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CHARACTERIZATION OF INCLUSIONS IN DINGOT URANIUM

by

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The nonmetallic inclusions in both as-reduced and fabricated dingot uranium have been studied for comparison with those in ingot uranium. Special attention was paid to the hydride for the purpose of determining the amount and distribution in the various types of uranium. The types and distribution of other inclusions were also studied. It was found that the dingot uranium was of a higher quality than ingot uranium and was comparable to as-reduced derby uranium on the basis of over-all inclusion count. The hydrogen content in dingot uranium, however, was found to be appreciably higher than in either ingot or derby uranium.

INTRODUCTION

Due to increased interest in the use of dingot* uranium for reactor applications, the types and distribution of nonmetallic inclusions in the material have been of special interest to the Savannah River Laboratories. Early examinations of this type of metal showed that the hydrogen content was much higher than in the vacuum-melted uranium now in common usage. In order to define the quality of dingot uranium, a program was initiated at Battelle to compare this metal in several conditions with ingot** uranium in comparable conditions. The results of this study are discussed in this report.

EXPERIMENTAL TECHNIQUES

Materials

Samples of as-cast ingot produced from magnesium-reduced uranium and dingot uranium in the as-reduced and the forged conditions were

*Dingot is the term used to refer to uranium which is cast into a shape suitable for fabrication during the reduction step.

**Ingot uranium can be defined as the normal production-grade metal which has been bomb reduced, vacuum melted, and cast into an ingot suitable for fabrication.

received from Mallinckrodt Chemical Works. No prior history of the material was furnished except that Dingot X-1073 and Ingot 2496 were considered as scrap and no analyses were made. The conditions of forging also were not reported, but it is presumed that the metal was forged from a salt bath at approximately 600 C.

Sections of extruded dingot and ingot uranium were available. The dingot material was extruded at SRL at a billet temperature of 1150 to 1170 F, but no information about the ingot tubing was available.

Sections of metal in the above conditions have been analyzed by chemical, spectrographic, and vacuum-fusion techniques and detailed metallographic studies were made of the material.

Metallographic Techniques

The specimens were ground on a water-lubricated revolving disk with 120-, 240-, 400-, and 600-grit silicon carbide papers. The final grinding on 600-grit paper was then repeated by hand on a well-worn paper (with water lubricant) in order to produce as fine a grind as possible and minimize the problem of imbedded particles of grit from the papers.

Mechanical polishing was carried out on a slow-speed wheel (240 rpm) covered with a medium-nap woolen cloth and employing Diamet Hyprez blue diamond paste (0 to 2 μ) as the abrasive with kerosene as a lubricant. Some specimens of higher purity (i.e., forged dingot uranium) required an additional polish with Diamet Hyprez gray diamond paste (1/4 μ), the remainder of the conditions being the same as above.

After washing thoroughly with ethyl alcohol, the specimens were electrolytically polished in a bath composed of 1 part stock solution of chromic acid (118 g CrO_3:100 cm^3 H_2O) and 4 parts glacial acetic acid. The cell was operated at an open-circuit potential of 40 v dc and required 2 to 5 sec to complete the polishing operation. A stainless steel cathode was employed and the electrolytic bath was kept at room temperature.

Electrolytic etching was accomplished in the above solution at 6 v dc on the open circuit. An alternate solution consisted of one part stock solution (100 g CrO_3:100 cm^3 H_2O) and 18 parts glacial acetic acid. This bath was operated at an open-circuit potential of 20 v dc.

Etching to delineate inclusions more sharply required 5 to 20 sec, but to bring out the structure of the metal a cell time of from 2 to 5 min was needed.

An etchant to darken carbides[1] was used extensively in this study. It was composed of equal parts of nitric acid and water and was applied either by immersion or swabbing. Usually, 5 to 15 sec was required to darken the UC inclusions.

Hydrogen Analysis by Metallographic Methods

Analyzing for hydrogen by metallographic means consisted of carefully examining the entire specimen surface at a magnification of 250X. A visually determined "average field" was then compared with uranium photomicrographs of known hydrogen content. The "analysis" was then made taking into account the size, number and distribution of the UH_3 inclusions. The result obtained by a careful examination of this type usually closely approaches the results obtained by vacuum-fusion analyses. The variation can be as little as ±0.2 ppm.

Vacuum-Fusion Analysis

The samples which were to be analyzed for both oxygen and hydrogen were dropped into a graphite crucible containing carbon-saturated iron at 1200 C (2192 F) which was then rapidly raised in temperature to 1750 C (3182 F). The specimens requiring only hydrogen analyses were dissolved in a carbon-saturated iron bath at 1650 C (3000 F). Gases evolved were analyzed by low-pressure fractional-freezing techniques.

Two samples of dingot uranium were analyzed by the "warm-extraction" method in order to preserve the identity of the metal for further metallographic examination. This analysis was performed by heating the specimens at 850 C (1562 F) in evacuated carbon-free Vycor reaction tubes until no more gases were evolved. These gases also were analyzed by the low-pressure fractional-freezing process.

