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INVESTIGATIONS OF SOME EXPERIMENTAL FUEL ELEMENT ALLOYS
WITH THE ELECTRON MICROPROBE

April 15, 1964



WELDON SPRING PLANT

MALLINCKRODT CHEMICAL WORKS
URANIUM DIVISION

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(TID-4500, 28th Edition)

TOPICAL REPORT

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by

L. A. Ferguson
D. L. Parker
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Mallinckrodt Chemical Works
Uranium Division
Weldon Spring, Missouri

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INVESTIGATIONS OF SOME EXPERIMENTAL FUEL ELEMENT ALLOYS
WITH THE ELECTRON MICROPROBE

by

L. A. Fergason
D. L. Parker
N. F. Neumann

ABSTRACT

The microstructures of seven alloys were investigated with the Cambridge microprobe. Six of the alloys were uranium containing the following combinations of other elements: S; P; Zr, Fe, and Al; Zr and P; Fe and Si; and Al, Fe, and Si. One was a section of a thorium fuel element.

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INTRODUCTION

The alloys of uranium and thorium, because of their varied physical and chemical characteristics, are under investigation at many AEC sites for their potential utility as fuel elements. Integral to the understanding of these alloys is the nature of their microstructures and phase relationships. These microstructures are revealed metallographically and may be characterized by classical techniques. The scanning electron microprobe is a powerful adjunct to these techniques in the identification and quantitative determination of micro-inclusions.

An extensive program is under way at the MCW Weldon Spring site employing the microprobe in uranium alloy studies. Specimens representing seven alloys prepared at the Hanford Atomic Products Operation were submitted for investigation with the Cambridge Mark II Microscan X-ray Analyzer. Six of these samples were alloys of uranium and one of thorium.

Metallographs taken at HAPO were submitted with the samples and used to aid in developing maximum information from phase identification with the probe. While detail is lost in reproduction, halftone copies are included here for ease of demonstrating the relationships observed.

GENERAL CONSIDERATION

The Cambridge microprobe used in this investigation was of conventional design and has been adequately described elsewhere.^{1,2}

Preparatory to analysis, the samples were mounted in conductive bakelite and diamond polished. Standard etching procedures were used, where necessary, for metallographic examination and qualitative identification of inclusions with the microprobe. For quantitative analysis, a very light etch was given in those cases necessary to remove metal smear; otherwise, none was used at all. If possible, etching is to be avoided before quantitative analysis because etching causes the various inclusions, matrix, and standards to be left in comparative relief. This difference in level of the specimen surface tends to change the focusing characteristics of the spectrometer. It is also important to avoid valleys and ridges because they may change the effective X-ray take-off angle, thus changing the self-absorption and secondary fluorescence effects.³ Finally, by its very nature the chemical etch may

preferentially remove different elements leaving a surface which is not chemically representative of the whole.

Two methods of quantitative analysis were used. One was of the conventional technique of comparing the characteristic X-ray emission of an element in the alloy with that of the pure element. Corrections for atomic number effects and self-absorption were usually made according to the method of Poole and Thomas⁴ and are described in a previous report.² Backscatter analysis was also performed on some of the inclusions and, as the name implies, was performed by measuring the quantity of electrons rejected or backscattered from the surface of the alloy. The magnitude of this backscattering is related to the average atomic number (\bar{Z}) of the area being measured.

The analysis was conducted by measuring (1) the total probe current with the aid of a Faraday cage in a sample mount position, (2) the residual sample current (after backscatter) in the alloy AB, and finally (3) the sample current of each of the pure elemental components A and B.

The backscatter coefficient, r , was then determined for each of the measurements by the following formula:⁴

$$r = \frac{\text{probe current} - \text{specimen current}}{\text{probe current}} \quad (1)$$

The concentration, C_A , was calculated from the following formula:

$$r_{AB} = C_A r_A + (1 - C_A) r_B \quad (2)$$

where r_{AB} , r_A , and r_B are backscatter coefficients of the alloy and each of the pure components, respectively.

The sample current measurements were taken with a Kiethely electrometer across a 100K resistor.

EXPERIMENTAL PROCEDURE AND RESULTS

Sample No. 1

The first sample to be investigated was thorium alloyed with 2.5 wt. % U and 1 wt. % Zr, coextruded with zircalloy-2 at 760°C with a reduction ratio of 17:1, and vacuum heat-treated for one hour at 750°C. Included with this sample was a thorium metal base stock specimen (Figures 1 and 2, respectively).

These samples were mounted together in a conductive bakelite mold suitable for probe analysis. Most of the observations were made on as-diamond-polished surfaces. Correlation of inclusions identified with the microprobe and inclusions as shown on the original metallographs were sometimes uncertain. For this reason, this specimen was polished and etched according to the recommendations of Mr. Rodger Todd of Hanford for some qualitative observations

