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A MICROGRAPHIC STUDY OF THE EFFECT OF MOISTURE  
IN THE AIR ON ARC-CAST URANIUM MONOCARBIDE AND  
URANIUM DICARBIDE AT ROOM TEMPERATURE OVER  
EXTENDED PERIODS

R. J. Gray and C. K. H. DuBose

## ABSTRACT

The development of fissures in uranium carbide metallographic specimens was observed over a four-year period.

Specimens consisting primarily of uranium monocarbide showed an increase in the severity of fissures after periodic removal from a storage desiccator for examination in ambient laboratory atmosphere. In uranium monocarbide and uranium dicarbide specimens, the amount of fissuring varied inversely with the uranium dicarbide content in the range of 10 to 90%. Uranium monocarbide specimens with minor amounts of  $\alpha$ -uranium were observed to develop fissures and minute eruptions in a short time if fully exposed to the ambient atmosphere, but could be sealed in a desiccator and remain inactive for a seemingly indefinite time.

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A MICROGRAPHIC STUDY OF THE EFFECT OF MOISTURE IN THE AIR  
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AT ROOM TEMPERATURE OVER EXTENDED PERIODS

INTRODUCTION

In the continuing search for better fuel materials, uranium carbide maintains a position of importance. Uranium monocarbide, in particular, offers considerable promise due to its high uranium density and a thermal conductivity near that of uranium metal. It is refractory and has a structure (face-centered cubic) that is theoretically capable of considerable resistance to radiation damage. It has been hailed as the fuel of the future<sup>1</sup> and undoubtedly would be in use today if it were not for some unfavorable features, such as instability in water, pyrophoricity, and inherent brittleness.

In a metallographic study of uranium carbides in 1956, the authors observed and later reported<sup>2</sup> that metallographic specimens containing a high uranium dicarbide content were more stable after exposure to ambient laboratory atmosphere than specimens containing primarily uranium monocarbide. Although environmental conditions were not the same, this observation did not seem to follow an assumption one might derive from earlier information by Litz<sup>3</sup> that uranium dicarbide was more reactive in vapor-phase hydrolysis studies in the temperature range of 144 to 307°C than uranium monocarbide. During the following four years, the authors made periodic microscopic examination of a series of arc-melted uranium carbide metallographic specimens with varying carbon content, and the results verified the original observation. These observations were substantiated by Secrest et al.<sup>4</sup> in their reporting

<sup>1</sup>F. A. Rough and R. F. Dickerson, "Uranium Monocarbide - Fuel of the Future?" Nucleonics 18, 74-77 (March, 1960).

<sup>2</sup>R. J. Gray, W. C. Thurber, and C. K. H. DuBose, Preparation and Metallography of Arc-Melted Uranium Carbides, ORNL-2446 (Dec. 27, 1957).

<sup>3</sup>Lawrence Marvin Litz, Uranium Carbides - Their Preparation, Structure, and Hydrolysis, TID-NP-1453 (1948).

<sup>4</sup>A. C. Secrest, Jr. et al., Preparation and Properties of Uranium Monocarbide Castings, BMI-1309 (Jan. 2, 1959).

that graphite mold castings of uranium monocarbide were more stable while standing in air than similar castings which had been machine ground. This stability was attributed to a thin layer of uranium dicarbide resulting from contact of the molten monocarbide with the graphite mold.

It is the intent of this report to present a micrographic comparison of the degree of fissuring in metallographic specimens of arc-cast uranium carbide in the 4.3 to 9.16 wt % C range. The comparisons involve specimens exposed entirely to ambient laboratory atmosphere, stored in a desiccator and exposed intermittently to the laboratory atmosphere, and complete storage in a sealed desiccator. In addition to presenting the fissuring characteristics of uranium carbide metallographic specimens, the importance of proper storage is shown for reactive metallographic samples intended for an extended time study.

#### SPECIMEN PREPARATION

The specimens were obtained from uranium carbide buttons of approx 100 g each which had been arc-cast in an inert-gas atmosphere. Due to the difficulty in cutting these brittle carbides, the buttons were fractured by impact and suitable fragments were chosen for examination. The fragments were mounted in a conventional Bakelite 1 1/4-in. mount and rough ground on a motor driven, flat 240-grit diamond wheel at 250 rpm using kerosene as a coolant. The specimens were polished successively on two canvas laps and a Microcloth lap using 30 to 40, 4 to 8, and 0 to 1  $\mu$  diamond paste,<sup>5</sup> respectively. Lubricating oil<sup>6</sup> designated for the diamond paste was used in all the polishing steps.