The data gathered from these analyses were quite comparable to results previously obtained for high-purity uranium. The only exception was in the oxygen analysis from a section from the top of Ingot 2496 (see Table 1).

(1) References at end.

TABLE 1. VACUUM-FUSION-ANALYSIS RESULTS[a]

Material	Analysis, ppm by weight	
	Oxygen	Hydrogen
As-reduced Dingot X-1073 top	12	2.6
As-reduced Dingot X-1073 top	8	2.7
As-reduced Dingot X-1073 bottom	--	2.5
As-reduced Dingot X-1073 bottom	5	2.6
Forged Dingot 1176B	--	0.6
Forged Dingot 1176B	--	0.7
Extruded Dingot 4169	6	4.4
Extruded Dingot 4169	--	2.5
As-cast Ingot 2496 top[b]	28	0.9
As-cast Ingot 2496 top[b]	88	1.2
As-cast Ingot 2496 top[b]	43	--
As-cast Ingot 2496 center	--	0.3
As-cast Ingot 2496 bottom	--	0.7
Extruded ingot	6	0.5
As-reduced Dingot X-1073 top[c]	--	3.0
As-reduced Dingot X-1073 bottom[c]	--	2.6

(a) The sensitivity of the apparatus in which these analytical measurements were made is equivalent to ±2 ppm oxygen and ±0.2 ppm hydrogen for a 4-g sample and varies inversely with the sample weight.
(b) This sample was reanalyzed in order to determine the correct value for oxygen. There evidently was oxygen segregation, as consistent results could not be obtained.
(c) Analyses made by warm-extraction method.

Chemical and Spectrographic Analyses

Representative samples from each type of material were analyzed for carbon and nitrogen by chemical means. The results of these analyses are shown in Table 2. Spectrographic-analysis data from selected specimens are given in Table 3.

CHARACTERIZATION OF INCLUSIONS

To simplify the reporting of the metallographic examinations, each type and condition of metal will be considered separately.

Dingot Uranium

As-Reduced Dingot

Metallographic examinations showed that Dingot X-1073* was relatively clean. The only visible inclusions are the UH_3 and UN. Immersion in the HNO_3-H_2O etchant for carbides produced only a slight edge darkening of the angular inclusions present. It is felt that this is due to a pickling effect on the exposed edges of the UN inclusions rather than an indication that carbon is present. The chemical analysis for carbon supports the view that no carbon should be seen microscopically, since samples from the dingot material analyzed only 0.004 w/o carbon (see Table 2).

Over-all inclusion distribution was quite uniform from top to bottom. However, random areas within any sample may show marked differences in the appearance of the fields. Typical variations can be seen in Figures 1 through 10. Similar areas may be found in any sample that was examined. Figures 9 and 10 show the results of the carbide etchant mentioned above.

The metallographic estimation of the hydrogen content was 3 to 3.5 ppm in the top of the dingot and 2 to 3 ppm at the bottom. Vacuum-fusion analyses (see Table 1) showed about 2.6 ppm of hydrogen throughout the dingot. One specimen from the top and one from the bottom was analyzed by the warm-extraction method to preserve the identity of the samples; the samples were photographed before and after analysis to show depletion of the hydrogen. Photomicrographs of these samples after extraction are shown in Figures 11 and 12.

*Numbers reported are those assigned by MCW.

TABLE 2. CHEMICAL-ANALYSIS RESULTS

Material	Analysis, w/o	
	Carbon	Nitrogen
As-reduced Dingot X-1073 top	0.004	0.002
As-reduced Dingot X-1073 center	0.004	0.003
As-reduced Dingot X-1073 bottom	0.004	
Forged Dingot X-1176B	0.005	0.003
Forged Dingot X-1176B	0.004	0.002
Forged Dingot X-1176B	0.005	0.002
Extruded Dingot 4169	0.006	0.003
Extruded Dingot 4169	0.004	0.003
Extruded Dingot 4169	0.004	0.002
As-cast Ingot 2496 top	0.042	0.008
As-cast Ingot 2496 center	0.043	0.009
As-cast Ingot 2496 bottom	0.043	0.007
Extruded ingot	0.035	0.008

TABLE 3. SPECTROGRAPHIC-ANALYSIS RESULTS

Material	Analysis, ppm in U_3O_8												
	Be	Si	Mn	Fe	Mg	Pb	Cr	Sn	Ni	Al	Mo	Cu	Co
As-reduced Dingot X-1073 top	0.4	10	6	30	3	3	10	--	30	50	50	5	20
As-reduced Dingot X-1073 bottom	0.15	20	5	20	3	1	10	--	30	50	5	2	40
Forged Dingot X-1176B	0.25	10	6	30	3	1	10	--	20	40	5	8	30
Extruded Dingot 4169	0.05	20	5	20	3	1	7	--	10	100	5	40	40
As-cast Ingot 2496 top	0.7	20	7	30	2	1	10	--	15	30	5	10	40
As-cast Ingot 2496 bottom	0.25	30	7	40	2	1	10	--	20	40	5	10	40
Extruded ingot	0.05	40	6	40	2	2	8	20	10	50	5	2	30

Polarized-light examination showed the structure to be typical of cast uranium. Hydrides were shown to occur in grain boundaries in all specimens. This was also true in the examinations described below. Figures 13 and 14 show structures at the center and bottom of the dingot.

