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FORMATION OF CORROSION-RESISTANT
OXIDE FILM ON URANIUM

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE GASEOUS DIFFUSION PLANT

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OXIDE FILM ON URANIUM

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ABSTRACT

A vacuum heat-treatment method has been developed for coating uranium metal with a protective uranium oxide film. No corrosion was observed on coated uranium coupons after they were exposed for several hundred hours in a corrosion test bath at 95°C and 100% relative humidity. The metallic uranium was coated by vacuum heat treatment at 625°C, using a controlled amount of oxygen. Varying the amount of oxygen added to the furnace provided control of film thicknesses in the range from 0.0002 to 0.001 in. The hard, blue film was nonwetting and very adherent; it had a surface finish equivalent to that on the original uranium metal.

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FORMATION OF CORROSION-RESISTANT OXIDE FILM ON URANIUM

INTRODUCTION

Coating or plating metallic uranium to protect it from corrosion under moist atmospheric conditions has been investigated by many researchers. The principal objective of these investigations was to prevent deterioration of the metal and formation of urano-uranic oxide (U_3O_8) on its surface. Many approaches have been used to coat metallic uranium with an adherent film that protects it from oxidation. Some of these efforts were directed toward applying a protective uranium oxide layer. Flint, et al¹ formed a thin film of uranium dioxide (UO_2) with a thickness of about 2,000 Å on cold-rolled uranium by anodic oxidation in an organic electrolyte; they obtained moderate passivity. Campbell, et al² vapor deposited thin films of chromium, molybdenum, niobium, and zirconium on metallic uranium with generally poor adhesion and porosity. Waldrop, et al³ applied coatings of organic materials to metallic uranium and also plated uranium with nickel. Gore and Seegmiller⁴ electroplated uranium with nickel, but had difficulty in obtaining nonporous deposits of about 0.001 in. thickness. All of these coatings, when exposed to a moist atmosphere, protected the uranium for only a short period of time.

Watts and Cayless⁵ coated metallic uranium by exposing it to the atmosphere to form UO_2 and U_3O_8 and then heating it in a vacuum to form uranium monoxide (UO). They also formed the monoxide layer by heating uranium in steam at a pressure of < 10 mm of mercury. The monoxide layer was bright and metallic, and protected the metal from corrosion at room temperature. Nevertheless, the monoxide layer did not protect the uranium very long in a humid atmosphere at an elevated temperature.

The authors of this report worked concurrently on two methods for protecting uranium metal. In one method, they electroless plated uranium with nickel⁶ to form a thin, adherent, corrosion-resistant coating. The second method, which is described in this report, was the controlled oxidation heat treatment of uranium metal to form a protective uranium oxide film on the surface.

SUMMARY

A vacuum heat-treatment method has been developed for coating metallic uranium with an adherent protective film of uranium oxide. Uranium coupons with the protective film have been exposed for several hundred hours in a corrosion test bath at 95°C and 100% relative humidity without corroding. The film is prepared by vacuum heat-treating the metallic uranium at 625°C for 1 hr while controlling the amount of oxygen being metered into the furnace.

Film thicknesses ranging from 0.0002 to 0.001 in. have been prepared and corrosion tested; the film thickness can be controlled to less than ± 0.0001 in. The oxide film is hard, nonwetting, and very adherent. The resulting surface finish of the metal is equivalent to that of the original finish.

EXPERIMENTAL

Protective films of UO and UO₂ were formed on metallic uranium during studies involving improvement of the conditions in the heat-treatment process. Three methods were used to control the supply of oxygen. A very thin film (< 0.0001 in.) of UO and UO₂ was formed on the surface of the uranium by vacuum heat treatment. The oxygen supply, in this case, was from reduction of some UO₂ on the uranium surface and the limited O₂ available in the atmosphere at a low vacuum. A thicker oxide film was formed by using a limited and controlled supply of oxygen from specially prepared U₃O₈. A film of the desired thickness was more readily formed during the heat-treatment process by using standard leaks to supply the exact amount of oxygen for the specified film thickness.

THIN OXIDE FILMS BY VACUUM HEAT TREATMENT

Prior to nickel plating⁶, heat-treating the metallic uranium at 625°C in a vacuum at a pressure of $< 10 \mu$ for 1 hr outgassed the metallic uranium and also made it more resistant to oxidation in the 95°C plating solution. Photomicrographs at 2,000X of a cross section of the heat-treated uranium show the formation of a very thin film (< 0.0001 -in.-thick) on the surface, figure 1. X-ray diffraction patterns of the film identify it as a mixture of UO and UO₂.

Metallic uranium which had not been cleaned with acid to remove the natural brown-colored oxide became silvery in appearance during the heat-treatment process. The reaction of the metallic uranium with the oxide on the surface is theorized⁷ as follows:

The appearance of the silvery film remained unchanged in the laboratory environment at room temperature over an observation period of several months; the film deteriorated in a few hours, however, when exposed in a corrosion test bath to 100% relative humidity at 95°C.

