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PROTECTION OF URANIUM: VAPOR-DEPOSITED COATINGS



by

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Report No. **BMI-887** Metallurgy and Ceramics



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PROTECTION OF URANIUM: VAPOR-DEPOSITED COATINGS

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I. E. Campbell, E. M. Sherwood, C. F. Powell, and R. P. Jones

The most satisfactory vapor-deposited coatings on uranium were obtained by a displacement-diffusion process similar to pack chromizing, employing the vapors of the lower zirconium iodides. Coatings of zirconiumuranium alloy up to 5.9 mils thick were obtained during a 24-hr treatment at 1050 C. These coatings, of undetermined composition, were adherent, nonporous, and exhibited corrosion rates in boiling water of the order of 0.001 to 0.006 mg/cm²)(hr). The average life of the coatings in boiling water is about 500 hr.

Chromium was deposited on uranium by thermal decomposition of chromous iodide vapor. Niobium was deposited by hydrogen reduction of niobium pentachloride vapor at reduced pressure. Molybdenum was deposited by thermal decomposition of molybdenum carbonyl. Zirconium was deposited by thermal decomposition of, or displacement from, zirconium $2rI\omega$ tetraiodide vapor by disproportionation of the vapors of lower zirconium iodides $(Zrl_2 + Zrl_3)$ and by reduction of the lower zirconium iodides with magnesium and zinc vapors. /2

This latter group of coatings was unsatisfactory because of porosity, poor adhesion, or the presence of underlying salt deposits.

The development of the pack-zirconizing process is being continued.

INTRODUCTION

The current practice of canning uranium slugs in aluminum jackets to prevent corrosion by the cooling water in Hanford reactors is not entirely satisfactory. The jackets occasionally develop pinholes, which, when penetrated by water, result in serious failure. Also, aluminum does not possess the desired corrosion resistance and strength at the higher temperatures desired for future reactor operation. Both of these problems might be solved by the application of protective coatings of other materials.

The ideal coating would be completely nonporous, metallurgically bonded to the base metal, ductile, and would have a low thermal-neutronabsorption cross section and a negligible corrosion rate. An ideal coating could be used as primary protection. A less-perfect coating, one having a





corrosion rate substantially less than that of pure uranium, would still be of value as secondary protection, as a "sweater" beneath the jacketing material used at present. This sweater would prevent the catastrophic type of failure while allowing a period during which incipient jacket failure could be detected.

This phase of the work on developing protective coatings for uranium is concerned with the vapor-deposition of chromium, molybdenum, niobium, vanadium, and zirconium coatings. These metals were chosen because of their corrosion resistance, the physical properties of their alloys with uranium, and their nuclear properties. Vapor-phase deposition of these metals can be accomplished by reduction or thermal decomposition of, or displacement from, their volatile halide vapors. In addition, molybdenum can be deposited at low temperatures by thermal decomposition of its carbonyl. The development of the vapor-deposition processes for applying protective coatings has been utilized primarily as a means of applying those materials which cannot be readily deposited by other means. Molybdenum, niobium, vanadium, and zirconium are excellent examples of such materials. Some of the vapor-deposited coatings have proven to be highly satisfactory and the processes commercially practicable. Based on this background, the prospects of developing a satisfactory vapor-deposited, protective coating for uranium appeared sufficiently promising to warrant investigation.

The criteria for evaluating the coatings were adhesion, freedom from pinholes or porosity, and corrosion behavior. These were determined by exposure of the coating specimen to boiling, distilled water and measuring the rate of weight change, or the time required for pinhole attack or spalling to occur.

EXPERIMENTAL WORK

In all instances the uranium specimens were cleaned by degreasing followed by anodic etching for 15 min in a bath containing 5 parts (by volume) phosphoric acid, 5 parts ethylene glycol, and 8 parts ethyl alcohol, operated at room temperature at 12 v with sheet-lead cathodes. The etched specimens were dipped in 5 per cent oxalic acid solution to remove the thin film of phosphate remaining on them, washed, dried, weighed, and placed in the deposition chamber.

Since the presence of a diffusion layer in a coating tends to improve adhesion and reduce porosity of the coating, conditions favorable to the formation of a diffusion layer during coating were chosen, or coated specimens were heat treated after coating to increase the thickness of the diffusion layer.



