

ELECTROLESS NICKEL PLATING
PART I. PLATING OF URANIUM AND IRON

by

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SUMMARY

This investigation showed that a sound, weather-resistant coating can be applied to uranium and iron provided that the surface to be plated is cleaned and etched properly.

Using the proposed two-bath plating method at 80°C., a four-mil nickel coat can be deposited in thirteen hours.

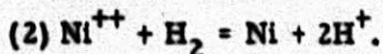
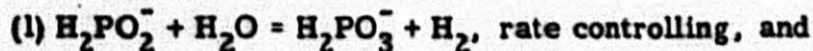
EXPERIMENTAL

A. Introduction

Electroless nickel plating is done in baths containing nickel salts, sodium hypophosphite, and buffering agents. The formulas of the plating solutions are based on two types of baths, alkaline and acid. In suitable temperature and pH ranges, nickel is deposited from these baths onto metallic surfaces immersed in the solutions. The nickel coatings produced by the electroless method vary in appearance from a dull grey color to a shiny lustre, depending on the plating conditions. The plate is hard and brittle. It is not entirely nickel; it contains as much as 7% phosphorus.

The variation of plating rate with temperature and with the concentrations of the chemical components has been studied by Brenner and Riddell.⁽¹⁾ As might be expected, at temperatures below 90°C., the rate decreases.

In an alkaline bath at 90°C. with a pH of 9 the kinetic data indicate a reaction which may be represented by:



Thus hydrogen evolution and a decrease in pH are always observed during the nickel deposition.

Baths of somewhat different composition are useful in the pH range 4.5 to 6. In this case the rate of plating is not directly dependent on the concentration of the reagents, so the mechanism must depend on a diffusional process. However, the over-all reaction still is such that nickel is reduced, hypophosphite is oxidized, hydrogen ions are produced and hydrogen is evolved.

B. Plating Technique

1. Surface Preparation

The plating reaction is catalyzed by metallic surfaces, especially nickel, and can be started only on suitably prepared metal surfaces. Also, proper surface preparation is required in order to obtain adherent coatings.⁽¹⁾

The surface preparation of iron is comparatively simple. Solvent degreasing, pickling in 96% sulfuric acid (3 min.), plus a water wash provide a suitable surface for plating.

The surface preparation of uranium is more involved. Mechanical cleaning is not enough; the surface must be etched. Evidently there is little or no chemical or intermetallic bond between uranium and nickel; a satisfactory bond must be formed by interlocking crystals, as shown in Figure 5. This bond is made possible by an etching treatment.

The surface preparation (and plating) was investigated with discs of uranium metal sawed from cold-rolled slugs. These discs were 1 1/2 inches in diameter and 3/16-inch in thickness. They weigh about 100 grams.

Early experiments with these discs showed that nitric, sulfuric and hydrochloric acid pickling gave a clean surface, but an adherent coating could not be obtained consistently. An anodizing procedure using phosphoric acid and ethylene glycol was likewise unsatisfactory.

The present surface treatment of uranium is based on a procedure by Wehrmann⁽²⁾. The procedure, although complex, produces the desired degree of etching. One mil is removed in this process.

(a) The surface is ground with a belt grinder to remove oxide and expose the metallic surface.

(b) The uranium is degreased by immersion in Permachlor (trichlorethylene). Hanging the cold piece in vapor of boiling Permachlor for a few seconds provides effective final degreasing.

(c) The uranium piece is pickled in 45% nitric acid for three minutes and then washed with water.

(d) The piece is anodized for 10 minutes in a trichloroacetic acid (600 g./l.) solution containing 0.1 M HCl. This operation is done at 50-60°C. and a current density of 50 milliamperes per square centimeter. Then the anodizing solution is washed off. The anodizing procedure forms a black layer on the surface.

(e) The piece is immersed in 45% nitric acid at 45°C. for three minutes. The black surface layer formed in the anodizing procedure dissolves, leaving a clean, etched, grey surface. After a quick water rinse, the piece is immersed in the plating bath.

2. The Plating Operation

(a) Bath Composition

Brenner and Riddell⁽¹⁾ reported higher plating rates in acid baths than in alkaline baths. Earlier experiments here showed that uranium could not be plated in an acid bath. However, it was possible to initiate plating in an alkaline bath, then switch to an acid bath to take advantage of the higher plating rate. Thus a two-bath process evolved.

