E-11 Fracture of Uranium Dioxide [1]

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## Abstract

Experimental evidence has been obtained to demonstrate room temperature microplasticity of $UO_2$. Electron microscopy of microhardness indenter marks shows increased dislocation etch pit densities, oriented slip bonds, and definite plastic flow of the $UO_2$. Single crystal fracture surfaces show similar evidence, but the effect appears to be overidden by other phenomena in irradiated polycrystalline $UO_2$.

## Introduction

$UO_2$ is usually considered to be a brittle material, and does behave so in normal applications. But "brittle" is a relative term, and depends partly on the frame of reference for measurement. It has been shown (1)(2)(3)(4) that $UO_2$ possesses microplasticity even at room temperature. Data on both single crystal and sintered $UO_2$ showed that the effect of compression stressing may be interpreted as due to plasticity resulting from multiplication and movement of dislocations under stress.

In the course of several research programs we have obtained further visual evidence of microplasticity in $UO_2$ at room temperature. It is of interest here to examine this evidence of microplasticity, consider how it may manifest itself generally in $UO_2$, and note the way it may be strongly affected by low amounts of irradiation.

## Experiments and Discussion

Most of this work has been on single crystals, prepared by arc fusion of high purity $UO_2$ in inert atmosphere. Such material is nearly stoichiometric ($2.00 \pm .005$), of high purity ($\sim$200 ppm impurity, comprising mainly C, N, Fe and Al), and low porosity (99 + % of theoretical density)(Table I). It should be recognized that on a microscale each grain of a polycrystalline solid will behave to some extent like the single crystal.

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A typical single crystal cleavage surface obtained by impact fracture is shown in Fig.1. Natural cleavage of $UO_2$ occurs on the (111) plane, and is influenced by minor impurities and by the residual stresses resulting from the rapid cooling used in fabrication. Solidification after fusion may occur stepwise, perhaps resulting in the layered structure shown along one edge of this specimen; this layering effect is not normally encountered, however. Looking at the fracture surface a little more closely, using reflection electron microscopy of a freshly fractured specimen (Fig.2 and 3), it is readily evident that a variety of fracture modes may occur on a single specimen, the predominant type displaying the typical steps and river patterns of Fig.3. There is nothing immediately evident here to suggest the presence of plastic flow, but fracturing by impact does not lend itself to observation of micro effects. However, a microhardness diamond point indenter, as used by Honda, et al.(3) provides an easily controlled method of introducing local concentrated stresses and defect structure. Applied stress will vary continuously, from a maximum at the instant of point contact, to the minimum at the final indenter position; both plastic and elastic deformations may contribute to the final indent size. The approximate minimum pressure may be calculated from the applied load and the indented surface area; for these tests the calculated pressure was of the order of $10^4$ $kg/cm^2$ (Table II). Indenting a single crystal fracture surface with an equiaxial (Vickers) diamond point using a 300 g load at room temperature and subsequently etching, a combination of microcracking and microplasticity is revealed by the dislocation etch pits (Fig.4). The dislocations extend 25 to 100 microns from the indent edges, about twice as far as the longest microcrack. In some regions the triangular array typical of the (111) planes of $UO_2$ is apparent.

The dislocation density is pressure and temperature dependent (Fig.5), probably accounting in part for the observations that microhardness values are very sensitive to the indenter load(5). Indenting at 200°C produces the regular array of well defined etch pits shown in the top figure; alignment and distribution again are typical of (111) $UO_2$ planes. Indentation at 500°C (center micrograph) increases the dislocation density by about 10 times; the step passing through the area appears to have no affect on dislocation density. However, nearly all these dislocations can be annealed out at 1500°C in 1 hour or less (lower micrograph) (Table II).

