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ELECTROLESS NICKEL PLATING FOR
CORROSION PROTECTION OF URANIUM

AUTHORS:

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE GASEOUS DIFFUSION PLANT

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ELECTROLESS NICKEL PLATING FOR
CORROSION PROTECTION OF URANIUM

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ABSTRACT

Two electroless nickel plating methods have been developed for corrosion protection of metallic uranium. In one method, the uranium is heat-treated in a vacuum furnace and given an electrostrike in a nickel sulfate bath to initiate the electroless plating process prior to placing it in the standard high-temperature electroless plating bath. In the second method, the plating is done in a low-temperature electroless bath, initiated by making the uranium cathodic for a few seconds. The nickel-plated uranium from either bath is heat-treated in a vacuum furnace to form a uranium-nickel alloy at the interface.

Metallic uranium pieces varying in area from 7 sq in. to 17 sq ft have been plated with nickel in the standard high-temperature electroless plating bath. Nickel deposits ranging in thickness from 0.0005 to 0.002 in. were readily plated with the thickness controlled to within ± 0.0002 in. There was no porosity in the deposit and no peel-back of a freshly cut edge after 165 hr in a steam test bath.

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ELECTROLESS NICKEL PLATING FOR CORROSION PROTECTION OF URANIUM

INTRODUCTION

The interest of the Atomic Energy Commission in developing methods for coating metallic uranium with a thin protective film has stimulated the development of such techniques at the Oak Ridge Gaseous Diffusion Plant (ORGDP), where a general capability of plating for corrosion protection has prevailed for many years. The goal was to establish a method whereby a thin protective coating on uranium metal would prevent its oxidation in a humid atmosphere. Nickel is the preferred coating metal, because it is hard, lustrous, and does not oxidize readily. The two principal methods for applying nickel to another metal are electroless plating and electroplating. The electroless plating method is preferred when it is desired to deposit a uniform film over all surfaces and edges, especially when there are unusual shapes or a variety of shapes and sizes. By comparison, electroplating could not easily achieve such uniformity even with special anodes for each shape to be plated.

Uranium is one of the most difficult metals to plate because of the ready tendency of the metal surface to be oxidized and become passive. Previously, most of the emphasis for coating uranium with nickel has centered on adaptations of the electroplating process. Gore and Seegmiller (1) reported on the electroplating of nickel on uranium after the metal was given an electrostrike of copper or silver. They found that pickling solutions containing stannous chloride substantially roughened the surface and removed uranium in the thickness range of 0.0007 to 0.003 in. Gore and Seegmiller also discovered that with proper cleaning and pickling, the nickel plating can be done from the Watts bath (2) without an initial copper or silver strike. They had difficulty in obtaining nonporous deposits of about 0.001-in. thickness on severely etched, partially passive uranium surfaces. They found, furthermore, that the deposit did not retard corrosion but actually accelerated it, as the uranium functioned like the anode of a cell through the pores in the nickel deposit. They suggested that uranium should be left unplated for normal atmospheric exposures.

Rebol and Wehrman (3) reported that satisfactory coatings of nickel may be electrodeposited on uranium which has been pretreated by pickling in trichloroacetic acid. The heat treatment of the plate at 540°C to form a uranium-nickel alloy increased the corrosion resistance of the deposit.

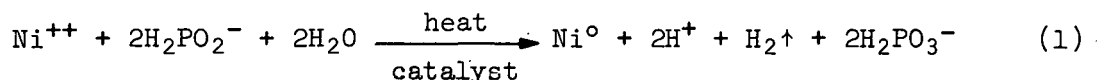
Lundquist, Braun, and Stromatt (4) reported on the electroplating of uranium with nickel. They anodized the uranium in a H₂SO₄-HCl solution to provide a surface onto which a nickel coat with good adherence and low pore density could be plated. Nickel plates thinner than 0.001 in. provided no significant protection to the uranium in an autoclave test at 165°C. Plates ranging in thickness from 0.0022 to 0.0028 in. failed after 25 to 400 hr in the autoclave.

Waldrop, Bezik, and Wilson (5) applied coatings of organic materials to

metallic uranium and also electroplated uranium with nickel. They reported good adherence of the nickel plate on the uranium.

Dalton, Gentry, Stevens, High, Clouse, and Dodson of ORGDP (6) attempted to adapt the standard electroless nickel plating process (7) to the plating of uranium. Prior to the investigation described in this report, the technique at ORGDP included pickling the uranium in a stannous chloride-nitric acid solution (8, 9, 10), plating it in an electroless bath at 65°C, and heat-treating the nickel-plated uranium at 550 to 600°C to improve the adherence and corrosion resistance. The technique was not capable of plating a nickel deposit that protected the uranium from corrosion for 90 hr in a steam bath, a major objective of the effort.

In the electroless nickel plating process (11), the nickel ion is reduced to the metal according to the reaction:



On passive surfaces the reaction is initiated by an electrostrike of a very thin film of nickel onto the surface. This brief electrostrike of nickel serves to activate the surface and to catalyze the electroless reduction of the nickel cations to metallic nickel by the hypophosphite anions. The electroless nickel deposit, acting as the catalyst, causes the plating reaction to proceed until either the coated items are removed from the bath or the metal or reductant ions are depleted.

The goal of the present development was to deposit a uniform, smooth, non-porous, adherent, and corrosion resistant nickel coating on uranium. The nickel should have a thickness uniform to ± 0.0002 in., a root-mean-square (rms) surface finish of 100 $\mu\text{in.}$ or less, no visible porosity, and less than 0.25 in. peel-back of a freshly cut edge after exposure for 90 hr in a steam test bath. In addition, it was desirable that less than 0.001 in. of uranium be removed from the surface during the cleaning and pickling processes. To meet these requirements, the pickling process had to be improved, and conditions for electroless plating the uranium had to be developed to prevent the formation of uranium oxide (3) on the surface before it could be completely covered with nickel. Previous work with the stannous ion indicated that a milder etchant in the pickling solution was desirable for better control. Furthermore, it was necessary to eliminate tin, because it would impede the electroless deposition of nickel on the uranium and could produce unattached nickel particles, causing decomposition of the plating bath.

Two approaches were considered for the electroless plating of uranium with nickel: one was to use a low-temperature electroless plating bath, decreasing the tendency for uranium oxidation; the second approach involved coating or treating the uranium to prevent or minimize oxidation during the initial plating in the standard high-temperature (95°C) electroless plating bath (7, 11).