The alkaline bath finally adopted has the following composition:

- 30 g./l. nickel acetate,
- 10 g./l. sodium hypophosphite,
- 100 g./l. sodium citrate, and
- 50 g./l. ammonium acetate.

Ammonium hydroxide is added to give a pH of 9; frequent additions of ammonium hydroxide are necessary to maintain the pH. This bath is operated at 80-90°C.

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When one mil of nickel has been deposited from an alkaline bath, the uranium piece may be transferred to an acid type bath. The one employed here has the following composition:

30 g./l. nickel sulfate,
10 g./l. sodium hypophosphite, and
50 g./l. sodium glycolate.

The pH of this solution as made up is close to 6, a satisfactory value; sodium hydroxide is added periodically to maintain the pH. The bath is operated at 80-90°C.

The plating rates of uranium, drill rod, and mild steel in the above alkaline and acid plating baths are presented in Table I. The acid bath rates are for pieces which had first been plated in the alkaline bath. The mild steel tested was in the form of hex nuts. Their unfavorable geometry may explain the low plating rates observed, as compared with drill rod.

TABLE I
PLATING RATE IN MILS PER HOUR

<u>Material</u>	<u>80°C.</u>		<u>90°C.</u>	
	<u>Alkaline</u>	<u>Acid</u>	<u>Alkaline</u>	<u>Acid</u>
Uranium	0.24	0.34	--	--
Drill rod	0.25	0.34	0.37	0.49
Mild steel	--	--	0.25	0.36

b. Variations in Bath Composition

In order to improve the homogeneity, durability, and adherence of the plate, various materials were added to the baths to test their effect.

The composition of the alkaline bath was varied by employing ammonium and nickel salts in the form of chloride or sulfate instead of the acetate. The results did not yield satisfactory plates and it was felt preferable to use acetate.

In the acid bath the glycolate was replaced by acetate in one experiment. After plating for one hour, a precipitate formed when the pH was adjusted to its original value with base. The reason may lie in the weaker complexing action of acetate as compared with glycolate. The life of an acid

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bath is limited chemically by the build-up of phosphite ion, which will eventually precipitate with nickel ion if nickel is maintained at its original concentration. Glycolate defers such precipitation longer than does acetate.

The effect of the wetting agent Nacconal NRSF was tested in an alkaline plating bath at 0.05% concentration. Since much foam formed, it was used in an acidic bath at 0.01%. Of two uranium pieces plated, one showed severe cracks in the coat. This wetting agent is of no help.

An attempt was made to incorporate molybdenum in the nickel plate by co-reduction from the plating solution. The alkaline plating bath contained 0.01 M MoO_3 . After three hours the uranium piece had blackened, but there was no evidence of any nickel deposition. When attempting to plate from a bath 0.001 M in MoO_3 , a plate formed on the uranium, but cracked after three hours. The attempt to co-deposit molybdenum was abandoned.

The commercial electroless nickel plating process known as "Lustralloy" was investigated. Chemicals from a "Lustralloy" kit were dissolved to furnish a plating bath similar in color to the one used here. A clean uranium piece was plated according to the directions. After half an hour the solution deteriorated with general precipitation of nickel black and failure of the coat. A second run was made employing one-third concentrations. Some trouble was had due to nickel plating on the walls and bottom of the beaker. Nevertheless, the rate of plating at 80°C . was the same as in our alkaline bath, 0.24 mil per hour. The resultant plate was quite shiny.

c. Apparatus and Methods

The required apparatus are a jar with lid, stirrer, hot plate, filtering device, thermometer, constricted funnel, and high temperature electrodes with pH meter. The lid is to minimize evaporation and the volatilization of ammonia from the alkaline bath. The filter employs an air lift operated with nitrogen. The air lift raises liquid to a sintered glass filter through which it drips back into the bath. The purpose of the constricted funnel is to permit gradual addition of reagents. With the electrodes already immersed in the plating bath, instant pH readings can be made.

The filtering device proved useful since the resulting clean solutions lasted longer and showed less tendency to form nickel deposits on the bottom of the beaker or on the supports. Filtering removes lint and particles which act as nuclei for the deposition of nickel.