This technique may be taken a step further by applying a Knoop diamond-shaped indenter to a polished single crystal surface, controlling the indenter orientation(5). Using a 1000 gram load, and with the long axis of the indenter parallel to the direction of intersection of (111) and (100) planes of the crystal, slip bands result parallel to the identer, and cracking is minimal (Fig.6, upper micrograph). On the other hand, rotation of the specimen by 30° (lower figure 6) leads to much more extensive microcracking, and again slip lines corresponding to the main crystallographic directions of the $UO_2$ crystal. Etching (Fig.7) shows the extent of dislocation formation more clearly. Nearly all the dislocations occurred along the slip lines evident before etching, for a distance of about 50 microns, 4 or 5 times the width of the indentation.





The evidence shown so far relies entirely on dislocation multiplication and slip line formation, and the assumption that these are manifestations of plasticity. Direct observations of plastic flow under the stressing of the diamond indenter can be achieved by use of reflection electron microscopy (Fig.8). In this case a 100 g load was applied, resulting in a smaller indentation with no cracking. Using a 17° angle of specimen tilt in the electron microscope, the raised lips of the indentation are readily seen. The indentation is about 35 microns long and 10 microns wide; the $UO_2$ edges have extruded 2 or 3 microns above the original specimen surface. In addition, slip lines can be seen extending from one end of the indentation. It is obvious that plastic flow has occurred, under conditions very similar to those producing dislocation etch pits in the previous examples.

Let us now consider the significance of these observations in the interpretation of the general behavior of $UO_2$ specimens. Examination of the etched fracture surface of a $UO_2$ single crystal shows several features similar to those produced by the diamond indenter (Fig.9). In particular, impurity inclusions are surrounded by dislocation etch pits, suggesting that some plastic flow occurred at that point. Similarly, etch pits are found along fracture steps, indicating that microplasticity may have permitted a limited plastic deformation in the vicinity of the fracture step preceeding final fracture. Electron micrographs of replicas show that the fine detail of apparent slip lines includes etch pit structure similar to that introduced by the diamond indenter (Compare Fig.5 and 9).

Sintered polycrystalline $UO_2$ presents a more complicated problem of interpretation; the fracture behavior has not been studied in sufficient detail for complete understanding. However, on a micro scale the individual grains may be considered as separate crystals, undoubtedly influenced to some extent by the adjacent grain boundaries. On a fracture surface (Fig.10) the typical river pattern structure (6)(7) is observed in the nonetched surface. The observations that pores and small amounts of impurities play a significant role in the occurrence of fracture, and that fracture ordinarily considered "brittle" may involve localized plastic flow on a micro scale immediately proceeding fracture, suggest that in the transgranular fracture normally occurring in sintered $UO_2$ as shown here the sites of impurity inclusions may have been centers of plastic flow initially.

Upon irradiation (right micrograph), the fracture changes to primarily intergranular. Apparently the fission products which are formed, and the porosity initially present, tend to agglomerate in grain boundaries during irradiation; on subsequent stressing these area serve as sites of fracture initiation. Probably microplastic deformation also occurs with intergranular fracture, but the other effects causing grain boundary weakening may predominate.

Although most observers have found that the fracture character generally changes from transgranular to intergranular upon irradiation, other types of changes may occur as well. For example (Fig.11), both of these specimens received about $1.5 \times 10^{19}$ fissions/cc. No river patterns typical of transgranular fracture occur in either, but while one appears to be a rather featureless transgranular fracture, the other is distinctly intergranular. The reason for the difference in behavior is not understood, but may stem from differences in initial material or irradiation conditions, including irradiation time, temperature, and flux rate.

## Conclusions

It has been demonstrated that "brittle" $UO_2$ actually displays microplasticity behavior, with dislocation movement on the order of 100 microns at room temperature; this plasticity appears to influence the fracture characteristics of the material. It is reasonable to expect a similar microplasticity to occur in other brittle materials as well. More study will be required to evaluate the role of this plasticity in fracture behavior under complicated conditions such as in polycrystalline materials or upon irradiation.