SUMMARY

Two methods have been developed for the electroless plating of uranium with nickel. In both methods, the same cleaning, degreasing, and pickling methods were used before plating. Prior to plating in the standard high-temperature electroless plating bath, the uranium was heat-treated in a vacuum and electroplated with a very thin film of nickel. In using the low-temperature electroless baths, the uranium was made cathodic for a few seconds and then plated electrolessly. The nickel-plated uranium from both methods was heat-treated to form a uranium-nickel alloy at the interface.

Several hundred small uranium test coupons have been plated with nickel in the two baths. Also, several pieces of uranium, up to 17 sq ft, have been plated in the standard high-temperature bath. In the final evaluation of the nickel-plated items, the deposits from the high-temperature bath were better. They were free of cracks and more resistant to corrosion.

EXPERIMENTAL

The methods and processes used for preparing and plating uranium with nickel were: (1) cleaning and pickling the uranium surface, (2) low-temperature electroless plating, (3) standard high-temperature electroless plating, and (4) heat treatment of the uranium before and after plating.

OBJECTIVES

The development of procedures and techniques was directed toward meeting the following requirements: the variation in the plated film thickness was not to exceed ± 0.0002 in.; the final rms surface finish was to be 100 μ in. or less, when the initial finish was not greater than 40 μ in.; and the plate was to have no porosity and less than 0.25-in. peel-back of a freshly cut edge after exposure for 90 hr in a steam test bath (10, 12).

QUALITY EVALUATION

The corrosion resistance of the plated deposit is evaluated by exposing a piece of the nickel-plated uranium with a freshly cut edge in a steam test bath for 90 hr or more. The amount of peel-back of the freshly cut edge is estimated by visual observation. The porosity of the exposed deposit is judged by visual observation of the number of apparent pores in the deposit. The adherence is judged by attempting to peel off the deposit.

Corrosion Test Bath Exposure

The corrosion test steam bath consists of a controlled temperature hot water bath with a Lucite enclosure over it. A reflux condenser is attached to help maintain the desired water level in the bath. For this study, the chamber was operated at 100% relative humidity and at a temperature of 95°C. The nickel-plated uranium samples were suspended on a wire in the steam atmosphere.

Plate Thickness

The thickness of the deposit was measured with a beta-backscattering thickness gauge made by Micro-Derm, Unit Process Assemblies, Inc., Woodside, New York. The thickness was also observed on photomicrographs of nickel-plated uranium cross sections. The variation in thickness was determined from systematic measurements.

Surface Finish

The surface finish of the nickel deposit was measured with a profilometer manufactured by Brush Instruments, Division of Clevite Corporation, Cleveland, Ohio. The surface finish was also observed on the photomicrographs of the nickel-plated uranium cross sections.

METHODS

Two methods were developed for the electroless plating of nickel on uranium: (1) standard high-temperature plating, and (2) low-temperature plating. The flow schemes for these methods are presented in figure 1. In both methods, the uranium is cleaned with laboratory scouring powder and degreased in trichloroethylene vapor. It is pickled in a nickel chloride-nitric acid solution and dipped several times in nitric acid, followed by a thorough distilled water rinse. In the high-temperature plating method, the uranium is then heat-treated in a vacuum furnace, given an electrostrike in a nickel sulfamate bath at room temperature, and nickel plated to the desired thickness in the hot electroless bath. After the nickel-plated uranium is given a second heat treatment in the vacuum furnace, it is ready for testing or use. In the alternative low-temperature plating method, the pickled uranium is made cathodic for a few seconds in a low-temperature electroless bath and then the plating proceeds catalytically, finally completed in a bath at slightly higher temperature. The nickel plated uranium is heat-treated in a vacuum furnace to complete either the high-temperature or the low-temperature method.

Cleaning and Pickling

Uranium coupons ($1/8 \times 1 \times 3$ in.) and large pieces of uranium with areas up to 17 sq ft had grease, wax crayon marks, finger prints, and other contaminants on the surface when received for plating. The surface was also covered with uranium oxide. These foreign materials had to be removed to provide a clean surface for plating.

Scrubbing the uranium pieces with a laboratory scouring powder removed most of the contaminants and some of the uranium oxide from the surface. Trichloroethylene vapor was used to remove any remaining grease on the surface. The vapor atmosphere was produced by heating the trichloroethylene in a container with a reflux condenser at the top. After degreasing, the pieces were rinsed in distilled water. An alternative, more economical method for uniformly cleaning the surface was to dip the uranium coupons in chromic acid. This eliminated the scrubbing and degreasing except for removing some crayon marks deeply embedded in the surface of the uranium. Following