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Continuous addition of replacement chemicals was tested, but no improvement was found over the system of periodic additions at frequent intervals. The improvement hoped for was the elimination of a layer structure to be discussed later. If 100 cm² are being plated in a one liter alkaline bath, 20 ml. of 50 g./l. NaH₂PO₂ in 5 M NH₄OH are added every fifteen minutes, and additional NH₄OH is added to maintain the deep blue color of the bath.

In the acid bath, 20 ml. of 50 g./l. NaH₂PO₂ and 8 ml. of 1 N NaOH are added every fifteen minutes.

Occasionally loose nickel particles form and are not raised by the air lift, but fall to the bottom of the beaker. Here they act as nuclei for nickel deposition and a nickel surface will grow on the bottom of the beaker. The uranium pieces must be removed to a fresh bath at once since general decomposition of the solution usually follows, with nickel black being formed throughout.

Variation of pH within the range 8-10 is permissible in the alkaline bath. Below this range deterioration of the bath commences. In the case of the acid bath a pH range 5-6 should be maintained. Below pH 5 the rate of plating drops off sharply, while above pH 6 there is a tendency for nickel salts to precipitate.

During the course of a plating operation it is inadvisable to remove a plated piece from the bath and permit it to dry out. If the plating is stopped momentarily by drying in air or otherwise interrupted and then recommenced, the nickel which now plates will form a poor bond to the undercoat and can be easily stripped from the piece.

3. Polishing

The nickel platings on two pieces were polished using #2, #1/0, #2/0, #3/0, and #4/0 sandpaper, followed by alumina on polishing cloth. This procedure gave a bright mirror finish which was still perfect six months later.

C. Evaluation of the Nickel Plate

1. Physical Characteristics

A four mil plate produced as above (but not polished) feels rough to the touch, and is dull grey in color. As viewed through an 18x microscope it appears shiny and metallic with a pebble grain texture, as in Figure 1.

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The plate is quite hard, being difficult to grind off even with a Behr Manning #120 belt. However, the plate is brittle, and is liable to chip if given a sharp hard blow.

Defects which were sometimes noted in plated pieces include blisters, cracks, (Figure 2) and peeling of one nickel layer from another, referred to as double layering. Those coatings on which no defects were observed were considered sound until proven otherwise.

Occasionally plated pieces removed from the bath have blackened surface areas. The cause is not understood, but these spots behave normally and polish to a bright metallic finish.

Of the last twenty uranium discs plated to four mils thickness according to the above cleaning and plating procedure, sixteen were without visible defects. Twelve drill rod pieces have been successfully coated using the above plating procedure and the special cleaning treatment. Of the sound pieces mentioned above, no piece has yet developed a defect from aging in the laboratory atmosphere.

One thorium disc was cleaned with a power grinding tool, then plated in an alkaline plating bath to a depth of one mil. The coating appeared sound, but several weeks later showed severe cracking.

2. Chemical Tests

Through the cooperation of F. C. Telfer of the Analytical Services Section, seven coated uranium pieces were subjected to a weatherometer test simulating a year's outdoor exposure. Of these pieces, three were initially defective due to blisters and double layering, although in no case was the uranium base metal revealed. All seven pieces were exposed in the weatherometer at 110°F. for 368 hours over a period of one month. The time cycle employed one and one-half hours of water spray, one and one-half hours ultraviolet irradiation, two hours spray, and sixteen hours ultraviolet light.

At the close of the run the pieces were examined and no changes detected. Each piece known to be defective had increased in weight an average of three milligrams per 30 cm², whereas the sound pieces gained less than one-half milligram. Thus sound nickel coats are protective against ordinary surface weathering as indicated by the weatherometer test.

The seven coated pieces from the above experiment were immersed in boiling water to see if they would withstand this medium. The defective

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pieces failed in seven hours; the sound pieces failed in fifteen hours, as indicated by cracks and appearance of UO_2 .

Two uranium pieces coated with nickel to a depth of four mils were treated with 1 M hydrochloric acid at $60^{\circ}C$. for one-half hour. The presence of five and fifty milligrams of uranium, respectively, in the leachings indicated pinholes in the coating. The 1 M hydrochloric acid treatment dissolves nickel plate at an average rate of 0.4 mils per hour.