THICKER OXIDE FILMS USING URANO-URANIC OXIDE

A thicker oxide film was formed on the surface of uranium coupons (1 x 1-1/2 x 1/8-in.) by having a small amount of modified urano-uranic oxide (U₃O₈) in the vacuum furnace during the heat treatment. This special oxide was prepared by heating uranium peroxide at 700°C for 30 min. This temperature and conversion time produced an oxide of uranium⁸ containing more oxygen than the stoichiometric amount (U₃O_{8+x}

2000X

Figure 1
OXIDE FILM ON URANIUM
AFTER HEAT TREATMENT IN VACUUM AT 625°C.

where x represents the variation from stoichiometry). This superstoichiometric oxide provides a limited supply of oxygen under the conditions in the vacuum furnace.

The thicker oxide film was prepared by placing the U_3O_8 in a platinum dish in the furnace as a source of oxygen when heat-treating uranium coupons. The sample uranium coupons were preliminarily cleaned by vapor degreasing with trichloroethylene, scrubbing with a scouring powder, rinsing with distilled water, dipping in an 8 N nitric acid solution for 20 min, and rinsing again with distilled water. The coupons were dried with acetone and immediately placed in the furnace along with the container of U_3O_8 . The furnace was evacuated, then purged three times with argon and evacuated to $< 10 \mu$ before starting the heating cycle. The temperature of the furnace was raised to 625°C at the rate of about 250°C/hr and maintained at 625°C for 1 hr. The furnace was then allowed to cool, under vacuum, to room temperature. The coupons were removed from the furnace and evaluated for corrosion resistance in the corrosion test bath; the resultant surfaces are shown in figure 2. The blue coating was unaffected after long periods of exposure in the corrosion test bath.

Initially, films were heat-treated 1/2 to 2 hr. The period of heat treatment appeared to have no significant effect on the corrosion resistance of films having the same thickness. For consistency, however, it was decided to standardize the time of heat treatment at 1 hr for the tests with U_3O_8 in the furnace.

Coupons were heat-treated for 1 hr at temperatures of 500, 550, 600, and 625°C . The corrosion resistance of the oxide film improved as the temperature was increased. To avoid the alpha-beta phase change which occurs at 662°C^9 in the uranium, only a few coupons were heat-treated above 625°C . During this phase change, there is a growth in the size of the crystals; when the uranium cools and returns to the alpha phase, warpage can occur in large pieces.

Oxide films were prepared by heat-treating uranium coupons in the presence of 0.55, 1.1, and 1.65 g of $U_3O_8/\text{sq in.}$ of coupon surface area. Cross sections in figure 3 show the film thickness to be approximately proportional to the amount of U_3O_8 used in the preparation; i.e., the use of twice the amount of oxide in the heat-treatment process produced a film about twice as thick. Using varying amounts of U_3O_8 , oxide films were formed with thicknesses ranging from 0.0002 to 0.001 in. These blue films were exposed in the corrosion test bath for evaluation of their resistance. Some of the films showed no visible deterioration after 525 hr in the test bath. The optimum film thickness for resisting corrosion was found to range from 0.0002 to 0.0005 in.

CONTROLLED THICKNESS OF OXIDE FILM USING PURE OXYGEN

Various thicknesses of the oxide film were formed on metallic uranium coupons using a controlled gas supply of oxygen in place of the superstoichiometric U_3O_8 . The oxygen was injected at the front of the furnace,

PHOTO NO. PH-67-1011

AFTER 525 HR IN TEST BATH

383 HR IN TEST BATH

525 HR IN TEST BATH

11

Figure 2
URANIUM COUPONS HEAT-TREATED AT 625°C WITH U_3O_8

0.55 g U_3O_8 /sq in.

500X

1.1 g U_3O_8 /sq in.

500X

1.65 g U_3O_8 /sq in.

500X

Figure 3
OXIDE FILM THICKNESS
Varied U_3O_8 /sq in. Uranium Surface Area

figure 4, with a manifold containing three standard leaks (each rated 900 micron-cu ft/hr) and attached to an oxygen supply (purity > 99.9%). The exhaust and vacuum pump were attached at the back of the furnace to evacuate the oxygen flow over the uranium coupons.

The uranium coupons were cleaned, pickled, and heat-treated as previously described, except for oxygen being admitted through one, two, or three leaks when the temperature of the furnace reached 625°C. The first heat treatments were made to determine the feasibility of controlling the film thickness by the amount of oxygen metered into the furnace, and whether films heat-treated by this process were corrosion resistant, and to establish the proper range of oxygen flow. Approximately 30 standard cc of oxygen was injected through a single leak during the 1-hr period. All tests were conducted using two 1 x 1-1/2 x 1/8-in. coupons and, for the defined surface area, the film thickness was approximately 0.00025 in. per leak (figure 5). This value is in close agreement with the calculated thickness (0.0003 in.), using the theoretical density of UO_2 . This calculation was used to determine the leak capacity desired for these experiments.

