FUSED FLUORIDE -- INCONEL SYSTEM UNDER CYCLOTRON IRRADIATION -- PRELIMINARY RESULTS

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ABSTRACT

The fused fluoride-Inconel reactor system was studied under irradiation with nominal 19 Mev deuterons as supplied by the Berkeley 60-inch cyclotron. Chemical, metallographic, magnetic susceptibility, electron diffraction and X-ray diffraction studies were made on the as-received materials, one control run and two irradiated runs. No changes in the fused fluoride fuel were noted. Accelerated intergranular corrosion and increased grain size were observed in the irradiated Inconel specimens.

This report is based upon studies conducted for the Atomic Energy Commission under Contract AT-40-1-GEN-1064.

I. INTRODUCTION

As part of the ANP Program, a study was undertaken of the fused fluoride-Inconel reactor system under irradiation with nominal 19 Mev deuterons, while maintained at or near the ARE design condition of 1500° F (815° C). The objective of this project was the determination of: (a) the possible radiation-induced decomposition of the UF_4-NaF-KF eutectic and (b) the accelerated corrosion of Inconel by UF_4-NaF-KF under irradiation.

Preliminary irradiations have been made with the Berkeley 60-inch cyclotron, utilizing existing capsule designs and apparatus with only minor alterations. Deuteron exposures of approximately 20 μa hours on the target were obtained in two cases and a third (control) run was made at the same temperature without irradiation.

The fused fluoride mixture was contained in an Inconel capsule under vacuum and irradiated through a window which was approximately 0.006 inches thick. The range of the deuterons in the fluoride charge was 0.022 to 0.024 inches. The approximate power densities in the two irradiated runs were 650 and 1600 watts/cubic centimeter.

The detection of free fluorine formed by decomposition of the fuel was attempted by placing a polished nickel rod in the capsule just above the

fused fluoride. Any decomposition products containing fluorine formed during an irradiation should react with this nickel to form a very thin layer of nickelous fluoride, NiF_2. This is the only compound formed between nickel and fluorine and is very stable, having a free energy of formation of -147 K cal/mole.[1]

The following analyses were performed after each run as well as on the stock materials.

1. Chemical Analysis. The fused fluoride charge from the capsules was ~~carefully~~ analyzed for (a) uranium and fluorine and (b) the major constituents of Inconel: nickel, chromium and iron. The results of (a) would provide an indication of the decomposition of the fluoride mix, while (b) was a measure of the corrosion of the Inconel by the fused fluoride. In addition to the above determinations, the stock material was also analyzed for sodium and potassium.

2. Metallographic Examination. These studies consisted of an examination of the Inconel window for grain-growth and/or corrosion.

3. Magnetic Susceptibility. Measurements of magnetic susceptibility were proposed as one means for following radiation damage to the fused fluoride fuel. Since the specific susceptibility of UF_4 is about 10×10^{-6}, while that of UF_6 is vanishingly small by comparison (-0.1×10^{-6}), small changes in the state of ionization of U^{4+} ions might be detected, limited only by the precision of the measurements.

4. Electron Diffraction. The surface of the nickel rod was examined for traces of NiF_2 as a means of detecting decomposition of the fluoride mix.

5. X-ray Diffraction. Powdered fluoride specimens were examined for crystallographic changes.

II. EXPERIMENTAL

A. Materials

Two bars of wrought Inconel were available. Capsule bodies were fabricated from 1 1/2-inch diameter bar stock while a 1-inch bar was used for

the windows. The composition of this material, as determined by chemical analysis, is given in Table I.

The fused fluoride eutectic mixture was supplied by Oak Ridge National Laboratory and identified as "ORNL Batch No. 1855, A.R. No. 603922." It had a reported nominal composition of 27.5 mole - % UF_4, 26.0% KF and 46.5% NaF.

Nickel rod, 99.99 per cent pure, was obtained from Sigmund Cohn, New York.

B. Capsule Construction

The component parts of a capsule are shown in Fig. 1. The window thickness was 0.0064 ± 0.0003 inches. The uniformity of the window was determined by measurements with a ball micrometer at sixteen evenly spaced locations. Any windows with thin spots were discarded.