Forged Dingot

Sections from forged Dingots X-1176B, X-1317, X-1319, and X-1324 were sampled and examined.

The general appearance of forged Dingot X-1176B was similar to the as-reduced dingot with the exception that the hydrogen content was much less, being estimated by metallographic means to be 1 ppm or less. This was borne out by vacuum-fusion analysis, which reported values of 0.6 and 0.7 ppm at the center of the forging.

Carbides again were not evident after immersion in the HNO_3-H_2O etchant. Some very small inclusions appeared to have darkened by the etchant but subsequent examination at high magnification showed only edge darkening (or pickling), as previously noted. Figures 15 through 17 show typical photos (in the polished condition) of the forged material.

Forged Dingots X-1317, X-1319, and X-1324 showed appreciably more hydrogen than was present in Dingot X-1176B. Metallographic analysis indicated the hydrogen in forged Dingot X-1317 to be on the order of 3.5 to 4.5 ppm while forged Dingots X-1319 and X-1324 contained somewhat less. These were estimated to contain 2.5 to 3 ppm.

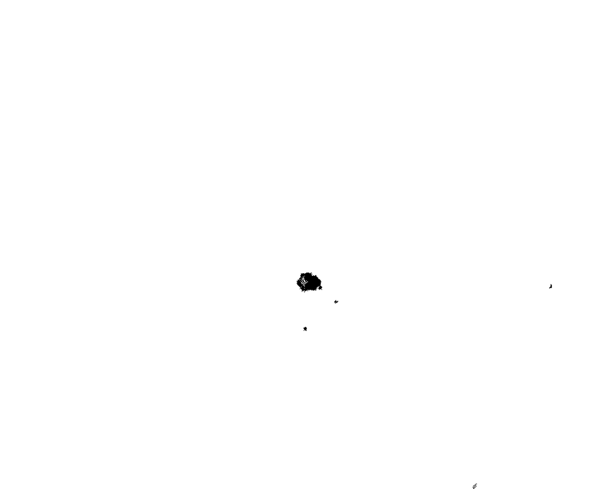
These samples also showed no visible UC inclusions. The UN inclusions, however, were approximately 2-1/2 times more numerous than in forged Dingot X-1176B above.

Structure evident in all samples were of recrystallized alpha uranium with average grain diameters ranging from 0.075 to 0.120 mm, as determined by comparison with the uranium grain-size chart prepared by HAPO.

Extruded Dingot

The tubes examined were extruded from Dingot 4169 after scalping and forging from a 1120 F salt bath to a billet 5-5/8 in. in diameter by 46 in. long. During extrusion the billet temperature was 1150 to 1170 F and the container and die temperatures were 900 F. The tubing was beta transformed after forging.

250X N37083

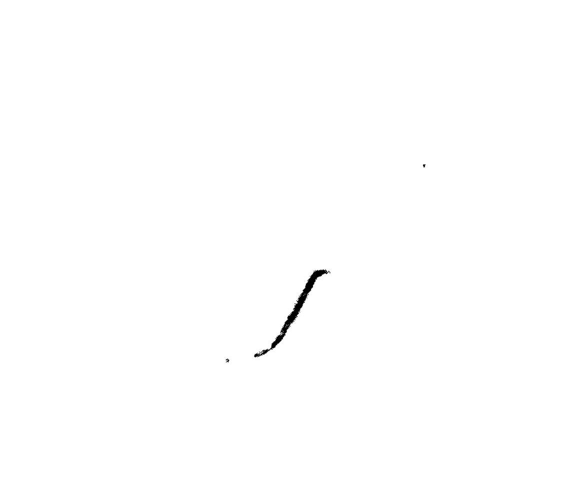


250X N37084

FIGURE 1. AS-REDUCED DINGOT TOP, SHOWING UN INCLUSIONS

As polished.

FIGURE 2. ANOTHER AREA OF THE SAME SPECIMEN SHOWN IN FIGURE 1



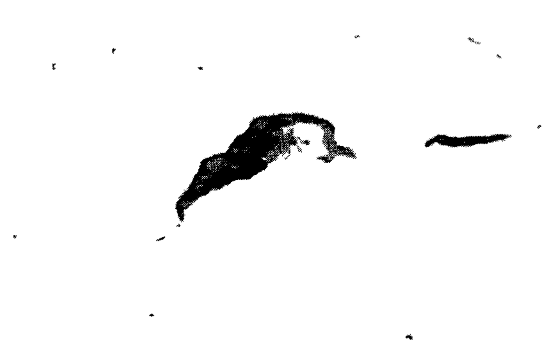
250X N37085

250X N37086

FIGURE 3. AS-REDUCED DINGOT TOP, SHOWING UN AND UH_3 INCLUSIONS

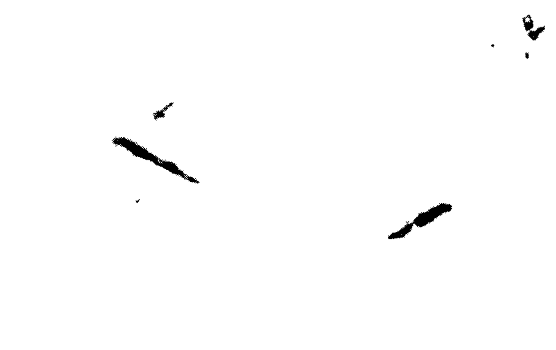
As polished – before warm-extraction hydrogen analysis.

