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FINAL REPORT

Contract AT(30-1)-2264

November 15, 1958 through November 14, 1959

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Classification code: UNCLASSIFIED

by authority of *Mr. H. S. Gatter, Chief, New York*

Opera Talent Group, dated 7-5-60

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Nuclear Materials and Equipment Corporation
Apollo, Pennsylvania

Final Report

Contract AT(30-1)-2264

November 15, 1958 through November 14, 1959

ABSTRACT

Metal coatings approximately two to ten microns in thickness were successfully applied to UO_2 spheres on a laboratory scale by a variety of methods including the reduction of halides for niobium, chromium, molybdenum and tungsten; chemical immersion plating for nickel and copper; and electroplating for chromium, nickel, and copper. In addition, copper and nickel were plated on uranium metal by electroplating. Also a small extrusion consisting of chromium coated UO_2 particles dispersed in a Zircaloy-2 matrix was successfully made without stringing or evidence of reaction between the oxide and the matrix. Small plates consisting of niobium coated UO_2 spheres homogeneously distributed in a matrix of pure niobium were also made entirely by the halide reduction process.

The integrity of coatings was evaluated by metallographic examination, oxidation tests, and acid immersion tests. The hardness of coatings and the crushing strength of particles before and after coating were also determined. In addition, the various coatings were analyzed chemically.

I. Introduction

Considerable effort has been expended over a period of years in the development of pure or slightly alloyed metallic uranium fuel elements that are both corrosion resistant and dimensionally stable under long irradiation. Such elements would provide high thermal conductivity and loading density, and allow operation at lower costs than presently possible with clad oxide or clad high uranium alloy elements. To date, however, only limited success has been achieved in meeting these objectives, particularly in water-cooled power reactors. The active chemical nature of pure or slightly alloyed uranium is such that high temperature coolant water penetrating the smallest clad defect tends to react and rupture the entire element, possibly causing blocking of the coolant channel and progressive failure of the entire fuel bundle. In addition, the anisotropic nature of α and β uranium and the instability of the γ phase of uranium contribute to the generally poor radiation damage resistance of the material.

It is conceivable, however, that these difficulties could be circumvented by plating particles of uranium with thin, strong, inert, impervious, metallic coatings having low cross sections, and consolidating these into fuel elements by one of the methods listed in Table I. (An external protective cladding could be applied simultaneously with, or subsequent to consolidation.) Such an element would consist of tiny randomly oriented spheres of uranium uniformly separated from each other

by a continuous matrix of corrosion resistant material. Thus, if a particle of uranium were exposed to the coolant, only that small particle would corrode and multiple barriers of corrosion resistant matrix would have to be penetrated before serious damage could result. These barriers would also provide mechanical constraint to the uranium and thus aid in maintaining the dimensional stability of the mass under irradiation and/or thermal cycling.

In another application, coatings for the fuel particles in dispersion-type elements could also be used to prevent detrimental reactions between fuel and matrix materials which would normally be incompatible. Moreover, the coatings would inhibit breakup and stringing of the ceramic particles during extrusion or rolling. The dispersion in a zircaloy matrix of UO_2 particles coated with a metal such as niobium which is compatible with both materials is an example of such an application. An element of this type provides the possibility of longer life by allowing greater fuel loading and enhancing the radiation damage resistance over comparable uranium-zirconium alloys. At the same time, the utilization of zirconium rather than stainless steel as the matrix material enables greater fuel economy.

Coated spheres of uranium, ThO_2 , and UO_2 could also serve as fuels for fluidized or static bed type reactors. The protective coatings should not only eliminate erosion and abrasion of fuel particles, but at the same time should minimize fission product escape and consequent contamination of the primary system.

Although it would be expected that the protective nature of coatings would improve with an increase in thickness and a decrease in the size of the particle (since a break in the coating would expose less material) it

is apparent that the portion of inert material rises in relation to the amount of fuel as shown in Fig. 1. Accordingly, it is necessary to compromise on both particle size and coating thickness in order to achieve optimum results (Fig. 2).

II. Coating of UO_2 Spheres

Since, as indicated above, coated particles can be applied in a variety of reactor types, i.e., thermal, epithermal and fast; water, liquid metal or gas-cooled; at low, intermediate, or high temperatures, coating with metals of comparatively high as well as low thermal absorption cross section was studied. These metals included niobium, chromium, nickel, copper, molybdenum and tungsten.

Depending on the metal, plating on UO_2 may be accomplished by a number of techniques, including chemical displacement, reduction of the halide, reduction of the oxides, decomposition of the iodides or the carbonyls, evaporation and electroplating. The following sections discuss the methods selected and the results obtained in the application of the various coatings.

A. Nickel

There are two rather obvious methods by which nonmetallic particles may be coated with nickel, viz., immersion coating from a hypophosphite bath and decomposition of the carbonyl. While these are outwardly simple in application, the first depending on the autocatalytic reduction of the hypophosphite and the second on thermal decomposition of the vapor, both have difficulties associated with them. The composition of the hypophosphite bath must be tailored to yield a dense, nonporous, adherent deposit at a

reasonable rate and bath life and the salt-bearing liquid must not be trapped in the pores of the material being coated where it may cause cracking and spallation on subsequent heating. On the other hand, the carbonyl is very toxic; moreover, the temperature of decomposition and the flowrates must be meticulously adjusted to yield smooth, nonporous, tightly adherent coatings. Because the immersion coating appeared to promise the greatest simplicity, uniformity and ability to coat particles in substantial quantity, this was selected for the principal avenue of attack. In addition, electroplating was also studied as a cheap convenient method of increasing the thickness of the initial conducting coating applied by immersion techniques as well as for applying other metals such as chromium:

The plating of nickel on UO_2 by immersion in a hypophosphite bath underwent a series of progressive improvements involving changes in bath composition, bath sensitizing techniques as well as methods of preventing cracking and spallation.