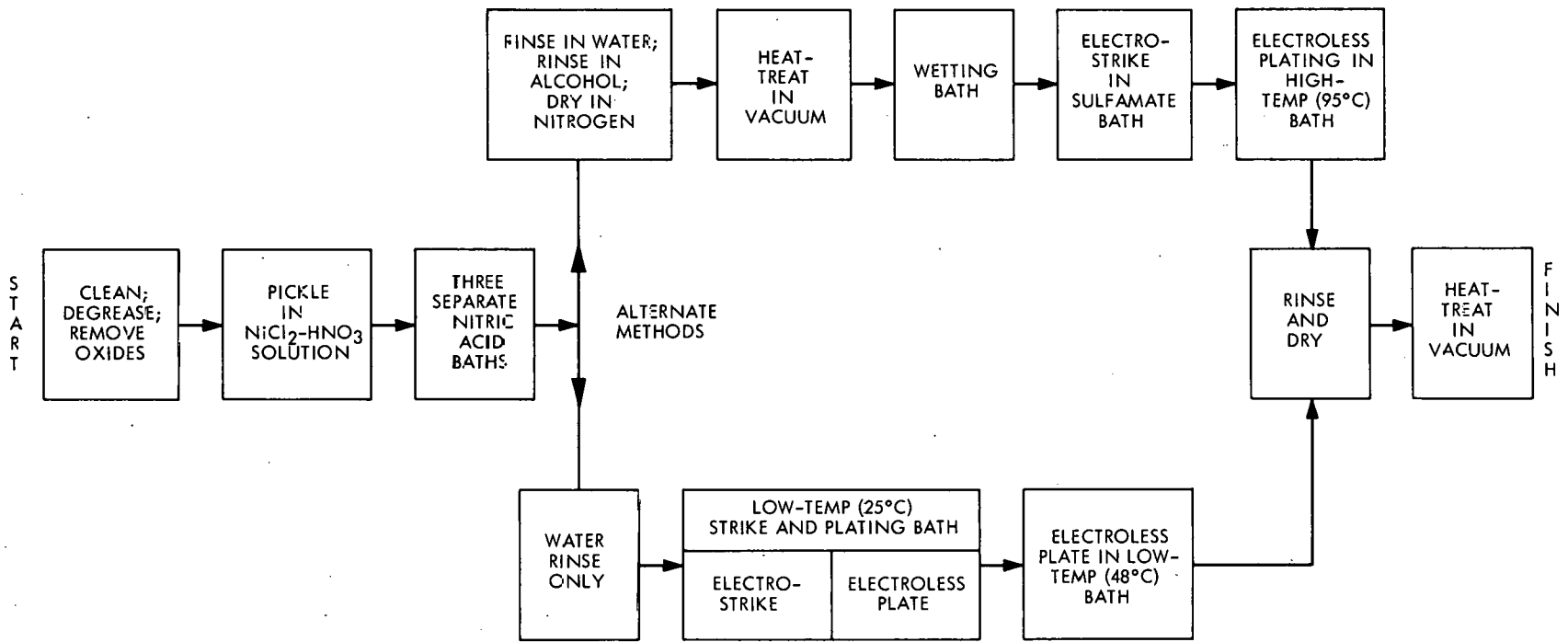


Figure 1
 FLOW SHEET FOR ELECTROLESS PLATING PROCESSES

the degreasing, the remaining oxide film was removed with a solution of 8 N nitric acid.

In the initial investigation, the surface of the uranium was pickled with a stannous chloride-nitric acid solution as performed by others (6). This pickling solution attacked the uranium very rapidly, leaving a rough surface and making it very difficult to control the etching and the amount of uranium removed. Also when even a very small amount of tin is left on the surface, it interferes with the plating of the nickel on the uranium and may produce unattached nickel particles, causing decomposition of the plating bath. Nickel chloride was selected to replace the stannous chloride since a residue of nickel ions on the uranium surface would have no detrimental effect on the plating rate or the bath. The chloride ion, when left on the surface, reacts with the uranium, forming a film (1) which interferes with the bonding of the nickel deposit. However, rinsing in three separate baths with 8 N nitric acid followed by distilled water was effective in reducing the chloride ion concentration to a level where the deleterious effects no longer occurred.

The concentrations of nickel chloride and nitric acid were varied in several pickling solutions to determine the optimum conditions. The optimum concentration was determined empirically to be about 2.5 M nickel chloride in a 4.8 N nitric acid solution. After evaluating temperatures ranging from 25 to 60°C, it was decided to maintain the temperature of the pickling solution at 42°C. The optimum period for pickling the uranium coupons was found to be 50 to 60 sec. This pickling process removed approximately 0.0007 in. of uranium from the surface and exposed the uranium crystals, producing a very clean surface for plating. The rms surface finish was 80 μ in. or less, after pickling. Before optimizing the concentration of the pickling solution and the period of pickling, the surface of uranium coupons with an rms finish of 40 μ in. before pickling increased to approximately 200 μ in. after pickling; and about 0.0014 in. of uranium was removed in the pickling process.

After removing the chloride ion with the nitric acid and water rinses the uranium metal was rinsed with ethyl alcohol and dried with a nitrogen gas stream. The metal was then ready for heat treatment prior to plating in the standard high-temperature bath (see figure 1). Alternatively, the alcohol and nitrogen drying steps could be omitted, and the wet pickled uranium piece would be introduced to the low-temperature plating process.

Low-Temperature Electroless Plating Baths

The conventional electroless nickel plating baths (7, 11) normally operate at 95°C. The plating of uranium metal at this temperature produced a film of oxide on the surface before the uranium was completely covered with nickel. The oxide film prevented chemical bonding of the nickel to the uranium. Some provision was necessary, therefore, for protecting the surface until it was adequately coated.

A low-temperature (25°C) electroless plating bath, UC No. 3 (described in appendix A), had been developed earlier for plating a very thin film

(0.0001 in.) of nickel on thorium (13). This film was adherent and protected the thorium from becoming oxidized in the high-temperature electroless bath. Although the bath produced a good nickel deposit on uranium, it plated at a rate of only 0.00004 in. of nickel per hour and, therefore, was not practical for applying the total required 0.0005 to 0.002 in. of nickel. A faster plating bath was needed after the uranium was protected with a very thin film (0.0001 in.) of nickel. The UC No. 3 bath was modified by decreasing the concentration of both the ammonium sulfate and the succinic acid by about one-third and the sodium hypophosphite by one-half (as shown in appendix A). The plating temperature was then raised to 48-50°C. This modified UC No. 3 bath had a nickel deposition rate of 0.0002 in./hr. The plating reaction was usually initiated in the UC No. 3 bath by making the uranium cathodic (electrostrike) with a 6- to 7-volt potential from a dc rectifier for 3 to 5 sec.

Uranium coupons were plated with 0.0001 in. of nickel in the UC No. 3 bath and then to 0.002 in. in the UC No. 3 modified bath. The nickel-plated deposit showed very small stress cracks in it, figure 2. Some of the coupons were cut into two pieces, and half of the pieces were heat-treated. The pieces were then placed in the corrosion test bath. The nickel deposit on the pieces which had not been heat-treated peeled off in less than 2 hr; the heat-treated nickel deposits were in excellent condition after 168 hr as shown in figure 3. The fine cracks in the deposit were not detrimental to the uranium; it was protected from corrosion by the formation of a protective oxide coating at the interface. An examination of the heat-treated piece, following the 168-hr corrosion test, showed very little deterioration; peel-back of the freshly cut edge was less than 0.06 in. Thinner deposits (0.0005 to 0.001 in.) which had been heat-treated showed some deterioration after 95 hr in the test bath.

The nickel deposit on the uranium coupons which were plated in these two low-temperature baths, and then heat-treated, was smooth, uniform, adherent, and corrosion resistant. Thus, it met the previously discussed criteria for a protective nickel plate.

Standard High-Temperature Electroless Plating Bath

Although the low-temperature electroless plating baths produced acceptable deposits, the desired goal was to adapt or develop a bath with a faster plating rate. A plate free of cracks was also desired, from the standpoint of apparent integrity. The standard high-temperature plating bath appeared to meet these goals. The plating rate in the high-temperature bath is about 0.0007 in./hr, which is approximately three times as fast as that of the UC No. 3 modified bath; furthermore, in early examination there was no evidence of cracks in the nickel plate.