The polishing procedure described above was in use at the time the specimens were prepared for this report; however, the technique has been improved and replaced with vibratory polishing.<sup>7</sup> In this new technique, alumina, silicone oil, and graphite<sup>8</sup> are used in one operation.

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<sup>5</sup>Elgin Dymo Diamond Abrasive, Elgin National Watch Company, Elgin, Ill.

<sup>6</sup>Dymo Thinner.

<sup>7</sup>E. L. Long, Jr., and R. J. Gray, Preparation of Metallographic Specimens Through Vibratory Polishing, ORNL-2494 (Sept. 10, 1958).

<sup>8</sup>C. K. H. DuBose and R. J. Gray, "Metallography of Pyrolytic Carbon Coated Uranium Carbide Spheres," Paper presented at Proceedings of 15th AEC Metallography Group Meeting, Savannah River Laboratory, May 17-18, 1961.

The specimens were etched with equal parts glacial acetic acid, concentrated nitric acid, and water. Although water must not be used in the specimen polishing because of the fissuring or erosion-corrosion which could develop during the comparatively long polishing procedure, it plays a vital part in the short time required for etching to produce the proper uniform staining effect. The specimens were immersed in the etchant for 10 to 50 sec. The longer etching time was necessary with the alloys of higher carbon content.

#### SPECIMEN EXPOSURE CONDITIONS

Five uranium carbide metallographic specimens, A, D, E, F, and G, representing analyses of 4.3 to 9.17 wt % C, received the same treatment over a four-year period. The specimens were metallographically prepared in August, 1956, and representative photomicrographs were made. The specimens were stored in a desiccator containing an indicating desiccant but removed periodically as a group and examined microscopically. During the examinations, the specimens were exposed to the ambient laboratory atmosphere. Examinations were made on an average of once a week during the first three months, then were examined on an average of once a month for the remainder of the four years.

Specimen B, containing 4.8 wt % C, was prepared in May, 1959, and a representative photomicrograph was made. The specimen was exposed entirely to the ambient laboratory atmosphere for one year and three months.

Specimen C, containing 4.3 wt % C, was prepared in August, 1957, and a representative photomicrograph was made. The specimen remained in a sealed desiccator containing calcium sulphate and was not removed for three years.

#### RESULTS

Photomicrographs were made of each specimen in the originally prepared condition. Additional photomicrographs were made later of each specimen to show the condition of each specimen in relation to its environment and time. The results of the examinations are presented for each individual specimen; likewise, each panel shows the changes or lack of changes in the microstructure of each specimen. A summary of the exposures and results for all the specimens is shown in Table 1.

Table 1. Fissuring of Uranium Carbide Metallographic Specimens  
Exposed to Different Environments and Periods of Time

Specimen	Metallographic Specimen No.	Composition (wt % C)	Microstructure			Exposure Period	Type of Environment*	Results
			% $\alpha$ -U	% UC	% UC <sub>2</sub>			
A	14162	4.30	3	97	--	4 yr	2	Developed fissures
B	20144	4.80	< 1	> 99	--	15 months	3	Severe fissuring - erupted particles
C	16884	4.46	3	97	--	3 yr	1	No fissuring
D	14156	6.08	--	90	10	4 yr	2	Developed fissures
E	14151	7.04	--	50	50	4 yr	2	Less fissuring than Specimen D
F	14129	8.00	--	20	80	4 yr	2	No evidence of fissuring
G	14155	9.16	--	10	90	4 yr	2	No evidence of fissuring

\*Type of Environment:

1. Complete confinement in sealed desiccator.
2. Stored in desiccator but removed periodically for examination.
3. Exposed to ambient laboratory atmosphere.

Specimen A, Panel 1, Uranium Carbon Alloy (4.3 wt % C) 97% Uranium Monocarbide  
with 3%  $\alpha$ -Uranium

The microstructure of the freshly prepared specimen as shown in Fig. 1 has a matrix of uranium monocarbide with a semicontinuous grain-boundary phase of  $\alpha$ -uranium. The globular phase within the grain is also  $\alpha$ -uranium. After three-months storage in a desiccator with intermittent removal for examination, some fissuring had developed as shown in Fig. 2. After the same handling over a four-year period, the amount of fissuring had increased as shown in Figs. 3 and 4. The fissuring did not appear to be associated with the  $\alpha$ -uranium phase nor did it seem to be related to the crystallographic orientation of the uranium monocarbide matrix.