Oxide films, figure 5, were subsequently prepared by using one, two, or three oxygen leaks. The injection of oxygen through two and three leaks into the furnace gave film thicknesses of about twice and three times, respectively, that of a film formed using only one leak.

A uranium coupon prepared using one standard oxygen leak was exposed in the corrosion test bath for 378 hr and showed no visible deterioration, figure 6. A photomicrograph at 500X of a cross section of the same coupon, figure 7, shows the film to be in excellent condition.

Uranium coupons were heat-treated with sufficient oxygen to form oxide films ranging in thickness from 0.0002 to 0.001 in. The film thickness was controlled to less than ± 0.0001 in. by using the correct number of leaks for a predetermined period of time. These bluish oxide films were then exposed in the corrosion test bath. The optimum film thickness for resisting corrosion was again found to range between 0.0002 and 0.0005 in.

CORROSION TEST RESULTS

Several hundred metallic uranium coupons were heat-treated under various conditions to determine the best technique for preparing a corrosion resistant oxide film. These films were corrosion tested in 100% relative humidity air at 95°C; the results are summarized in table 1.

Figure 4

VACUUM FURNACE EQUIPPED WITH THREE STANDARD LEAKS

ONE LEAK

500X

TWO LEAKS

500X

THREE LEAKS

500X

Figure 5
OXIDE FILM THICKNESS
USING STANDARD LEAKS OF OXYGEN

Figure 6

2X

URANIUM COUPON HEAT-TREATED AND
EXPOSED IN TEST BATH FOR 378 HOURS

Figure 7

500X

CROSS SECTION OF OXIDE FILM
AFTER EXPOSURE IN TEST BATH FOR 378 HOURS

Table 1
OXIDE FILMS ON METALLIC URANIUM

Preparation		Properties			
Oxygen Source	Heat-Treatment Temperature, °C	Film Thickness, in.	Color of Film	Test Bath Exposure Before Corroding, hr	
				Avg	Range
None*	625	< 0.0001	Silvery	10	5 to 50
U ₃ O ₈	625	0.0002 to 0.001	Blue	200	100 to > 500**
Metered Pure Oxygen	625	0.0002 to 0.001	Blue	600	350 to > 1700***

*Except sample and furnace residuals and leaks.

**See figure 2.

***See figure 8.

All corrosion resistant films have a hardness value of 60 to 65 Rockwell C, as compared to 20 to 25 for the metallic uranium. The surface finish is equivalent to the original finish. The film thickness was readily controlled to less than ± 0.0001 in., in the range of optimum thickness, by controlling the amount of oxygen metered into the furnace.

CORROSION RESISTANCE OF FILMS PREPARED WITH U₃O₈ AND PURE OXYGEN

The blue films prepared with metered pure oxygen have greater corrosion resistance than those prepared in the presence of U₃O₈. The film on three coupons prepared with pure oxygen showed no deterioration after being exposed in the test bath about 1,700 hr, figure 8. The film prepared with U₃O₈, figure 2, showed a slight deterioration on one of the coupons after 383 hr of exposure in the test bath, although other samples withstood more than 500 hr of testing. The use of standard leaks to meter the oxygen into the furnace provided much better control of the oxygen supply in the furnace and the film thickness. The excess oxygen in the superstoichiometric U₃O₈ possibly varied from batch to batch, thereby varying the amount of oxygen available during the heat treatment. The use of standard

PHOTO NO. PH-67-1013

AFTER 1680 HR IN TEST BATH

AFTER 1704 HR IN TEST BATH

AFTER 1792 HR IN TEST BATH

Figure 8
URANIUM COUPONS HEAT-TREATED WITH OXYGEN BLEED

leaks, furthermore, permitted the injection of the oxygen only at the heat treatment temperature of 625°C ; the excess oxygen in the U_3O_8 was available in the system during the heating of the furnace and probably reacted with the uranium at lower temperatures. These differences in conditions probably accounted for the better quality of the film when the oxygen leaks were used.

EFFECT OF SMOOTH SURFACE FINISH

The best protective oxide film was obtained on coupons with a surface finish of 80 $\mu\text{in. (rms)}$ or better. Pits and irregularities in the surface of the uranium metal were the weakest areas of the film; corrosion first occurred here. Inclusions, or metal edges, were more susceptible than the flat, clean surfaces, figure 9. However, when the corrosion occurred in these small areas, it did not readily spread over the entire coupon, but was usually confined to a small area, as shown in the upper left hand corner of the coupon in figure 9. Magnification of the corroded spot area shows good adherence of the film around the spot and adherence of some of the film in the corroded area.