An evaluation was made to determine whether the standard electroless plating bath could be used in place of the UC No. 3 modified bath. Uranium coupons were plated to a thickness of 0.0001 in. of nickel in the UC No. 3 bath and then to a thickness of about 0.001 in. of nickel in the standard high-temperature electroless plating bath. Photomicrographs of cross sections of coupons from the high-temperature bath showed no stress cracks in the plate;

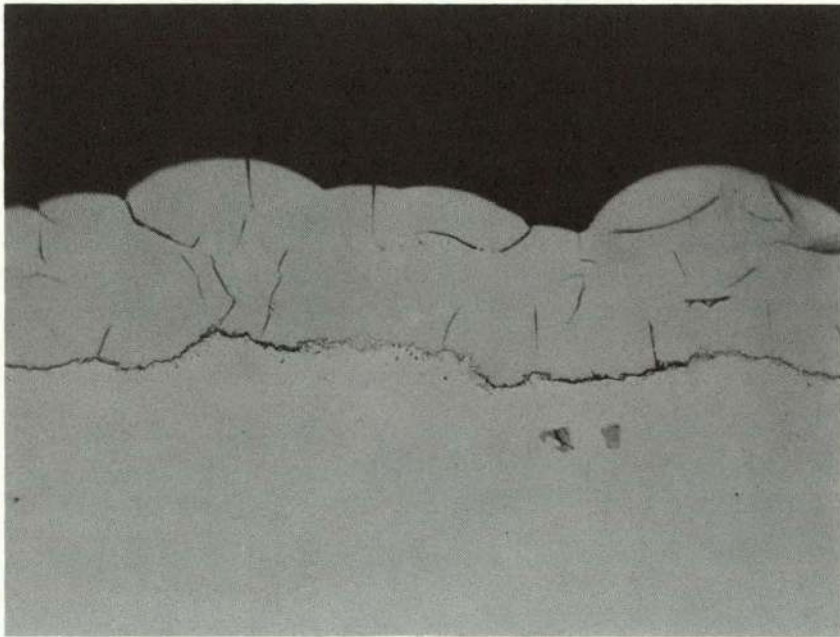


Figure 2
0.002-INCH NICKEL DEPOSIT
PLATED IN LOW-TEMPERATURE BATH

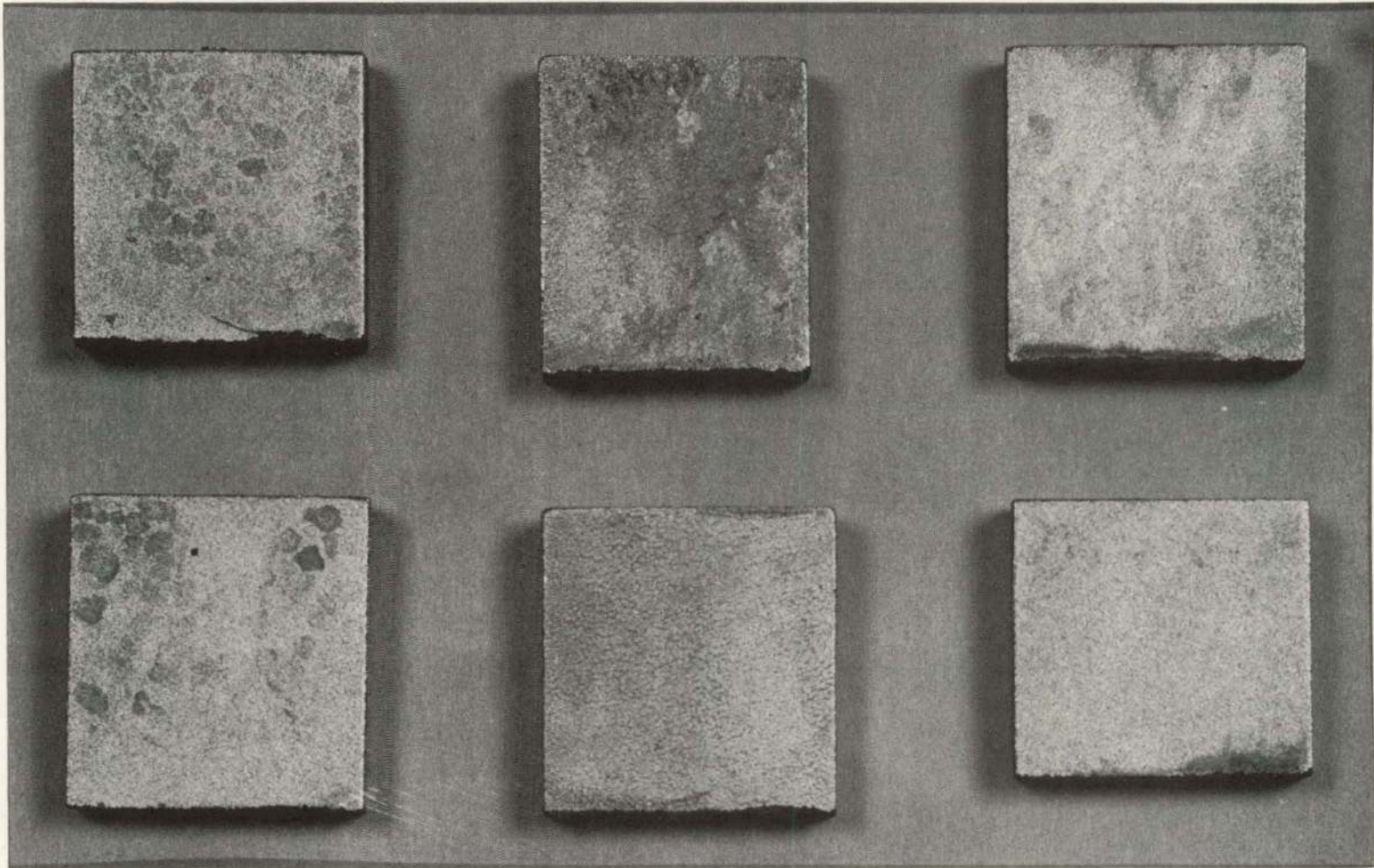


Figure 3
0.002-INCH NICKEL DEPOSIT ON COUPONS PLATED IN LOW-TEMPERATURE BATH
After 168 Hours Exposure in Corrosion Test Bath

however, after these were heat-treated to form the diffusion bonding layer, small blisters formed during the early stages of corrosion testing. These blisters were believed to be caused by the outgassing of the uranium during the heat treatment. In contrast, the nickel deposit plated in the UC No. 3 modified bath, figure 2, contained small cracks, permitting the gases to escape without injuring the nickel plate during the heat treatment.