FIGURE 4. ANOTHER AREA OF THE SAME SPECIMEN SHOWN IN FIGURE 3



250X N37087

FIGURE 5. ANOTHER AREA OF THE SAME SPECIMEN SHOWN IN FIGURE 3



250X N37088

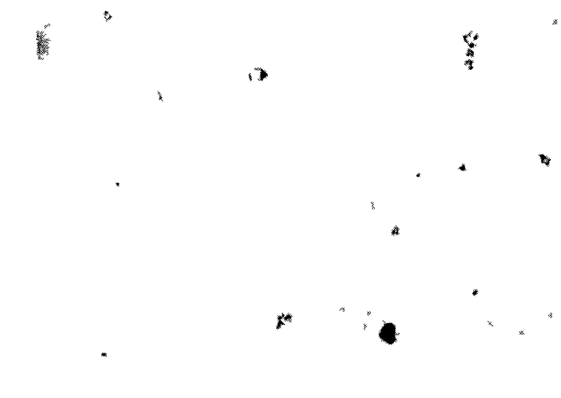
FIGURE 6. AS-REDUCED DINGOT CENTER, SHOWING UN AND UH_3 INCLUSIONS

As polished.

250X N37089

FIGURE 7. AS-REDUCED DINGOT BOTTOM, SHOWING UH_3 INCLUSIONS

Before warm-extraction hydrogen analysis.



250X N37090

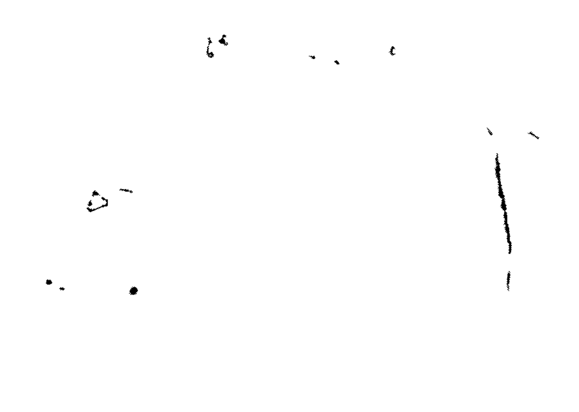
FIGURE 8. AS-REDUCED DINGOT BOTTOM, SHOWING UN AND UH_3 INCLUSIONS

As polished.

250X N37091

FIGURE 9. AS-REDUCED DINGOT TOP, SHOWING UN INCLUSIONS

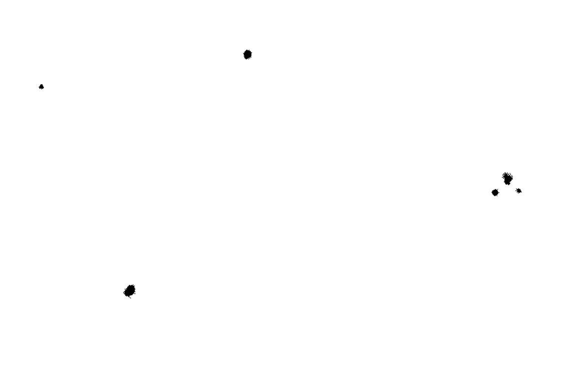
HNO_3-H_2O etch.



250X N37092

FIGURE 10. AS-REDUCED DINGOT CENTER, SHOWING UN AND UH_3 INCLUSIONS

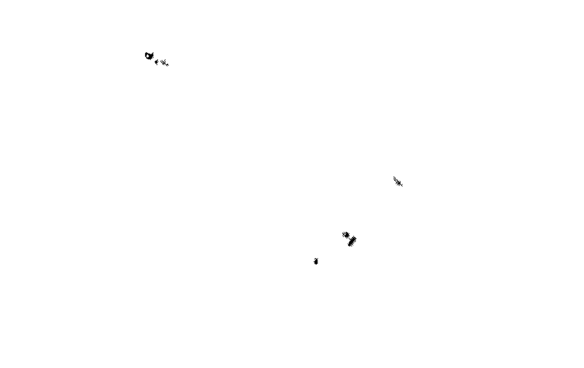
HNO_3-H_2O etch.



