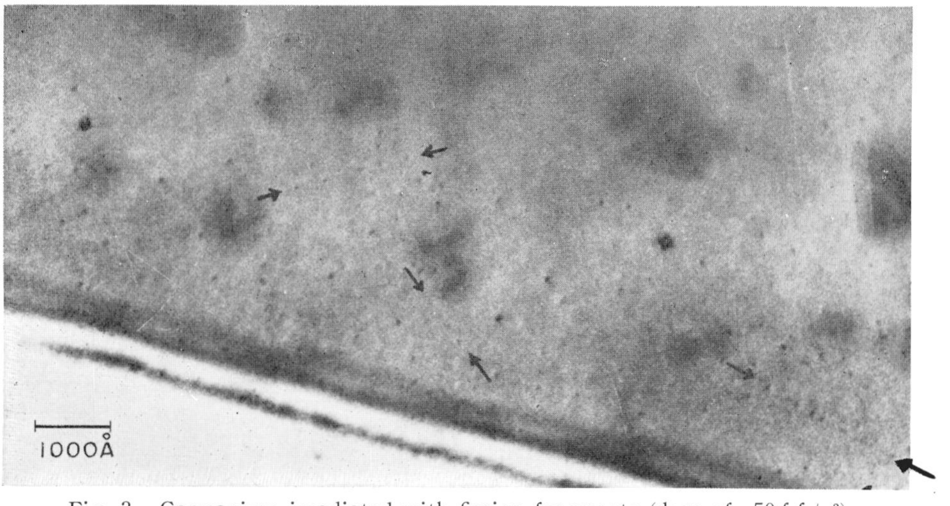

Fig. 3. Germanium irradiated with fission fragments (dose of ~50 f.f./μ^2)

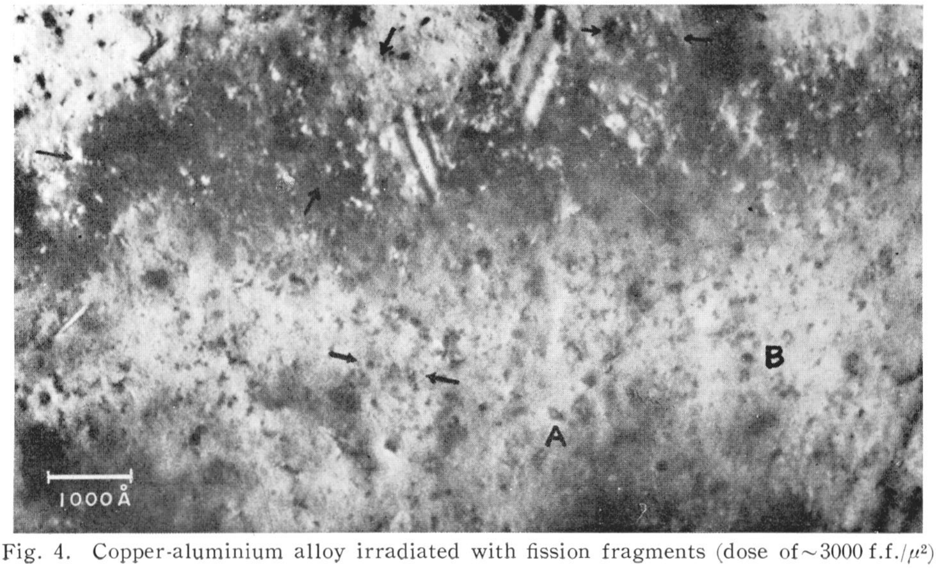

Fig. 4. Copper-aluminium alloy irradiated with fission fragments (dose of ~3000 f.f./μ^2).

to suggest that the image contrasts of spots are mainly due to the strain field around the defect regions. Some of the spots took linear arrangement as shown by arrows in Fig. 4. The distances between these spots will be discussed in relation to the mean free path for nuclear collisions in the following section.

In the aluminium-copper-uranium alloy, no appreciable defects such as linear tracks nor spots were observed, which was similar to the result of observations on neutron-irradiated aluminium.

