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Corrosion Behavior, Mechanical Properties, and Long-Term Aging of Nickel-Plated Uranium

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CORROSION BEHAVIOR, MECHANICAL PROPERTIES, AND LONG-TERM AGING OF NICKEL-PLATED URANIUM

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ABSTRACT

The behavior of nickel-plated uranium upon exposure to moist nitrogen was evaluated. Plating thicknesses of 0.051 mm (2 mils) were adequate to prevent corrosion. Specimens with thinner coats showed some corrosion and some reduction in mechanical properties during subsequent testing. Plated samples exposed to dry air at ambient pressure for 10 years showed no corrosion and no degradation of mechanical properties.

Surface and bulk hydrogen content, as well as free hydrogen generated during the test, were measured to determine the extent of corrosion. The results support an earlier proposed mechanism for uranium corrosion at low humidities.

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CORROSION BEHAVIOR, MECHANICAL PROPERTIES, AND LONG-TERM AGING OF NICKEL-PLATED URANIUM

Introduction

Since uranium is readily oxidized in air or by water even at room temperature, metallic coatings such as nickel are used to provide corrosion resistance for uranium. The work described herein is a continuation of some earlier work undertaken by us.[1] Objectives included the following:

1. To evaluate the influence of nickel plating thickness on the corrosion protection of uranium.

2. To measure the amount of hydrogen picked up by uranium as a result of corrosion.

3. To determine the influence of corrosion of nickel-plated uranium on the mechanical properties of uranium.

4. To evaluate the long-term performance of nickel-plated uranium.

Corrosion Reactions

The rate of corrosion of unprotected uranium is very dependent on the presence of oxygen. In humid air the rate of oxidation is independent of water vapor pressure between the approximate limits 1-90% relative humidity, and the only major product is an oxygen-rich uranium dioxide[2]:

$$U + O_2 + H_2O \rightarrow UO_{2.3} + H_2O$$

In pure water vapor, oxidation occurs at 30-100 times the rate observed in the presence of oxygen. The rate of oxidation increases with increasing water vapor pressure, reaching a maximum in the region 60-90% relative humidity. The products of the reaction are uranium dioxide, uranium hydride and hydrogen[2]:

$$2U + 2H_2O \rightarrow UO_2 + UH_3 + {}^{1}/2H_2$$

Once any free oxygen is consumed, the available water then reacts as above, producing free hydrogen. For this reason, a sensitive test of uranium corrosion is a determination of the amount of hydrogen generated. Orman et al[2] used this technique to study the corrosion behavior of nickel-plated uranium, and Couch[3] used it for determining the porosity of nickel-plated uranium. The reaction of amounts of uranium as small as 10^{-6} moles (0.0002 grams) may be detected in this manner.

Test Procedure

For our work, unalloyed uranium tensile samples were etched, nickel plated, and sealed in glass ampoules containing moist nitrogen for varying periods of time. After this they were removed from the ampoules, tensile tested, and then sectioned for hydrogen analysis and metallography.

Sample Preparation

Unalloyed uranium tensile samples 6.25 mm (0.25 inch) in diameter with a 25-mm (1-inch) gage length (per ASTM E8-69, 1972, Figure 8 and Federal Standard 151) were used for this work. They were etched in 1400 g/l ferric chloride solution and then nickel plated in sulfamate solution at 214 A/m^2 (20 A/ft^2). Metal removed during etching ranged from 0.02 to 0.036 mm (0.8 to 1.4 mil) on the diameter. After plating, the ends of the specimens were dipped in molten solder so that only the reduced gage length of the samples was left with exposed nickel plating. A mildly activated flux, Alpha 611®, was used on the sections given the solder dip.

Test Environment

The specimens were sealed in glass ampoules about 100 ml in volume (Figure 1). The tubes were evacuated for at least 1 hour under hard vacuum (<0.1 micron), backfilled with gas containing 2.8% (volume) H_2O and 97.2% (volume) N_2, sealed, and placed in an oven at 74°C. At this temperature, the relative humidity inside the ampoules was 8.4%.

The tubes had side arms with break seals for extracting gas samples for analysis. The hydrogen generated during the exposure was measured by a mass spectrometer if the volume percent was greater than 0.2 percent and by gas chromatography if the content was less than 0.2 percent.

Exposure times varied from 8 days to 37 weeks.

® Alpha Metals, Inc., Jersey City, N. J.