The above tests indicate small pinholes or cracks in the coatings. The laboratory atmosphere penetrates these and attacks the uranium at a negligible rate, but hot hydrochloric acid reacts rapidly enough to disrupt the coating in one-half hour. Steam disrupted this coating in fifteen hours.

3. Metallographic Examination

Through the cooperation of T. C. Nelson and L. A. Hartcorn of the Metallurgical Section, metallographic examinations were performed on several of the plated discs. A layer structure was indicated by the many alternate light and dark bands (Figure 3). A columnar structure perpendicular to the layers is apparent in Figure 3. In each case where an examination was made a sharp discontinuity in the plate characteristics was observed where the acid bath plating had commenced.

The above features were thought due to some discontinuous process during the plating, such as a sudden temperature change, or a change in solution composition. However, the same features were found in plates from experiments in which temperature was held constant to within one degree and reagents were added continuously.

One examination indicated that the coating formed in the alkaline bath was more homogenous than that produced in the acid bath (Figure 4). Upon plating five steel pieces in an alkaline bath to a depth of four mils and examining them metallographically, it was seen that the layer structure was still present (Figure 6), at least thirty layers being observable.

The uranium-nickel interface in Figure 5 contained no voids, the nickel apparently following the etched uranium contour exactly, forming a tight interlocking bond.

It was hoped that annealing would yield a more ductile coat and diffuse the layers sufficiently to give a homogenous coating. No change was evident

after annealing for three hours at 300°C. in an inert atmosphere. Two other pieces annealed at 400°C. for one hour showed no change upon metallographical examination.

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2. CT-2443, Electroplating, R. Wehrmann, 5-6, June 2, 1945.

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2. HW-17838, pp 11-12, April, 1950.
3. HW-18203, pp 29-32, May, 1950.
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5. HW-18880, pp 6-7, August, 1950.