The high-temperature electroless plating bath and the heat-treatment method required techniques serving to: (1) outgas the uranium before plating, (2) increase the resistance of the uranium to oxidation, and (3) initiate the electroless plating process by producing a catalytic surface on the uranium. The uranium was outgassed by heat treatment before plating to prevent the blistering of the plate during the heat treatment after plating. Outgassing the uranium and increasing its resistance to oxidation were accomplished by a heat-treatment process discussed in the next section. The uranium piece (following heat treatment) was given an electrostrike at room temperature in a nickel sulfamate bath (see appendix A) to initiate the electroless plating process. The standard nickel sulfamate bath (14) was modified by increasing the concentration of the nickel sulfamate to provide a rapid electroplating rate at room temperature; the electrostrike was applied to the uranium using a dc current density of 4 amp/sq ft for 20 min. The uranium was then immediately transferred into the standard electroless plating bath and plated with nickel to the desired thickness. In preparing the electroless plating bath, care was taken not to add chloride or fluoride ions (3, 4) which attack the uranium and prevent the deposition of an adherent film of nickel.

Plating of Coupons. Uranium coupons were plated with 0.0005-, 0.001-, 0.002-, and 0.003-in. thicknesses of nickel in the standard electroless plating bath and then heat-treated as described in the next section. The deposit was smooth, lustrous, uniform, nonporous, and adherent. The nickel plate had no stress cracks in it, figure 4. The plated coupons were evaluated in the corrosion test bath, after forming a fresh-cut edge on each. The coupons with a 0.0005-in. deposit were inspected after 95 hr in the test bath and were in good condition with very little porosity and no peel-back, figure 5. Some coupons were removed after 200 hr in the test bath; the plated deposit showed only a slight porosity. These nickel deposits were superior to those from the low-temperature bath, table 1.

Plating Large Pieces of Uranium. Large pieces of uranium (up to 17 sq ft) were plated with thin films of nickel in the high-temperature bath and then heat-treated. Coupons taken from these large plated pieces were evaluated in the test bath. The coupons were inspected after 38, 92.5, 165, and 240 hr in the test bath. There was no visible deterioration of the nickel plate at 165 hr. After exposure for 240 hr, there was evidence of a few pinholes in the plate. Photomicrographs, figures 6 and 7, of cross sections were made after 92.5 and 240 hr, respectively. These photomicrographs showed the plated surface and interface to be in excellent condition even after the 240-hr exposure.



500X

Figure 4
0.0005-INCH NICKEL DEPOSIT FROM STANDARD ELECTROLESS BATH
With Uranium-Nickel Alloy at Interface After Heat Treatment

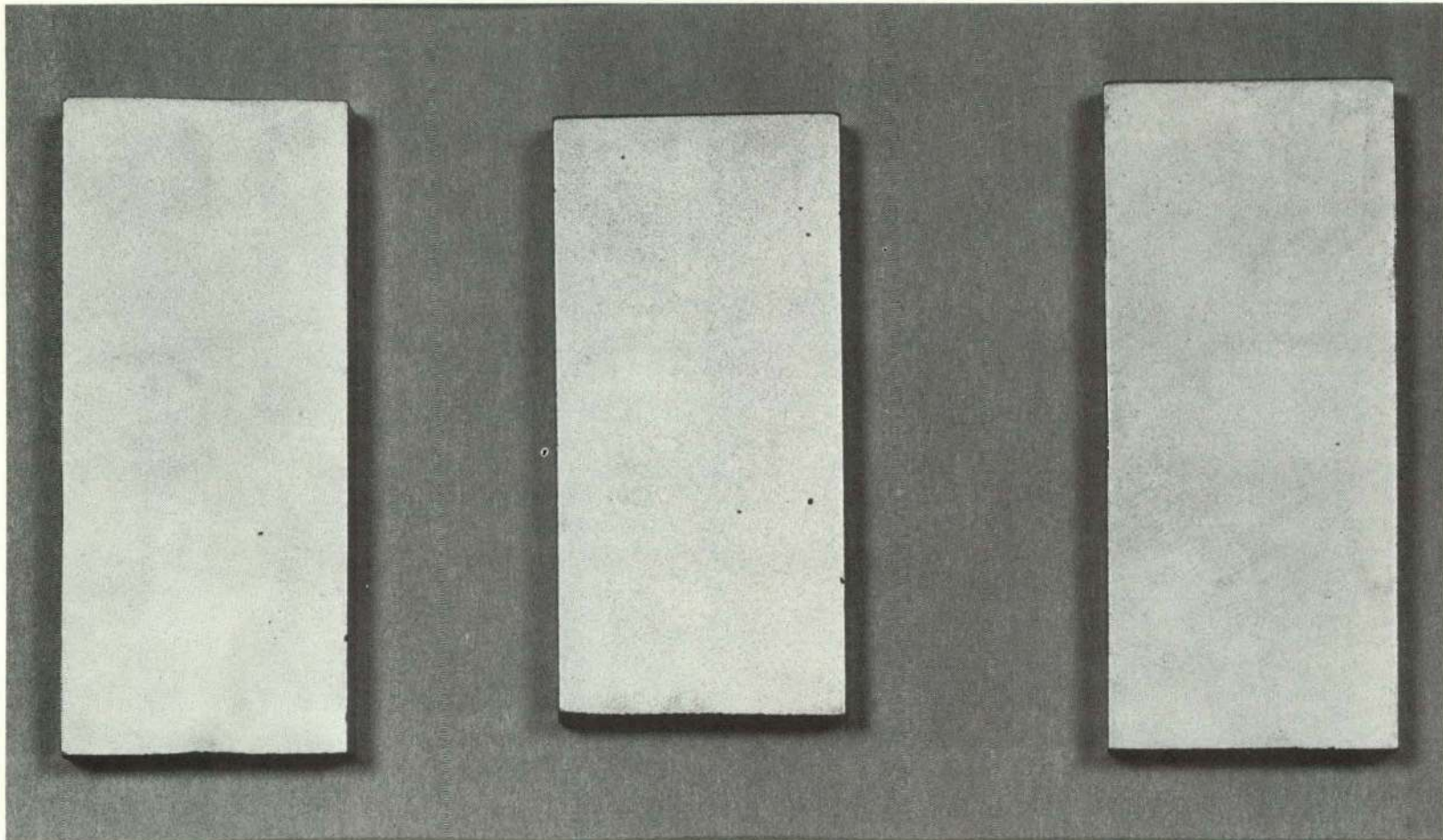


Figure 5
0.0005-INCH NICKEL ON COUPONS PLATED IN HIGH-TEMPERATURE BATH
After 95 Hours Exposure in Corrosion Test Bath