The chamber just behind the window contained the fused fluoride mixture. This chamber had a volume of approximately 0.75 cubic centimeter. The nickel rod extending into the free space above the fused fluoride mixture was metallographically polished on the flat end surface prior to being press fitted to the rear plug. Since the rod was not in direct contact with the charge, any corrosion observed after a run must have been caused by fluorine or volatile fluorides.

The capsules were assembled by Heliarc welding and all seals were carefully leak tested for vacuum tightness.

C. Capsule Loading

Two and one-half grams of the eutectic mixture were used for each charge, corresponding to a volume of 0.66 cubic centimeter at the operating temperature of 815° C.[2] Only small (about 1 millimeter on a side) pieces were used.

The assembly and loading procedure was as follows. All Inconel surfaces were well cleaned with solvents and vacuum dried. The rear plug was put in place and leak tested. If it was not tight, the seat and plug were reworked until a vacuum tight seal was obtained. The plug was then removed and the window Heliarc welded into place (using chill blocks to prevent an undue rise

in temperature of the Inconel). This weld was leak tested and re-welded if not satisfactory. The fused fluoride was then dropped into the capsule through the stem end. The capsule was subsequently placed in a Vycor tube which extended into a furnace and was connected to a high vacuum line. The temperature was slowly raised to 550° to 575° C and held there for 15 to 30 minutes to allow the mixture to melt and flow down into the window chamber. Some rise in pressure during this process was noted, but as the pressure returned to near the original value (about 10^{-5} millimeter Hg) after a few minutes at 550° C, this indicated only an out-gassing of the mixture.

After cooling to room temperature, the capsule was placed in a vacuum loading rig, evacuated to a pressure of less than 10^{-3} millimeter Hg, and the rear plug put into place by means of a modified screw driver working through a Wilson seal. To insure a tight seal at elevated temperatures, the plug was welded to the capsule body.

D. Irradiations

The irradiations were made with deuterons having a nominal initial energy of 19 Mev as produced by the 60-inch Berkeley cyclotron. The capsules were mounted in a sleeve-shaped heater of type 347 stainless steel, which was held between water-cooled electrodes contained within a water-cooled target box. Grade A helium, fed directly from a storage cylinder at a rate of several cubic feet per hour, provided the circulating atmosphere which was isolated from the cyclotron chamber by a series of two windows consisting of one 0.00025-inch tantalum and one 0.0014-inch dural foil. The tantalum foil was selected for its high melting point. It was located 0.922 inch from the heated target, and it served as a thermal radiation shield as well as to monitor the beam distribution on

during the runs necessitated interchanging the recorder units to obtain suitable control of heater power.

A beam integration unit was used to record the total exposure in micro-ampere hours received by the target capsule. This unit was calibrated before and checked after each run to obtain the correct total exposure on the capsule. Since the exposure received only by the window was somewhat less than the total exposure, a correction factor was applied by use of the monitoring foil which provided the necessary horizontal and vertical exposure profiles obtained by suitable slicing and counting techniques. Alignment of the monitoring profiles were finally checked by comparison with autoradiographs of the sectioned window.

E. Post Irradiation Examinations

Following an irradiation, the capsule was set aside to permit decay of the short-lived induced activities. (Capsule No. 1 measured several R/hr shortly after it was removed from the cyclotron, but decayed to 200 mr/hr in 30 days. The activity of the fused fluoride was only 1 to 2 mr/hr when it was removed, the majority of the activity being in the Inconel window.)

The capsules were opened by cutting off the rear plug with a pipe cutter at the indentation on the stem. The nickel rod was removed and stored in a desiccated jar to await electron diffraction studies of the surface. The window was then cut off in the same manner and submitted for metallographic examination. The charge of fused fluorides was removed and two small (few milligram) samples were used for magnetic susceptibility measurements and X-ray diffraction work. The balance was used for chemical analysis.

1. Chemical Analysis. The chemical analytical methods used for the determinations in the UF_4-KF-NaF mixture were the following:

a. Potassium, Sodium and Uranium. By one procedure, the mixture was dissolved in perchloric acid and, in sequence, potassium perchlorate and sodium chloride were separated and weighed, while uranium was hydrolyzed out with hexamethylene tetramine, fired, and weighed as U_3O_8. A mixture of nitric and boric acids readily dissolved the complex. This method of solution was used as an alternate solution technique.