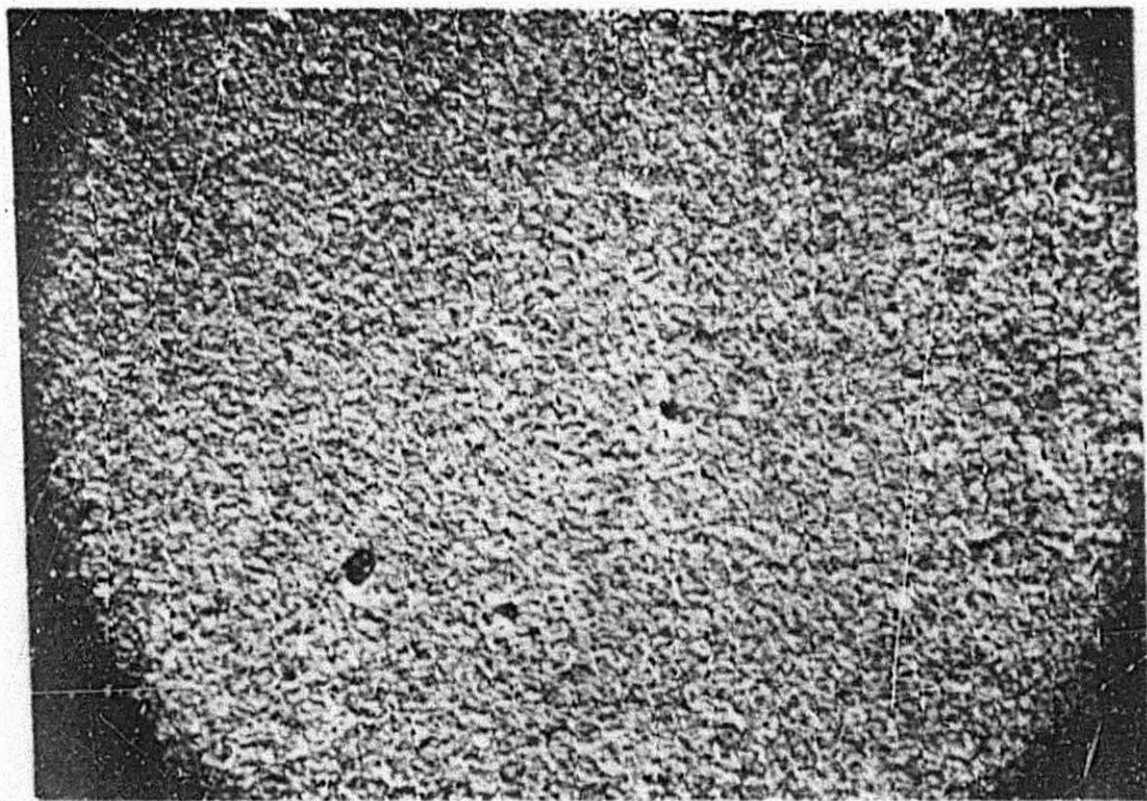
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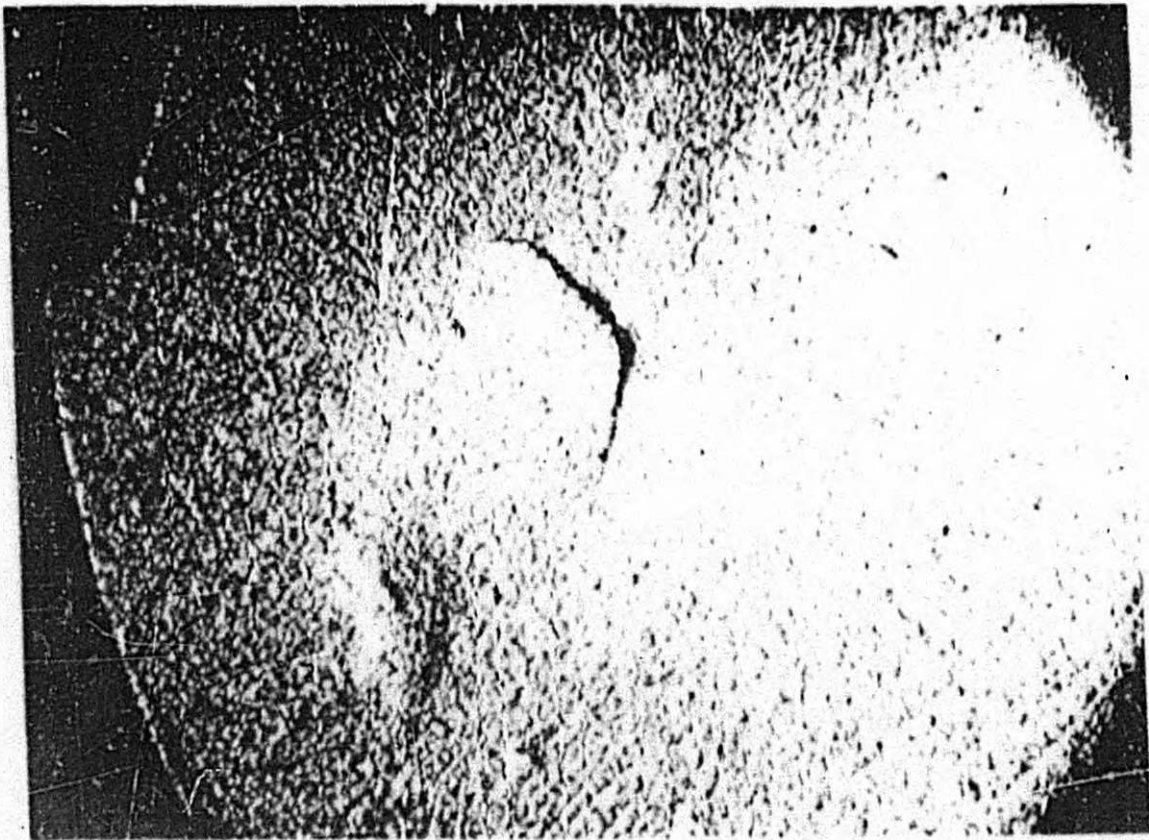
Figure 1.