Table 1

COMPARISON OF NICKEL DEPOSITS ON URANIUM PLATED IN LOW- AND HIGH-TEMPERATURE BATHS

Type of Plating Bath	Thickness of Deposit, in. $\times 10^3$	Heat-Treated Before Plating	Heat-Treated After Plating	Time In Test Bath, hr	Results	
					Porosity of Deposit	Peel-Back of Deposit At Cut Edge, in.
Low-Temperature	0.5	No	No	2	Deposit Destroyed	---
	0.5	No	Yes	90	~ 20 Spots	~ 1/8
	1.0	No	No	2	Deposit Destroyed	---
	1.0	No	Yes	90	~ 10 Spots	~ 1/8
	2.0	No	Yes	90	Minor Porosity*	~ 1/16
	2.0	No	Yes	168	Minor Porosity	~ 1/16
	3.0	No	Yes	168	Minor Porosity	Trace
	1.0	Yes	No	22	Deposit Destroyed	---
	1.0	Yes	Yes	96	Minor Porosity	Trace
	Standard High-Temperature	0.5	Yes	No	22	Deposit Destroyed
0.5		Yes	No	41	Minor Porosity	3/16
0.5		Yes	Yes	95	No Visual Porosity	None
0.5		Yes	Yes	95	No Visual Porosity	None
0.5		Yes	Yes	95	Minor Porosity	None
0.6		Yes	Yes	95	No Visual Porosity	None
0.3		Yes	Yes	90	Minor Porosity (Dark Alloy Showing through the Plate)	None
1.0		Yes	No	46	No Visual Porosity	1/16 One Side
1.0		Yes	Yes	95	No Visual Porosity	None
1.0		Yes	Yes	95	No Visual Porosity	None
1.0		Yes	Yes	90	Minor Porosity	None
2.0		Yes	No	46	No Visual Porosity	1/4 Avg
2.0		Yes	Yes	90	No Visual Porosity	None
3.0		Yes	No	46	No Visual Porosity	None
3.0		Yes	Yes	90	No Visual Porosity	None

*Minor Porosity - 4 or less pinpoint spots on 1 \times 3 \times 1/8-in. coupon.

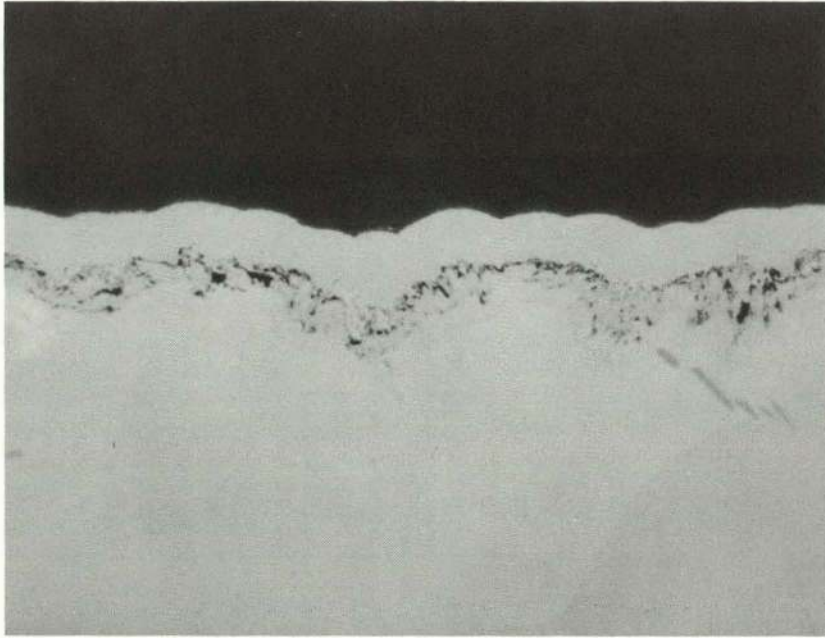


Figure 6

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0.0005-INCH NICKEL DEPOSIT PLATED IN HIGH-TEMPERATURE BATH
After 92.5 Hours Exposure in Corrosion Test Bath

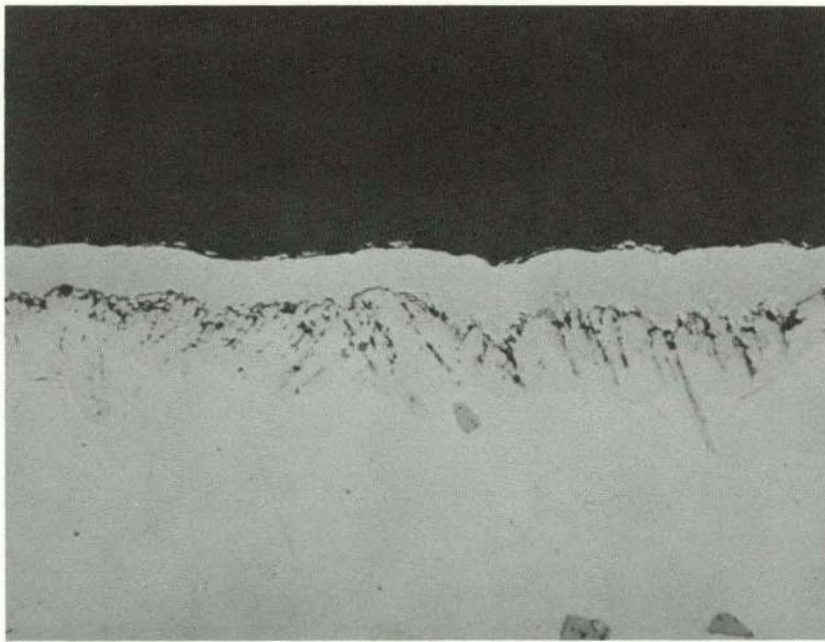


Figure 7

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0.0005-INCH NICKEL DEPOSIT PLATED IN HIGH-TEMPERATURE BATH
After 240 Hours Exposure in Corrosion Test Bath

Heat Treatment

The nickel deposits plated with the standard high-temperature bath were uniform and smooth, but as formed were not sufficiently adherent in the corrosive test atmosphere, table 1. Since the interface between the nickel and the uranium was clean, as shown in figure 4, a better metal-to-metal bonding could be achieved by heat-treating the plate to form a uranium-nickel alloy at the interface.

