

[54] **PROCESS FOR PLATING URANIUM WITH METAL**

Primary Examiner—Reuben Epstein
Attorney—Roland A. Anderson

[72] **Inventors:** George S. Petit; Ralph R. Wright, both of Oak Ridge, Tenn.

[57] **ABSTRACT**

[73] **Assignee:** The United States of America as represented by the United States Atomic Energy Commission

A process for providing a uranium metal article with a tenaciously adhering metal plating deposited from aqueous solution. Prior to plating, oxides and other contaminants are removed from the surface of the article. The article then is heated in vacuum under selected conditions to form thereon a very thin and highly protective oxide film which is non-wettable by water. The surface of the oxide-coated article is made wettable by water by contacting the article with a basic wetting solution. The resulting wettable, oxide-coated article is then electroplated with metal in an aqueous metal-plating bath.

[22] **Filed:** June 10, 1970

[21] **Appl. No.:** 45,085

[52] **U.S. Cl.**.....204/1.5, 204/29, 204/38, 204/49, 117/50

[51] **Int. Cl.**.....C01g 43/00

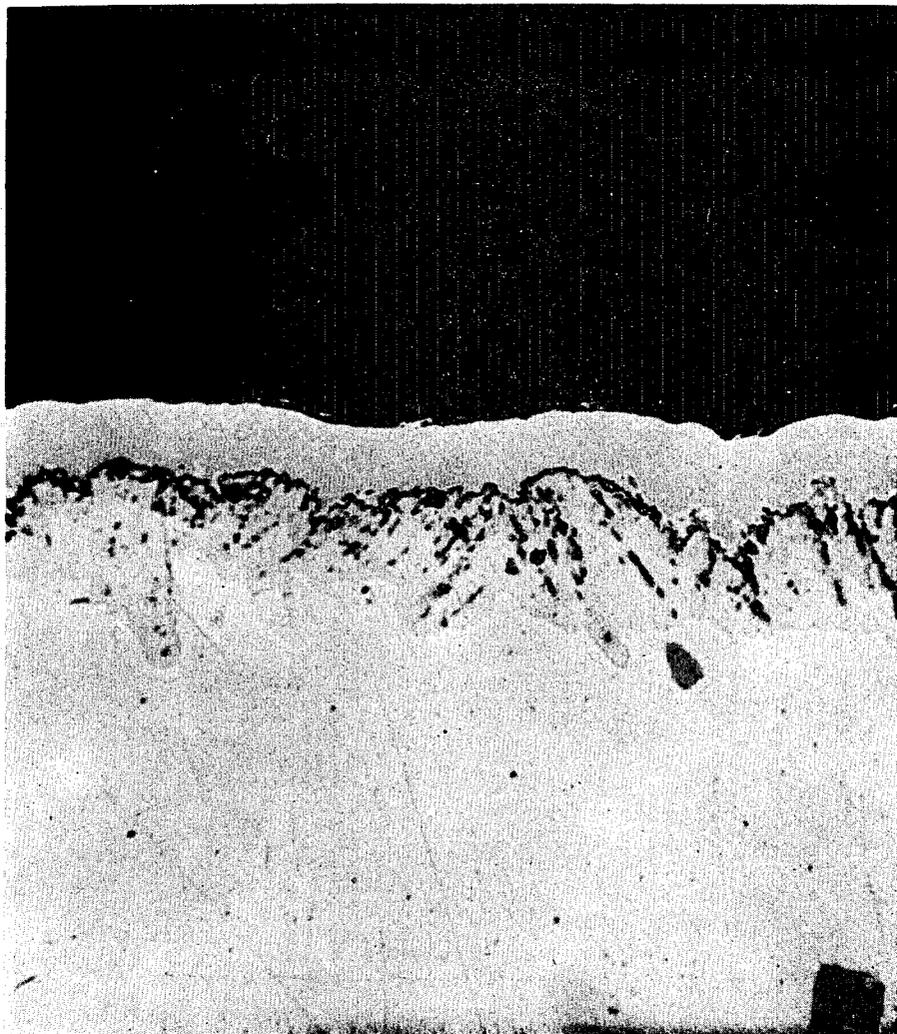
[58] **Field of Search**.....204/1.5

7 Claims, 1 Drawing Figure

[56] **References Cited**

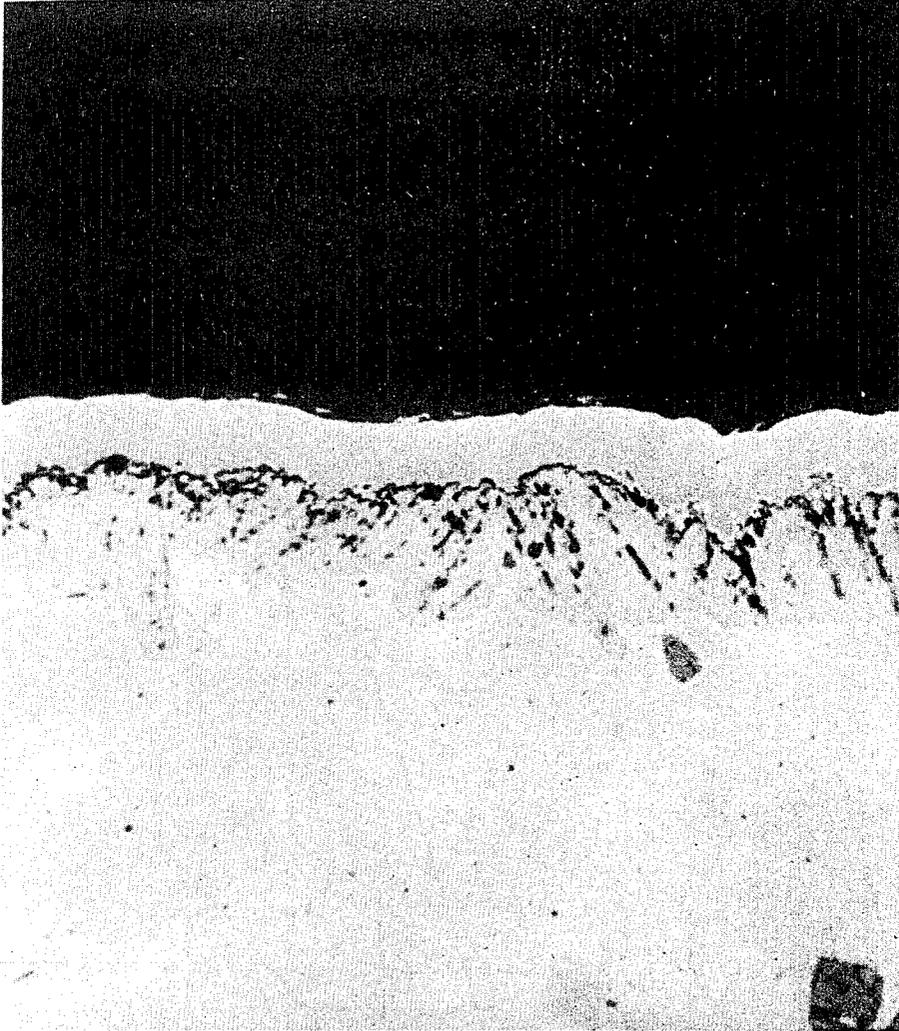
UNITED STATES PATENTS

2,894,884 7/1959 Gray.....204/1.5



PATENTED JUN 6 1972

3,668,084



INVENTORS.

George S. Petit
Ralph R. Wright

BY

Colman A. Anderson

ATTORNEY.

PROCESS FOR PLATING URANIUM WITH METAL

BACKGROUND OF THE INVENTION

This invention was made in the course of, or under, a contract with the U. S. Atomic Energy Commission.

The present invention relates generally to processes for depositing an adherent metal plating on uranium, and more particularly to such processes where the plating is deposited from aqueous solution.

Uranium is one of the most difficult metals to plate because uranium surfaces readily oxidize, forming comparatively thick and poorly adherent oxide films which prevent satisfactory plating by either electrodeposition or chemical (electroless) deposition. Thus, it is conventional practice to precede uranium-plating operations with various cleaning steps in which the uranium surfaces are scrubbed, abraded, and pickled to remove surface oxide. To prevent re-oxidation of the uranium surfaces prior to plating, it is common practice to maintain the cleaned uranium in an essentially oxygen-free environment, or, if feasible, to immediately immerse the uranium in the plating bath.