Uranium was also separated and weighed as oxyquinolate.

b. Fluorine. The sample was fused with sodium carbonate, dissolved in nitric acid and the fluorine precipitated as lead chloride fluoride at pH 3.6 and weighed.

c. Impurities: Chromium, Nickel and Iron. Using the nitric and boric acid solution method, iron and chromium were determined colorimetrically while nickel was separated and weighed as glyoxime.

2. Metallographic Examinations. These studies consisted of an examination of the sectioned Inconel window for signs of grain-growth or corrosion. The windows were sectioned vertically through the center normal to the face, mounted in plastic, etched with a glycerine-aqua regia mixture and examined. The same examination, plus a photomicrograph of the outside surface, was made on a window which had not been used for a run, in order to have a comparison.

3. Magnetic Susceptibility. Measurements were performed in an apparatus which provided a constant magnetic force over a volume larger than the specimen, and as a result accurate comparisons of susceptibilities were obtained. The contribution of variable degrees of ferromagnetic impurity, that might have been added on handling the specimens, was removed by making observations in two different, precisely known field strengths above that required for saturation; e.g., 8,000 and 16,000 oersteds.

Initial observations on chips of the stock material revealed a measurable anisotropy when the specimens were rotated in a magnetic field. Differences of the order of 5 per cent in the susceptibility were observed. From this it was concluded that the crystalline forms present were not entirely of the cubic system.

To search for changes of less than 5 per cent due to irradiation, a more complex procedure was adopted. Measurements were made of the sum of three susceptibilities observed in mutually perpendicular directions on the same specimen. The sum is known to be invariant, and independent of the degree of anisotropy.

To give the specimens the cubical form desired for these observations, weighed amounts of the powdered material were cast in styrene resin. The cubes were one-tenth inch on edge and the fluoride weight varied from 7 to 15 milligrams. The styrene had a comparatively negligible susceptibility.

4. Electron Diffraction. The nickel rods were taken to the AEC group at UCLA for electron diffraction of the surface. This work was performed with an RCA electron microscope equipped for diffraction work. An untreated nickel rod was used for obtaining the pure nickel pattern, while one which had been treated with bromine trifluoride was used to determine the NiF_2 pattern.

5. X-ray Diffraction. Samples of irradiated, unirradiated and original fused fluoride were subjected to X-ray analysis. Standard techniques were employed using a powdered sample.

III. RESULTS

Three runs were completed; two irradiated and one control. The data for these runs are shown in Table II.

The results of the chemical analyses are given in Table III. The error in the uranium-fluorine ratios is ± 0.04, so that these data indicate that there was no change in this ratio. A small increase in the chromium content and slight decrease in iron content were noticed. The nickel content of the material from the irradiated runs was only half that of the stock material, while the unirradiated control had doubled in nickel content.

Photomicrographs of the Inconel windows are shown in Figs. 2 through 6. The grain size in the window used for the control run is similar to that of the original material, but the grain size is much larger in the two windows which were irradiated. The corrosion of the control window is very slight, but there is considerable intergranular corrosion in the irradiated specimens. The outside of these latter two windows also appear slightly attacked, probably due to impurities in the helium which flowed over the capsule during the irradiations.

The results of magnetic susceptibility measurements on the fused fluoride fuel are given in Table IV.

The tabulated errors vary because the powdered and cast specimens acquired considerable ferromagnetism in their preparation, SLIGHTLY reducing the precision of the determinations. The cube formed from one piece of the stock material displayed a ferromagnetic contribution of less than one tenth of 1 per cent of the susceptibility, that is, zero within the precision of the individual

force determinations. This is equal to one-half part per million of metallic iron or its ferromagnetic equivalent.

Differences between the material from run 2 (heated only) and run 1 (irradiated and heated) are not to be considered significant. anisotropy - paper

Electron diffraction work on the nickel rods was inconclusive. Some of the fused fluoride mixture had distilled onto the rods, but very little of the rods' surface had any coating and only a few almost imperceptible spots were obtained for a diffraction pattern. The BrF_3 treated nickel rod gave only a faint pattern. No pattern was obtained with pure nickel.