Specimen B, Panel 2, Uranium Carbon Alloy (4.8 wt % C) 99% Uranium Monocarbide  
and < 1%  $\alpha$ -Uranium

The microstructure of the freshly prepared specimen is shown in Fig. 5. A small amount of  $\alpha$ -uranium is present at the grain boundaries and is dispersed in fine globules within the matrix grains of uranium monocarbide. The specimen was placed in an open box in the laboratory. After fifteen months, minute explosions had scattered particles over the specimen and the mount as shown in Fig. 6. The condition of the specimen did not permit making a photomicrograph.

Specimen C, Panel 3, Uranium Carbon Alloy (4.46 wt % C) 97% Uranium Monocarbide  
and 3%  $\alpha$ -Uranium

A photomicrograph was made of the specimen immediately after it was prepared (Fig. 7). After the uninterrupted storage in a sealed desiccator for three years, the only observable change was a slight staining of the  $\alpha$ -uranium (see Fig. 8). No fissuring was detected.

Specimen D, Panel 4, Uranium Carbon Alloy (6.08 wt % C) 90% Uranium Monocarbide  
and 10% Uranium Dicarbide

The specimen was prepared and photomicrographed as shown in Figs. 9 and 10. After the four-year storage with periodic removal as described previously (see Specimen Exposure Conditions), some fissuring was evident as shown in Figs. 11 and 12.

EFFECT OF MOISTURE IN THE AIR ON ARC-CAST URANIUM CARBIDE  
METALLOGRAPHIC SAMPLES AT ROOM TEMPERATURE

SPECIMEN NO. 14162

4.3 wt % C

EST. vol %  $\alpha$ U = 3

EST. vol % UC = 97

SPECIMEN A

PANEL 1

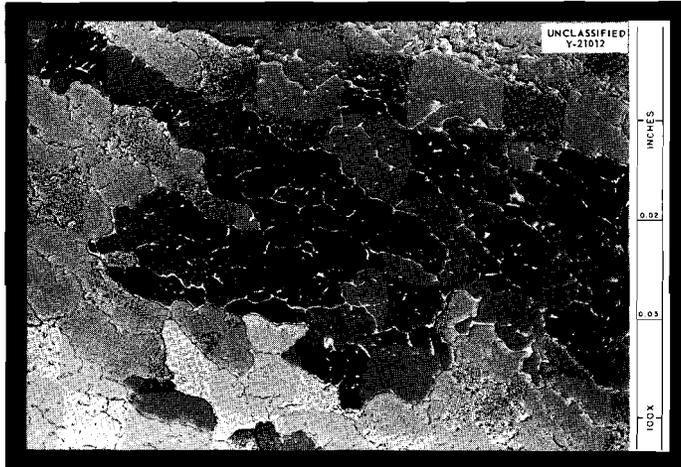


FIG. 1. AS POLISHED AND ANODIZED. (100X)



FIG. 2. SAME SPECIMEN - 3 MONTHS LATER (100X)

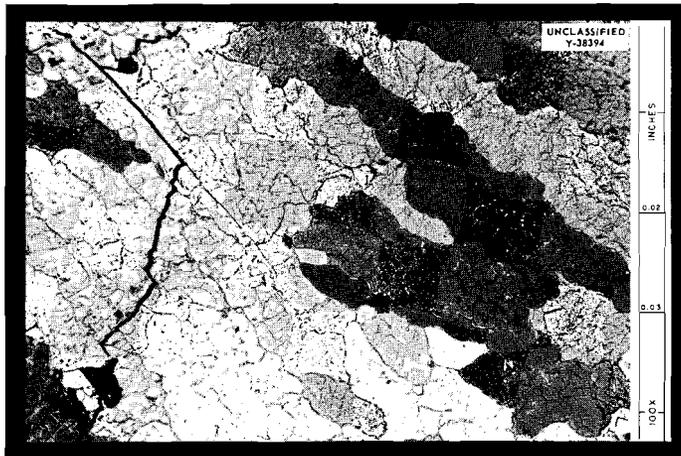


FIG. 3. SAME SPECIMEN - 48 MONTHS LATER. (100X)