Unfortunately, most of the baths used for plating uranium articles are aqueous solutions, and thus re-oxidation of the cleaned uranium surfaces begins as soon as the uranium is immersed in the aqueous bath. If the bath operates at a low temperature, as at room temperature, the rate of oxidation may be sufficiently low so that the resulting oxide film does not interfere appreciably with the deposition of a tenaciously adherent plating. This advantage is offset, however, by the fact that low-temperature baths are characterized by comparatively low plating rates. If the bath is of the high-temperature type, higher plating rates are obtained, but at the expense of serious deficiencies in the quality of the plating-to-uranium bond.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a process whereby a uranium metal body is provided with an adherent metal strike plating deposited from an aqueous electroplating bath.

It is another object to provide a process whereby a uranium metal body is provided with an adherent metal plating deposited at least in part from an aqueous plating bath maintained at an elevated temperature.

It is another object to provide a process for metal-plating uranium wherein the uranium to be plated is made resistant to oxidation by aqueous plating solutions.

Other objects of this invention will be apparent from the following description and appended claims.

In accordance with this invention, oxides and other surface contaminants are removed from the uranium article to be plated. The resulting clean uranium article is confined in an enclosure which is then evacuated to a pressure below about 500 microns. The confined uranium body is heated under vacuum to a temperature above about 500° C. and below the temperature at which uranium changes to the beta phase for a time sufficient to form thereon a continuous uranium oxide coating having a thickness below about 2.5 microns. This film is composed of uranium dioxide and lesser oxides, is non-wettable by water, and is virtually impervious to dry air, moist air, and water. The oxygen content of the film gradually decreases from the outer surface inward toward the film-and-substrate interface.

The oxide-coated uranium article is immersed in an aqueous ammoniacal solution containing a wetting agent, to render the oxide film wettable by water. The wettable, oxide-coated uranium article is immersed in an aqueous metal-electroplating bath and plated with metal.

BRIEF DESCRIPTION OF THE DRAWING

The single FIGURE is a microphotograph (magnification, 500) of a sample obtained by cross-sectioning a plated portion of a uranium article processed in accordance with this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Out invention first will be illustrated in terms of a preferred application: providing a uranium article with an adherent nickel plating which is alloy-bonded to the uranium. The operations involved in this form of invention are discussed below.

Removal of Surface Contaminants

Oxides and other contaminants are removed from the surface of the uranium article by any suitable techniques. For example, the article may be successively scoured, degreased, soaked in acid, pickled, and then dipped in acid to remove chloride residue. The resulting cleaned article is rinsed with water and dried rapidly, as by dipping in alcohol and ten exposing to a stream of nitrogen.

Formation of Protective Oxide Coating

The cleaned uranium article is transferred rapidly to a vacuum furnace which preferably is filled with a dry inert gas, such as argon. The vacuum furnace may be of conventional design. On completion of the transfer, the furnace promptly is evacuated and then purged with dry inert gas. Preferably this procedure is repeated several times to ensure removal of oxygen, nitrogen, and water vapor. The furnace then is evacuated to a pressure below about 500 microns, after which heating of the furnace is initiated. The furnace temperature is increased gradually, at a rate facilitating outgassing, successively to a temperature in the range of about 500° to 625° C. The furnace is maintained at this temperature for a period ensuring that a selected thickness of a protective uranium-oxide film (discussed below) has formed on PROTECTIVE article. A temperature in the range cited is (a) high enough to form the desired protective film within a few hours and (b) safely below the temperature ($\approx 665^\circ \text{C.}$) of the alpha-beta transition. Heat treatment at a temperature below the transition temperature is preferred to avoid undesired changes in the crystal structure of the uranium.

The above-described vacuum treatment forms on the uranium a semimetallic-appearing uranium oxide film or coating, composed of the dioxide and lesser oxides. This film is non-wettable by water, is characterized by a gradually decreasing gradient of oxygen content from the outer surface inwardly toward the film- and-substrate interface, and is virtually impervious to, and free from reaction with, dry air, moist air, and water. As taught in our co-assigned, copending application Ser. No. 728,910, now U.S. Pat. No. 3,547,709 issued Dec. 15, 1970, very thin films of this character can be formed by heating uranium articles to a selected temperature in an evacuated volume in the absence of specially provided sources of oxygen. Films so produced are comparatively thin but, as shown in the single table presented in U.S. Pat. No. 3,547,709, prevent corrosion of the uranium substrate for from about 5 to 50 hours when exposed to atmospheric air at 100 percent relative humidity and 95° C.