Uranium plated with 3.5 mils of nickel by the "electroless" method. Illustrating pebble-grained surface. 18x

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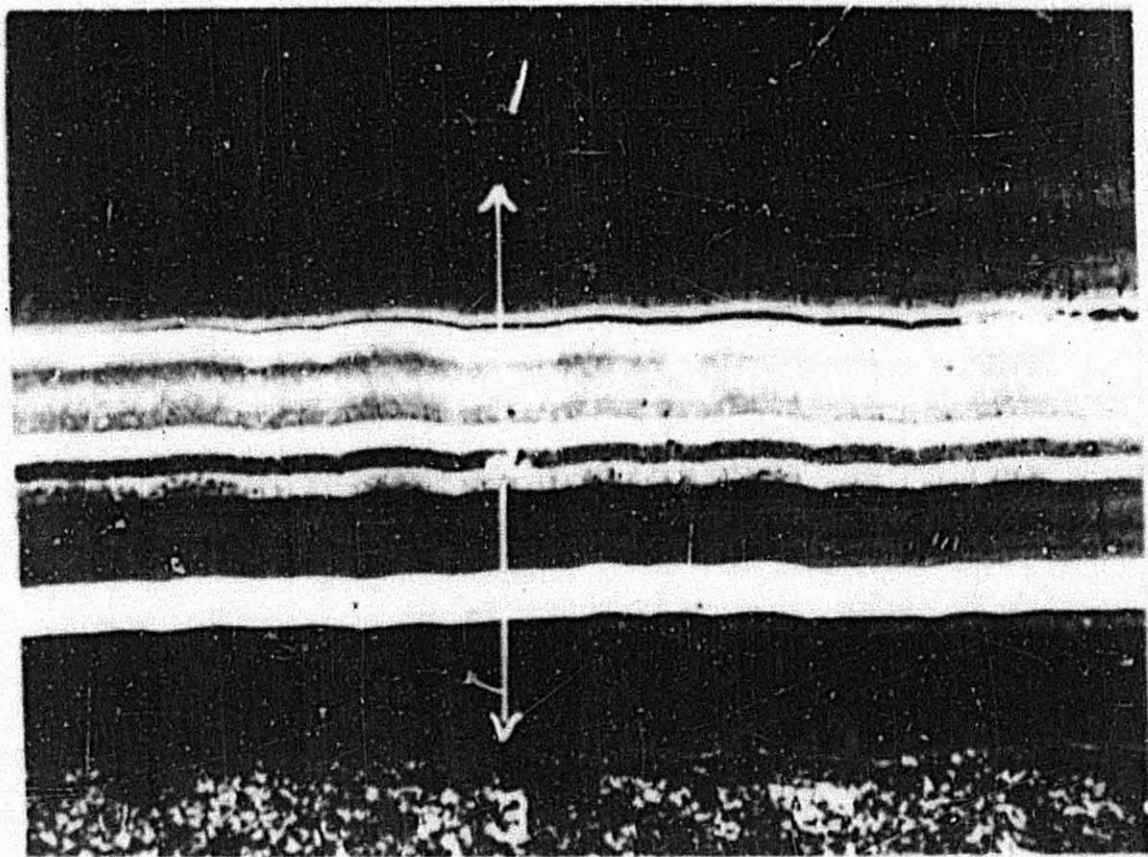
Figure 2



Uranium plated with 3.5 mils nickel by the "electroless" method. Illustrating crack in coat. 18x