Chromium

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Chromium was deposited by thermal decomposition of chromous iodide vapor on $3 \times 1 \times 1/8$ -in. specimens. Chromous iodide was prepared by outgassing granular electrolytic chromium at 900-950 C in vacuo and subjecting it, at 900 C, to iodine vapor at 0.5 atmosphere pressure. The chromium was contained in a perforated molybdenum boat which permitted the chromous iodide to drip to the bottom of the Vycor deposition tube as it was formed. After iodination, the chromous iodide was heated to 600-700 C and the excess iodine was pumped out of the system. After cooling under vacuum, the tube was filled with dry CO₂ and the iodination apparatus (iodine and chromium boats) removed and a cleaned specimen suspended on a molybdenum support over the chromous iodide cake in the bottom of the tube. The system was then evacuated to a pressure of 1 micron or less and the uranium specimen slowly heated inductively to deposition temperature. The heating was carried out at such a rate that the pressure in the system did not rise above 5 microns. With the specimen hot, the chromous iodide was heated to its vaporization temperature by means of an external sleeve furnace. Specimen temperatures between 740 and 850 C, and CrI₂ vaporization temperatures between 670 and 740 C, were used with coating periods of 3 to 4 hr.

It was difficult to avoid the formation of a condensed uranium iodide phase on the specimen during chromium deposition. One specimen, coated for 4 hr at 830 C, with the chromous iodide vaporized at 717 C, appeared to be completely coated with chromium. The metal deposit, however, was underlaid by a thick layer of purple UI₃, which rapidly absorbed moisture when the specimen was exposed to air. The formation of a condensed UI₃ layer was avoided by using a specimen temperature as high as possible and a low CrI₂ vaporization temperature. The specimen temperature was limited by the melting point of the chromium-uranium eutectic, 860 C. Specimen temperatures were measured by an optical pyrometer. However, the uncertainties of specimen emissivity and light absorption by walls clouded with iodide deposits made temperature determinations inaccurate. Chromel-Alumel thermocouples could not be used in contact with the uranium, because the desired temperatures exceeded the eutectic temperatures of uranium with the thermocouple alloys.

Chromous iodide was sufficiently unstable to decompose appreciably at all vaporization temperatures used, depositing a layer of chromium on the tube walls between the CrI₂ vaporization region and the specimen location. This premature decomposition would add considerable free iodine to the coating atmosphere and tend to cause excessive attack of the specimen as well as reduce the throwing power of the coating reaction. All of the specimens coated showed signs of being attacked on the downstream ends; some





were severely pitted. The few apparently adherent coatings obtained were confined to small areas on the upstream ends of the specimens. The remainder of these specimens were either not coated or covered with a thin, nonadherent, porous coating. No corrosion-resistant coatings were obtained.

Pack chromizing of a $3 \ge 1 \ge 1/8$ -in.uranium specimen was attempted in one experiment. The pack consisted of 25 per cent 16-mesh, crushed, fused chromium, and 75 per cent 60-mesh crystalline alumina. The chromizing pack was evacuated to 0.7 micron, heated to 800 C, and subjected to iodine vapor at 0.08-mm mercury pressure for 4 hr. The specimen appeared to have a thin, corrosion-resistant coating on one end, but the other end was uncoated. The low maximum treatment temperature (860 C) which can be used in the chromizing process with uranium is a severe limitation, since this process depends on solid-solid diffusion for continued coating action.

Molybdenum

One flat uranium specimen was coated with molybdenum by thermal decomposition of molybdenum carbonyl vapor. The specimen was outgassed at 500 C, cooled to 475 C, and then subjected to the vapor from molybdenum carbonyl that had been resublimed at 30 to 50 C. The total coating time was 6 hr. The pressure in the coating apparatus varied from 20 to 50 microns during deposition. The coating period was divided into two parts, the specimen being electropolished and shifted in its holder before applying the second coating, in order to avoid uncoated support points. The first coating was adherent except at the point covered by the electrode during the initial electropolish. The second coating was adherent all over. The total coating was so thin, however, that several pinholes developed during a 2-hr test in boiling water.