The temperature selected for heat treatment of the uranium was 625°C. This temperature was below that for the alpha-beta transition in which there is a change in the crystalline structure (15). It was also far enough below the melting points of the uranium-nickel alloys (785°C and up) so that it would not cause distortion of thin pieces of nickel-plated uranium. It was desirable, however, to provide sufficient alloying for good bonding of the nickel deposit in a short period of time, about 1 hr.

The first nickel-plated uranium coupons that were heat-treated were those plated in the low-temperature bath. The plated coupons were heat-treated at 625°C for 1 hr in a vacuum furnace at < 10 microns pressure; the heat treatment increased considerably the corrosion resistance of the nickel plate that had cracks in it; evidently, the uranium was outgassing through the cracks during the heat treatment. The nickel deposits without the cracks blistered during corrosion testing unless the uranium had been heat-treated prior to plating.

Heat Treatment Before Plating. Uranium coupons without a nickel plate were heat-treated for 1 hr at 625°C in a vacuum furnace; a rise in pressure was observed, confirming the outgassing theory. The main constituent of the outgasses was determined by mass spectrometry to be hydrogen.

The heat treatment of the unplated uranium coupons at 625°C for 1 hr in a vacuum furnace produced a protective film on the surface of the uranium that retarded oxidation of the uranium in a moist environment. It protected the uranium from oxidation in the high-temperature electroless plating bath, table 1. It was determined by X-ray diffraction to be UO and UO₂ (110 crystal plane highly oriented).

The oxide film did not wet in the plating bath; the surface was, therefore, wetted by a very dilute sodium lauryl sulfate solution, made basic with ammonium hydroxide (see appendix A). The wetted surface was suitable for an electrostrike and for plating in a standard electroless plating bath.

Heat Treatment After Plating. Nickel-plated uranium coupons which were heat-treated prior to plating were heat-treated again at 625°C for 1 hr in a vacuum furnace. A uranium-nickel alloy formed at the interface, figures 4, 6, and 7; there were no blisters in the deposit. The thickness of the alloy was approximately 0.0002 in. which agrees with the thickness calculated by the diffusion equation (16) and the constants of Kittel (17).

$$x^N = K_0 t e^{-Q/RT} \quad (2)$$

or

$$X^N = kt,$$

where

- X = distance of metal diffusion,
- N = reaction index (3 for nickel-uranium),
- Q = activation energy,
- R = gas constant,
- T = absolute temperature,
- K_0 = a constant,
- t = annealing time,
- e = base of natural system of logarithms, and
- k = a constant, at constant temperature.

As shown by equation 2, the thickness of the alloy depends on the temperature and the time the nickel-plated uranium is heated. The alloy formed by the heat treatment of the uranium plated in the low-temperature bath increased the life of the plate from about 2 to 90 hr in the corrosion test bath, table 1. The alloy formed on the uranium plated in the high-temperature bath increased the life of the plate from 22 to over 95 hr in the test bath. The life of the plate depended on its thickness and that of the alloy formed. The alloy, which starts forming at about 500°C, also improves the bonding of the nickel plate. An alloy thickness of 0.0002 in. appears to be adequate for both protection and adherence.

RESULTS AND DISCUSSION

CLEANING

Scrubbing the uranium pieces with laboratory scouring powder was a very satisfactory method for cleaning and removing contaminants from the surface. This method, however, requires considerable manual labor and is time consuming. An alternative cleaning method using a chromic acid dip was found to be satisfactory, except for removing deeply embedded crayon marks on the surface of the uranium.

PICKLING

The desired pickling was achieved by dipping the uranium in a nickel chloride-nitric acid bath for about a minute. During the development of these pickling conditions, it was noted that the period of time for pickling could be increased by decreasing the concentration of the nickel chloride-nitric acid bath or the temperature of the solution. Further work should be done to optimize these conditions.

PLATING

The plating of the uranium was accomplished by two processes. The standard high-temperature process is preferred over the low-temperature process; it

plates at a faster rate than the low-temperature bath, and the deposits have no stress cracks and are more corrosion resistant.

The use of the standard electroless plating bath for plating uranium, however, requires more preparation of the uranium prior to plating than the low-temperature baths (appendix B). The uranium must be outgassed by a heat treatment process and plated with a very thin film of nickel by an electrostrike in a nickel sulfamate bath. These steps are not necessary when plating in a low-temperature bath.

The deposits from the low-temperature and high-temperature electroless plating baths contained approximately 4 and 8% phosphorus, respectively. There was no evidence that the phosphorus content of the deposit was detrimental to the successful application of heat treatment or to the corrosion protection which the methods provided.

The deposits plated by both methods were uniform, lustrous, smooth, non-porous, adherent, and corrosion resistant. The quality of the plated deposits is summarized in table 2. The results indicate that the better method for plating nickel on uranium is the standard high-temperature electroless plating process which requires special preparations prior to plating.

Table 2

COMPARISON OF QUALITY OF PLATED NICKEL DEPOSITS ON
URANIUM METAL AFTER HEAT TREATMENT

Characteristic	Type Bath	
	Low-Temperature	High-Temperature
Thickness of Plated Deposits, in.	0.0005 to 0.003	0.0003 to 0.001
Variation in Thickness, in.	± 0.0001	± 0.0001
Uranium Removed in Pickling, in.	0.0007	0.0007
Surface Finish, μ in., rms	100-150	80
Time to Failure in Test Bath, hr	90-160	168-300
Bonding Quality	Alloy-Excellent	Alloy-Excellent
Hardness, Rockwell C	55-60	60-65
Plate Integrity	Stress Cracks	Excellent

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Chemical analyses of the plating baths were performed by analysts under the supervision of P. F. Shorten of the Chemical Analysis Department. The mass spectrometer scans were made by J. C. Horton of the Isotopic Analysis Department. The X-ray diffractions were made by F. N. Bensey and P. W. Pickrell of the Materials Development Department.