250X N37093

FIGURE 11. AS-REDUCED DINGOT TOP, SHOWING UN INCLUSIONS

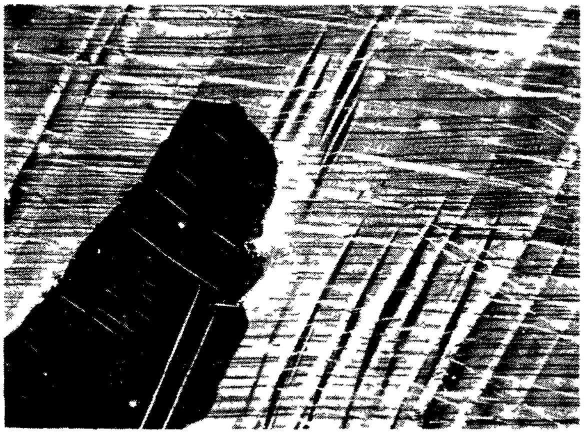
After warm-extraction hydrogen analysis. As polished.



250X N37094

FIGURE 12. AS-REDUCED DINGOT BOTTOM, SHOWING UN INCLUSIONS

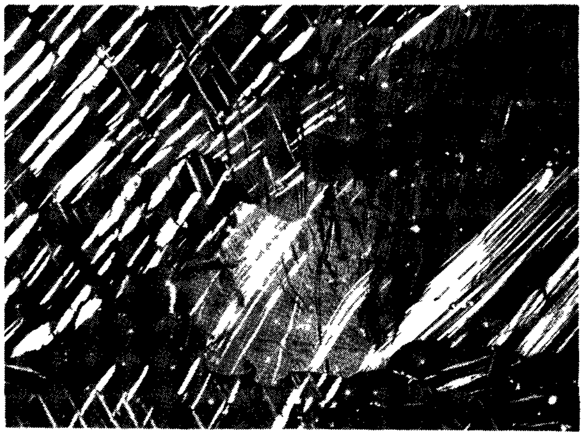
After warm-extraction hydrogen analysis. As polished.



100X N37095

FIGURE 13. AS-REDUCED DINGOT CENTER

Note UH_3 inclusions in grain boundary.



100X N37096

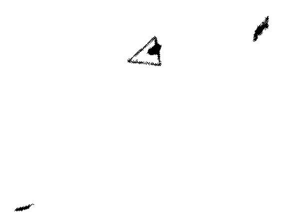
FIGURE 14. AS-REDUCED DINGOT BOTTOM

Polarized light.

250X N37097

FIGURE 15. FORGED DINGOT X-1176B, SHOWING UN INCLUSIONS

As polished.



500X N37098

FIGURE 16. FORGED DINGOT X-1176B, SHOWING UN AND UH_3 INCLUSIONS

As polished.

250X N37099

FIGURE 17. FORGED DINGOT X-1176B, SHOWING UN AND UH_3 INCLUSIONS

As polished.

Metallographic examination of this tubing revealed a duplex-type structure consisting of clusters of relatively large grains, similar in appearance to the transformed alpha structure after beta annealing, which were interspersed in the structure normally expected in alpha-fabricated material. Figures 18 and 19 show examples of this structure.

Thin sections from the forged dingot material were heat treated in an attempt to reproduce this structure. Water quenching after 5 min at 725 C and subsequent annealing at 600 C for 2 hr produced structures that would be expected after these treatments but which had no correlation with the structures present in the extruded material. These results are shown in Figures 20 and 21.

The hydrogen content of the samples examined was appreciably higher than in the as-reduced or forged dingot uranium. Metallographic estimation placed the value at 3.5 to 4 ppm; this was partially verified by vacuum-fusion analyses, which reported amounts of 4.4 and 2.2 ppm in the two samples analyzed.

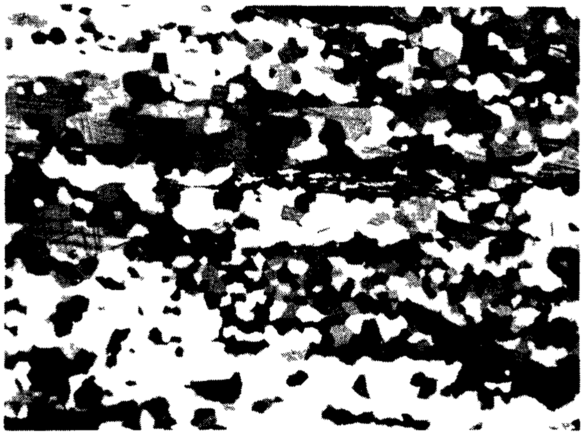
General inclusion content, excepting the high amount of hydrogen, was quite low (Figures 22 and 23), no carbides or oxides being visible. Nitride inclusions were present in approximately the same distribution as in derby bottom.

An attempt to rate stringering of inclusions(2) due to extrusion was unsuccessful. This could be attributed to the over-all cleanliness of dingot metal.