Figure 1. Glass Tube With Break Seals Used for Corrosion Study

Post-Test Analysis

The test specimens were removed from the ampoules, and tensile tests were performed in vacuum at 10^{-6} torr at 22°C. Crosshead speed was 1.3 mm/min (0.050 inch/min).

The specimens were then sectioned for hydrogen analysis and metallography. Both surface and bulk hydrogen analysis were performed by G. L. Powell, using the technique he described earlier.[4] This consists of mass spectrographic determination of the instantaneous rate at which hydrogen is thermally evolved from a sample, thus allowing the hydrogen produced by the decomposition of surface contamination to be distinguished from the hydrogen evolved from the sample bulk.

Test Results

Corrosion Test Results

Increasing the nickel plating thickness reduced the amount of corrosion and, concurrently, the amount of hydrogen generated (Table I). An uncoated sample generated 180,000 ppm of hydrogen during 6 weeks of testing. By comparison, a sample plated with 0.013 mm of nickel generated 35,000 ppm of hydrogen and one plated with 0.025 mm of nickel generated only 15 ppm of hydrogen during a similar 6 week exposure. Use of thicker nickel (0.076 mm) resulted in no hydrogen generation during 30 weeks of exposure.

Table I

Corrosion of Nickel-Plated[a] Uranium in Moist Nitrogen[b]

Thickness of Plating (mm)	Thickness of Plating (mils)	Length of Test	Hydrogen Evolved (ppm)
No Plating		6 Weeks	180,000
0.013	0.5	8 Days	7,000
0.013	0.5	6 Weeks	35,000
0.025	1.0	6 Weeks	15
0.025	1.0	24 Weeks	29
0.051	2.0	6 Weeks	10
0.051	2.0	37 Weeks	10
0.076	3.0	7 Weeks	0
0.076	3.0	30 Weeks	0

a. Specimens were plated in nickel sulfamate solution after etching in ferric chloride solution. Surface area of each specimen was approximately 3870 mm^2 (6 in^2).

b. The nitrogen contained 2.8% H_2O, 97.2% N_2; temperature was 74C. The specimens were sealed in glass tubes, evacuated for at least one hour under hard vacuum (<0.1 micron), backfilled with the desired gas mixture, sealed off and then placed in the oven for test. Relative humidity inside the ampoules at test conditions was 8.4%.

Data showing surface and bulk hydrogen content after corrosion testing, as well as the amount of hydrogen generated during testing, are included in Table II.

For the 0.013-mm (0.5-mil) coatings, hydrogen generation data indicate that considerable corrosion had taken place. This is confirmed by the noticeable increase in surface hydrogen of these samples.

For the 0.051-mm (2.0 mil) coatings, hydrogen generation during testing was minimal, and there was no increase in surface hydrogen after completion of testing. The results show that in the duration of this test (37 weeks for the 0.051-mm samples), corrosion did not occur.

For the 0.025-mm (1.0-mil) coatings, the results were contradictory. Measurement of the hydrogen generated in the ampoules during testing indicated that a very slight amount of corrosion was occurring. For example, three of the four specimens showed 29 ppm of hydrogen, most likely due to a defect on one end of the sample which ruptured near the end of the test period. Discounting this result because of the location of the failure, very little indication of corrosion was obtained for the 0.025-mm specimens. Yet when these samples were analyzed for surface hydrogen, they showed as much hydrogen as the *0.013*-mm samples.

Figure 2 shows cross sections of samples of all three coating thicknesses. Definite corrosive attack is seen for both the 0.012-mm and 0.025-mm samples. The sample with 0.053 mm of nickel shows no signs of attack, which is in agreement with the hydrogen analysis data. Figure 3 is a plot of the surface hydrogen versus nickel plating thickness, clearly showing the beneficial effect obtained with the 0.051-mm coating.

Use of an electrolytic oxalic acid etch, per Jackson[5], revealed uranium hydride platelets beneath the 0.013-mm and 0.025-mm coatings, as shown in Figure 4. These platelets are quite similar to those seen by Beevers and Newman[6] and by Adamson et al[7] with thermally or cathodically charged uranium.

The significance of this work is twofold: (1) it confirms the mechanism proposed by Orman et al.[2] on corrosion of uranium at low humidities, and (2) it shows that surface and bulk hydrogen analyses, used in conjunction with hydrogen generation data obtained during corrosion testing, provides a more complete picture of the corrosion reaction.