Nickel bath A-1 (Table II) was the first partially successful immersion formulation used in this work. However, as illustrated in Fig. 3-A by the photomicrograph of typical cross sections of coated oxide particles, the two micron thick coatings applied with this bath were not entirely continuous. Moreover, it was found that the coatings contained approximately 7% phosphorous, and during subsequent high temperature degassing and coating operations a nickel phosphide eutectic apparently caused spheres to weld together. Additional voids and cracks were then generated on separation.¹

¹Work carried on simultaneously on plating chromium on the nickel substrate indicated that continuous base coats were essential for the achievement of continuous overcoats.

Modifications made on Nickel Bath A in an attempt to improve base coatings are shown in Table II. As in the previous case, plating was dependent upon bath activation with a few milligrams of aluminum powder and best results were obtained at bath temperatures between 95 and 98°C. Improvements achieved as a result of these composition changes were not outstanding. Accordingly, Nickel Bath A was modified with hydroxyacetic acid in the manner shown under Nickel Bath B (Table II). As the pH of these baths was increased from 5.5 to 8 the plating rate increased but the plates were dendritic and porous (Fig. 3-B). Best results were obtained at a pH of 6 with formulation B-2, Table II, which contained six times as much hydroxyacetic acid as formulation B-1. With this bath (B-2) dense, uniform, coatings five microns thick could be obtained in 45 min. (Fig. 4-A). Unfortunately, however, the hydroxyacetic acid baths had poor stability and were shortlived.

Baths C and C-2, Table III, based on lactic acid proved to be far superior to the previous baths in many respects. Not only did these have good stability, but they produced dense, uniform coatings containing only 3-4% phosphorous at satisfactory plating rates. In contrast to the previous baths which required sensitization with aluminum powder, these formulations required only that the oxide spheres be sensitized by a prior dip in chloride ion. A typical result achieved with these formulations is shown in Fig. 4-B while a graph illustrating plating thickness as a function of time is shown in Fig. 5.

Since tests performed to determine the porosity of the plates involving the heating of the coated oxide spheres for 10 min. at 550°C

resulted in cracking of the coatings, although visual examination indicated the coatings were sound prior to the tests, it was assumed that small amounts of moisture had become entrapped in the pores of the oxide spheres during immersion in the baths, which upon vaporization caused the rupture. Accordingly, the following technique was successfully employed for the application of the coatings.

The bare spheres were heated in a vacuum at 400°F, chemically flashed with a one micron thick coating of nickel and again vacuum baked at 400°F before application of the final thickness of nickel.

B. Electroplating of Nickel

The electroplating of nickel proved to be very simple after a one or two micron thick conducting coating of nickel was applied to the UO_2 by the immersion techniques described above. A standard bath composed of nickel sulfate, ammonium chloride and boric acid in the proportions and under the conditions indicated in Table IV was quite satisfactory. The plating was carried out in a rotating copper cup cathode and a stationary platinum screen anode. Figure 6 illustrates the type of plate obtained with this technique.

Since the results achieved by the methods outlined above proved satisfactory, further work on the application of nickel coatings to oxide particles was terminated.

C. Copper

As in the case of nickel, copper may also be applied by immersion coating. In this connection a number of plating baths were tried. Best results were achieved with an ammoniacal formaldehyde bath, the composition

of which is given in Table III. This formulation yielded comparatively uniform, dense coatings, the thickness of which varies with time, as indicated in Fig. 5. It will be noted that thicknesses of approximately 4-6 microns were obtained after an hour at room temperature. Although the coatings (Fig. 7) were not of the quality obtained with nickel, additional work was not done since use of copper coating was anticipated primarily as a base for further coats of other materials or as a conducting coating for further electroplating, rather than as a principal barrier coat. In this latter connection, electroplating was easily achieved using the bath indicated in Table IV and the same apparatus used for electroplating nickel. A photograph of cross sections of particles coated in this manner is shown in Fig. 8.

D. Chromium

A variety of methods are possible for coating UO_2 particles with chromium. These include electroplating, vacuum evaporation, reduction of the halides, decomposition of the iodide, decomposition of the carbonyl, etc. In the interests of saving time, a number of approaches were investigated simultaneously with a view toward the selection of the most promising ones for a concentrated developmental effort.

1. Electroplating

The electroplating of chromium proved to be considerably more difficult than the plating of nickel or copper because of the high current density required. Adequate electrical contact was difficult to maintain and the usual chrom plating baths generally yielded dendritic and irregular deposits. It was found, however, that if the particles were well stirred

and good electrical contact made, adequate results could be obtained on a small scale with a bath consisting of chromic and sulfuric acids in the ratio of 100:1, providing that several drops of HF were added for each 100 cc of solution and the bath was maintained at a temperature between 35-40°C. An illustration of the coatings obtained in this manner is shown in Fig. 9. In the case of larger particles barrels made of Monel or stainless steel screen allowed the gases generated during plating to be conducted away without interfering with electrical contact. In the case of tiny particles, however, difficulty was encountered because of clogging of the screen with fine particles. Accordingly, the unit shown in Fig. 10 was devised to circumvent this difficulty. Essentially, this apparatus consisted of a 2 in. O.D. copper cathode barrel with a series of parallel v-shaped grooves machined around its internal circumference. This allowed the particles to roll freely without agglomeration and without interference from escaping gases.

Electrical contact for the normally nonconducting UO_2 particles was achieved by applying a nickel flash in one of the immersion baths previously described. Most consistent results were obtained with a fluosilicic acid modified bath under the conditions given in Table IV. A photomicrograph of polished cross sections of particles chrome plated in this manner is shown in Fig. 11.