## Acknowledgements

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## References

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### Table I

### Typical Analysis of Arc Fused $UO_2$ Crystal

| | | |
|---|---|---|
| Al | - | 20 ppm |
| Fe | - | 50 ppm |
| C | - | 40 ppm |
| N | - | 40 ppm |

Sum of all other metallic impurities: 100 ppm

| | | |
|---|---|---|
| O/U | - | 2.004±.005 |
| Density | - | 10.96 g/cc |

### Table II

### Dislocation Density and Plasticity in Indented $UO_2$(3)

(Specimen: Arc fused single crystal $UO_2$, cleavage surface)

| Indent Test Temperature | Calculated Minimum Mean Pressure/1 | Post-Indent Annealing | Dislocation Density(Avg.) | Plasticity/2 |
|---|---|---|---|---|
| Initial specimen | - | - | $8.5\times10^{6}$ $cm^{-2}$ | - |
| 20°C | $6.5\times10^{4}$ $kg/cm^{2}$ | none | $1.9\times10^{7}$ | $2.5\times10^{-2}$ mm |
| 200° | $4.1\times10^{4}$ | none | $5.4\times10^{7}$ | $3.6\times10^{-2}$ |
| 500° | $2.4\times10^{4}$ | none | $2.1\times10^{8}$ | $6.7\times10^{-2}$ |
| 500° | $2.4\times10^{4}$ | 1300°C, 1 hour | $6.4\times10^{7}$ | - |
| 500° | $2.4\times10^{4}$ | 1500°C, 1 hour | $1.5\times10^{7}$ | - |

/1 $\frac{\text{Indenter load}}{\text{Indent Mark Area}} = \frac{300\ g}{\text{Indent Mark Area}}$

/2 Average distance from the edge line of indentation to the outer slip line.

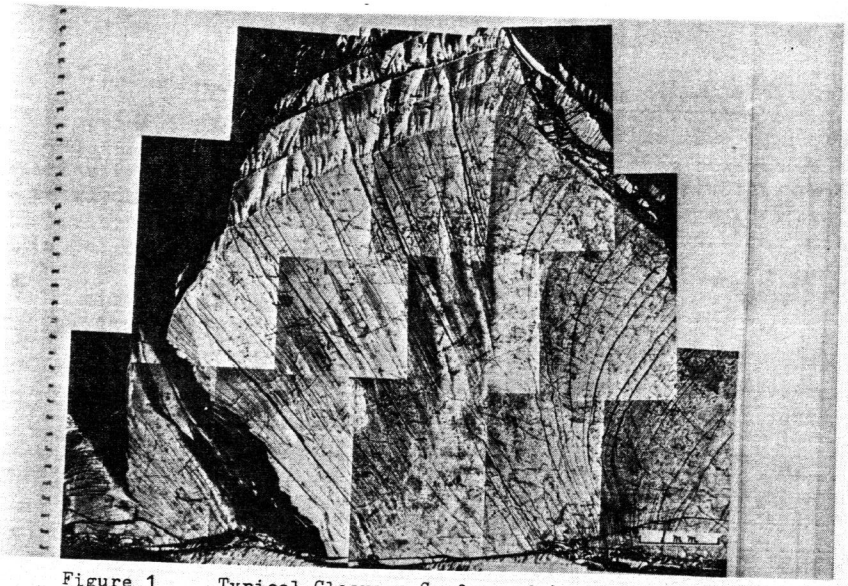

Figure 1 Typical Cleavage Surface of Arc-Fused Uranium Dioxide Single Crystal. Layered structure along one edge occurs occasionally, and may result from step-wise cooling of the fused melt.