Table II

Results of Hydrogen Analysis of Nickel-Plated Uranium[a]

Thickness of Plating		Length of Test (Weeks)[b]	Hydrogen Generated in Ampoule (ppm)	Hydrogen Content of Sample (ppm)[d]	
mm	mils			Surface	Bulk
0.011	0.44	Control[c]	---	0.99	0.69
0.012	0.48	6	30,000	7.57	0.81
0.012	0.47	13	17,800	18.0	1.3
0.011	0.44	13	1,700	5.85	0.82
0.009	0.37	24	6	10.0	1.9
0.022	0.87	Control[c]	---	1.11	0.81
0.030	1.2	24	500	15.5	2.1
0.025	0.98	24	3	18.0	3.74
0.024	0.96	24	20	15.05	1.00
0.023	0.9	24	4	6.96	1.98
0.046	1.81	Control[c]	---	1.10	0.62
0.061	2.4	Control[c]	---	1.20	0.38
0.053	2.1	37	3	0.94	0.48
0.053	2.1	5	10	1.31	0.67
0.058	2.3	37	10	0.52	0.90

a. See Table I for information on etching and plating.

b. Exposed to moist nitrogen in sealed glass ampoules.

c. The control samples were not subjected to the moist nitrogen.

d. Determined by technique of Powell, Reference 4.

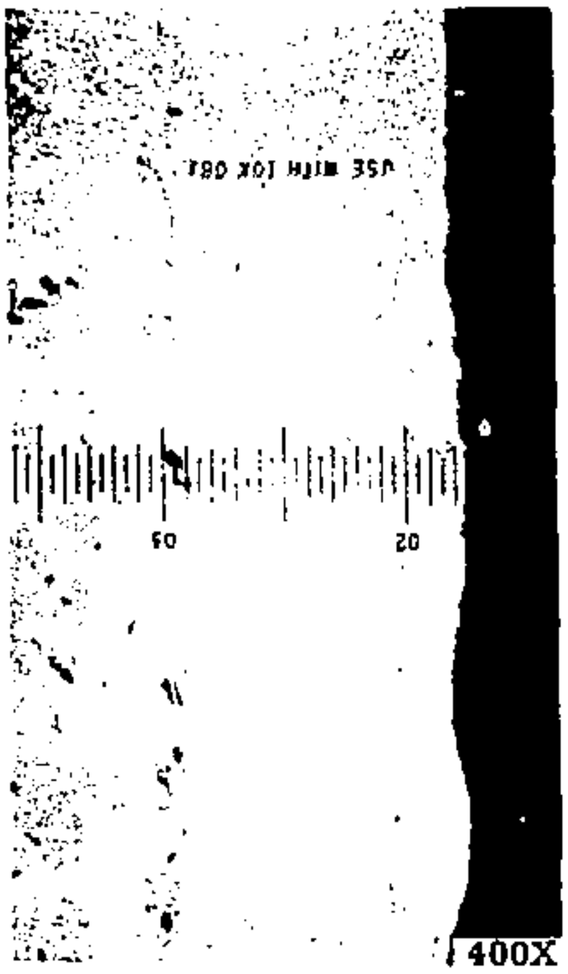


Plate thickness 0.053 mm (2.1 mil), 37 weeks of exposure.