2. Vacuum Evaporation

The chrome plating of UO_2 particles by vacuum evaporation was investigated primarily as a means of obtaining a thin, continuous flash coating which would prevent the UO_2 particles from absorbing liquids or

being chemically attacked during subsequent processing. It also provided a method of obtaining an undercoat of the same material for subsequent chemical or electrolytic plating operations.

To determine the feasibility of the approach a simple device was constructed consisting of a small bell jar and base plate fitted with a suitable vacuum system, pressure gauges, an electrical feed-through device for heating a tungsten filament, and a small stainless steel pan fixed to a shaft which could be oscillated by hand from outside of the base plate.

In operation, lumps of commercially pure chromium metal were placed in the tungsten helical coil (1/4 in. diam. and 3/4 in. long) arranged about one inch above the particle pan. The system was evacuated to approximately 5×10^{-5} mm Hg and the filament heated slowly to temperature to allow for gradual heating and outgassing of the system and particles before vaporization of chromium occurred. The pan was oscillated in a horizontal plane during vaporization to rotate the particles so that all surfaces would be presented more or less uniformly to the vapor. Because of the proximity of the pan to the filament, the particles attained temperatures between 600°-800°C by the conclusion of a run (approximately 10 min. for complete vaporization of the chromium contained in the filament coil). A layer approximately one micron thick could be deposited on the particles during the course of a single run. Accordingly, a number of runs were required for the deposition of thicker plates.

Although a deliberate study was not carried out during the course of the vapor deposition work reported herein, it was noted that the rate of vaporization and the proximity of the particles to the filament had a

definite effect on the character of the deposit. It was noted, for example, as the distance of the particles to the filament was decreased and the rate of vaporization increased, the chromium deposited as tiny droplets and the surface took on a mat rather than a bright metallic appearance. Moreover, the deposit appeared to become somewhat more porous in character.

In addition to observing the gross character of the deposits under the stereoscopic microscope, particles were mounted, sectioned and polished for further microscopic examination. In general, it was found that coatings made in the crude apparatus under the conditions described were more granular than coatings produced by electrodeposition and chemical decomposition, but were generally adequate as a reaction and diffusion barrier. While a more elaborate apparatus capable of yielding much better results could have been constructed, additional work along these lines was not considered necessary for the time being.

E. Reduction of the Halides

Preliminary experiments quickly established that chromium could not be deposited directly on UO_2 by vapor phase reduction of the halides because of reaction of the UO_2 with the by-product gases at the temperatures required to maintain an adequate concentration of the halide vapor in the reaction chamber. For example, in the case of the reduction of chromium chloride with hydrogen, the sintered UO_2 particles disintegrated completely in the by-product HCl atmosphere at 950°C . While it was not severe, chloride attack was evident and it was found that the adherence of chromium to the spheres was adversely affected at temperatures as low as 700°C .

Accordingly, it was necessary to apply an initial protective metal coating prior to chromium deposition, and the spheres used in all experiments with chromium, reported on below, were initially plated with a nickel undercoat as previously described. Nickel coatings two to four microns thick were found to be sufficient as a protective metal base for subsequent chromium deposition.

1. Reduction of Chromous Iodide

Because chromous iodide of adequate purity could not be obtained commercially, it was prepared by passing hydrogen over iodine at approximately 100°C, then over chromium metal at 800-850°C. The product consisting of chromous iodide in excess hydrogen was passed over nickel coated UO_2 spheres at 900-1000°C. Experiments were conducted at various flowrates and with varying proportions of hydrogen to iodide. However, difficulty was continually encountered in the production of uniform adherent chromium coating on the spheres. Accordingly, this method was temporarily set aside in favor of those described below.

2. Reduction of Chromic Chloride

Preliminary experiments involving the passage of H_2 and HCl mixtures over chromium metal heated to 800-900°C and finally over nickel coated UO_2 pellets at 950-1050°C were unsuccessful. However, favorable results were obtained when chromic chloride was used as a starting material. The successful procedure involved the heating of a mixture of chromic chloride, nickel coated particles, and quartz chips to 750° in a hydrogen atmosphere. The quartz chips prevented the formation of agglomerates during the reduction process.

It was especially noted in carrying out these experiments that it was essential to keep the reduction temperature below the melting point of chromous chloride (824°C) in order to obtain good results. The mechanism by which reduction occurs involves the initial formation of the chromous chloride by the decomposition of chromic chloride in the following manner:

The chromous chloride then reacts with the hydrogen as follows:

Thus, if the chromous chloride melts, the hydrogen is inhibited from diffusing to the interface of the particle and the chromous chloride, and reduction of the salt on the surface of the particle is prevented.

In a typical experiment 10 grams of 60 mesh UO_2 spheres with a 2-4 micron nickel coating were mixed with five grams of CrCl_3 and sufficient quartz chips to prevent agglomeration. This mixture was heated to 750°C with constant agitation in a hydrogen atmosphere flowing at the rate of 0.5 liters/min. Well bonded chromium coatings 4-8 microns thick were obtained in three to four hours with no evidence of chloride attack.

As a result of this success a larger apparatus affording better control over the process variables was designed and constructed (Fig. 12). As can be noted, the reaction mixture is contained in a small cell comprising the reaction chamber which in turn is housed in a larger tube. Before reaching this chamber the hydrogen is preheated to the desired temperature in a coil within the larger tube. The entire apparatus is rotated inside a stationary resistance furnace through a 180° cycle approximately 25 times/min.

After a number of experimental runs conditions giving optimum results were established. Single batches of 35 grams of spheres containing 4-6 microns of nickel base were coated in single runs through this apparatus. A batch of spheres was mixed with 10 grams of finely divided chromic chloride and 40 grams of 1/8 in. diam. quartz chips and loaded into the reaction chamber. The mixture was first heated at 500°C in a hydrogen atmosphere for one-half hour with constant agitation to convert the chromic chloride to chromous chloride. The temperature was then raised to 750°C with a hydrogen flowrate of 0.6 liters/min.