IV. Discussions

(*a*) *Effect of electron excitations*

Since the width of the track in molybdenum oxide was about 150Å, the number of atoms vaporized was estimated as 1200 atom/Å, which indicate the energy dissipation along the track being larger than about 1000 ev/Å.

The great majority of the energy of fission fragments is dissipated in electron excitation. Using the Bethe's formula the value of energy loss by electron excitation was calculated for each crystals as shown in Table I. assuming that the energy of the fission fragment is 80 MeV, the mass number 100 and the charge 20.

The value for molybdenum oxide is in good agreement with the order of magnitude of the value estimated from the observation, that is about 1000 eV/Å. The amount of dissipated energy is so large that the material in the cylindrical region with the diameter of about 100Å can melt or vaporize if the energy of electron is transferred to the lattice instantaneously. This may be responsible for the track registration in molybdenum oxide crystal, as in the case of uranium oxide[3] and molybdenum sulphide[6].

The fact that no linear track registration took place in germanium and copper-aluminium alloy indicates that no effect such as melting or vaporization results from the energy dissipated in electron excitation by the fission fragments in spite of the large amount of energy loss as listed in Table I.

This observation implies that the energies transmitted to the electrons may disperse over the wide range before these are transferred to the lattice, because the relaxation time for electron lattice interaction may be much longer in germanium and copper aluminium alloy than in molybdenum oxide. Thus the energy dissipated in electron excitation cannot give rise to high temperature sufficient for melting or vaporization.

Recently T. S. Noggle and J. O. Stiegler[9] have found that fission fragment tracks can be registered on very thin evaporated films of platinum (~25Å thick) and palladium (<100Å) and no track in thicker films. They account for this phenomenon on the basis of a model in which reflection of the excited free electron by a free surface of a thin film would confine the energy to a smaller volume and consequently raise the average energy density. Their observations and interpretation are very suggestive and would support our view described above.

(*b*) *Effect of nuclear collisions*

In parallel with the electron excitation, fission fragments make nuclear collisions with atoms in crystals and produce knock-on atoms. Although the average energy transfer in this collisions is very small, such collision processes may be expected to produce appreciable defects in the crystals.

The effect of fast neutrons involved in reactor irradiation is negligible in this experiment in comparison with the effect of fission fragments, because the numbers of primary knock-ons produced by fast neutrons may be expected to be less than 1% of those produced by fission fragments.

Accordingly the major part of spots observed in germanium and copper-aluminium alloy are thought to be defect regions produced by fission fragment irradiation. These defect regions seem to represent displacement spikes produced by primary knock-ons which are ejected from the lattice sites by collisions of fission fragments. The energy transferred

Table I. Energy loss by electron excitation

	MoO_3	Ge	Cu-Al (95.5-4.5%)	Al-Cu-U (95.7-4-0.3%)
$\frac{dE}{dx}$ (ev/Å)	6.6×10^3	7.2×10^3	11×10^3	7.2×10^3

to a primary knock-on would be required to be large enough for producing a displacement spike. The distances between the observed spots in linear arrangement seem to represent the free paths for Rutherford collisions in which the energy transfers are large enough for producing observable defect regions. (Note that the collision processes of fission fragments can be treated as Rutherford type in almost entire range of them.)

The mean free paths for Rutherford collisions were calculated for each crystal on the suitable assumptions for the energies of fission fragment and the energy transfers in these collisions, as shown in Table II where the observed distances between the neighbouring spots in a straight line are listed for comparisons. In this calculation the transferred energies were taken to be above 400 eV and the lower value of L_R came from the assumption that the energy of fission fragment $E_1=50$ MeV, the mass number $M_1=150$, the charge $Z_1=57$ and the upper value came from that $E_1=100$ MeV, $M_1=80$, $Z_1=35$.

Table II. L_R; Calculated mean free paths for Rutherford collisions in which the transferred energies are above 400 eV.
L_{obs}; The distances between the observed spots in a straight line.