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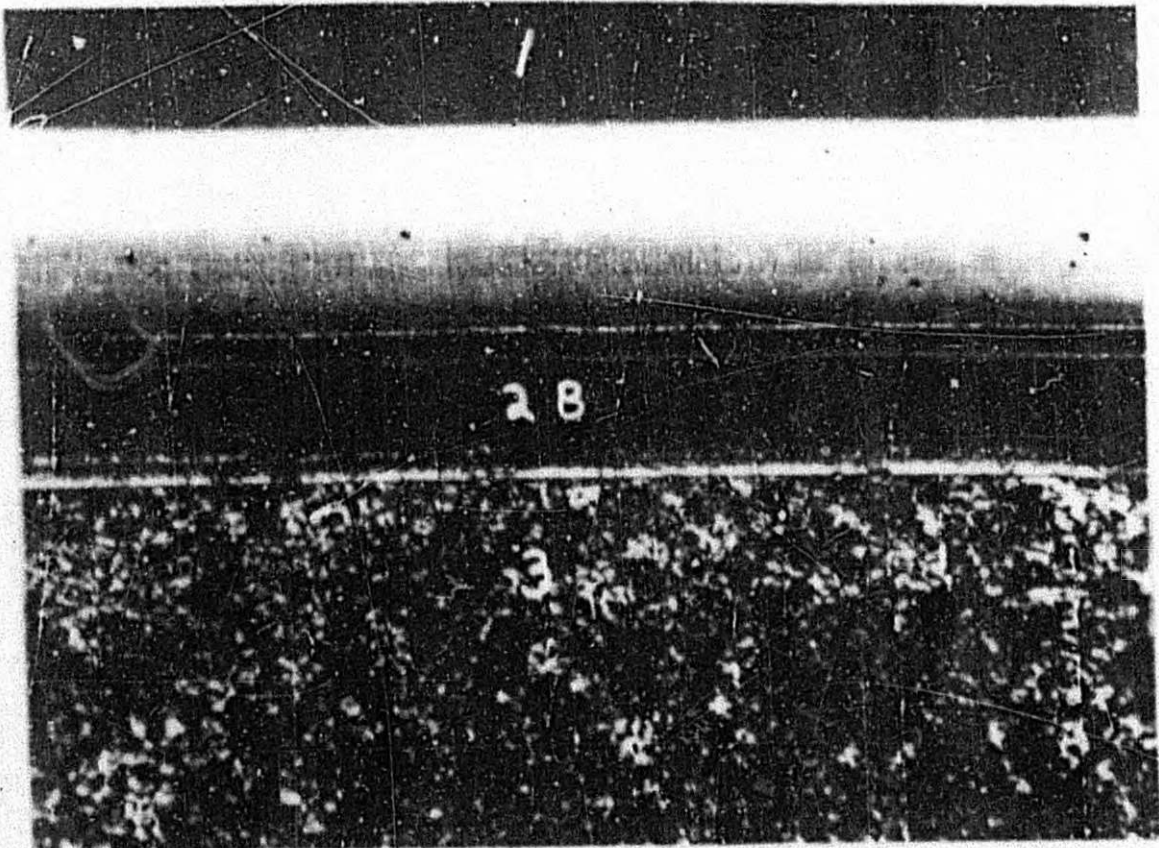
Figure 3.



Drill rod plated with 5.5 mils nickel by the "electroless" method, 500x. Illustrating layer structure and also columnar structure within layers. (1) Bakelite, (2) Nickel coating, (3) Drill rod.

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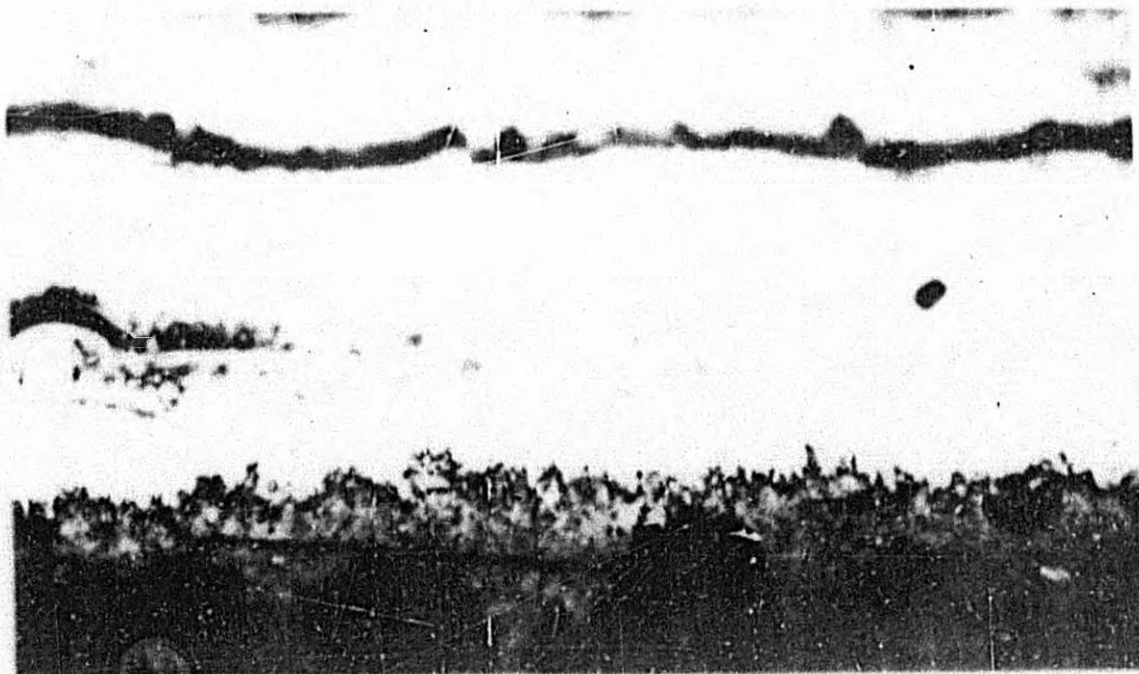
Figure 4.