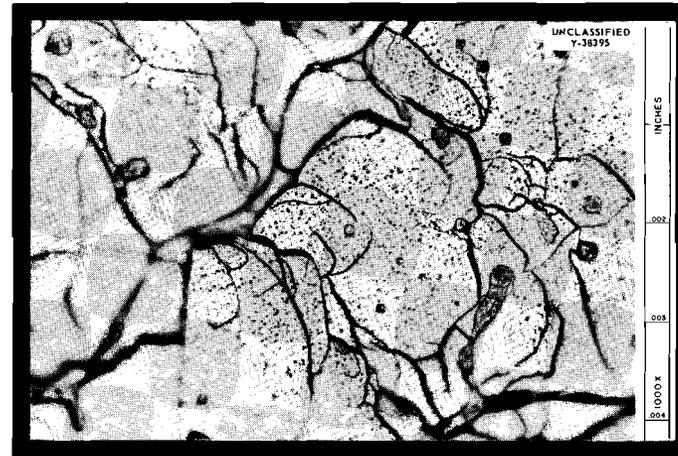


FIG. 4. SAME AS FIG. 3 AT HIGHER MAGNIFICATION. (1000X)

EFFECT OF MOISTURE IN THE AIR ON ARC-CAST URANIUM CARBIDE  
METALLOGRAPHIC SAMPLES AT ROOM TEMPERATURE

SPECIMEN NO. 20144

4.8 wt % C

EST. vol %  $\alpha$ U = < 1

EST. vol % UC = > 99

SPECIMEN B

PANEL 2

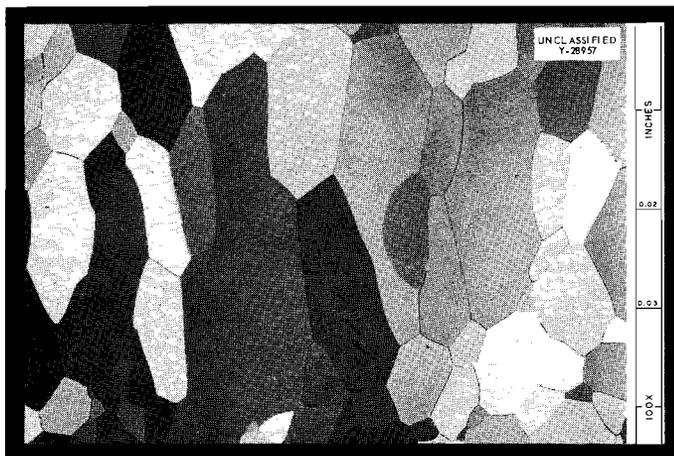


FIG. 5. AS POLISHED AND ANODIZED. (100X)

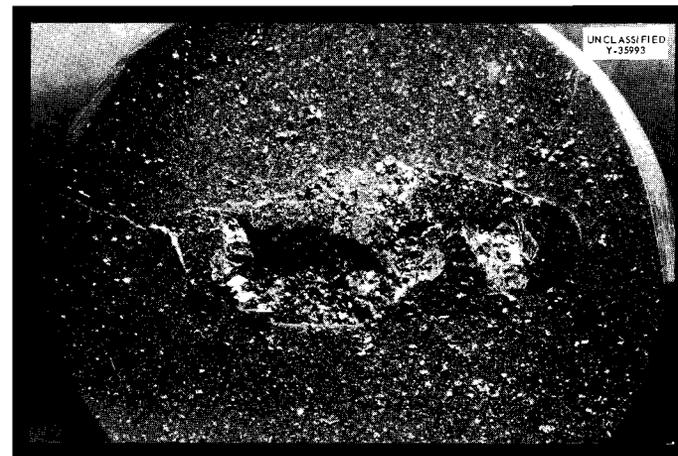


FIG. 6. OVERALL VIEW OF SAME SPECIMEN IN MOUNT AFTER 15 MONTHS EXPOSURE TO ROOM TEMPERATURE. (5X) NOTE SCATTERED PARTICLES OVER SPECIMEN AND MOUNT DUE TO MINUTE EXPLOSIONS ON SPECIMEN SURFACE.

EFFECT OF MOISTURE IN THE AIR ON ARC-CAST URANIUM CARBIDE  
METALLOGRAPHIC SAMPLES AT ROOM TEMPERATURE

SPECIMEN NO. 16884

4.46 wt% C

EST.vol %  $\alpha$ U = 3

EST.vol % UC = 97

SPECIMEN C

PANEL 3

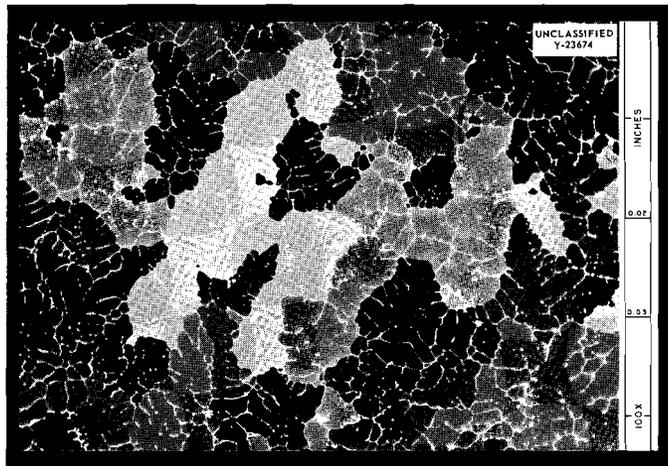


FIG. 7. AS POLISHED AND ANODIZED. (100X)