	Germanium	Copper-aluminium alloy (95.5-4.5%)
L_R	100-1000Å	64-600Å
L_{obs}	100-300 Å	70-300Å

The value of L_R decreases proportionally with decreasing the energy of fission fragment. Some of the small values of L_{obs} may, therefore, arise from collisions of low energy fission fragments.

L_R depends also upon the lower limit of transferred energy in the above mentioned calculation. The limiting energy, of 400 eV, seems to be reasonable in relation to the restriction in sizes of defect regions which are observable with the electron microscope as discussed in the following paragraph.

(c) *The nature of the displacement spikes produced by primary knock-ons*

An energetic primary knock-on ejects the shower of secondary knock-ons, and its energy is transferred instantaneously to the atoms in a small volume through the secondary knock-ons. M. Yoshida[10] has calculated the spatial distribution of the secondary knock-ons in germanium. His calculation may be useful to estimate the extension of the region where the energy of the primary knock-on is transferred instantaneously. The results, however, seems to be very sensitive to the closed shell interaction potential, and, therefore, the region will be assumed to be a sphere with the diameter of 30Å. Then the energy required to melt the material in this volume is about 400 eV in germanium. Applying the equation of macroscopic thermal conduction, the time interval heated above melting point is of the order of 10^{-12}sec. Thus we may suppose that the region can melt by the primary knock-on with the energy larger than 400 eV, if the above assumption is correct. The crystallization of the melted material in the covalent crystal requires a high activation energy, because the covalent bonds should be broken during the rearrangement. The cooling rate of the melted region is sufficiently high and there is not enough time for recrystallization. The displacement spike in germanium, therefore, may be in amorphous state.

If the region of a displacement spike is a sphere with 40 Å diameter, the energy required to melt this volume is about 800 eV. Although the limiting energy for producing a displacement spike may have some ambiguity of factor 2, the value near 400 eV seems to be reasonable in view of the good agreement between calculated mean free paths and observed ones and the restriction in spot sizes observed in the electron micrographs.

F.E. Fujita and U. Gonser[11] have observed small angle scattering in deuteron-irradiated germanium at liquid nitrogen temperature. The scatterer was particles of about 35 Å in radius. The size of the spiked region agreed with the electron microscopic observation. Since the specific volume of germanium in amorphous state is less than in crystalline state, contraction may take place around the spiked region. R. O. Simmons and R. W. Balluffi[12] have, however, found that germanium crystals always expand by deuteron irradiation. The collision events of low energy transfer predominates in the case of deuteron irradiation, so the great majority of the primary knock-on results in Frenkel pairs which induce the lattice expansion.

A similar estimation on the macroscopic temperature in the spiked region in copper-aluminium alloy gives the following picture. If 800 eV energy is given within the sphere of 40 Å diameter, it might melt, but the time interval heated above the melting point is of the order of 10^{-13} sec. In order to melt the region the energy of a few KeV should be given within the volume. Although the conclusion depends sensitively upon the assumed closed shell interaction potential, the spiked region in copper-aluminium alloy does not seem to melt.

Acknowledgments

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DISCUSSION

Barnes, R. S.: Recent work at Harwell by Whapham and Makin has shown that the grain size is very important in determining the nature of the fission track in uranium dioxide. When the grain size is less than 100Å the track takes the form of a surface furrow as seen on many occasions in evaporated films of uranium dioxide. Above this grain size such tracks are not seen and in large grains very fine tracks, with diffraction contrast indicating strains around the track, are seen. Intermittently along these tracks that are believed to be point defect clusters are seen. It is believed that the grain boundary is able to confine the released energy to the vicinity of the track to give more violent effects when the grain size is small.

Fujita, F. E.: Concerning the comment by Dr. Barnes, I should like to point out that the film thickness is also important to get the contrast by the evaporation of material along tracks of fission fragments. For instance, Dr. J. J. Kelsch found that, in evaporated thin films of various metals, tracks are very clear in case of very thin films and are not observable in case of films thicker than a certain thickness. Anyhow, these comments concerning the visibility of tracks depending upon the grain size or the film thickness have little relation with Drs. Izui and Suzuki's experiment, because they used only single crystals and they observed spotty structures which are not formed by the evaporation of the material.