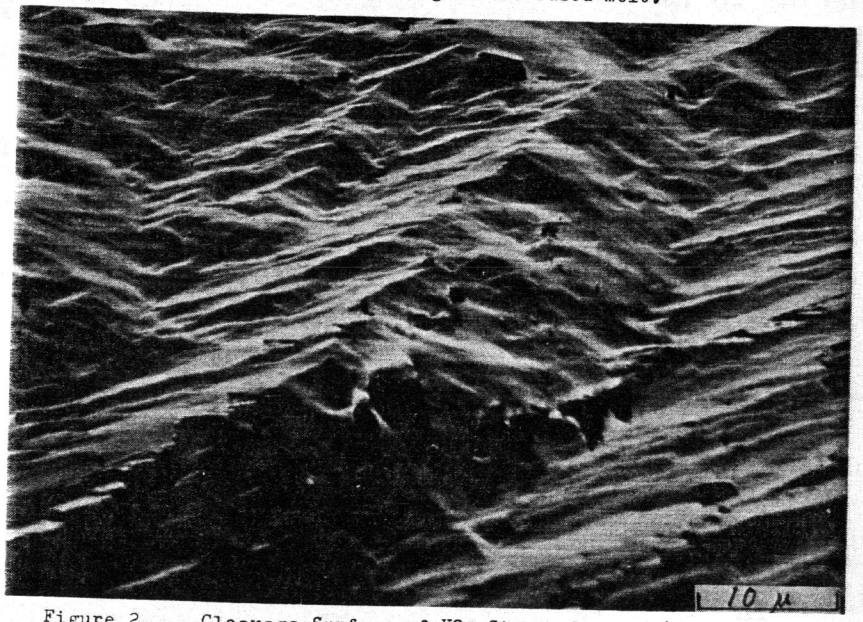


Figure 2 Cleavage Surface of $UO_2$ Single Crystal (Reflection Electron Microscopy). One of two most common surface structures encountered.





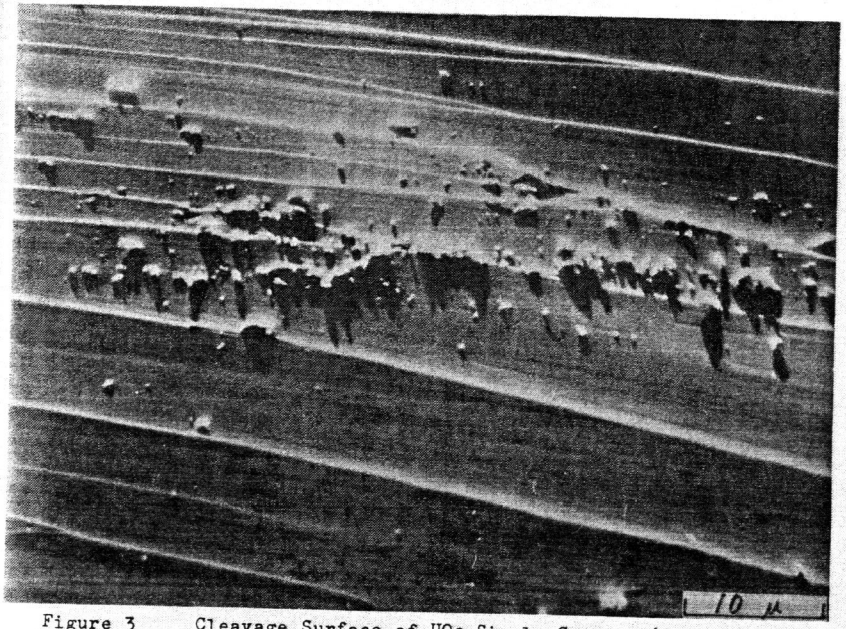


Figure 3 Cleavage Surface of $UO_2$ Single Crystal (Reflection Electron Microscopy). Most common cleavage surface structure.