Ingot Uranium

As-Cast Ingot

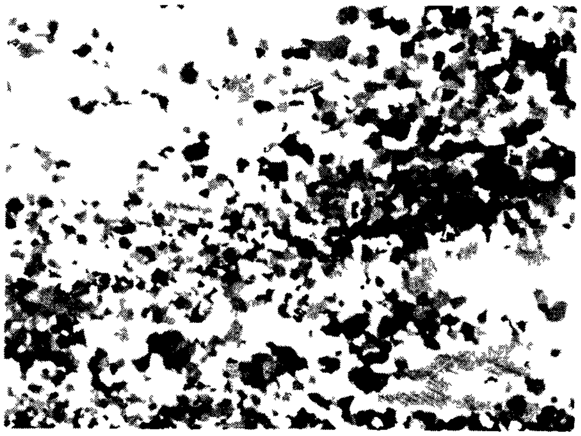
Samples from Ingot 2496 representing top, center, and bottom were evaluated. The inclusion content of this material was radically different than that in the dingot uranium. The extreme top of the ingot showed a profusion of UN inclusions and scattered particles of MgF_2 slag, and was quite similar in appearance to a sample from the top of as-reduced derby uranium (Figure 24). This layer extended approximately 1/4 in. from the upper surface of the ingot. Immediately beneath the UN layer were inclusions that appeared to be UN-UC combinations, as shown in Figure 25. These, in turn, were followed by rather large carbide inclusions and then by smaller particles which again seemed to be UN and UC in combination, as the centers of some of the inclusions were not affected by the HNO_3-H_2O etchant. Examples of these types of inclusions are shown in Figures 26



100X N37100

FIGURE 18. EXTRUDED DINGOT URANIUM

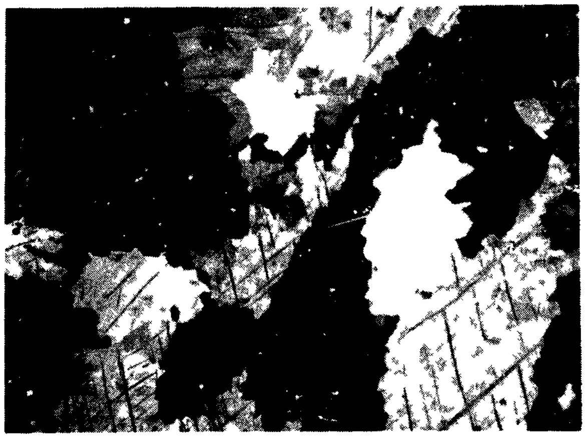
Polarized light.



100X N37101

FIGURE 19. EXTRUDED DINGOT URANIUM, SHOWING THE VARIATION IN STRUCTURE

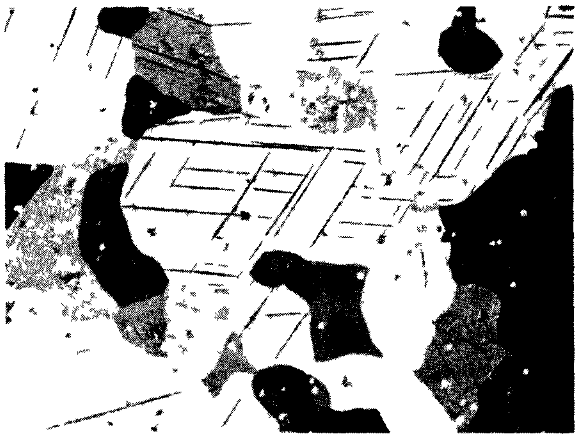
Compare with Figure 18. Polarized light.



100X N37102

FIGURE 20. FORGED DINGOT URANIUM HEAT TREATED 5 MIN AT 725 C AND WATER QUENCHED

Polarized light



100X N37103

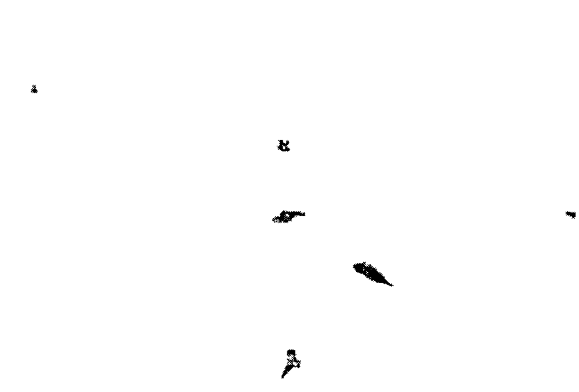
FIGURE 21. FORGED DINGOT URANIUM HEAT TREATED 5 MIN AT 725 C AND WATER QUENCHED, AND 2 HR AT 600 C AND WATER QUENCHED

Polarized light.

250X N37104

FIGURE 22. EXTRUDED DINGOT URANIUM, SHOWING UN AND UH_3 INCLUSIONS

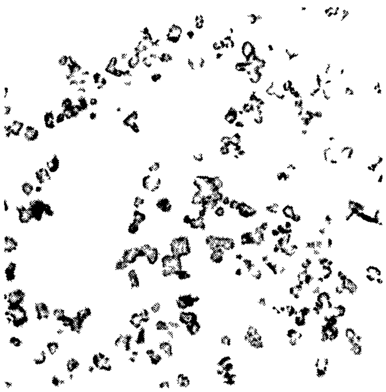
Longitudinal section. HNO_3-H_2O etch.