Uniform deposits of chromium 4-6 microns thick were produced in 3-1/2 hr by this process. Polished cross sections of these coatings are shown in Fig. 13-A.

Minor design changes were made in the apparatus shown in Fig. 12 in order to increase the load capacity and facilitate the coating of larger quantities of spheres per run. As a result chromium coatings 8-10 microns thick were produced on 200 grams of nickel undercoated spheres in five hours time in a single run (Fig. 13-B).

F. Thermal Decomposition of Chromium Carbonyl

As indicated above, plating of chromium by hydrogen reduction of the halide creates a by-product such as HCl, which attacks the UO_2 and necessitates the protection of the oxide by a thin coating of nickel. Since nickel may sometimes be undesirable from a physics standpoint, it was attempted to deposit a chromium coating directly on the UO_2 from a material which produced no obnoxious by-products. Accordingly, a number of pilot experiments were performed in which chromium carbonyl was used as the deposition agent. In general, these experiments were carried out by

holding the carbonyl at 100°C and vaporizing it into a stream of purified argon which flows into a deposition chamber containing UO_2 particles. The chamber was varied in temperature from 200 to 600°C.

A deposition temperature of approximately 450°C was found to be critical; higher temperatures produced chromium carbide and oxide in addition to the metal, while lower temperatures did not favor the deposition of chromium. However, in all the experiments it was found that the deposit was powdery and not well bonded to the pellets. Moreover, carbide and oxide formation could not be completely eliminated. The powdery nature of the chromium was attributed to premature decomposition of the carbonyl in the gas phase prior to contact with the pellets.

G. Coating of UO_2 with Niobium

Of the various approaches to the preparation of metallic niobium, the hydrogen reduction of the pentachloride appeared to be most applicable to coating of UO_2 particles. However, as in the case of the reduction of the chromium chloride a number of difficulties are inherent in the process.

Niobium pentachloride, like the other niobium halides may be prepared by direct synthesis as well as by reaction of the oxide with carbon and the halogen or by reaction with carbon halogen compounds such as carbon tetrachloride. The halides are covalent compounds and as such are characterized by comparatively low melting and boiling points as follows:

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	<u>Melting Point (°C)</u>	<u>Boiling Point (°C)</u>
NbF ₅	76	230
NbCl ₅	209	245
NbBr ₅	227	272-362
NbI ₅	327 (d)	347

The compounds hydrolyze easily producing the oxyhalides or the oxides and the corresponding halogen acids and must therefore be handled under anhydrous conditions. Moreover they may undergo a series of side reactions during deposition such as

in the case of niobium pentachloride in addition to the reaction of principal interest

Thus, extremely close control of the reaction is required in order to avoid major difficulties during deposition of Nb.

Reduction of the pentachloride begins at a very slow rate at approximately 600°C and becomes very rapid at temperatures in excess of 1000°C. Accordingly, attempts were made to deposit niobium on bare UO₂

spheres near the top of this temperature range (800-1000°C) in the hopes of obtaining rapid enough deposition to prevent detrimental attack of the UO_2 by the by-product chlorides. However, in spite of the comparatively high rate of niobium formation, the initial formation of uranyl chloride at these temperatures was sufficient to prevent the deposition of adherent coatings. Subsequently it was found that uniform, adherent coatings could be applied despite slight chloride attack by reducing the deposition temperature to 700°C.

The procedure which produced the best coating of niobium involved the vaporization of niobium pentachloride at 220°C into a stream of argon flowing at the rate of 0.2 liters/min. The one inch quartz reaction chamber was maintained at 700°C and hydrogen gas, preheated to this temperature, was introduced at a rate of 0.5 liters/min. The reaction chamber was agitated constantly during the coating process. By this method coatings 1-2 microns thick were obtained in two hours.

On completion of the pilot experiments outlined above the apparatus was scaled up to 50 grams and later to 200 grams in the manner illustrated in Fig. 14. The apparatus operated in the following manner.

Pre-purified hydrogen was preheated to the selected temperature by passing through the stainless steel preheating coil into the reaction chamber through a series of jets. The niobium pentachloride was carried into the chamber by saturating a stream of pure preheated argon with the vapor as the gas passed over the halide into the reaction zone through a set of jets which directed the vapor toward the oxide spheroids. The deposition chamber was constantly rotated on its axis in order to agitate the spheres to achieve uniform deposition.

The best niobium coatings deposited in these modified reactors were achieved by vaporizing niobium pentachloride at temperatures of 150-160°C in an argon carrier passing through the reactor at a flowrate of 1.2 - 1.4 liters/min. Uniform coatings up to 8 microns thick were deposited by this process on 100 micron spheroids in only four hours as shown in Fig. 15-A.

The ratio of hydrogen to argon and the concentration of the pentachloride in the carrier were among the most important variables. Best results were obtained with a hydrogen to argon ratio of 3:1 when the argon was saturated at 150-160°C. Deposits produced under these conditions were lustrous whereas those produced at lower hydrogen to argon-halide ratios were dull. If the hydrogen-argon ratio was reduced below 2:1 niobium trichloride was formed due to partial reduction of the pentachloride.

It was also found that the results achieved were very sensitive to the materials from which the reaction vessels were constructed. Vessels made of nickel, Monel and Inconel were completely unsatisfactory because of severe reaction with the halides. Stainless steel, on the other hand, was only slightly affected and did not interfere with the chemistry involved in the plating process.