According to X-ray diffraction results, all of the samples (stock material and charges from the three runs) were identical crystallographically. A simple hexagonal crystal structure with constants a = 6.20 kx and c = 7.78 kx was indicated by a Hull-Davey chart fit. Further work is required to establish whether this fit represents a single phase, or a pure coincidence. An eutectic mixture is indicated by the phase diagram[3] for the composition used in the present experiment.

IV. SUMMARY

On the basis of the results from chemical analysis, magnetic susceptibility measurements and X-ray diffraction studies, there appears to be no change in the fused fluoride fuel caused by deuteron irradiation in vacuo at 815° C.

Metallographic examinations indicate an increased intergranular corrosion of Inconel by the fluoride mix under the above conditions. Considerable grain growth in the Inconel was also noted. These results could have been due to a higher window temperature in the irradiated specimens, although the thermocouple just behind the fuel charge might be expected to give a good approximation of the fuel and window temperature. Subsequent experiments may include a record of the window temperature during irradiations. Unirradiated control runs will be made at higher temperatures (900° to 1000° C) to see if the effects noted in the irradiated Inconel windows can be duplicated.

REFERENCES

1. Quill, L. L. (Ed), Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, McGraw-Hill, New York, 1950.
2. ANP News, August 15, 1951.
3. Aircraft Nuclear Propulsion Project, "Quarterly Progress Report for Period Ending March 10, 1951", ANP 60, June 19, 1951.

TABLE I

CHEMICAL ANALYSIS OF INCONEL

Bar	Use	Si %	Mn %	Cr %	Cu %	Fe %	Ti %	Ni %
$1\frac{1}{2}$-inches	Capsule Bodies	0.18	0.03	14.2	0.17	6.7	<0.1	Balance
1-inch	Capsule Windows	0.30	0.08	14.2	0.15	6.8	<0.1	Balance

TABLE II

IRRADIATION DATA

RUN NUMBER		1	2	3
RUN DESCRIPTION		IRRADIATION	CONTROL	IRRADIATION
Temperature, °C	Front (Window Ledge)	798 ± 6 (Estimated)	819 ± 2	815 ± 28
	Back (Body Well)	768 ± 6	819 ± 2	908 ± 28
Time at Temperature, Hours		8.5	8.9	21.1
Time under Irradiation, Hours		7.5	0	12.2
Integrated Beam Current, (Effective), μa hrs		23.5	0	15.4
Average Effective Beam Current, μa		3.16	0	1.26
Average Effective Beam Current Per cm^2, $\mu a/cm^2$		6.98	0	2.78
Probable Peak Beam Current, μa, (Effective)		4.3	0	2.9
Beam Energy Incident on Capsule Window, Mev.		18.0	0	18.0
Beam Energy Incident on Eutectic, Mev		13.6	0	13.1
Average Window Thickness, inches (cm)		0.00605 (0.0154)	0.00654 (0.0166)	0.00655 (0.0166)
Range in Eutectic, inches (cm)		0.0238 (0.0605)	0 0	0.0223 (0.0567)
Window Volume Irradiated, cm^3		0.00696	0	0.00749
Eutectic Volume Irradiated, cm^3		0.0274	0	0.0257
Power Dissipated in Window, watts/cm^3 (Avg.)		1995	0	828
Power Dissipated in Eutectic, watts/cm^3 (Avg.)		1568	0	644

Window Area = 0.250" high x 0.5625" wide = 0.1405 in^2 = 0.906 cm^2

Target Area = 0.125" high x 0.5625" wide = 0.0703 in^2 = 0.453 cm^2

*This temperature is believed to be low due to faulty thermocouple circuit.

TABLE III

CHEMICAL ANALYSIS OF FUEL

Run	U %	F %	U/F	Fe %	Cr %	Ni %
Stock Material	53.9	28.7	1.88	0.01	Not Detected	0.14
1	53.7	28.7	1.87	0.005	0.02	0.06
2	53.8	29.0	1.85	0.005	0.02	0.27
3	53.7	28.8	1.86	0.005	0.001	0.05

TABLE IV

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Sample	$X_1 \times 10^6$	$X_2 \times 10^6$	$X_3 \times 10^6$	$X_T \times 10^6$
Stock Material (As Received, not Powdered)	7.25	7.5	7.6	22.35 ± 0.5%
Run 1	6.6	6.7	6.7	20.0 ± 1%
Run 2	6.8	6.7	6.8	20.3 ± 1%
Run 3	7.2	6.6	6.5	20.3 ± 2%