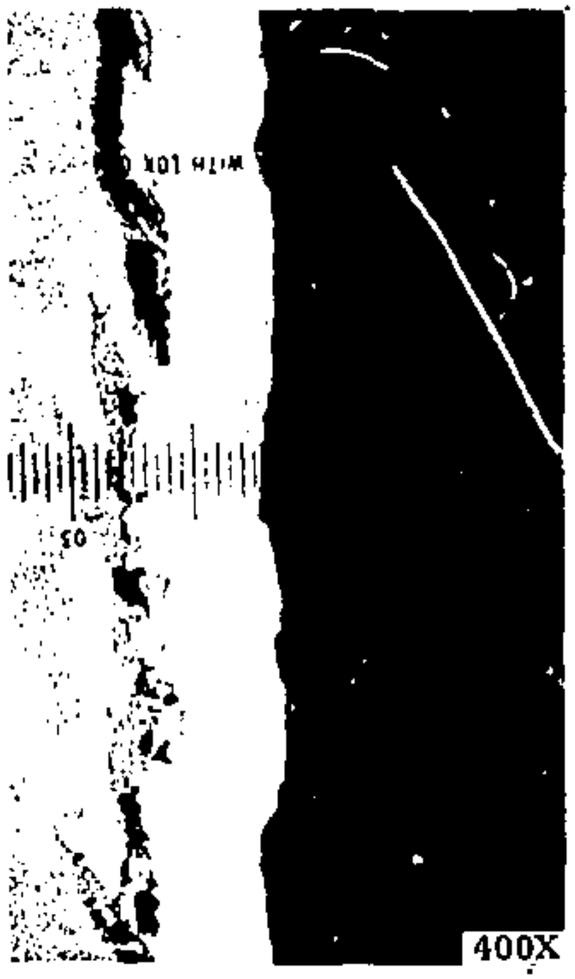


Plate thickness 0.025 mm (1.0 mil), 24 weeks of exposure.

Plate thickness 0.012 mm (0.47 mil), 13 weeks of exposure.

Figure 2. Cross Sections of Nickel-Plated Uranium After Exposure to Moist Nitrogen