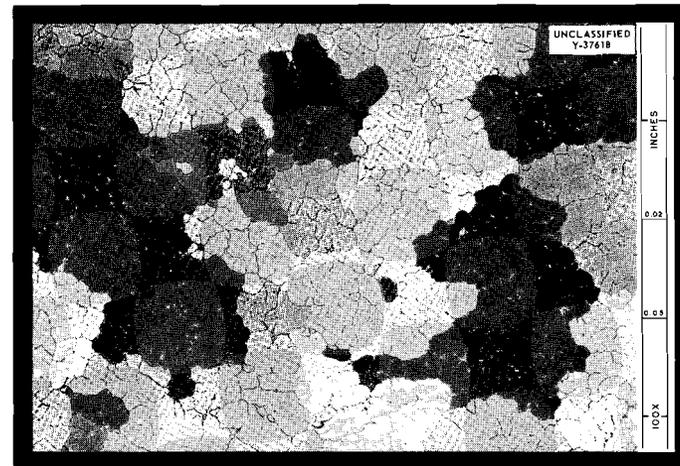


FIG. 8. SAME SPECIMEN 3 YEARS LATER - STORED IN A SEALED  
DESICCATOR. NOTE ABSENCE OF MICROCRACKS.

EFFECT OF MOISTURE IN THE AIR ON ARC-CAST URANIUM CARBIDE  
METALLOGRAPHIC SAMPLES AT ROOM TEMPERATURE

SPECIMEN NO. 14156

6.0 wt % C

EST. vol % UC = 90

EST. vol % UC<sub>2</sub> = 10

SPECIMEN D

PANEL 4



FIG. 9. AS POLISHED AND ANODIZED. (100X)



FIG. 10. SAME AS FIG. 9 AT HIGHER MAGNIFICATION. (1000X)



FIG. 11. SAME SPECIMEN AFTER STORAGE IN A DESICCATOR FOR 4 YEARS; REMOVED PERIODICALLY FOR EXAMINATION. (100X)

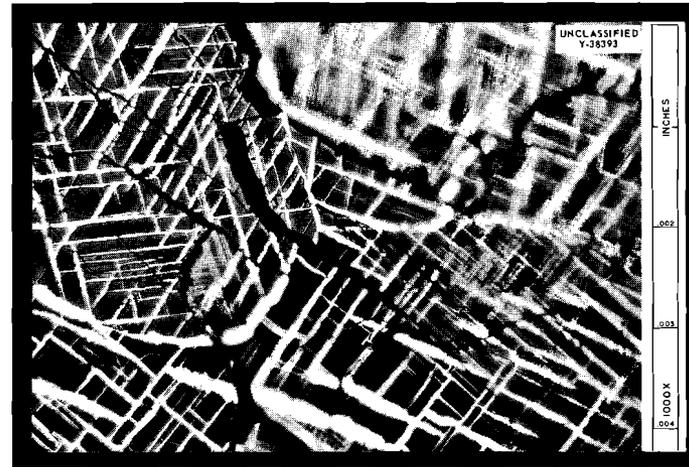


FIG. 12. SAME AS FIG. 11 AT HIGHER MAGNIFICATION. (1000X)

Specimen E, Panel 5, Uranium Carbon Alloy (7.04 wt % C) 50% Uranium Monocarbide and 50% Uranium Dicarbide

Photomicrographs of the specimen immediately after preparation are shown in Figs. 13 and 14. After the four-year storage (see Specimen Exposure Conditions), the specimen had a small amount of fissuring as shown in Figs. 15 and 16.

Specimen F, Panel 6, Uranium Carbon Alloy (8.00 wt % C) 80% Uranium Dicarbide and 20% Uranium Monocarbide

Photomicrographs of the as-prepared specimen are shown in Figs. 17 and 18. After the storage period of four years with intermittent removal for examination (see Specimen Exposure Conditions), no change in the microstructure or evidence of fissuring was detected as shown in Figs. 19 and 20.