Niobium

Niobium was deposited by hydrogen reduction of niobium pentachloride at reduced pressure. Niobium pentachloride was prepared by chlorination of Nb₂O₅ at 450-500 C with a mixture of chlorine and carbon tetrachloride vapor, and by chlorination of the metal powder at 400 C with chlorine carried in helium. Preparation from the metal was preferred, since the product obtained upon chlorinating the oxide was chiefly NbOCl₃. The crude chloride was purified by fractional sublimation in vacuo at 150 to 200 C. Where large amounts of NbOCl₃ were present, the initial separation was made by extraction of the NbCl₅ with CCl₄, followed by recrystallization and sublimation. The purified chloride was sealed under vacuum in glass bulbs with frangible seals.



The hydrogen used in deposition was purified by passage through a catalytic deoxidizer and dried with a cold trap at -70 C and with anhydrous magnesium perchlorate.

Deposition was carried out in Pyrex apparatus, using a vertical deposition chamber in which the specimen was hung on a molybdenum wire. A Vycor liner around the specimen prevented overheating of the Pyrex walls. The top of the deposition tube was connected to the vacuum system through a liquid-nitrogen trap, while the bottom of the tube was connected through a U-tube of 12-mm-diameter tubing to a vaporizing chamber containing the NbCl5 bulb and a glass-enclosed steel striker for breaking the NbCl5 bulb. Hydrogen was bled into the vaporizer bulb through a needle valve, and a barometric mercury column between the needle valve and the vaporizer bulb indicated the pressure at which the hydrogen entered the system. The U-tube between the deposition tube and the vaporizer tube was immersed in an oil bath which was heated, during deposition, to a temperature 30 to 50 C below that of the vaporizer bulb. Partial condensation of the NbCl5 vapor in the U-tube during deposition insured that the NbCl5 vapor concentration was fixed by complete saturation at the oil bath temperature, rather than by partial, and variable, saturation at the vaporizer temperature. The specimen was heated inductively, the vaporizer bulb was heated by an external sleeve heater controlled with the aid of a thermocouple and potentiometer, and the vapor lines outside of the oil bath were heated by an external Nichrome wire winding to prevent condensation therein.

In operation, the system was evacuated to 0.05 to 1 micron, warmed slightly to outgas the glassware, and the NbCl5 bulb broken. The specimen was slowly heated to 1000 C and outgassed. The hydrogen flow was then adjusted to the value used during deposition. The vaporizer was then warmed until condensation of NbCl5 occurred in the U-tube in the oil bath, following which the oil bath was heated to the desired vaporization temperature to start deposition. At the close of the deposition period, the vaporizer and oil bath were cooled, the hydrogen flow stopped, and the specimen outgassed for 15 to 30 min at 1000 to 1050 C and 1 micron pressure to remove any absorbed hydrogen. The coated specimen was cooled to room temperature before breaking the vacuum.

The best coating was obtained at a specimen temperature of 1050 to 1100 C, a NbCl5 vaporizer temperature of 70 to 115 C, and at a total pressure of 5 mm mercury. When deposition was started with the NbCl5 saturation tube at 70 C and the tube temperature was then slowly raised to 115 C during deposition, better results were obtained than when the NbCl5 saturation tube was operated at a higher starting temperature. High NbCl5 saturation temperatures and low specimen temperatures (900 to 950 C) produced metal deposits underlaid by a uranium chloride deposit. A low NbCl5 concentration at the start permitted a thin layer of niobium to be deposited, following which a higher NbCl5 concentration could be used





without danger of formation of a condensed chloride layer. A more adherent coating was obtained when the hydrogen flow was not started until the NbCl5 saturation tube was nearly up to temperature, than when the specimen was heated for a long period in a flow of hydrogen containing no NbCl5 vapor. This was probably caused by the trace amounts of impurities in the hydrogen. These impurities, in the absence of NbCl5 vapor, would form an oxide, nitride, or carbide layer at the surface of the uranium and render a subsequent metal coating nonadherent. When the hydrogen was mixed with NbCl5 vapor from the start, these impurities would deposit in the niobium itself and would have less effect on the coating bond.