We believe that the very thin, semimetallic films of interest to the present application are produced by reaction of the uranium and the highly limited amount of oxygen present (a) in the furnace after evacuation or (b) on the cleaned uranium body as oxides formed during transfer to the furnace. For convenience, such oxygen will be referred to herein as residual oxygen.

In the oxide-forming operation, the time- and-temperature combination is selected to form an oxide film having a thickness less than about 2.5 microns (100 millionths of an inch). Such a film protects the article against corrosion by aqueous plating solutions, permits the electrodeposition of a strike coat (to be described), and does not impair the formation of a satisfactory alloy bond in a subsequent heat-treatment operation (to be described).

After the uranium is oxide-coated as described, it may, if desired, be left exposed to the atmosphere for long periods without adversely affecting subsequent plating operations.

TREATMENT WITH WETTING SOLUTION

The oxide-coated uranium article is immersed in a non-caustic basic aqueous solution containing an anionic wetting agent. We have found that this renders the oxide film wettable by water without vitiating its protective properties. Acid or caustic wetting solutions are undesirable for this application, since they attack the oxide film. We prefer to use aqueous ammoniacal solutions, such as a dilute aqueous solution of sodium lauryl sulfate made basic with ammonium hydroxide or ammonium carbonate.

After the oxide film is made wettable as described, the film-coated uranium body can be metal-plated in aqueous baths with virtually no oxidation by the bath, even if it is operating at close to 100° C. We have demonstrated in numerous experiments that the protection provided by this thin wettable film, while limited to relatively short periods of exposure as compared with thicker films, is adequate to permit the deposition of adherent metal platings from cold or hot aqueous solutions. As described in our above-cited application, formation of this uranium oxide film is characterized by a highly preferred 100-crystal orientation. We postulate that this orientation, which is not changed when the film is made wettable, is at least in part responsible for the protectiveness of the film.

DEPOSITION OF STRIKE COAT

The wettable, oxide-coated uranium article is immersed in a conventional low-temperature aqueous electroplating bath and provided with a strike coat of nickel. This strike coat is provided to make the oxide surface catalytic for reactions involved in the chemical deposition of nickel in a subsequent step of the preferred form of this process. Preferably, the strike coat is a very thin nickel layer (e.g., 0.1 mil). The strike coat may be porous, since the underlying oxide film will protect the uranium against corrosion by aqueous solutions.

DEPOSITION OF FINAL NICKEL PLATING

Following deposition of the strike coat, the uranium article is transferred to a conventional high-temperature electroless nickel-plating-bath where nickel is deposited on the article at a comparatively high rate to provide a plating of the desired overall thickness. The plating deposited from the electroless bath is an amorphous alloy of nickel and phosphorus ($\approx 8\%$ P), which for brevity will be referred to herein as nickel.

FORMATION OF ALLOY BOND

After rinsing and drying, the plated uranium article derived from the preceding operation is heat-treated to form a nickel-uranium alloy at the interface of the uranium and the plating. Formation of this alloy provides a stronger metal-to-metal bond. Satisfactory alloying is accomplished by heating the article at subatmospheric pressure. A reduced pressure promotes removal of any gases trapped in the plating or in the interfacial region between the uranium and the plating. If desired, alloying can be conducted in the same furnace and under the same conditions referred to above in connection with the formation of the protective oxide film. Alloying is conducted at a temperature below the alpha-beta transition and can be effected in less than 2 hours at temperatures above about 600° C.

EXAMPLE I

A uranium coupon ($\frac{1}{8}$ inch thick, 1 inch wide, and 3 inch long) was hand-scoured with conventional cleansing powder, degreased in trichloroethylene vapor, rinsed in distilled water, soaked in 8 N nitric acid at 40° C. for 20 minutes to remove oxide, and then pickled for one minute at 42° C. in a solution of 600 g/l nickelous chloride hexahydrate and 300 ml/l concentrated nitric acid. The pickled coupon was dipped in three successive baths of 8 N nitric acid (28° C.) to remove chloride residue, and rinsed with distilled water. It was then rinsed with

ethyl alcohol and dried in a nitrogen gas stream. Examination of the coupon showed that pickling had removed about 0.0007 inch of uranium from the surface, exposing the metal crystals and thus providing a very clean and smooth surface (root-mean-square finish, 80 rms).