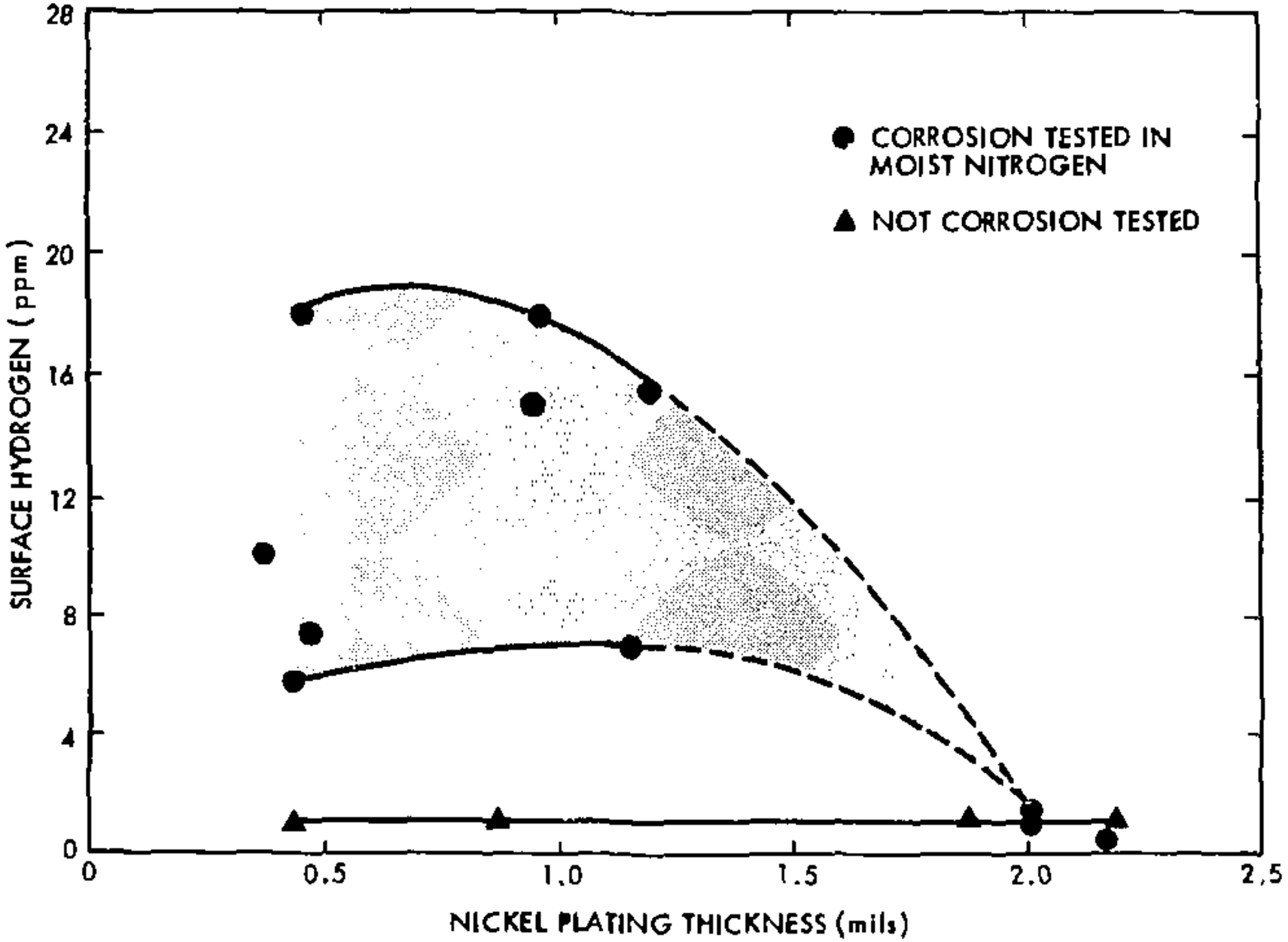
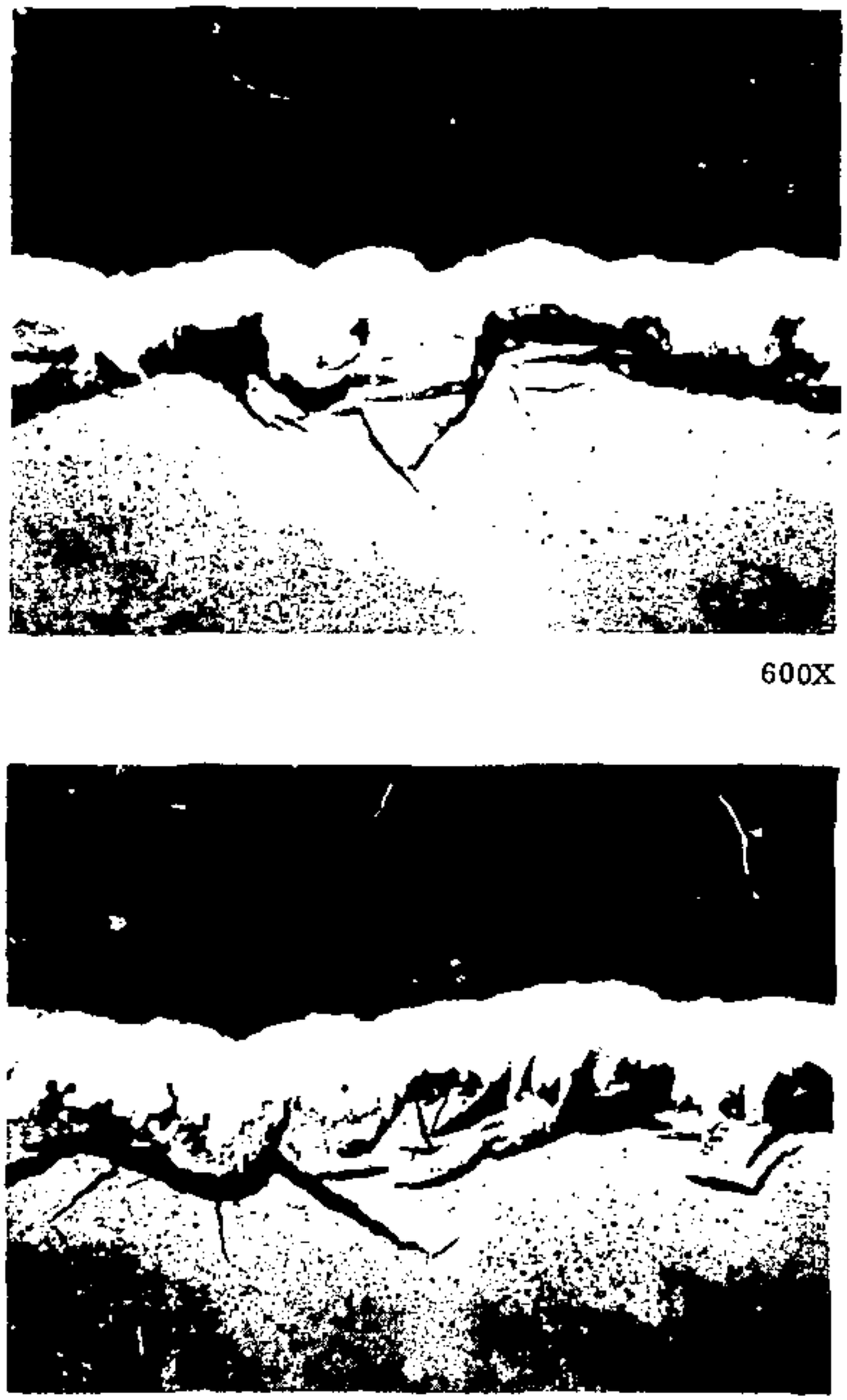


Figure 3. Influence of Nickel Plating Thickness on Surface Hydrogen.