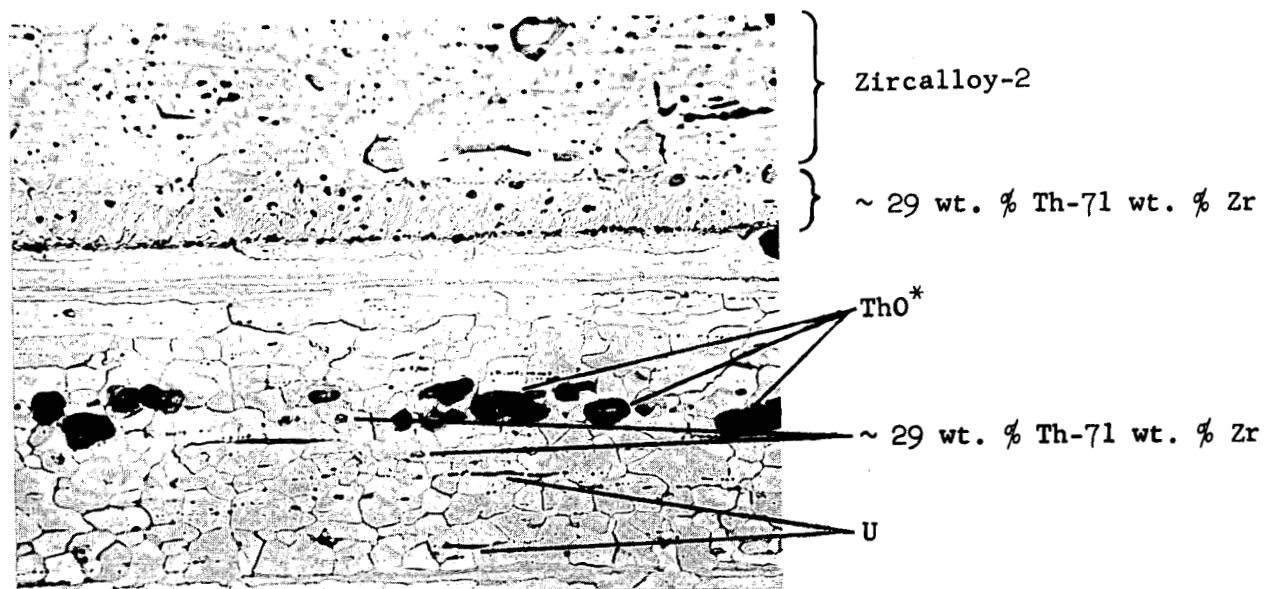


Figure 1. Sample 1. Thorium Alloyed with 2.5 wt. % U and 1 wt. % Zr
Coextruded with Zircalloy-2. 500X. (HAPO Neg. 4W-63-285B)

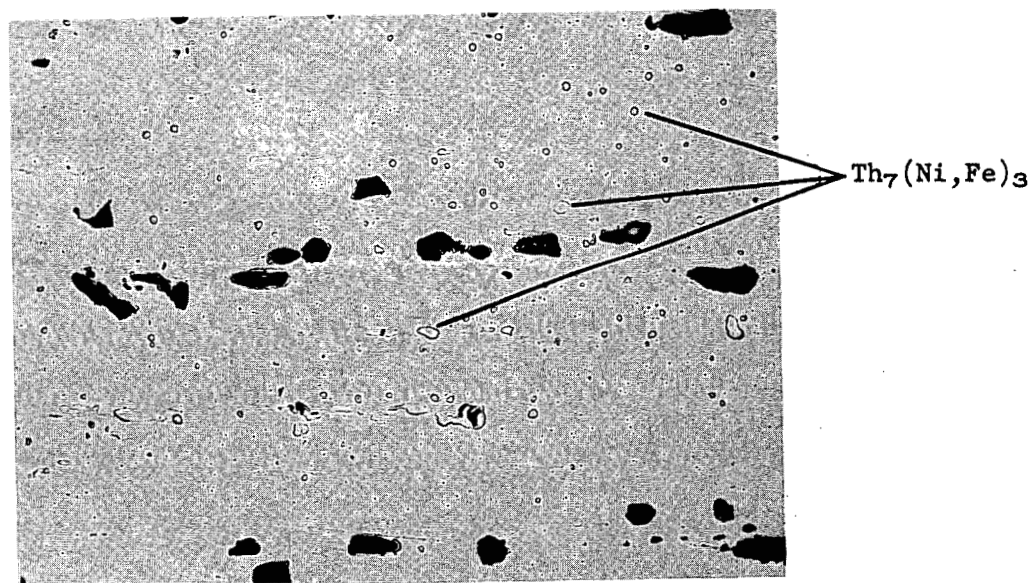


Figure 2. Thorium Metal Base Stock Used in Preparation of Sample 1.
250X. (HAPO Neg. 4Z-1862)

*See text.

in the probe. Accordingly, the sample was polished with a 1μ alumina abrasive (Linde "A," Linde Air Products Co.) in a liquid soap vehicle and electrolytically etched in an alcohol-perchloric acid bath at 25 volts for 10 seconds.

The chemical nature of the zircalloy-2-thorium bond layer was studied by traversing the electron beam slowly across the bond concurrently with the recording of Th $L\alpha$ and Zr $K\alpha$ X-ray emission intensities. A concentration plateau about 10μ wide was observed between the can and core. Subsequent electron backscatter analysis showed the plateau to be 71-72 wt. % Zr in Th.

These results coincide within the limits of error of an eutectoid composition of 69.5 wt. % Zr reported by Carlson.^{5,6,7} The various inclusions in the canned core metal and the base stock thorium were identified and the results are presented as follows:

Metallic uranium was seen to be present in the long strata-like inclusions and some of the smaller round inclusions found in the stringers (see Figure 1).

The large black inclusions tentatively identified as ThO by Hanford could not be positively identified with the microprobe other than to say that they were thorium containing. The refractory nature of these inclusions caused a surface charge to be built up when they were subjected to bombardment with the electron beam. Consequently, the electron beam would be repelled and become unstable, thus precluding any possibility of an accurate X-ray analysis without depositing a conductive layer on the surface of the sample. Obviously, electron backscatter analysis could not be effected under these conditions.

A scan of the specimen for Zr $K\alpha$ X-ray emission showed areas of high Zr concentration similar in appearance to those inclusions indicated in Figure 1. Both backscatter and Th X-ray analysis of several of these inclusions again showed a concentration of about 71 wt. % Zr. This corresponds to an atomic ratio of 6:1 for Zr and Th, respectively.