The purity of the pentachloride was another source of difficulty. It was found that commercially obtained pentachloride was spotty in quality and sometimes contained volatile impurities. Under these conditions the coatings were dark colored and nonmetallic in appearance and generally poor in character. In addition a white powdery residue accumulated in the reactor chamber during the run. No difficulty of this

nature was encountered when the pentachloride was prepared by direct chlorination of high purity niobium metal and redistilled prior to use.

In addition to the problems mentioned above, it was found that the reproducibility and uniformity of the coating was critically dependent on the degree of agitation of the spheres. Dead spots in the deposition chamber where the particles could hang up or become stagnant resulted in uneven coatings, agglomeration or no coating at all. This difficulty was particularly pronounced when it was attempted to coat quantities of 100 grams or more of UO_2 particles at a time in reaction chambers agitated by vibration only.

H. Coating of UO_2 Particles with Tungsten and Molybdenum

As in the case of other metals previously discussed, tungsten and molybdenum form volatile compounds which either decompose or can be reduced by hydrogen. Accordingly, the coating of UO_2 particles with these metals is most conveniently accomplished by reactions in the vapor phase.

Of the two more obvious processes available, viz., the thermal decomposition of the carbonyls is as follows:

or the reduction of the chlorides with hydrogen in accordance with the following reactions.

the latter is considerably more attractive from the standpoint of the purity of the deposit as well as from the standpoint of ease of handling, availability, purity, and cost of the starting material. The following table giving the approximate cost of depositing 0.001 in. of metal per square foot of surface illustrates the latter point.

MoCl_5 - \$ 0.53

$\text{Mo}(\text{CO})_6$ - 2.55

WCl_6 - 1.99

$\text{W}(\text{CO})_6$ - 18.05

The coating apparatus and general procedure used in the case of tungsten was the same as that used for niobium. The conditions were as follows.

The argon carrier was preheated to 230°C and saturated with tungsten hexachloride at the same temperature. The flow of hydrogen was maintained at 1 to 1.4 liters/min., while that of the carrier was regulated between 0.4 to 0.5 liters/min. The reaction container was maintained at 550°C. Under these conditions lustrous pure deposits of the type shown in Fig. 16 were obtained. Deposits of molybdenum were obtained under similar conditions.

III. Coating of Uranium Metal Particles

The problem of plating uranium metal is considerably different than that of coating sintered UO_2 of near theoretical density. Whereas the oxide is relatively inert and comparatively unaffected by many of the reagents and environmental conditions which might be employed in

plating, uranium metal is, in contrast, highly reactive and, as is well known, mere contact with water or air causes immediate formation of an oxide film which prevents or inhibits proper adherence of the plate. Moreover, the chemical reactivity of the metal interferes with proper operation of displacement and immersion plating baths. Thus, while nickel, copper, zinc and other materials may be displaced from appropriate chemical baths, the coatings slough off as they are formed. In addition, the immersion plating baths previously described which worked well in the case of UO_2 were poor for plating uranium. Not only were the plates thin, discontinuous and nonadherent, but the catalytic effect of the uranium caused rapid decomposition of the baths. Accordingly, it was necessary to devise some means of cleaning the surface of the uranium and protecting it from the plating environment. Several of the possible approaches in the solution of this problem are as follows:

(1) The uranium could be bright pickled in acid and almost simultaneously given a thin inorganic coating which would be both protective and compatible with the metal plate.

(2) Uranium shot could be formed in a vacuum and passed into a fused salt bath where it could be electroplated or plated by displacement.

(3) Uranium shot could be formed in a vacuum, or alternatively be cleaned by sputtering, and subsequently be vapor-plated with a thin coating of an appropriate metal which would offer protection during subsequent operations.

Although all of the above approaches appeared to have promise, the first was selected for initial consideration because of its apparent simplicity as well as the time limitations imposed by the contract.

In this connection, it was found that the oxide film could be reduced significantly by employing the method of surface preparation indicated in Table V prior to electroplating. The first step of the process dissolves the oxide film and displaces it with a phosphate film, leaving the uranium bright and passivated. The short dip in HNO_3 indicated in Step 2 of the process appears to reduce the thickness of the phosphate film somewhat and further conditions the surface so that it can be electroplated. As shown in Figs. 17-A and 17-B, acceptable electroplates of copper and nickel, with only slight oxide interface films, were applied from the modified acid-copper and nickel fluoborate baths listed in Table V.

IV. The Preparation of Dispersions of Coated Particles in Metal Matrices

A. Zircaloy-2 - UO_2

In order to evaluate the efficacy of the coatings on UO_2 particles in preventing a reaction between the zirconium matrix and UO_2 dispersion during actual working conditions, a small element was prepared by hot extrusion in the following manner.

Roughly spherical particles, 20-30 mesh in size were coated with chromium by vapor deposition to a thickness of 5 to 6 microns. Five grams of these were then blended with 45 grams of -60 +270 mesh Zircaloy-2 powder prepared from an ingot by mechanical attrition. The mixture was

then cold pressed at 40 T.S.I. into a 0.780 in. diameter Zircaloy-2 tube with 1/4 in. thick Zircaloy-2 end-plugs. After trimming the excess Zircaloy from the ends, the compact was enclosed in a copper jacket, evacuated and sealed. The billet was then heated to 1375°F and extruded at a ratio of 25:1 into a rectangular strip clad with Zircaloy-2. As shown in Fig. 18-A, which is a print of an X-ray taken of the finished strip after cold turksheading, the particles appear to have retained their shape and to have gone through the strenuous work without fragmenting and stringering as might have been expected. It was further noted in observing polished sections that in spite of the somewhat porous nature of the vapor deposited chromium, the coatings were retained by the particles and that the protection afforded by these coatings prevented reaction between the UO_2 and the Zircaloy. Moreover, the coatings themselves appear to have become consolidated and dense during the process (Fig. 18-B). Thus, the idea and the methods applied appear to have excellent promise for the development of a really practical, long-lived, radiation damage resistant dispersion of UO_2 in zirconium.