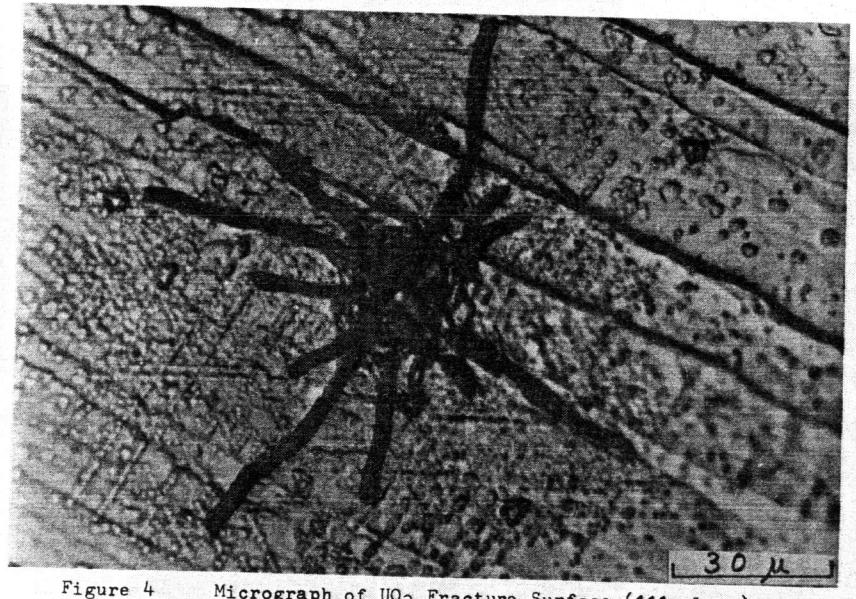


Figure 4 Micrograph of $UO_2$ Fracture Surface (111 plane) after Diamond Indentation at 20°C, and Subsequent Etching (300 gram load)

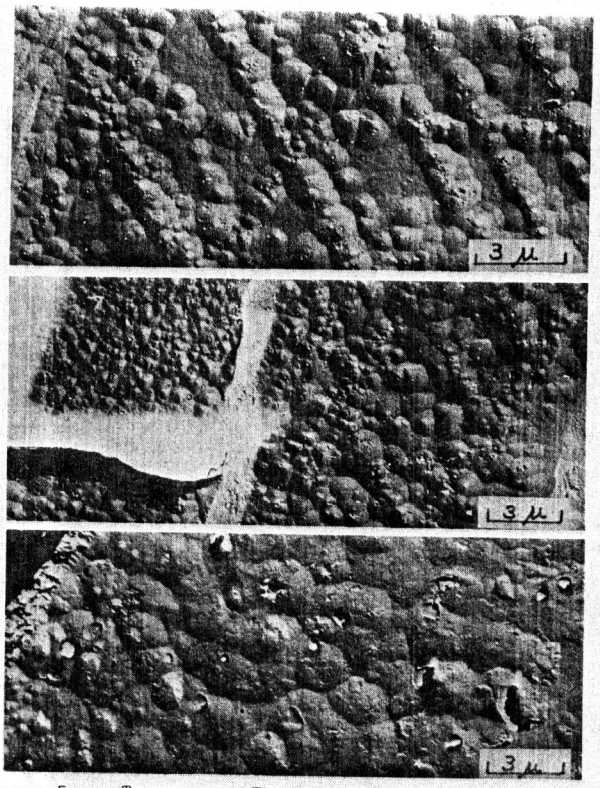


Figure 5 Temperature Effect on Dislocation Density Produced by Diamond Indentation (300 g load)

Top: Indented at 200°C; etched
Middle: Indented at 500°C; etched
Lower: Indented at 500°C and annealed at 1500°C for 1 hour; etched

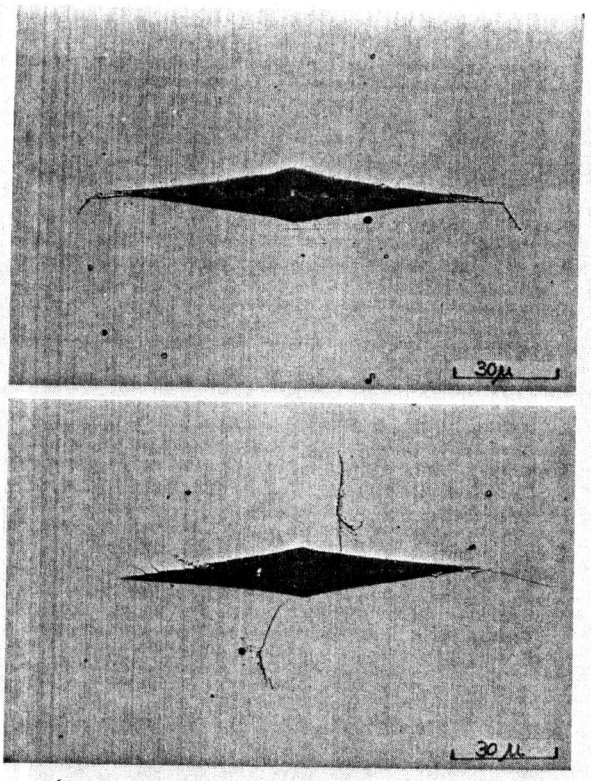


Figure 6 Indentation by Knoop Indenter (100 g load) on Polished (111) Plane of $UO_2$ Single Crystal