Inclusions of a Th-Fe-Ni complex were seen in the stock metal as indicated in Figure 2. Similar inclusions could not be located in the fuel element sample, although indications of Ni and Fe rich areas were detected that were too small to be resolved with the microprobe. The relative intensity of the Ni $K\alpha$ and Fe $K\alpha$ X-ray emissions was about 5 to 1, respectively. This ratio must be applied to relative concentrations with a degree of caution. The mass absorption coefficient of Fe for Ni $K\alpha$ radiation is much higher than for the converse and, in turn, iron is strongly fluoresced by Ni $K\alpha$ radiation. The appearance of these elements in a thorium matrix reduces the magnitude of these interatomic effects but at the same time complicates the correction procedures. All things considered, to assume that the as-measured intensity ratio is equal to the concentration ratio is as

good a data treatment as any other. At any rate, the tendency would be for the Fe $K\alpha$ X-ray intensity to be high and the Ni $K\alpha$ to be low relative to true concentration.

Analysis of several of these areas by electron backscatter analysis gave an average thorium concentration of 90.9 wt. %. This value agrees closely with the theoretical values of 90.2 wt. % Th in Th_7Ni_3 and 90.7 wt. % Th in Th_7Fe_3 and is compatible with intermetallic compounds as shown in published phase diagrams.⁷

Sample No. 2

This sample was uranium containing about 5000 ppm sulfur. This alloy was prepared by arc casting a button with dingot uranium feed stock and sulfur added as US. The button was heated four hours at 800°C and slowly cooled. Figures 3a and b are metallographs of this alloy prepared by Hanford. Analyses of the structure revealed the following:

The sample was a uranium-sulfur alloy. Figure 4 is a backscatter image taken of the as-diamond-polished surface. The dark, lower atomic number areas were determined to contain sulfur.

Uranium X-ray analysis of these areas resulted in an average value of 86 wt. % U after correction for absorption and atomic number effects.

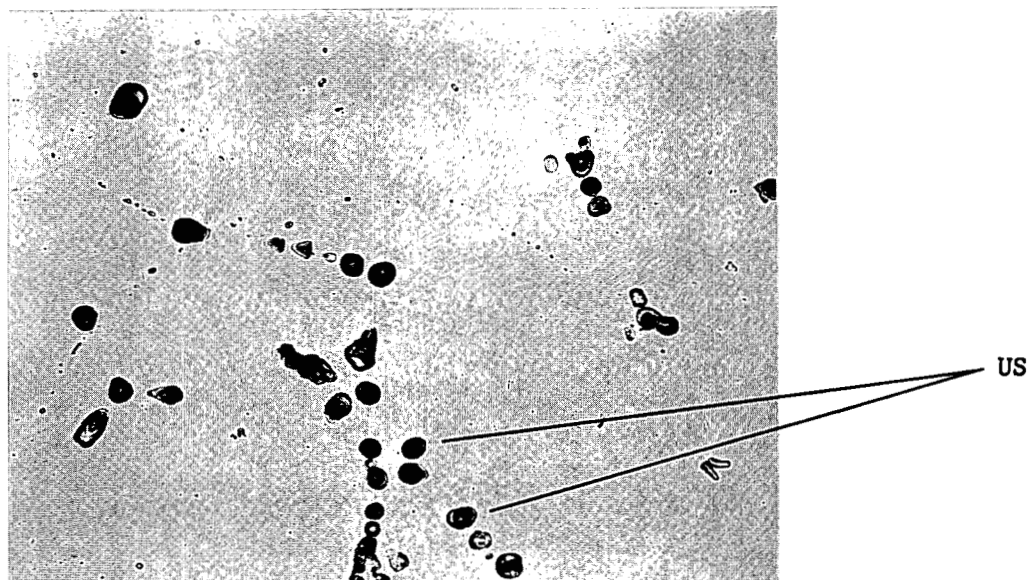
Backscatter analysis of the same areas gave a value of 89.5 wt. % U. The analytical technique for the backscatter analysis was the same as described previously for Sample No. 1 except the r value for sulfur had to be extrapolated from values measured for Mg, Al, and Si. The results of these analyses most closely fit the stoichiometry of US which is 88.2 wt. % U.

The eutectoid structure shown in the dark field picture (Figure 3b) could not be seen in the X-ray or backscatter images obtained with the microprobe. The probe diameter was about 0.5 μ when the attempt was made. An ortho-phosphoric acid etch failed to assist in revealing this structure.

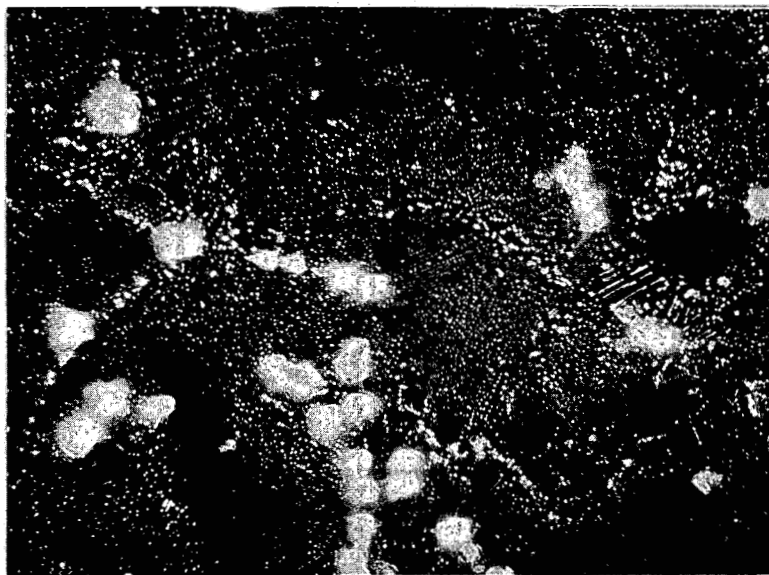
Sample No. 3

Sample 3 was U containing about 2700 ppm P prepared by arc casting. This sample exhibited four types of microstructure when investigated with the microprobe (see Figures 5 and 6). They were as follows:

Large angular inclusions containing phosphorus in quantity equal to that of UP were seen. Figures 7a and b show backscatter and P $K\alpha$ X-ray images, respectively, of areas containing this type of inclusion.



a) Brightfield 500X. (HAPO Neg. 4Z-1651B)



b) Darkfield 500X. (HAPO Neg. 4Z-1651A)

Figure 3. Sample 2. Uranium with 5000 ppm Sulfur.

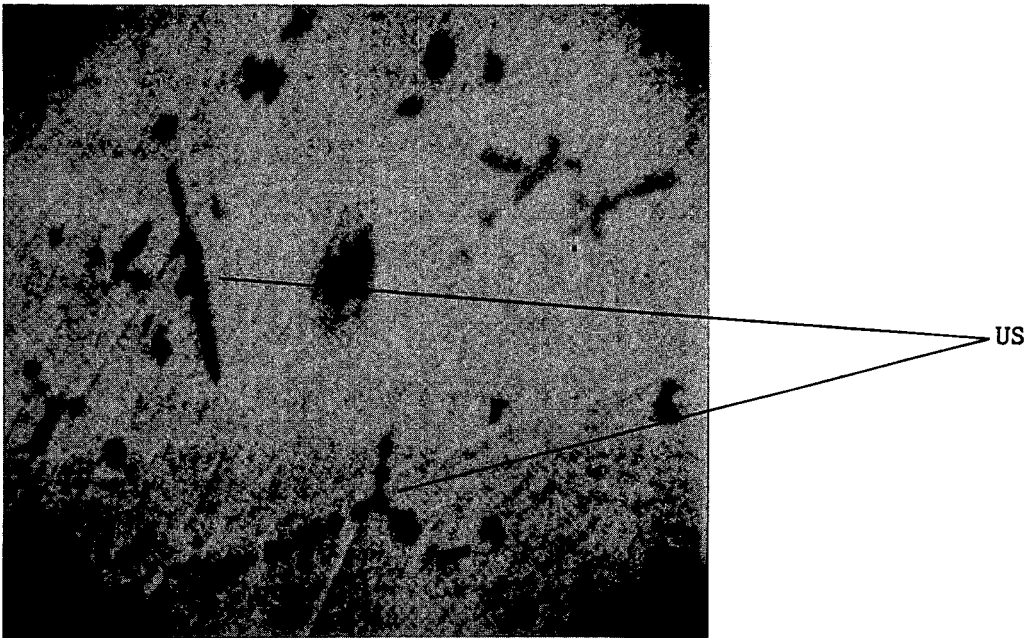


Figure 4. Sample 2. Electron Backscatter Image. 500X.

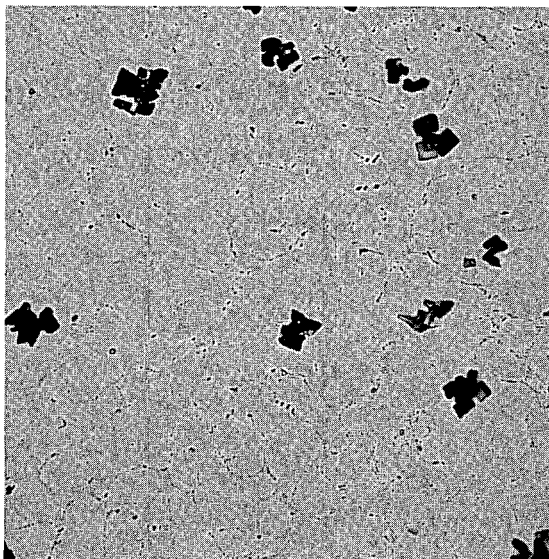


Figure 5. Sample 3. Uranium with 2700 ppm Phosphorus. 500X.
(HAPO Neg. 4Z-1628B)