Following cleaning as described, the coupon was transferred immediately to a conventional argon-containing vacuum furnace, which was immediately sealed, evacuated, and purged with pure argon. The evacuation-purging cycle was conducted four times. The furnace then was evacuated to approximately 10 microns pressure. At this time heating was initiated and the furnace temperature raised over a period of 3 hours to 625° C., at which it was maintained for an hour. The furnace then was cooled under vacuum to room temperature. Evacuation of the furnace was continued throughout the heating cycle.

The coupon removed from the furnace was covered with a continuous oxide film composed of uranium dioxide and lesser oxides, the oxygen content increasing gradually from the surface of the uranium outward. This film was semimetallic in appearance, was non-wettable by water, and was approximately 0.00006 inch thick. The coated coupon was immersed for 5 minutes in a basic wetting solution (2 g/l sodium lauryl sulfate and 125 ml/l ammonium hydroxide in distilled water) at 27° C.

The wettable oxide-coated coupon was immersed in a conventional aqueous electroplating bath and provided with a porous nickel strike coat approximately 0.00006 inch thick. Electroplating was conducted for 20 minutes at a temperature of 27° C. and an initial current density of 4 amps/ft². The bath composition (in distilled water) is given below.

77-86 g/l nickel as nickel sulfamate

30-39 g/l boric acid

2.5 g/l sodium lauryl sulfate (to lower surface tension and promote wetting)

pH 3.5 to 4.2 controlled with sulfamic acid and/or nickel carbonate

Following deposition of the strike coat, the coupon was transferred to a conventional aqueous electroless plating bath free from chloride or fluoride ions (Bath F-2B, General American Transportation Company; composition published in *Symposium on Electroless Nickel Plating*, A.S.T.M. Special Technical Publication No. 265, 1959). After immersion in the hot (95° C.) bath for 45 minutes, the plated coupon was removed and inspected. The nickel plating on the coupon was approximately 0.0005 inch thick, with a variation in thickness of ± 0.0001 inch.

The plated coupon was transferred to a vacuum furnace where it was heat-treated for 1 hour at a temperature of 625° C. and a pressure below 10 microns to form an interfacial nickel-uranium alloy. After removal of the coupon from the furnace, the nickel plating was found to have a hardness on the Rockwell-C scale of 60-65.

Following heat-treatment, the plated coupon was cut through transversely to provide a fresh-cut edge for testing. The coupon then was exposed to atmospheric air at a relative humidity of 100 percent and a temperature of 95° C. to determine the extent to which its nickel plating would be protective under severe conditions. At the end of 240 hours the plating exhibited no visual porosity and no peel-back at its cut edge. Examination showed that the alloy bonding was of excellent quality and that the plating was free of stress cracks. The figure is a sectional view (magnification, 500) of the plating and substrate as they appeared after the 240-hour exposure to steam. The nickel-uranium alloy can be seen as a gray band underlying the nickel layer. The dark spots in the region of the alloy represent the diffused protective uranium oxide layer.

EXAMPLE II

To determine the effectiveness of alloy bonding, 10 uranium coupons were prepared by the process described in connection with Example I. Five similar uranium coupons were processed in the same manner but were not heat-treated to

form an alloy bond between the uranium and the nickel plating. After processing, the coupons were exposed to steam at 95° C. for up to 95 hours. Table 1 gives the following information on each coupon: thickness of nickel plate; type of heat-treatment received; time exposed to steam bath; and condition of plating after exposure. All but one of the platings without alloy bonds withstood the test for at least 41 hours; however, as shown, the alloy-bonded platings were even more resistant to corrosion.