Upper: Indenter axis parallel to direction of intersection of (111) and (100) crystal planes
Lower: Same Crystal rotated 30° from original position





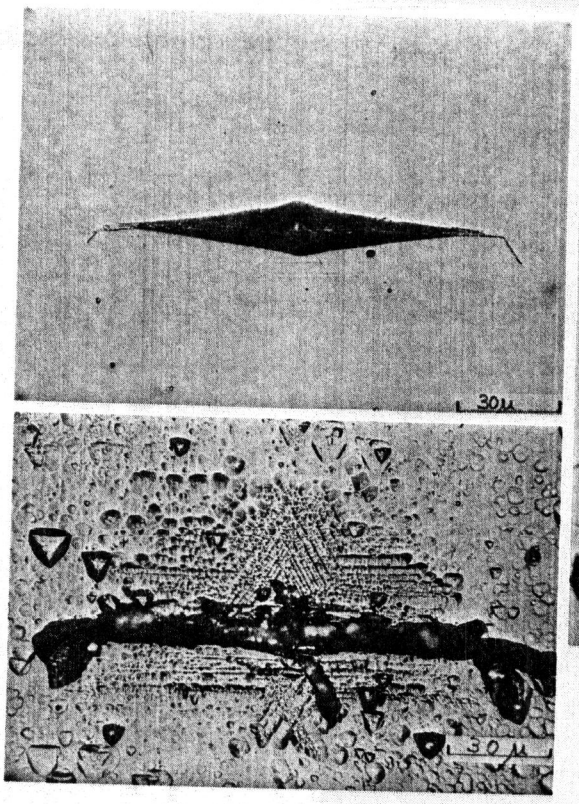


Figure 7 Knoop Indentation on (111) Plane of $UO_2$ Single Crystal

Upper: As indented on polished surface
Lower: After etching

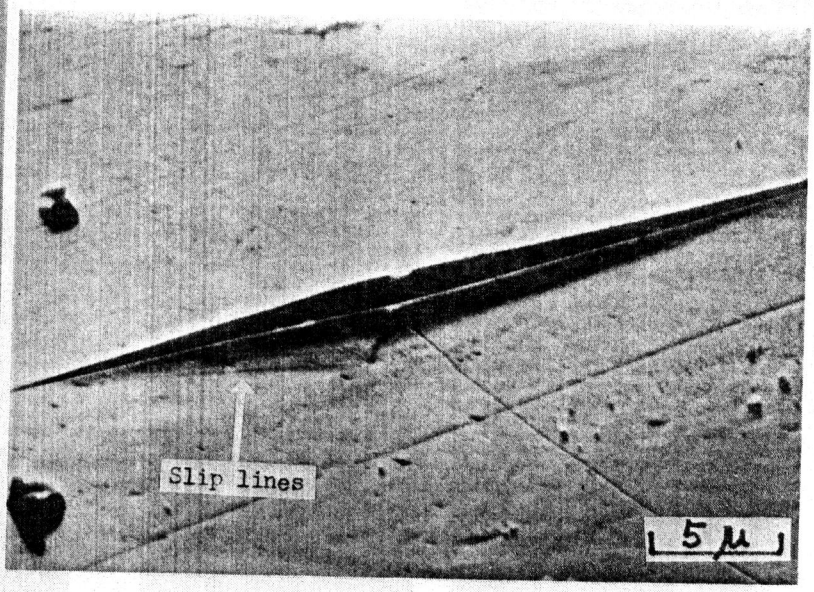


Figure 8 Indentation on Polished (111) $UO_2$ Plane (100 g load), showing material extruded by pressure of the indenter (Reflection electron micrograph; specimen angle 17°). Note the slip lines extending from the left end of the indentation.