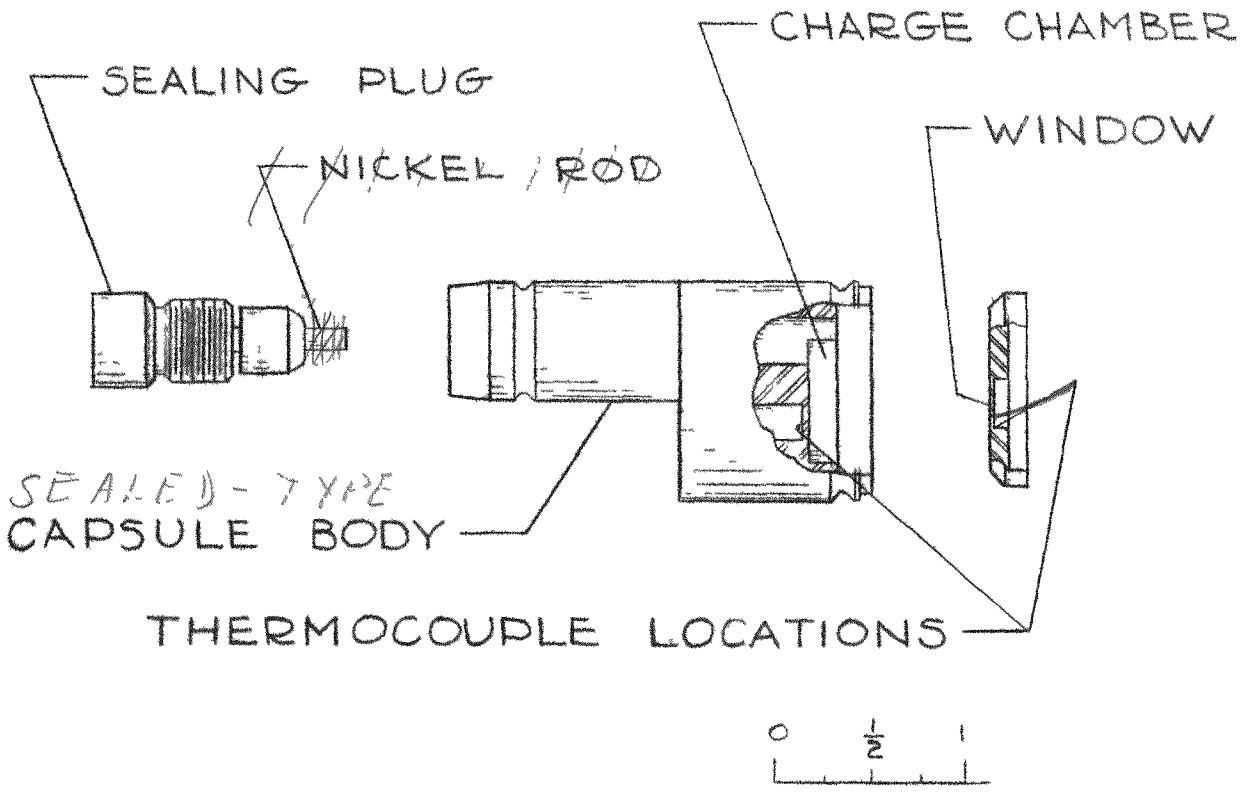

FIG. 1

INCONEL CAPSULE

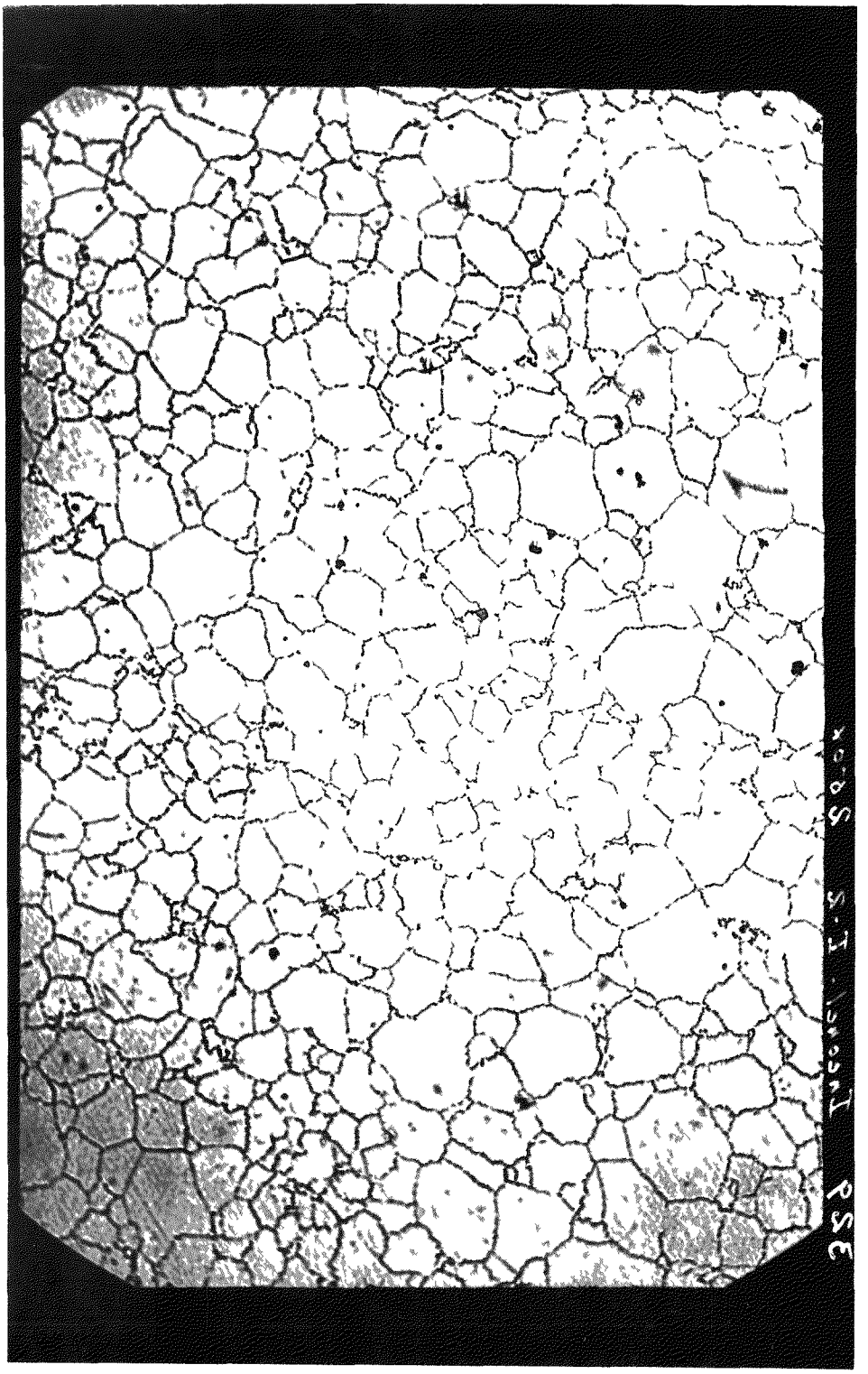

Figure 2. Photomicrograph of stock Inconel window surface. Magnification 250.