Specimen G, Panel 7, Uranium Carbon Alloy (9.16 wt % C) 90% Uranium Dicarbide and 10% Uranium Monocarbide

Photomicrographs were made of the specimen after it was prepared as shown in Figs. 21 and 22. After the four-year storage with intermittent removal for examination (see Specimen Exposure Conditions), no change in the microstructure or evidence of fissuring was detected as shown in Figs. 23 and 24.

#### DISCUSSION

The reaction of uranium monocarbide and uranium dicarbide metallographic specimens with the ambient atmosphere appears to be proportional to the quantity of uranium dicarbide present in the specimen. In vapor-phase hydrolysis tests, Litz<sup>3</sup> found the reaction of each carbide to be dependent on the test temperature; also, the reaction between uranium monocarbide and water vapor was found to proceed at a much slower rate than that between the dicarbide and water vapor. In fact, the dicarbide reacted faster at 125°C than the monocarbide did at 300°C. Apparently in ambient laboratory atmosphere, the reactivity rates are reversed.

EFFECT OF MOISTURE IN THE AIR ON ARC-CAST URANIUM CARBIDE  
METALLOGRAPHIC SAMPLES AT ROOM TEMPERATURE

SPECIMEN NO. 14151

7.04 wt % C

EST. vol % UC = 50

EST. vol % UC<sub>2</sub> = 50

SPECIMEN E

PANEL 5

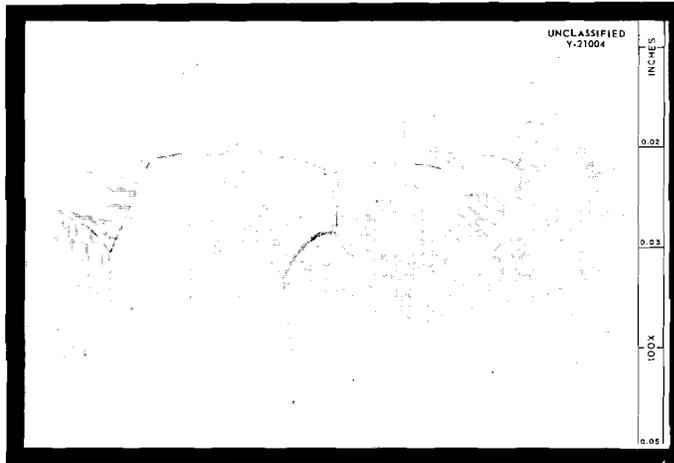


FIG. 13. AS POLISHED AND ANODIZED. (100X)

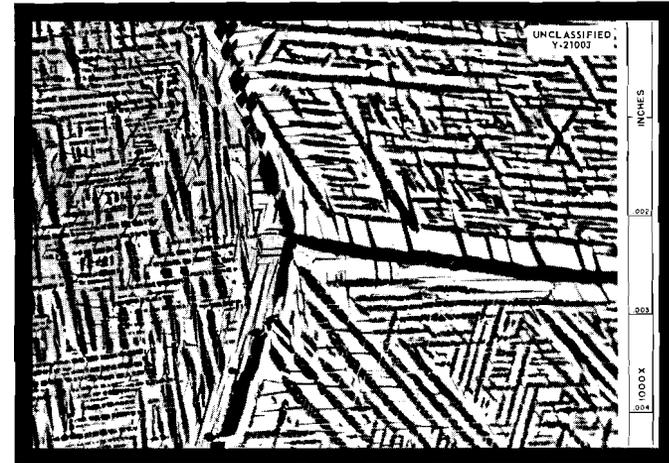


FIG. 14. SAME AS FIG. 13 AT HIGHER MAGNIFICATION. (1000X)

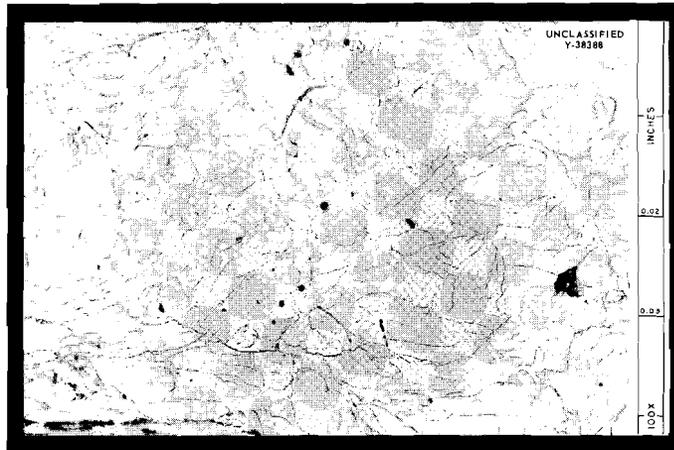


FIG. 15. SAME SPECIMEN AFTER STORAGE IN A DESICCATOR FOR 4 YEARS; REMOVED PERIODICALLY FOR EXAMINATION. (100X)