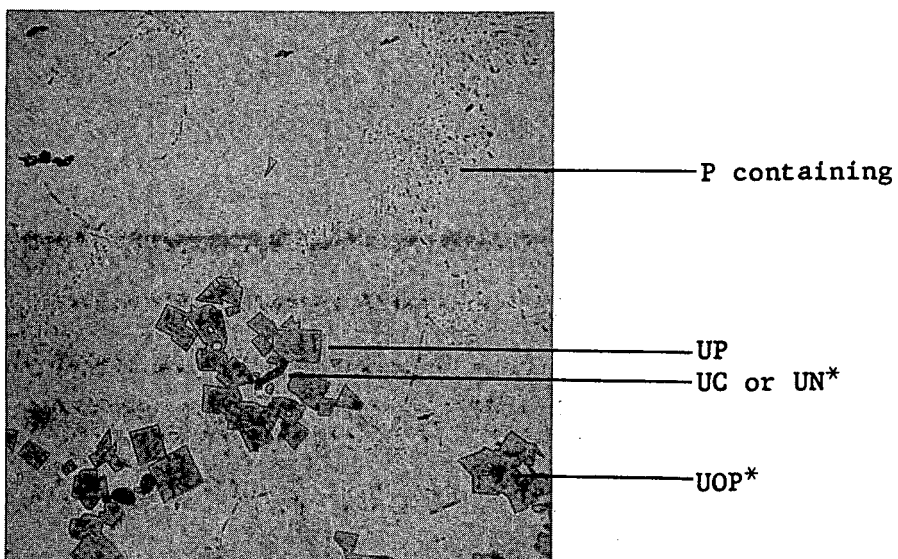
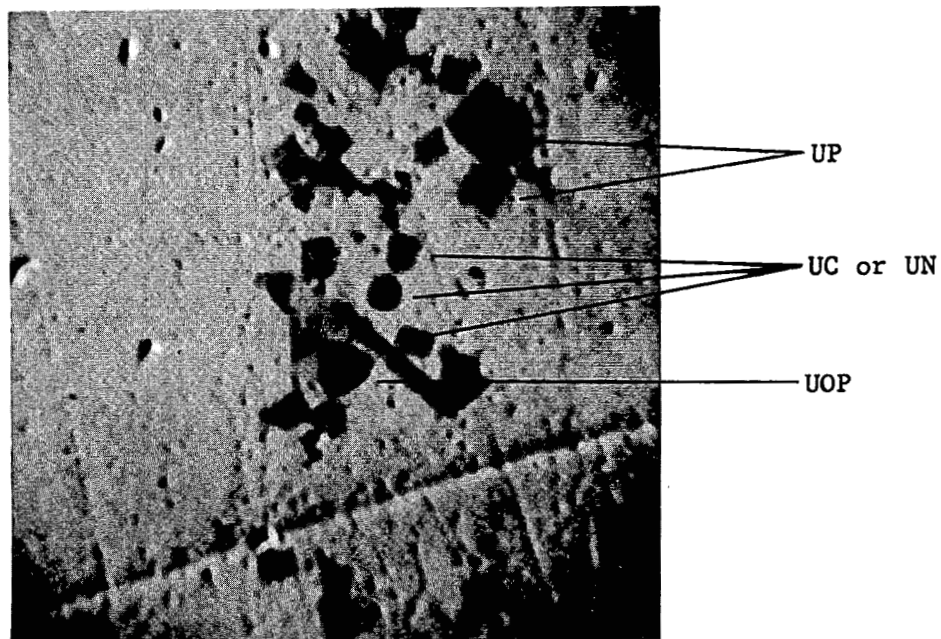
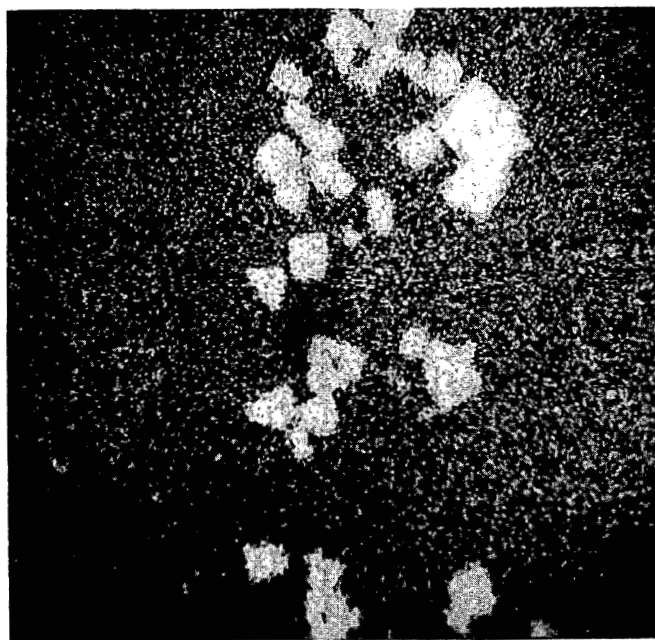


Figure 6. Sample 3. MCW Metallograph. 750X.

*See text.



a) Electron Backscatter Image. 750X.



b) P K α X-ray Image. 750X.

Figure 7. Sample 3. Images of Uranium-Phosphorus Alloy Taken from Microprobe.

Other phosphorus inclusions, fewer in number and containing less phosphorus than UP, approached the concentrations expected for UOP.

The large non-phosphorus containing inclusions shown in Figures 7a and b probably were uranium carbide or nitride. They contained approximately 95 wt. % U as determined by U L α X-ray emission. The limits of error of this analysis encompasses the uranium content of both UC and UN; therefore, positive identification could not be made. No other elements were found in the inclusions.

The eutectoid-like area contained phosphorus; however, quantitative analysis was not possible. The X-ray analytical area was two to three microns in diameter which was greater than the size of the inclusions; consequently, only qualitative analyses could be made.

Sample No. 4

This uranium alloy contained 1 wt. % Zr, 200 ppm Fe, and 350 ppm Al. Prior to examination, the arc-cast button was heated for three days at 800°C and then water quenched. This treatment was followed by a 100-hour anneal at 600°C from which temperature the sample was furnace cooled. Figures 8a and b and Figure 9a are photomicrographs showing the structure. The sample was diamond polished and then given a light ortho-phosphoric acid etch. Microprobe analyses gave the following results:

Figure 9b is an electron backscatter image of the same area as seen in Figure 9a with some of the inclusions identified. The light inclusions in relief on the backscatter pattern are U₆Fe. For the most part, the U₆Fe was randomly distributed; however, some subnetwork structure is made up of very small U₆Fe inclusions.

The small gray areas, found mostly in the major network, are UAl₂.