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Commercial products mentioned in this document may be substituted with other products of equal specifications.

APPENDIX A

BATH COMPOSITIONS

NICKEL CHLORIDE-NITRIC ACID PICKLING SOLUTIONChemical Composition*

600 g/l nickelous chloride, hexahydrate, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$
300 ml/l concentrated nitric acid, HNO_3

UC NO. 3 LOW-TEMPERATURE ELECTROLESS NICKEL PLATING BATHChemical Composition*

37.0 g/l nickelous sulfate, hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
67.0 g/l ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$
30.0 g/l succinic acid, $(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$
30.0 g/l sodium acetate, anhydrous, $\text{NaC}_2\text{H}_3\text{O}_2$
20.32 g/l sodium hydroxide, NaOH

Adjust pH to 6.6-6.8 with sodium hydroxide. Filter if necessary at this point.

Add 50 g/l sodium hypophosphite, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$.

Adjust pH to 9.0-9.5 with concentrated ammonium hydroxide.

Maintain pH 9.0-9.5 by addition of ammonium hydroxide.

Plating Rate ≈ 0.00004 in./hr at room temperature.

UC NO. 3 (MODIFIED) ELECTROLESS NICKEL PLATING BATHChemical Composition*

37.0 g/l nickelous sulfate, hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
40.0 g/l ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$
20.0 g/l succinic acid, $(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$
30.0 g/l sodium acetate, anhydrous, $\text{NaC}_2\text{H}_3\text{O}_2$
13.55 g/l sodium hydroxide, NaOH

Adjust pH to 6.6-6.8 with sodium hydroxide. Filter if necessary at this point.

Add 25 g/l sodium hypophosphite, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$.

Adjust pH to 9.0-9.5 with concentrated ammonium hydroxide.

*In distilled water.

Maintain pH 9.0-9.5 by addition of ammonium hydroxide.

Plating Rate \approx 0.0002 in./hr at 48°C.

NICKEL SULFAMATE STRIKE BATH

Chemical Composition*

77-86 g/l total nickel - added as nickel sulfamate, $\text{Ni}(\text{SO}_3\text{NH}_2)_2$
30-39 g/l boric acid, H_3BO_3
2.5 g/l sodium lauryl sulfate, $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$ (to lower surface tension to
34 dynes/cm)
pH 3.5 to 4.2 with sulfamic acid, $\text{NH}_2\text{SO}_3\text{H}$

Bath must have mild agitation and continuous filtration for best results.
Bath should not be filtered through carbon. Filter through No. 42 filter
paper or the equivalent.

SODIUM LAURYL SULFATE WETTING SOLUTION

Chemical Composition*

2 g/l sodium lauryl sulfate, $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$
125 ml/l ammonium hydroxide, NH_4OH

*In distilled water.

APPENDIX B

OPERATING PROCEDURES*

CLEANING AND PICKLING

The uranium metal is scrubbed with a laboratory scouring powder (Federal Specification Type 1, Class 1, P-S-00311B) to remove grease and wax crayon markings. It is rinsed with water, degreased in trichloroethylene vapor, and rinsed in distilled water. The piece of uranium metal is then dipped in 8 N nitric acid at a temperature of about 35 to 40°C for 20 min to remove the oxide film. The metal is pickled in a nickel chloride-nitric acid bath at a temperature of 42°C for about 1 min to etch the surface. The pickled uranium is dipped in three successive baths of 8 N nitric acid at room temperature to remove the chloride residue, and well rinsed with distilled water. The piece is then rinsed with ethyl alcohol and dried with a nitrogen gas stream to prepare it for heat treatment prior to plating in the standard high-temperature bath. If low-temperature plating is planned, the water-rinsed piece is introduced directly into the bath, without allowing it to dry.

PLATING IN LOW-TEMPERATURE BATH

The cleaned and pickled uranium is immediately transferred into the UC No. 3 bath at room temperature, and the electroless plating process is initiated by making the metallic uranium cathodic to a 6-volt-dc potential for 3 to 5 sec, the plating tank serving as the anode. In the same bath the piece is electroless plated for 3 hr at a rate of 0.00004 in./hr to obtain a coating which will protect the metallic uranium from oxidation in a higher temperature (48°C) electroless plating bath. The uranium with the thin film of nickel on it is removed from the room-temperature bath and immediately placed in the UC No. 3 modified plating bath where it is plated to the desired thickness, the plating rate being 0.0002 in./hr. The nickel-plated uranium is removed from the bath, rinsed with distilled water, then dried by spraying with acetone or ethyl alcohol. The plated uranium is now ready for the heat treatment to alloy the uranium and nickel at the interface.

PREPLATING HEAT TREATMENT

The pickled and dried piece of uranium is placed in a vacuum furnace at room temperature. The furnace is evacuated and purged with pure argon four times to assure complete removal of the oxygen and nitrogen. The furnace is evacuated to less than 10 microns pressure prior to initiating the heating cycle. The evacuation is continued during the heat treatment process to remove the outgasses and to prevent oxidation or nitridation of the uranium. The temperature of the furnace is raised in about 3 hr to

*See figure 1.

625°C and maintained for 1 hr. The furnace is cooled under vacuum to room temperature; then the uranium piece is removed from the furnace and is ready for wetting and plating.

PLATING IN STANDARD BATH

The heat-treated uranium metal is wetted for about 5 min in a dilute sodium lauryl sulfate solution made basic with ammonium hydroxide. The uranium is placed in a nickel sulfamate bath at room temperature and given a 20-min nickel strike using a current density of 4 amps/sq ft to initiate the plating process. The uranium is immediately transferred to a standard electroless nickel plating bath (which is free of chloride and fluoride ions) and plated at a rate of about 0.0007 in./hr to the desired thickness. The nickel-plated uranium is removed from the bath, rinsed with distilled water, then dried by spraying with acetone or ethyl alcohol. The metallic piece is now ready for the second heat treatment to form the uranium-nickel alloy at the interface.

HEAT TREATMENT FOR ALLOYING

The uranium plated with nickel by either the low-temperature process or the standard electroless plating process is given the same heat treatment which the pickled uranium receives, as described under the preplating heat-treatment section. After this final heat treatment, the piece of uranium is ready for testing or use.