The niobium coatings obtained by this method were nonuniform in that the upstream face of a specimen would be heavily coated, while the downstream face would have a thin coating, or none at all. The sides of the specimens had coatings of intermediate thickness.

Uniform adhesion was difficult to obtain in these coatings. The coatings on the sides of the specimens were usually well bonded, but the coatings on the upstream face frequently showed poor adhesion, sometimes blistering during the cooling from deposition temperature. Coating adhesion might be improved by using higher purity hydrogen and by slower heating of the specimen during the outgassing period (i.e., limiting the maximum pressure in the system during the outgassing period to 0.1 micron, or even lower).

The heaviest and most adherent niobium coating produced, 5 to 7 mils, was not 100 per cent pore free, so that some undercutting of the coating occurred during corrosion testing. Test lives up to 96 hr were obtained before serious undercutting occurred.

Vanadium

No attempts have yet been made to deposit vanadium. Because of the very promising results of corrosion studies of uranium-zirconium alloys, initial attention has been devoted to zirconium coatings. Conditions for the deposition of vanadium by thermal decomposition of vanadium diiodide vapor would be very similar to those used in depositing chromium from CrI₂ vapor, with the important exception that specimen temperatures up to 1000 or 1050 C could be used because of the absence of any low-melting eutectics in the vanadium-uranium system. For this reason, the deposition of vanadium should be more successful than was the deposition of chromium.

Vanadium-uranium alloy coatings could also be prepared by a packvanadizing process similar to the pack-zirconizing process used so successfully in preparing zirconium-uranium alloy coatings (see below). Such a process would be the most economical vanadium-coating process to carry out, and would give the highest percentage of satisfactorily coated specimens.



Zirconium

Zirconium was deposited by: (a) thermal decomposition of, or displacement from, ZrI_4 vapor; (b) disproportionation of the vapor of lower zirconium iodides (i.e., ZrI_2 , $ZrI_3 \rightarrow Zr + ZrI_4$); (c) reduction of the vapor of the lower iodides with magnesium and zinc vapor, and (d) displacement-diffusion in a pack-zirconizing process using the lower zirconium iodides.

Zirconium tetraiodide was prepared by passing iodine vapor at about 0.5 atmosphere pressure over Bureau of Mines Grade C zirconium sponge heated to 400 C. The product was resublimed once or twice in vacuo at about 250 C, and sealed in evacuated Pyrex bulbs with frangible seals.

Deposition from ZrI4 was carried out in a vertical, closed-end Vycor tube. The inductively heated specimen was suspended over the bulb of ZrI4 located at the bottom of the tube and heated by an external sleeve heater. The system was outgassed, the bulb of ZrI4 broken, and the specimen slowly heated to deposition temperature. The ZrI4 was then heated to the required vaporization temperature for the desired length of time.

Because of the stability of ZrI_4 , the highest possible deposition temperature was used. This resulted in the melting of a number of specimens, after which the specimen temperatures were maintained between 980 and 1050 C. The ZrI₄ vaporization temperatures ranged from 250 to 260 C. The measured pressure in the system during deposition ranged from 1 to 5 microns.

The coatings obtained by this process were very thin, but were uniformly adherent and appeared to consist entirely of a zirconium-uranium alloy, since they darkened upon exposure to air or moisture. For this reason, it is thought that deposition occurred entirely by displacement, with virtually no decomposition of the ZrI4 vapor. A coat thickness of 0.08 mil was obtained on one $3 \ge 1 \ge 1/8$ -in. specimen treated for 5 hr at 980 to 1030 C with a total of 16.3 g of ZrI4 (equivalent to 2.5 g zirconium). This specimen developed numerous pits during a 48-hr test in boiling water. A specimen coated for 2.5 hr at 1000 to 1030 C developed some pits during a 35-hr test in boiling water.

Because of the extremely slow and inefficient deposition of zirconium from the tetraiodide, and since the reports of work at the Knolls Laboratory indicated that much higher deposition rates could be obtained with conditions favoring the following reaction,

$$2ZrI_2 \rightarrow Zr + ZrI_4$$
,

the work with ZrI4 was abandoned.