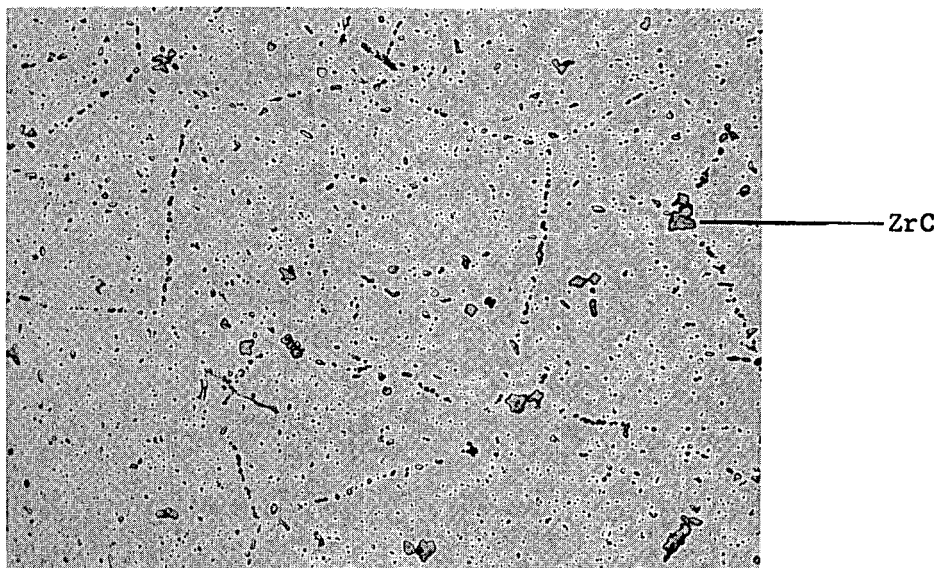
The larger dark inclusions are ZrC.

Quantitative analysis of the UAl₂ and U₆Fe was achieved by comparing the Al and Fe K α X-ray intensities to that of the known intermetallics of these species.

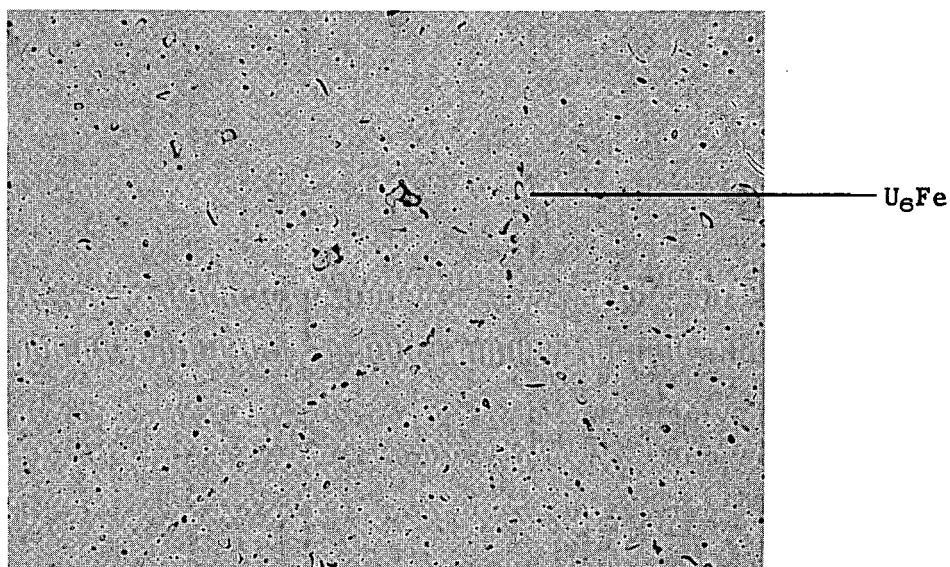
The Zr L α emission from the ZrC areas was compared with that of pure Zr. No uranium could be detected in these inclusions.

Sample No. 5

Uranium was arc cast with 1 wt. % Zr and 350 ppm P. The sample was annealed three days at 800°C, water quenched, annealed 100 hours at 600°C, and furnace cooled.



a) 500X. (HAPO Neg. 4Z-1669B)



b) 1000X. (HAPO Neg. 4Z-1669C)

Figure 8. Sample 4. Uranium with 1 wt. % Zr, 200 ppm Fe, and 350 ppm Al.