250X N37105

FIGURE 23. EXTRUDED DINGOT URANIUM, SHOWING UN AND UH_3 INCLUSIONS

Transverse section. As polished.



250X N37106

FIGURE 24. INGOT URANIUM TOP, SHOWING UN INCLUSIONS

HNO_3-H_2O etch.

250X N37107

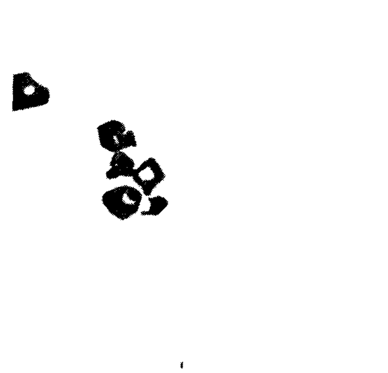
FIGURE 25. INGOT URANIUM TOP, SHOWING UN-UC INCLUSIONS

HNO_3-H_2O etch.

250X N37108

FIGURE 26. INGOT URANIUM TOP, SHOWING UC INCLUSIONS

HNO_3-H_2O etch.



250X N37109

FIGURE 27. INGOT URANIUM TOP, SHOWING UC-UN INCLUSIONS

HNO_3-H_2O etch.

250X N37110

FIGURE 28. INGOT URANIUM, SHOWING UC AND UC-UN INCLUSIONS 5 IN. FROM TOP

HNO_3-H_2O etch.

250X N37111

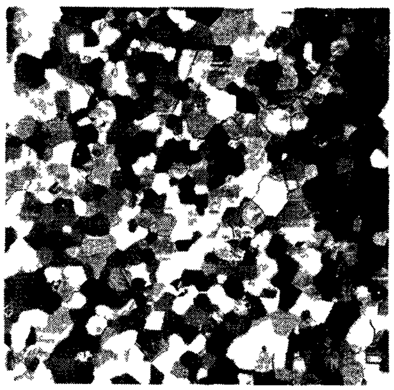
FIGURE 29. INGOT URANIUM CENTER, SHOWING UC AND UH_3 INCLUSIONS

As polished.

250X N37112

FIGURE 30. INGOT URANIUM BOTTOM, SHOWING UC AND UH_3 (IN GRAIN BOUNDARY) INCLUSIONS

Light electro etch.



100X N37113

FIGURE 31. EXTRUDED INGOT, SHOWING UNIFORM STRUCTURE

Polarized light.

250X N37114

FIGURE 32. EXTRUDED INGOT URANIUM, SHOWING UC INCLUSIONS

As polished.

through 28. The predominant type of inclusion throughout the balance of the ingot was the carbide. Some hydrides were present, occurring in grain boundaries as in other types of uranium, but very few, if any, identifiable nitrides were present. Figures 29 and 30 present examples of inclusions and structures that were in the lower part of the ingot.

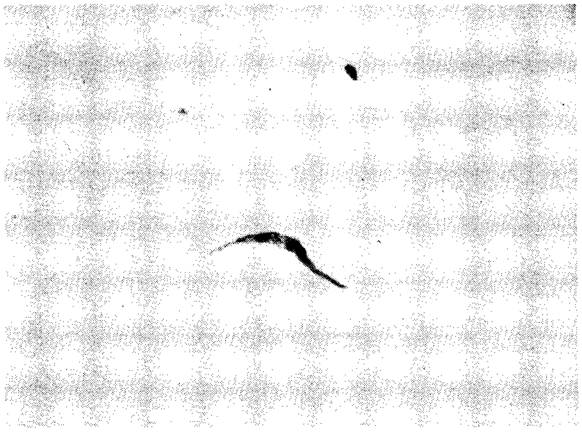
Extruded Ingot

No ingot material in the as-forged condition was available but a small sample of extruded ingot uranium was examined. There was no evidence of duplex structure in this material (see Figure 31) as was present in extruded dingot uranium. Inclusions present consisted primarily of UC, with a few hydrides being seen. UN inclusions were not noticed in this material. The carbides occasionally were in the form of stringers, as in Figure 32.

Hot-Stage Microscope

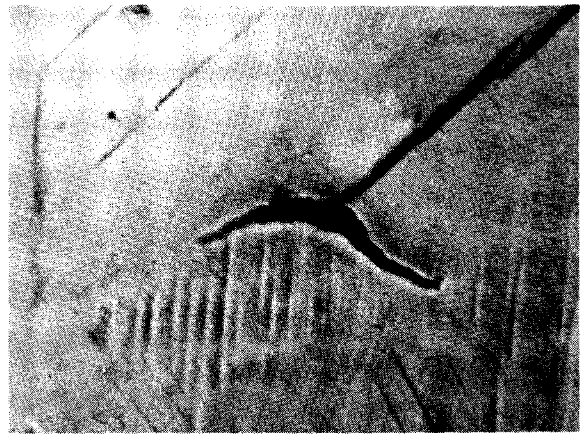
A section from the center of Dingot X-1073 was placed in the hot-stage microscope and examined at temperatures up to 1500 F. The maximum pressure in the system during the run was 2×10^{-5} mm of mercury. It required 30 min to reach 400 F and the temperature was held at this point for 20 min. Heating was resumed to about 1500 F, taking approximately 1 hr to reach that point.