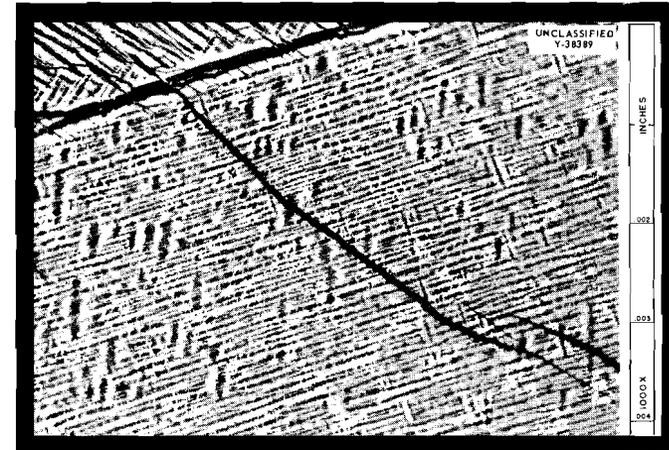


FIG. 16. SAME AS FIG. 15 AT HIGHER MAGNIFICATION. (1000X)

EFFECT OF MOISTURE IN THE AIR ON ARC-CAST URANIUM CARBIDE  
METALLOGRAPHIC SAMPLES AT ROOM TEMPERATURE

SPECIMEN NO. 14129

8.0 wt % C

EST. vol % UC = 20

EST. vol % UC<sub>2</sub> = 80

SPECIMEN F

PANEL 6



FIG. 17. AS POLISHED AND ANODIZED. (100X)

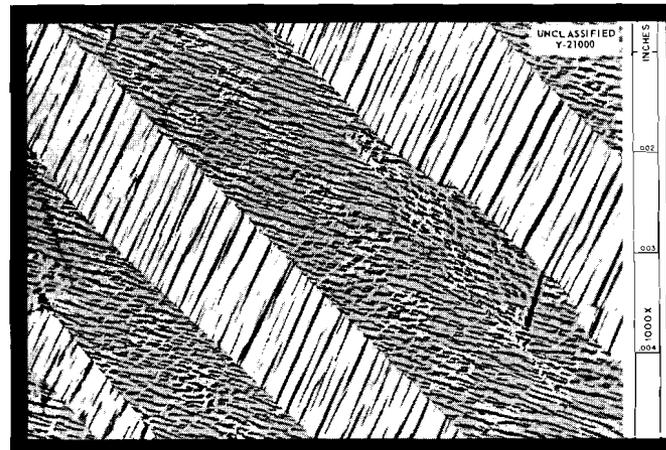


FIG. 18. SAME AS FIG. 17 AT HIGHER MAGNIFICATION. (1000X)

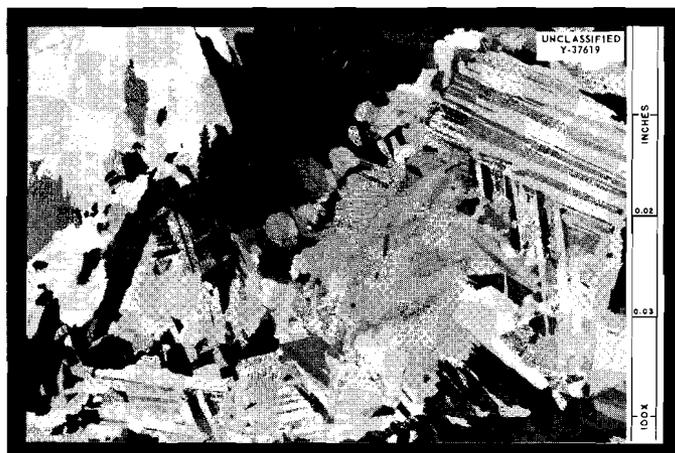


FIG. 19. SAME SPECIMEN AFTER STORAGE IN A DESICCATOR FOR 4 YEARS; REMOVED PERIODICALLY FOR EXAMINATION. (100X)