- a. cleaning the surface of said article to remove oxides and other contaminants therefrom;
- b. confining the cleaned article in an enclosed volume;
- c. evacuating the volume to a pressure below about 500 microns;
- d. heating said article in the evacuated volume to a temperature above about 500° C. and below the temperature at which the uranium changes to beta phase;
- e. maintaining said article in the evacuated volume at said

TABLE I.—COMPARISON OF NICKEL DEPOSITS ON URANIUM: WITH AND WITHOUT ALLOY BONDING

Thickness of deposit in. X10 ³	Vacuum heat-treated before plating	Vacuum heat-treated after plating	Steam time in bath, hr.	Results	
				Porosity of deposit	Peel-back of deposit at cut edge, in.
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	do	Do.
0.5	Yes	Yes	95	Minor porosity	Do.
0.6	Yes	Yes	95	No visual porosity	Do.
0.8	Yes	Yes	90	Minor porosity (dark alloy showing through the plate)	Do.
1.0	Yes	No	46	No visual porosity	1/16 one side.
1.0	Yes	Yes	95	do	None
1.0	Yes	Yes	95	do	Do.
1.0	Yes	Yes	90	Minor porosity	Do.
2.0	Yes	No	46	No visual porosity	1/4 avg.
2.0	Yes	Yes	90	do	None
3.0	Yes	No	46	do	Do.
3.0	Yes	Yes	90	do	Do.

* Minor porosity—4 or less pinpoint spots on 1X3X1/8-in. coupon.

In another experiment, 10 alloy-bonded coupons, prepared as described above and having nickel platings from 0.0003 inch to 0.001 inch thick, were subjected to the steam test until failure. The coupons resisted corrosion for periods of from 168 to 300 hours.

It will be apparent that this process is not limited to the plating of the strike-coated uranium by electroless techniques. For example, after the uranium article is provided with the above-described protective oxide film and the resulting film has been made wettable by water, the article may be immersed in any suitable aqueous electroplating bath and plated with metal to the desired final thickness in a single plating operation. That is, the uranium article may be left in the strike bath for final plating. Or, if preferred, the uranium article may be plated to a selected thickness in a low-temperature electroplating bath and then transferred to a higher temperature electroplating bath for deposition of the final portion of the plating at a comparatively high rate. If desired, nickel platings so produced may be heat-treated as described to form a uranium-nickel alloy bond.

Also, it will be apparent that although this process has been illustrated above in terms of plating uranium with nickel, it is applicable wherever a metal can be plated on uranium from an aqueous bath. For example, the oxide-protected and water-wettable uranium body may be electrolessly plated with cobalt, using the aqueous electroless plating bath published in *Metal Finishing Guidebook Directory*, 1970, page 514 (Metals and Plastics Publication, Inc.). Similarly, the oxide-protected, wettable uranium article may be electroplated with various other metals (e.g., cobalt, copper, gold, and silver) deposited from aqueous solutions well known in the art.

Although the above-described preferred form of our invention includes an alloy-bonding operation, it will be understood that our process is not limited to that form but rather is limited only by the following claims.

What is claimed is:

1. The process of metal-plating a uranium metal article comprising the steps of

temperature for a time sufficient to form thereon, by reaction of said surface and residual oxygen, a continuous uranium oxide film having a thickness below about 2.5 microns, said film being composed of uranium dioxide and lesser oxides, the oxygen content of said film gradually decreasing from its outer surface inwardly toward the film- and-uranium interface, said film being non-wettable by water and virtually impervious to and free from reaction with dry air, moist air, and water;

f. contacting the resulting film-coated article with a basic ammoniacal aqueous solution containing a wetting agent, to render said film wettable by water; and

g. making the resulting water-wettable film-coated article cathodic in an aqueous metal-electroplating bath to electrodeposit a metal plating of selected thickness thereon.

2. The process according to claim 1 wherein said metal-electroplating bath is operated substantially at room temperature.

3. The process according to claim 1 wherein the electrodeposited metal plating is nickel.

4. The process according to claim 1 wherein said article provided with an electrodeposited metal plating is removed from said bath and immersed in an aqueous electroless metal-plating solution to deposit additional metal plating thereon.

5. The process according to claim 4 wherein said electroless metal-plating solution is maintained at an elevated temperature.

6. The process according to claim 4 wherein both the electrodeposited and the electrolessly deposited metal platings are nickel.

7. The process according to claim 6 wherein said article provided with additional metal plating is confined in an enclosed volume maintained at subatmospheric pressure and is heated therein to a temperature above about 500° C. and below the temperature at which uranium changes to beta phase, to form a uranium-nickel alloy at the interface of said uranium article and said nickel.

* * * * *