B. Niobium - UO_2

In the course of experimenting with the use of vibratory agitation of particles for coating UO_2 particles by reduction of niobium pentachloride with hydrogen, it was found that in addition to being quite uniformly coated with 10-12 microns of niobium (Fig. 19-B) the individual particles were agglomerated in the plate-like form as shown in Fig. 19-A. Because of the possible application of this technique for the manufacture of dispersion elements, the experiment was repeated several times with comparable results.

A more practical approach to the making of given shaped dispersion fuel fillers by this method might be as follows:

1. Coat an adequate amount of the desired sized spheres with the required thickness of niobium.
2. Form the coated spheres into a porous platelet of the desired geometry by packing into a ceramic tray type mold and sintering.
3. Arrange the pre-formed porous plate in the reactor in such a manner that it forms a barrier dividing the chamber into two sections (Fig. 20).
4. Operate the reactor at a reduced pressure on the exhaust side of the porous disc.

Reducing the pressure on the exhaust side of the porous disc would first force the H_2 and the pentachloride vapor through the paths of least resistance or the larger pores. As these areas were filled with niobium the vapor would be forced through smaller pores, etc., until the last interconnected opening through the disc was filled with niobium. Although some closed porosity may remain in the completed disc, the amount should be small based on the previously observed niobium penetration of microscopic sized crevices. Moreover, the fuel filler could be coined to achieve higher density.

Such a method would not only eliminate some of the steps in preparing dispersion elements by more conventional techniques, but it would also be adaptable to making dispersion elements with materials such as chromium, molybdenum and tungsten, which are more difficult to work by commonly used methods.

In addition, spheres base coated with one material could be over-coated with and consolidated in a matrix of another material.

V. Evaluation and Testing of Coated Particles

A. Microscopic Examination

Microscopic examination of the gross coated particles by stereo, and of sectioned particles by reflected light, was the best means of evaluating the general uniformity, thickness, cross-sectional uniformity, porosity, penetration and character of the bond. Limitations of the method were primarily those usually encountered in the preparation of plastic mounts of small particles. Pressures required for satisfactory results with phenolic thermosetting mounting materials occasionally crushed the particles, and it was, therefore, necessary to exercise extreme care in mounting samples.

B. Crushing Tests

Dispersion elements may be prepared by a variety of techniques including powder rolling and sintering; compaction, sintering and rolling; compaction and hot extrusion. The crushing forces applied to the oxide particles will, of course, vary with the method of preparing the element. If the strength of the particles is insufficient to withstand these fabrication forces the particles will rupture and tend to stringer. Thus, the crushing strength may be an important parameter in determining what fabrication techniques may be utilized in making dispersion elements with the various types of coated particles. Accordingly, an apparatus was constructed for measuring the relative resistance to crushing of bare vs coated UO_2 spheres. It consisted of a hardened, round, flat-faced, tool-steel

anvil and flat-bottomed cup that could be affixed to the Tukon hardness tester for applying constant controlled loads (Fig. 21). It was equipped with a sensitive sound detection and amplifying system for audible determination of the point of fracture. To perform a test, spheres were first arranged in a close packed single layer on the bottom of the cup, such that the entire anvil face would be effective. Various loads from 10 gms up to several hundred grams were tried until a particular lot of spheres was crushed. Two or more lots from each type of coating were tested to check the reproducibility of results.

While the results are qualitative at best and only give relative trends they do indicate (Table VI) that the addition of these thin metal coatings has, in most cases, contributed to increasing the resistance of the particles to crushing.

C. Knoop Hardness Tests

Although it is difficult to get good impressions in coatings only several microns thick, hardness numbers even for these thin films have some value in establishing the relative hardness and quality of the coatings.

The Knoop hardness test was especially selected for this work because the narrow 172° included angle diamond indenter is more suited for thin metal films than the Vickers or D.P.H. indenter which because of a square base and an apex angle of 136° makes a wider impression.

The hardness values obtained for the various coatings are listed in Table VI. The softness of the niobium coatings should be especially noted.

D. Helium Leak Rate

It was expected that significant differences would appear in the degree and rate of helium desorption from coated and uncoated particles based on the assumption that spheres having good continuous coatings would exhibit much lower porosity than bare UO_2 spheres. Accordingly, data were taken on an empty container, on 1/4 g of 100 micron diameter glass beads and on one gram of 100 micron diameter bare UO_2 spheres. The slope of the straight portion of the curve was used for comparing the cases. However, results were erratic and a definite correlation could not be made (Fig. 22).

Thus, while it is conceivable that very large test samples might have shown significant differences, the method appeared sufficiently insensitive to be reliable.

E. Oxidation Tests

Oxidation of UO_2 to U_3O_8 results in a considerable decrease in density and a corresponding increase in volume. Thus, an obvious method of evaluating the soundness of the coatings on the particles is to heat the spheres in air to a temperature which would easily cause oxidation and burst those having inferior coatings. The technique must be applied with care, however, since significant differences in the thermal expansivity of the coating and base material, as well as poor oxidation and/or thermal shock resistance of the coating can cause spheres with good coatings to burst.

Ten minute tests at 550°C were applied to particles coated with nickel, chromium and niobium and, in most cases, the results indicated that the coatings were sound.

F. Nitric Acid Leach Test

Due to the solubility of UO_2 in HNO_3 it was suggested that the integrity of the coatings be tested by immersing in acid and checking the resulting solution for uranium content. The method as applied to niobium-coated spheres was as follows: The spheres were first rinsed in a 1:1 HNO_3 , H_2O solution to remove any possible surface contamination by uranium. The spheres were then immersed for 15 min. in a fresh solution of the same composition. Thus, the presence of any porous or cracked coatings or the presence of any uncoated spheres would cause the solution to become sufficiently contaminated to allow detection of uranium by scintillation techniques. Although this is a severe test, batches of niobium-coated spheres found satisfactory by other tests also withstood this test.