Drill rod plated with 3.5 mils nickel by the "electroless" method, 500x, illustrating interface between alkaline bath and acid bath plate. (1) Bakelite, (2A) Acid bath plate, (2B) Alkaline bath plate, (3) Drill rod.

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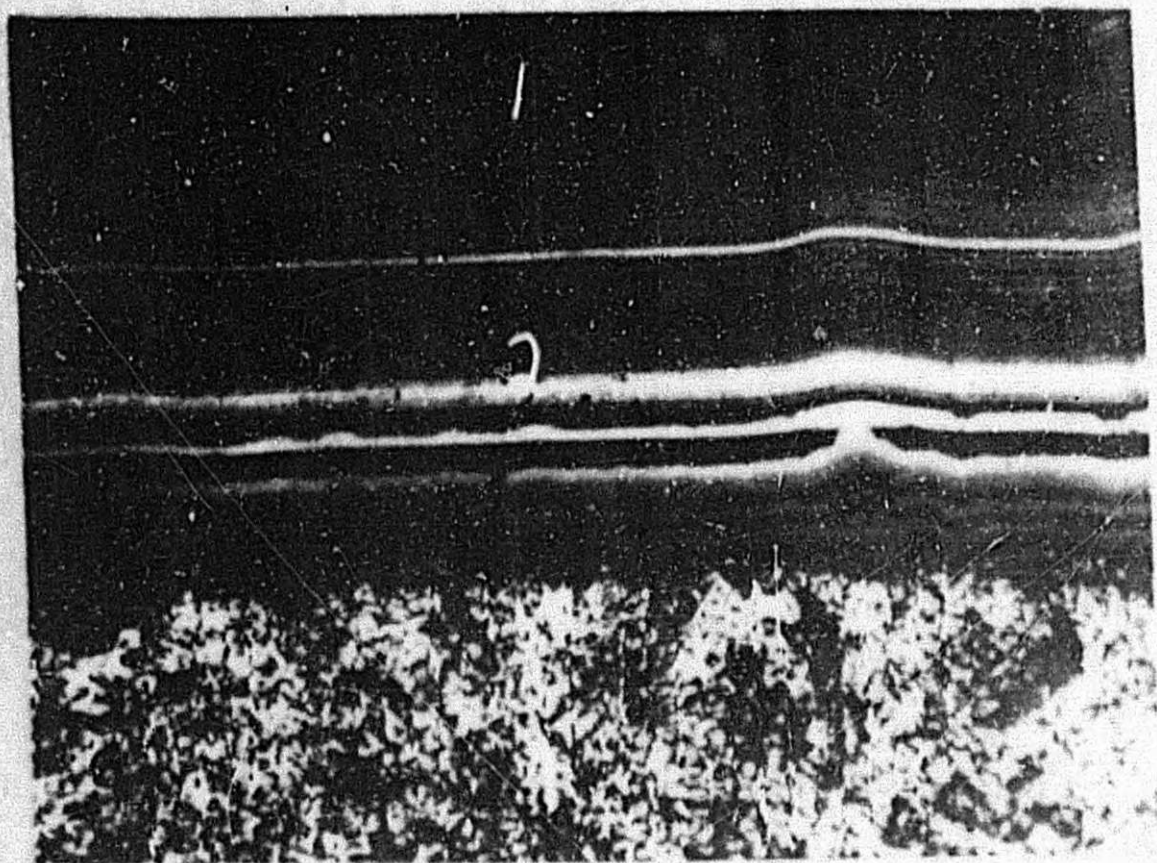
Figure 5.



Uranium plated with 5 mils of nickel by the "electroless" method, 500x. Illustrating interlocking uranium-nickel interface.

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Figure 6.



Drill rod plated with 4 mils of nickel by the "electroless" method, 500x. Illustrating plate produced entirely in alkaline bath. Note inclusion. (1) Bakelite, (2) Nickel plate, (3) Drill rod.

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