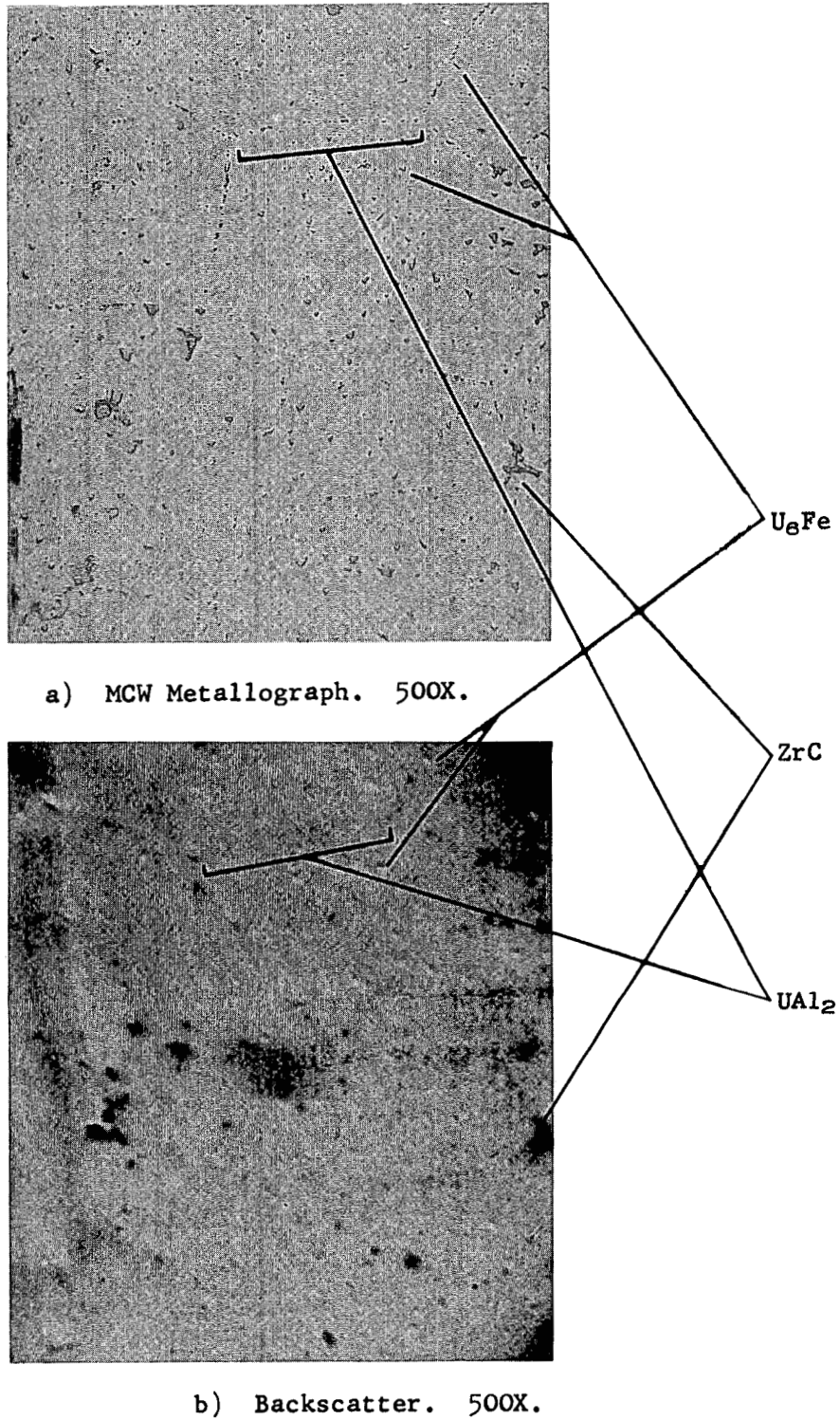


Figure 9. Sample 4. Comparison of Metallograph with that of Backscatter Image.

The inclusions indicated on the photomicrographs (Figures 10a and b) contain Zr and U, with P as a minor constituent. No Zr or P inclusions were found without the presence of the other element. Quantitative analysis was not attempted on these inclusions. Phosphorus, zirconium, and uranium together present a special problem in quantitative analysis. Zirconium $K\alpha$ X-radiation is interfered with by U $L\beta$ X-radiation, and the Zr $L\alpha$ and P $K\alpha$ lines interfere with each other. The presence of P and Zr together in the inclusions was determined by scanning with the gypsum crystal spectrometer in the region of Zr $L\alpha$ and P $K\alpha$ emissions. The resolution of the spectrometer was fully adequate for qualitative analysis.

Sample No. 6

An alloy of uranium containing 130 ppm Fe and 107 ppm Si was beta heat-treated and held at 400°C for 72 hours.

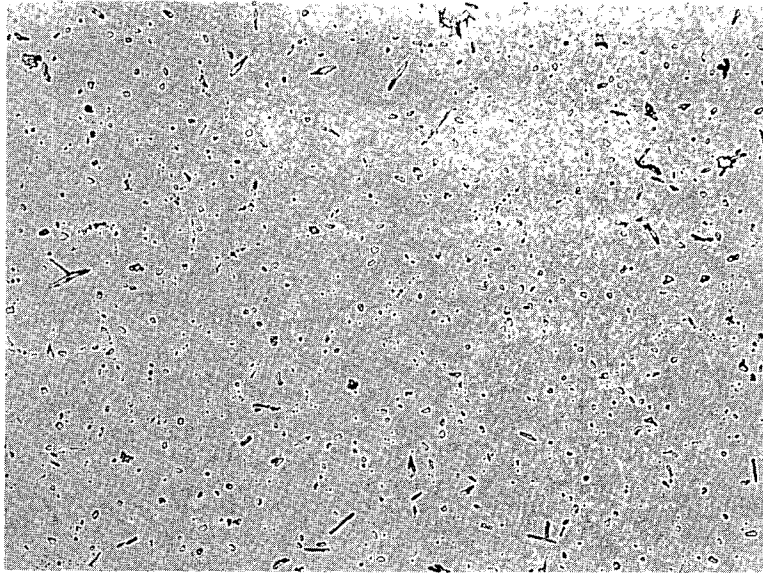
The inclusions identified as U_6Fe are shown in Figure 11. Silicon containing inclusions could not be detected; however, U_3Si inclusions in a uranium matrix are difficult to detect with the microprobe if they are less than 0.5 micron in diameter.