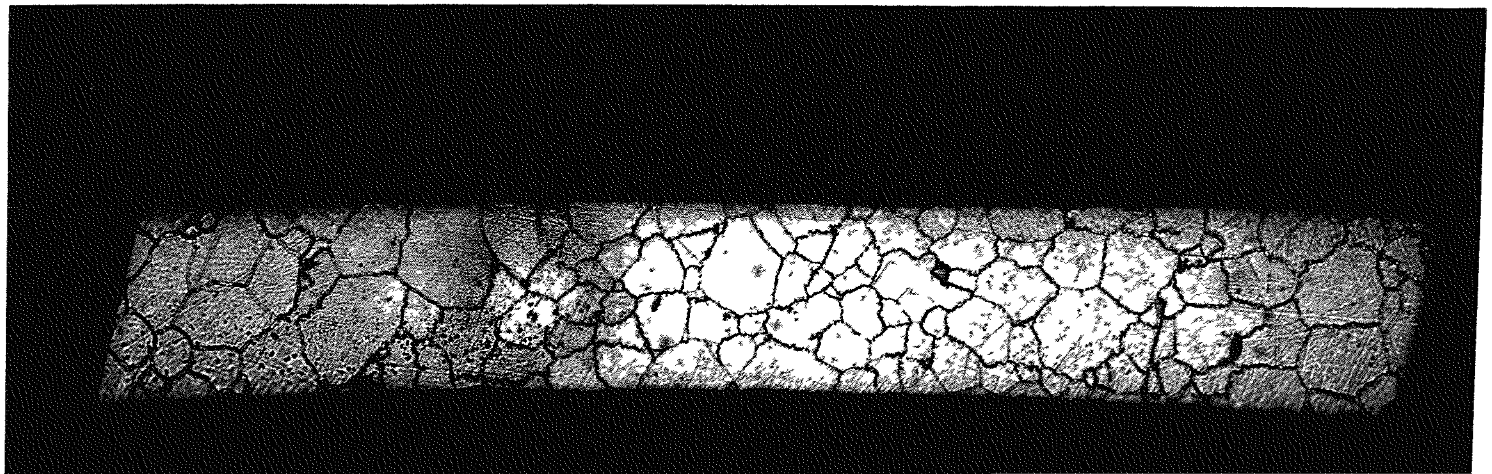

Figure 4. Photomicrograph of Inconel window cross section. Run No. 1: irradiated and heated. Deuterons impinged on lower surface. Fused fluoride was in contact with upper surface. Magnification 250.

Figure 5. Photomicrograph of Inconel window cross section. Run No. 2: heated only. Fused fluoride was in contact with upper surface. Magnification 250.

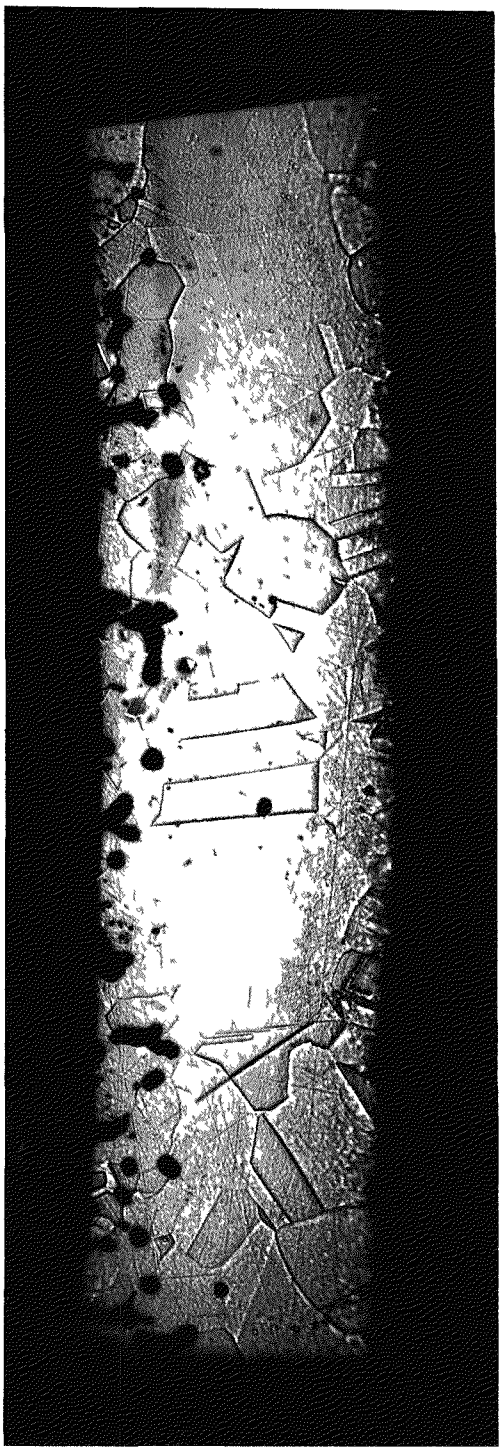

Figure 6. Photomicrograph of Inconel window cross section. Run No. 3: irradiated and heated. Deuterons impinged on lower surface. Fused fluoride was in contact with upper surface. Magnification 250.