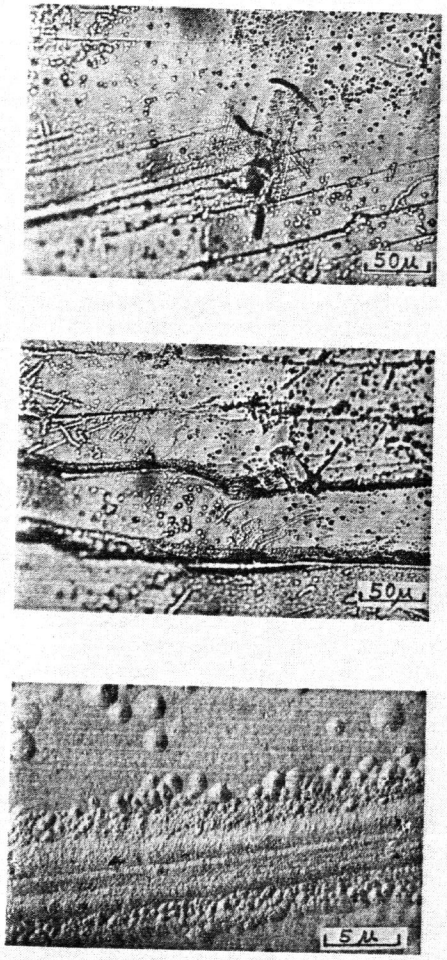


Figure 9 Dislocation Etch Pits on $UO_2$ Cleavage Surface

Upper: Impurity inclusion
Middle: Slip lines
Lower: Microslip lines





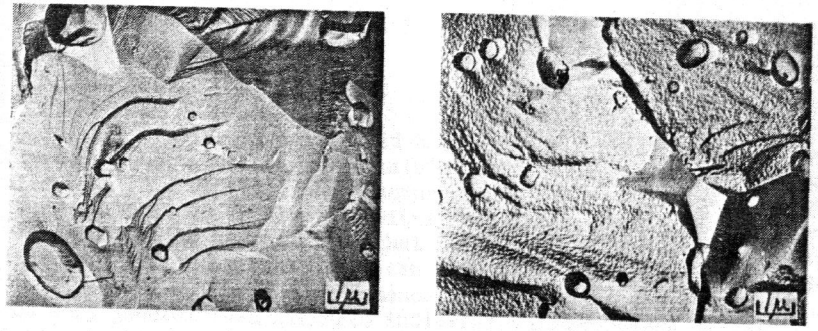


Figure 10 Polycrystalline $UO_2$ After Fracture

Left: As fabricated by pressing, and sintering at 1700°C in hydrogen
Right: After low-flux irradiation to $1.4 \times 10^{19}$ f/cc; Maximum irradiation temperature $< 100°C$

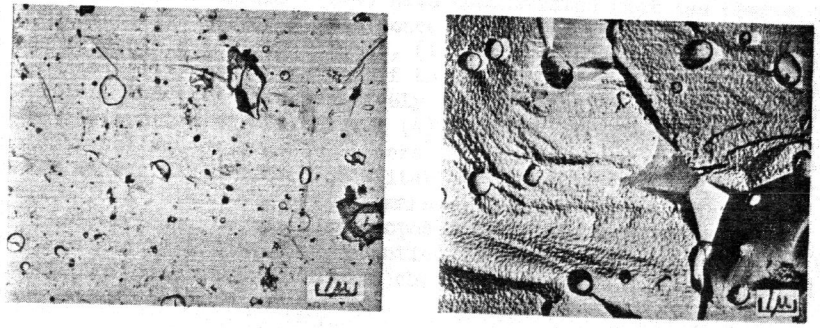


Figure 11 Irradiated Polycrystalline $UO_2$

Left: $1.7 \times 10^{19}$ f/cc; irradiated at temperatures 400° - 900°C
Right: $1.4 \times 10^{19}$ f/cc; irradiated at temperature $< 100°C$
(Specimens prepared independently from different starting materials.)