G. Chemical Analyses

Coatings of the various metals were analyzed for impurities to determine the purity of the starting materials, as well as the adequacy of control during processing. The results are listed in Table VII. It will be noted that the Nb coatings were of excellent purity.

SUMMARY

The work described in this report was exploratory and therefore qualitative in nature and designed primarily to demarcate the areas which would be most fruitful for more quantitative work. Nevertheless, the accomplishments were very significant in that methods were devised for coating UO_2 with nickel and copper by immersion and electrolysis, chromium by electrolysis, and niobium, chromium, molybdenum and tungsten by hydrogen reduction of the corresponding chlorides. Moreover, substantial progress was made in developing a technique for cleaning and passivating uranium metal so that it could be electroplated with copper and nickel from an aqueous solution. In addition, methods were devised for testing the integrity of the coatings. While further work must be done to delineate the optimum coating conditions and to effect further improvements, the areas in which this work should be done were well defined.

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TABLE I

Scope of Items Warranting Consideration for Coated Particle Program

Fuel Particles

U
U-Mo
U-Zr
U-Nb
U-Si
UO₂
UC₂
UN
U Be

Coatings

Cu	Al
Ni	Al ₂ O ₃
Nb	BeO
Mo	Nb-V
V	Nb-Mo
Fe	Si
Mg-Be	Mo-Si
Be	Fe-Ni-Cr
Zr	SiC
Y	ZrO ₂ - CaO
	C

Matrix Materials

Al
Zircalloys
Stainless
Niobium
Niobium Alloys
Graphite

Consolidating Methods

Cold Press and Sinter
Cold Press and Extrude
Cold Press and Swage
Hot Press
Hot Press and Roll
Hot Press and Forge
Hot Press and Extrude
Hot Press and Swage
Powder Rolling and Sintering

Environments

H₂O
Steam
Liquid Metals
Na
NaK
Gases
CO₂
Organics

TABLE II

Chemical Nickel Immersion Coating
Baths for UO₂ Spheres

Nickel Bath A

<u>Constituent</u>	<u>g/l</u>			
	<u>A-1</u>	<u>A-2</u>	<u>A-3</u>	<u>A-4</u>
Nickel Chloride Hexahydrate	30	30	30	37.5
Sodium Acetate	5	2.5	10	7.5
Sodium Citrate	10	15	10	15
Ammonium Chloride	10	10	10	15
Sodium Hypophosphite	10	10	10	15
pH	5.5	5.5	5.75	5.5
Coating Temp.	95-98°C	95-98°C	95-98°C	95-98°C

Nickel Bath B

<u>Constituent</u>	<u>g/l</u>			
	<u>B-1</u>	<u>B-2</u>	<u>B-3</u>	<u>B-4</u>
Nickel Chloride Hexahydrate	40	40	40	40
Hydroxyacetic Acid	10	60	40	20
Ammonium Chloride	10	10	10	
Sodium Hypophosphite	25	25	25	25
Sodium Citrate			20	10
Sodium Acetate				3
pH	8	6	6	5.75
Coating Temp.	90°C	90°C	90°C	90°C

Note: It is necessary to activate Baths A and B with a few mg of Al powder before coating will commence.

TABLE III

Chemical Immersion Coating
Baths for UO₂ Spheres

Nickel Bath C

<u>Constituent</u>	<u>C-1</u>	<u>C-2</u>
Nickel Chloride Hexahydrate	50 g/l	50 g/l
Lactic Acid 85%	50 cc	50 cc
Ammonium Chloride	- - -	10 g/l
Sodium Hypophosphite	15 g/l	15 g/l
pH	5	5
Coating Temp.	90-95°C	90-95°C

Note: Spheres must first be sensitized by a prior dip in Bath A or B, Table I.

Copper Bath

<u>Constituent</u>	<u>g/l</u>
Copper Sulphate	30
Rochelle Salt	75
Ammonium Hydroxide (28%)	150 cc/l
Formaldehyde (37%)	30
pH	9 - 9.5
Coating Temp.	R. T.

TABLE IV

Electrolytic Barrel Plating Baths
For UO₂ Spheres

<u>Bath</u>	<u>Constituent</u>	<u>g/l</u>	<u>Current Density</u>	<u>pH</u>	<u>Bath Temp.</u>
Nickel	Nickel Sulphate	150	10-30 amps/ft ²	5-5.5	90°F
	Ammonium Chloride	30			
	Boric Acid	30			
Chromium	Chromic Acid	250	100-300 amps/ft ²		120-140°F
	Fluosillicic Acid	2.5			
Copper	Copper Sulphate	45	5 amps/ft ²		R. T.
	Sodium Cyanide	67.5			
	Sodium-Potassium Tartrate	60			
	Potassium Carbonate	11.3			

TABLE V

Electrolytic Barrel Plating Baths
and Surface Preparation
For Uranium Metal Spheres

<u>Bath</u>	<u>Constituents</u>		<u>Current Density</u>	<u>Bath Temp.</u>
Acid Copper	CuSO ₄ H ₂ SO ₄	210g/l 55cc/l	20-30 amps/ft ²	R. T.
Modified Acid Copper	CuSO ₄ H ₂ SO ₄ Na Lauryl Sulphate	210g/l 55cc/l 7 mg/l	30-50 amps/ft ²	R. T.
Nickel Fluoborate	Ni(BF ₄) ₂ 42% H ₂ O	300cc 600cc	100 amps/ft ²	R. T.