Sample No. 7

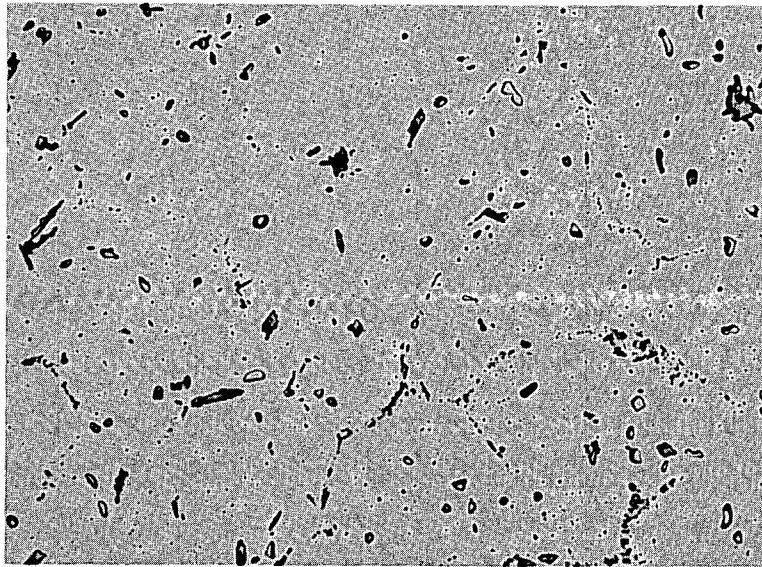
This beta-treated sample containing uranium with 640 ppm Al, 400 ppm Fe, and 85 ppm Si was held 24 hours at 600°C and furnace cooled.

As shown in Figure 12, the larger inclusions are U_6Fe areas containing Si.

Neither U_3Si nor UAl_2 could be resolved.



a) 500X. (HAPO Neg. 4Z-1667A)



b) 1000X. (HAPO Neg. 4Z-1667B)

Figure 10. Sample 5. Uranium with 1 wt. % Zr and 350 ppm P.

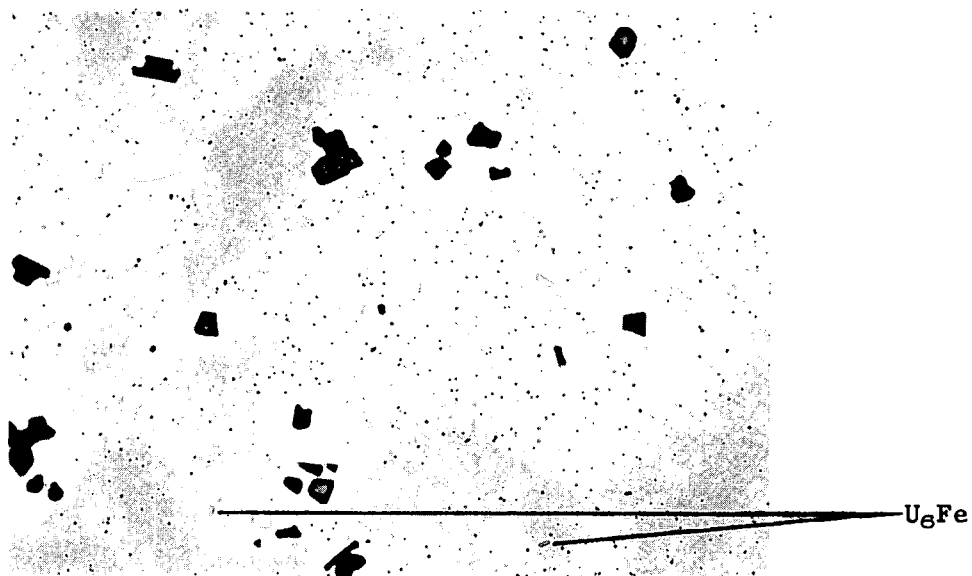


Figure 11. Sample 6. Uranium with 130 ppm Fe and 107 ppm Si.
500X. (HAPO Neg. 4Z-1749B)

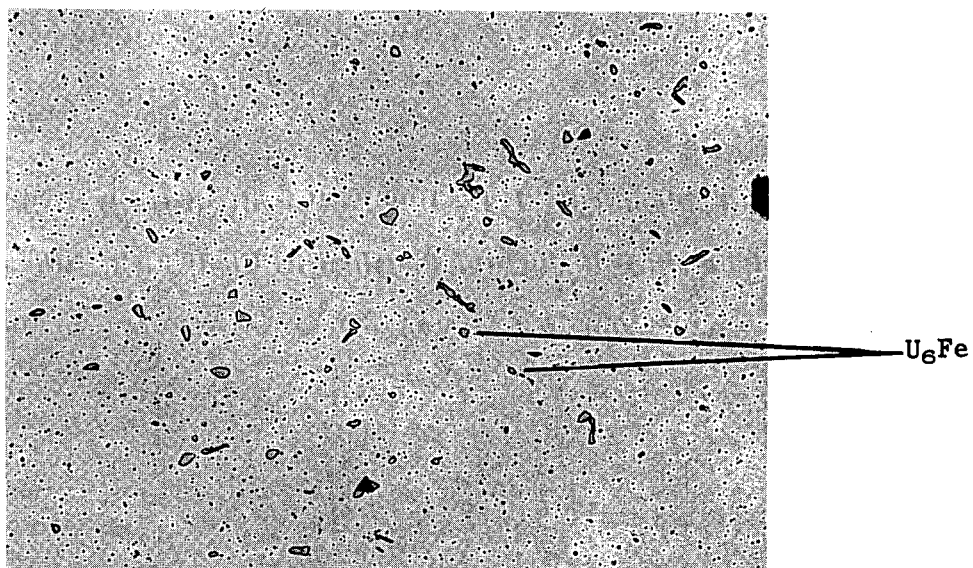


Figure 12. Sample 7. Uranium with 640 ppm Al, 400 ppm Fe,
and 85 ppm Si. 500X. (HAPO Neg. 4W-62-2276C)

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