600X

600X

Figure 4. Uranium Hydride Platelets Observed in Specimens Exposed to Moist Nitrogen (electrolytically etched in oxalic acid)

With regard to the former, Orman et al.[2] observed that uranium hydride could form at the nickel-uranium surface, and that this could account for the apparent cessation of hydrogen evolution. They postulated that the hydride can be formed as a result of hydrogen diffusion through the nickel film and/or along the interface between the uranium and nickel, resulting in interface bond rupture at sites remote from the original pores.

Mechanical Properties Test Results

Data included in Table III show that nickel plating did not adversely affect the tensile properties of plated uranium when testing was performed in vacuum. Thinly-plated specimens subjected to corrosion in moist nitrogen did exhibit less elongation and reduction in area than unexposed, unplated specimens. This was probably due to porosity in the coatings leading to increased corrosion at pore sites.[8] However, specimens coated with at least 0.051 mm (2 mils) of nickel did not exhibit these reductions, even though they were subjected to moist nitrogen for much longer times. This observation is in accord with the surface hydrogen analysis data, which showed that samples with at least 0.051 mm of nickel were not picking up hydrogen as a result of exposure to the corrodant.

Long-Term Exposure Tests

Samples plated approximately ten years ago and subjected to dry air at ambient pressure (relative humidity < 10%) were also evaluated. The samples were in a closed container, i.e., they did not have opportunity to breathe, and therefore they retained their original atmosphere. Hydrogen analyses, metallography, and electrochemical porosity[9] data were obtained on this material, which had been etched in ferric chloride solution and plated with 0.025 mm (1.0 mil) of nickel. In addition, some mechanical property data were obtained.

Metallographic inspection revealed no signs of corrosion products nor any type of degradation at the nickel-uranium interface. Figure 5 shows representative photomicrographs of the material. Electrochemical porosity tests[9] performed after masking the edges of the samples with stop-off lacquer revealed an exposed uranium area fraction below 10^{-10}. This indicates that for all practical purposes, the plating was pore free.

Tensile properties were obtained from sheet tensile specimens, and stress intensity at fracture and delayed failure results were obtained using precracked mini-Charpy specimens.[10] No unplated material of the original heat was available to include in these tests, so some current unalloyed uranium was used for control properties.

Table III

Mechanical Property Data For Nickel-Plated Uranium[a]

Nickel Plating Thickness		Exposure time (Weeks)[d]	Yield Strength[b]		Tensile Strength		Elongation (%)[c]	Reduction in Area (%)
mm	mil		MN/m^2	KSI	MN/m^2	KSI		
None		Not exposed to	807	117	1069	154	10.5	30.0
None		moist nitrogen	807	117	1076	156	11.6	16.0
0.011	0.44	↓	676	98	1069	154	21.5	24.0
0.022	0.87		731	106	1069	155	--	21.6
0.046	1.81		745	108	1034	150	17.3	21.2
0.061	2.4		724	105	1034	150	18.0	29.4
None		6	800	116	1117	162	13.6	16.0
0.012	0.48	6	814	118	1028	149	7.6	14.2
0.012	0.47	13	697	101	1028	149	8.4	13.7
0.011	0.44	13	717	104	1000	145	8.1	15.7
0.009	0.37	24	786	114	1014	147	5.4	9.4
0.030	1.2	24	814	118	1020	148	4.8	9.7
0.025	0.98	24	759	110	1014	147	5.4	9.4
0.024	0.96	24	828	120	1020	148	8.2	16.3
0.023	0.91	24	814	118	1020	148	5.0	12.4
0.053	2.1	37	828	120	1028	149	12.6	12.5
0.053	2.1	6	752	109	1033	150	10.0	19.0
0.050	2.3	37	686	100	1028	149	13.5	16.9

a. See section on preparation of samples for details on specimen configuration and testing. Tensile tests were performed at 22C in vacuum (10^{-6} torr). Crosshead speed was 1.3 mm/min (0.050 inch/min).
b. Determined by using 0.2 percent offset.
c. In 25.4 mm (1 inch).
d. Sealed in glass ampoules containing 2.8% H_2O, 97.2% N_2, and kept at 74C for duration of test.