Surface Preparation

Step No. 1	2 min immersion in	H ₃ PO ₄ 70 v/o HNO ₃ 20 v/o H ₂ O ₂ 10 v/o
Step No. 2	5 sec immersion in	HNO ₃ 70 v/o
Step No. 3	immerse immediately	in desired plating solution

TABLE VI

Coating Evaluation Results

<u>Type of Coating</u>	<u>Thickness of Coating in u</u>	<u>Relative Load in Grams Required to Crush a Test Lot of Spheres*</u>	<u>Calculated Load in Grams Required to Crush a Single Sphere</u>	<u>Knoop Hardness of Coating</u>
Bare UO ₂ Spheres		300	1	
Ni	4	900	3	569
Cr on Ni Base	4 to 8	1100	3.7	336
Nb	4	300	1	52
W	2	325	1.08	846

*That amount of spheres that could be close packed in a single layer under the anvil area.

TABLE VII

Analytical Results of Coatings

PPM

Coatings

Element	Nb*	Cr*	Ni ☐
C	16-100		
H	13-40		
N	40		
Fe	50		
B	0.2		
Co	5		
Mn	10		
Cd	1		
W	10		
Al	50		
Sn	2		
Cu	5		
Pb	2		
Cr	10		
Si	50		
Ti	50		
Ni	15		
Mo	2		
V	1		
Ag	0.2		
Li	10		
Cl	60	35	5
P			3 w/o

* Halide Reduction
☐ Chemical Immersion

TABLE VIII

Coatings Successfully Applied

UO₂ Spheres

<u>Coating</u>	<u>Thickness Microns</u>	<u>Coating Process</u>	<u>Application</u>
Ni	12	Chemical immersion	Conducting medium for subsequent electro-plating - protective barrier for Cr coating by halide reduction
Ni	20-40	Electro-plating	Final coating
Cr	8-10	Halide reduction	Final coating
Cr	10-30	Vacuum Evaporation	Finals and barrier coating
Cr	15-20	Electro-plating	Final coating
Cu	4-6	Chemical immersion	Conducting medium for subsequent electro-plating
Cu	30	Electro-plating	Final coating
Fe	4-6	Electro-plating	Conducting medium for subsequent electro-plating
Nb	8-10	Halide reduction	Final coating
Mo	2-4	Halide reduction	Final coating
W	2	Halide reduction	Final coating

Uranium Metal Spheres

Cu	15-50	Electro-plating	Protective barrier for subsequent coating
Ni	15-50	Electro-plating	Protective barrier for subsequent coating

AL COATED U-PARTICLES

FIGURE 1

FIGURE 2

A. 2 micron thickness - 45 minutes in bath A-1, Table II.

B. 8-10 micron thickness - 40 minutes in bath B-1, pH of 8, Table II.

Fig. 3. Chemical Immersion
Nickel Coatings on UO₂ Spheres. X100.

A. 5 micron thickness - 45 minutes
in bath B-2, pH of 6, Table II.

B. 8-10 micron thickness - 1 hour
in bath C, Table II.

Fig. 4. Chemical Immersion
Nickel Coatings on UO_2 Spheres.
X100.

Fig. 5. Thickness of Ni and Cu by Chemical Immersion as a Function of Time.

Fig. 6. Ni 8-12 Microns.
Electrolytic Barrel Coatings from
Baths Listed in Table IV. X100.

Fig. 7. Chemical Immersion
Copper Coating, 6 Microns Thick,
1 Hour Immersion Time. X100.

Fig. 8. Cu 12-20 Microns.
Electrolytic Barrel Coatings from
Baths Listed in Table IV. X100.

Fig. 9. UO_2 Particles Coated with Chromium by Electro-deposition From a Chromic-Sulphuric Acid Bath. X100.

A. Top view of barrel

B. Barrel and rectified power supply.

Fig. 10. Electrolytic Barrel Plating Apparatus.

Fig. 11. Cr 3-5 Microns.
Electrolytic Barrel Coatings from
Baths Listed in Table III. X100.

SCHEMATIC DIAGRAM OF CrCl_2 REDUCTION APPARATUS

FIGURE-12

A. 4-6 micron thickness in 3-1/2 hours time using apparatus shown in Fig. 12. X100.

B. 8-10 micron thickness in 5 hours time from the 200 gram reactor.

Fig. 13. Chromium Coated UO_2 Spheres by the Reduction of Chromic Chloride.

SCHEMATIC DIAGRAM OF VAPOR REDUCTION APPARATUS

FIGURE-14

A. 8 micron thickness in 4 hours time
from the 50 gram reactor. X100.

B. 12 micron thickness in 8 hours time from
the 200 gram vibratory agitated reactor.
X250.

Fig. 15. Niobium Coated UO_2 Spheres
by Reduction of NbCl_5 . X100 and X250

Fig. 16. Tungsten Coated UO_2 Particles
Thickness 2-4 Microns. X100.

A. Copper plate, using surface preparation and modified acid copper bath. X100.

B. Nickel plate, using surface preparation and $\text{Ni}(\text{BF}_4)_2$ bath. X100.

Fig. 17. Electroplated Uranium Metal Spheres.

A. X-ray showing distribution of particles.

B. Polished longitudinal section of element. X75.

Fig. 18. Dispersion Element Containing Chromium Coated UO_2 Particles.

A. External appearance of platelets

B. Metallographic cross section. X100.

Fig. 19. Platelets of Niobium Coated Spheres
Formed in Vibratory Agitated Reactor.

Fig. 20. Sketch of Halide Reduction Reactor Arrangement for Making Dispersion Elements.

A. Cup and anvil.

B. Set-up on Tukon hardness tester.

Fig. 21. Apparatus for Determining Crushing Resistance of Coated Spheres.

DESORPTION RATE OF COATED & UNCOATED UO₂ SPHERES

• - EMPTY COMPARTMENT

+ - COATED

○ - UNCOATED

FIGURE-22

057 063