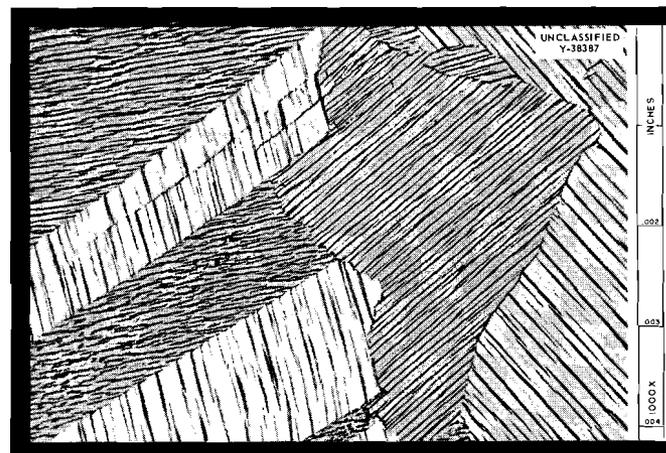


FIG. 20. SAME AS FIG. 19 AT HIGHER MAGNIFICATION. (1000X)

EFFECT OF MOISTURE IN THE AIR ON ARC-CAST URANIUM CARBIDE  
METALLOGRAPHIC SAMPLES AT ROOM TEMPERATURE

SPECIMEN NO. 14155

9.16 wt % C

EST. vol % UC = 10

EST. vol % UC<sub>2</sub> = 90

SPECIMEN G

PANEL 7

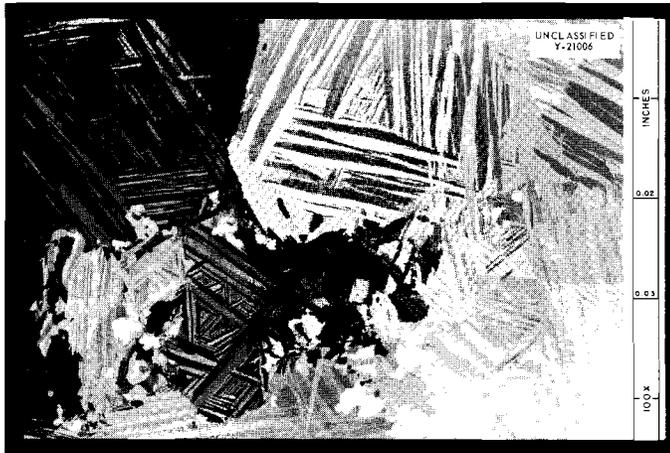


FIG. 21. AS POLISHED AND ANODIZED. (100X)



FIG. 22. SAME AS FIG. 21 AT HIGHER MAGNIFICATION. (1000X)



FIG. 23. SAME SPECIMEN AFTER STORAGE IN A DESICCATOR FOR  
4 YEARS; REMOVED PERIODICALLY FOR EXAMINATION. (100X)  
NOTE ABSENCE OF MICROCRACKS



FIG. 24. SAME AS FIG. 23 AT HIGHER MAGNIFICATION. (1000X)

Judging from the gaseous products reported by Litz<sup>3</sup>, the minute explosions in the metallographic specimen exposed to the open air were due to a sub-surface build-up of methane and hydrogen gases. Analysis by x-ray diffraction has shown the powder particles produced from these minute explosions were uranium monocarbide. No change in composition was evident due to the explosions or the room-temperature exposures.

Some postulations can be made concerning the behavior of the metallographic specimens. The presence of  $\alpha$ -uranium in the uranium monocarbide may have influenced the instability of these specimens in periodic exposure to the open air; however, the microstructure showed no indication of a concentration of the fissuring near or in relation to the  $\alpha$ -uranium. The stability of the uranium dicarbide specimens could be attributed to a threshold humidity and temperature value under which no reaction occurs in an air-conditioned laboratory. In an aqueous vapor-phase solution test, the threshold value is exceeded and reaction is quite rapid.

Another postulation could be the metallographic stain etch or anodization on the uranium dicarbide specimens produces a more protective oxide film than the  $\alpha$ -uranium-uranium monocarbide specimens or uranium monocarbide specimens with minor amounts of uranium dicarbide. No attempts were made to determine the storage characteristics of unstained specimens.

#### CONCLUSIONS

Uranium monocarbide metallographic specimens containing minor amounts of  $\alpha$ -uranium or uranium dicarbide tended to fracture after short exposures to ambient laboratory atmosphere; the stability of the specimens was extended slightly with intermittent laboratory exposure and desiccator storage. Metallographic specimens containing 80% or more uranium dicarbide were significantly more stable under similar exposure conditions.

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