300X

300X

Figure 5. Cross Sections of Nickel-Plated Uranium Subjected to Long-Term Exposure

No effect of plating on mechanical properties was noted. The average tensile properties for six specimens in each condition are included in Table IV. Much more scatter exists in the data for unplated than for plated material, for which we have no explanation. Nevertheless, there is no statistically significant difference in yield strength, ultimate strength, or elongation between plated and unplated material.

Sustained loading tests were performed on precracked, reduced-thickness Charpy specimens.[10] Plated and unplated specimens were loaded in tension in dry air at 75-80% of the stress intensity required for instantaneous fracture to determine if delayed fracture would occur in long testing times. Overload controls were essentially the same for both types of specimens at approximately 37 MN-$m^{3/2}$ (34 KSI-$in^{1/2}$). Four unplated specimens loaded at 75-80% of this value for 5200 hours did not fail and showed no evidence of crack propagation. Two plated specimens loaded at approximately 80% of the overload value did not fail in 3800 hours; however, there was some evidence of slow crack growth. A third specimen loaded at greater than 90% of the overload failed almost instantly, indicating that this was most probably a mechanical overload.

These data showed that both plated and unplated uranium were able to sustain a very high load for long periods of time in dry air without failure. However, because the plated specimens indicated that slow growth was occurring which would lead to failure given enough time, it does not appear advisable to subject this material to high sustained loads for very long periods of time.

Summary

Increasing the nickel plating thickness reduces the amount of corrosion of uranium and, concurrently, the amount of hydrogen generated. This was confirmed by utilizing surface and bulk hydrogen analyses, in conjunction with hydrogen generation measurements obtained during corrosion testing. The results confirmed those of Orman et al[2] who showed that at low humidities, a plateau is obtained in the hydrogen generation curve.

Mechanical property tests showed that nickel plating caused no degradation. Plated specimens subjected to corrosion in moist nitrogen did exhibit less elongation and reduction in area than unexposed, unplated specimens. However, when the plating was at least 0.051 mm thick, these reductions were not obtained even though the specimens were subjected to the moist nitrogen corrodant for relatively long times.

Long-term exposure (10 years) in a relatively non-corrosive atmosphere (dry air at ambient pressure) showed no degradation of the plated bond nor any harmful effects on mechanical properties.

Table IV

Mechanical Property Data For Aged Nickel-Plated Uranium[ab]

Condition	Yield Strength[d]			Tensile Strength			Elongation[e]	
	MN/m^2	psi	Deviation	MN/m^2	psi	Deviation	%	Deviation
Plated[c]	224	35, 500	0. 04	587	87, 100	0. 04	5. 5	0. 2
Unplated	224	32, 500	2. 1	604	87, 600	2. 5	8. 7	1. 7

a. Data of Rohde and Magnani, Reference 10.

b. Subjected to dry air at ambient pressure (relative humidity less than 10%) for 10 years.

c. Plate thickness 0. 025 mm (1. 0 mil); etched in ferric chloride solution before plating.

d. Determined by using 0. 2 percent offset.

e. In 50. 8 mm (2 inches).

References

1. H. R. Johnson, J. W. Dini and S. W. Zehr, "On the Embrittlement of Uranium and U-O. 8Ti Alloy by Hydrogen and Water", ASM/CMU Conference on Hydrogen in Metals, Seven Springs, PA, Sept. 22-27, 1973

2. S. Orman, L. W. Owen, and G. Picton, Corrosion Science, 12, 35 (1972)

3. D. E. Couch, Plating, 49, 363 (1962)

4. G. L. Powell, "A Method for Measuring the Hydrogen Content of Metals". ASM/CMU Conference on Hydrogen in Metals, Seven Springs, PA, Sept. 22-27, 1973

5. R. J. Jackson, private communication

6. C. J. Beevers and G. T. Newman, Jour. of Nuclear Materials, 23, 10 (1967)

7. P. Adamson, S. Orman, and G. Picton, Jour. of Nuclear Materials, 33, 215 (1969)

8. L. J. Weirick and D. L. Douglass, "The Effect of Thin Electrodeposited Nickel Coatings on the Corrosion Behavior of U-0.75 T_i," Sandia Laboratories, Livermore, SLL-74-5010, June 1974.

9. L. J. Weirick, "Electrochemical Determination of Porosity in Nickel Electroplates on a Uranium Alloy," Sandia Laboratories, Livermore, SLL-73-5316, October 1973.

10. R. W. Rohde and N. J. Magnani, private communication, January 21, 1974.