Figures 33 through 36 show the inclusion under study at room temperature, 290 F, 620 F, and 1300 F. It can readily be seen that there was little noticeable change in the inclusion except for a slight darkening. However, after removal from the hot stage, the area previously filled by the hydride inclusion was seen to be predominantly void. This can be seen in Figures 37 and 38. Light repolishing showed the entire surface to contain only voids or partial voids where hydrides had been previously present. A specimen heated to only 500 F and reground to a depth of 1. 5 mm below the original surface also showed voids where UH_3 inclusions presumably had been previously located.



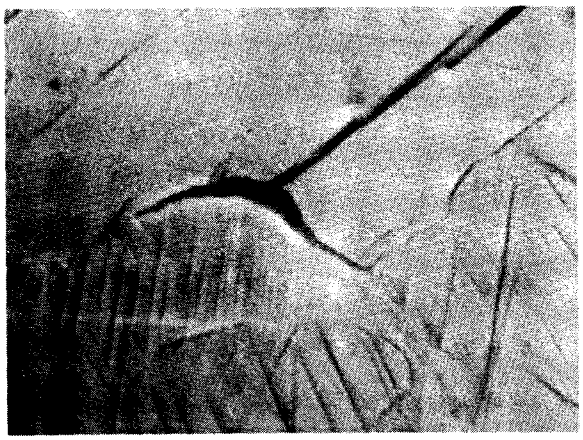
150X N37115

FIGURE 33. AS-REDUCED DINGOT CENTER IN HOT STAGE BEFORE HEATING



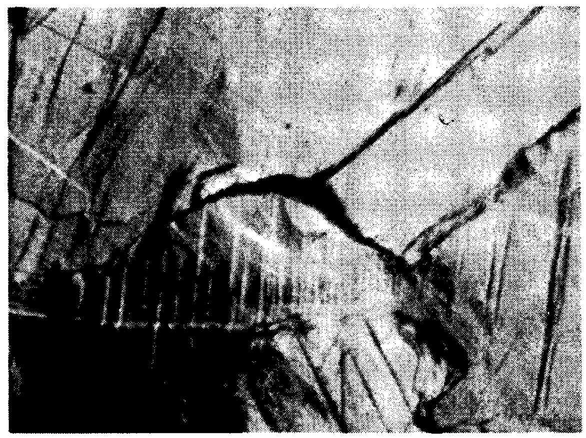
250X N37116

FIGURE 34. AS-REDUCED DINGOT CENTER IN HOT STAGE AT 290 F



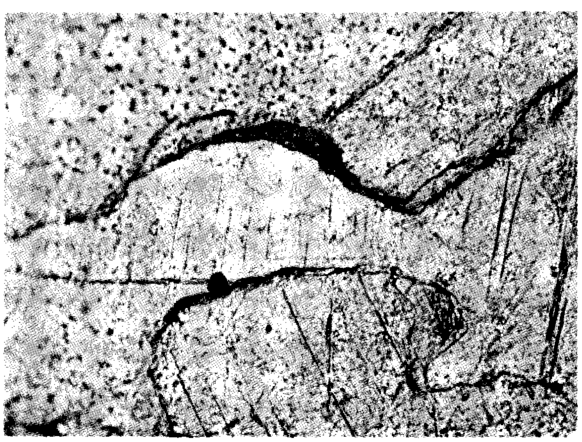
250X N37117

FIGURE 35. AS-REDUCED DINGOT CENTER IN HOT STAGE AT 620 F



250X N37118

FIGURE 36. AS-REDUCED DINGOT CENTER IN HOT STAGE AT 1300 F



250X N37119

FIGURE 37. AS-REDUCED DINGOT CENTER AFTER REMOVAL FROM HOT STAGE

No surface preparation.

500X N37120

FIGURE 38. AS-REDUCED DINGOT CENTER AFTER REMOVAL FROM HOT STAGE

No surface preparation.

CONCLUSIONS

The results of this study show that dingot uranium has over-all purity comparable with that of as-reduced derby uranium, with the exception of hydrogen content. If a means were found to lower this hydrogen to a level comparable with that of ingot uranium, there should be few problems in fabrication or other applications due to nonmetallic inclusions in the metal.

REFERENCES

(1) Dickerson, R. F., Gerds, A. F., and Vaughn, D. A., "Metallographic Identification of Non-Metallic Inclusions in Uranium", Transactions of the AIME, Journal of Metals 456 (April, 1956).

(2) Report of the Metallographic Subcommittee of the Metal Quality Working Committee, DPST-55-234 (April, 1955).

DMC:RFD/jpl