EXAMINATION BY ELECTRON MICROSCOPE

An electron micrograph at 36,000X, figure 10, was made of a replica of a cross section of a film exposed for 378 hr in the test bath, figure 7. The film had been prepared using pure oxygen in the heat-treatment furnace. There is no visible evidence of any deterioration of the film or damage to the uranium. The interface is visible in the electron micrograph; there appears to be very little difference between the metal and the film near the interface, indicating a high degree of continuity and integrity.

DISCUSSION

POSTULATED MODE OF OXIDE FILM FORMATION

A very thin film first forms on the metallic uranium; then as more oxygen is slowly admitted to the furnace, the original UO consumes the oxygen, forming some UO_2 and replenishing the UO at the uranium- UO interface.

The interface of the film and metal continues to move into the metal as more oxygen is added. The film probably maintains about the same chemical bonding as the initial film formed. There is probably diffusion of oxygen through the film to the metallic uranium, forming more UO at the interface. There appears to be a gradient of UO_2 to UO content from the surface inward, as illustrated in figure 11. A single analytical determination, performed by National Lead of Ohio, Cincinnati, Ohio¹⁰, on a sample provided by the authors, showed the oxygen-to-uranium ratio in the total film to be 1.9 in a film of about 0.0005-in. thickness using U_3O_8 as the source of oxygen. It was initially assumed that the corrosion protection from very thin films was from the UO and that the UO_2 present was

2 X

10 X

Figure 9
COUPON HEAT-TREATED WITH OXYGEN
AND EXPOSED IN TEST BATH FOR 1704 HOURS

↑
URANIUM METAL BASE

↑
OXIDE FILM

36,000X

Figure 10
ELECTRON MICROGRAPH OF A REPLICA OF A CROSS SECTION OF
THE URANIUM COUPON AFTER
EXPOSURE IN TEST BATH FOR 378 HOURS

Figure 11
POSTULATED MODE OF OXIDE FILM FORMATION

undesirable; however, the thicker films (0.0002 to 0.001 in.), which are very resistant to corrosion, are essentially all UO_2 (110 highly preferred crystal structure), according to X-ray diffraction study.

ADVANTAGES OF OXIDE FILM

The oxide film has several advantages over other films and coatings used for protecting uranium metal from corrosion in moist atmospheres. The life of the 0.0003-in.-thick film is several times longer than that of other coatings known to the authors, including their excellent electroless nickel plate⁶. A principal advantage over plating is there is no appreciable removal of uranium from the surface, only the thin adherent layer of oxide, in the preparation; whereas in plating⁶, an average of about 0.0007 in. of uranium is removed from all surfaces in the pickling step. In forming an oxide film of 0.0002 to 0.0003 in., half or more of the film thickness is below the level of the initial metal surface. Therefore, there are only very small changes in the dimensions of the uranium metal; the final protected uranium piece contains essentially all of the original uranium content.

DECREASED CORROSION RESISTANCE FROM AIR INLEAKAGE

A leak in the gasket seal at the front of the furnace permitted a small inleakage of atmospheric air during the initial heat treatment studies. Several coupons were heat-treated before the leak was eliminated. The oxide film which formed during the inleakage of air had a good appearance and was about the thickness expected; however, the film soon deteriorated in the corrosion test bath. A leaktight vacuum furnace is necessary to provide very precise control of the atmosphere in the furnace for producing a corrosion-resistant oxide film. A thicker gasket was made and installed, which reduced the leak rate to less than 1 micron-cu ft/hr. Thereafter, the quality of films prepared by all techniques was much improved, see table 1.

NONWETTABLE PROTECTIVE OXIDE FILMS

A quick test was recognized for estimating the corrosion resistance quality of the oxide film. Coupons coated with the oxide were dipped in a beaker of distilled water and observed for wettability, prior to quantitative testing in the corrosion test bath. Coupons that shed the water, figure 12, upon removal from the beaker, were found to be corrosion resistant; they withstood several hundred hours in the test bath. If the surface of the coupon *wetted* in the beaker test, it was also noted that they deteriorated in a short period of time in the corrosion test bath at 95°C and 100% relative humidity.

The nonwettability of the film is probably related to the crystal orientation of UO_2 . An X-ray diffraction pattern of a nonwetable film showed a highly preferred 110 crystal face. X-ray patterns of coupons which wetted showed little or no preferred orientation. Some U_3O_8 was detected

PHOTO NO. PH-67-1012

SAMPLE DOES NOT WET

SAMPLE WETS

Figure 12
CORROSION RESISTANCE OF
WETTABLE AND NONWETTABLE OXIDE FILMS ON URANIUM COUPONS

in the wettable film by X-ray diffraction, but it was not observed in the nonwetable film.

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