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Zirconium deposition by disproportionation of the lower zirconium iodides was carried out by passage of iodine vapor through a 4- to 6-in.bed, or column, of heated zirconium sponge (Bureau of Mines, Grade C), and then over an inductively heated uranium specimen (a 1-in.-diameter, 0.5inch-thick, round slug). This was done in a vertical Vycor tube. The iodine charge at the bottom of the tube was outgassed for 30 min at room temperature and then cooled to minus 70 C while the zirconium-sponge charge was slowly heated to 500 to 600 C and outgassed. After outgassing the zirconium, the specimen was outgassed at 250 to 350 C, after which it was heated to deposition temperature and the iodine warmed to its vaporization temperature. At the end of the coating period the iodine and zirconium charges were cooled before cooling the specimen.

Specimen temperatures were varied from 1050 to 1100 C in order to obtain maximum thickness in the diffusion layer. Iodine-vaporizer temperatures of 0 to 160 C, zirconium-metal temperatures of 450 to 830 C, and coating times of 2 to 5 hr were used. True iodine-vaporization temperatures were unknown but were much lower than the indicated temperatures. Molten iodine was not obtained in the vaporizer, even at temperatures (external) as high as 170 C. The temperature of the zirconium, over the range indicated, had little influence on the deposition rate. This rate was influenced, to a certain extent, by the iodine-vaporization temperature, especially over the temperature range 0 to 50 C. Extremely thin coatings were obtained with the iodine kept at 0 C. Deposition rates ranged from 0.9 to 1.2 mils per hr for iodine-vaporizer temperatures between 60 and 160 C.

These coatings appeared to consist of two phases: an outer layer of zirconium and an inner layer of zirconium-uranium alloy. This diffusion layer occupied about 10 per cent of the total coating thickness. The outer layer was always somewhat porous. The metal was quite ductile and could be compacted by peening or burnishing, but fine cracks always remained at the sites of the original pores. For this reason, test lives, in boiling water, longer than 20 hr were not obtained, even in coatings as thick as 3.8 mils. Some porosity always persisted.

These coatings were nonuniform, heavy on the upstream side and thin on the downstream side. The efficiency of the deposition reaction was also relatively low, generally being less than 10 per cent.

The efficiency of the deposition reaction and the coating uniformity were improved by adding a reducing agent to the atmosphere of ZrI₂ vapor. Hydrogen is too weak a reducing agent to use here, but both magnesium and zinc vapors were found to be satisfactory and could be obtained in highly pure forms. The method of utilization consisted of placing an Alundum crucible, containing the magnesium or zinc, on top of the column of zirconium sponge

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in the previously described setup and heating it with a separate sleeve heater. In this way the $ZrI_2 + ZrI_3$ vapor was mixed with magnesium or zinc vapor just before contacting the specimen.

Magnesium proved to be too strong a reducing agent; the zirconium iodide vapors were reduced upon contact with the magnesium vapor, depositing zirconium foil upon the tube walls, where it interfered with the induction heating of the specimen. (External heating would have been preferable here.) For this reason low magnesium-vaporization temperatures (560 to 530 C or under) gave best results.

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> Zinc vapor, being a weaker reducing agent, was best used in high concentrations (vaporization temperatures of 384 to 610 C), and did not produce secondary deposition on the tube walls. Both reducing agents produced coatings of good over-all uniformity. Magnesium seemed to produce slightly more adherent coatings than did zinc, in that no blistering was noted in the magnesium-reduced coatings. Consistently good adhesion was obtained in the zinc-reduced coatings by treatment of the specimen with a small amount of magnesium vapor at the start of deposition. The deposition efficiency in one zinc-reduction experiment was 28 per cent for a deposition rate of about 2.5 mils per hr. In this run, the specimen was heated to 1040 to 1100 C, the iodine to 100 C, the zirconium to 580 to 590 C, and the zinc to 384 to 560 C. Deposition rates as high as 3 mils per hr were obtained.

> All of the magnesium- and zinc-reduced coatings were porous in their outer layers, although the diffusion layers appeared to be nonporous. This porosity appeared to consist of both intercrystalline and intracrystalline porosity, one caused by voids trapped between intersecting crystal growths, the other apparently caused by gas evolution within, or beneath the deposits during deposition. The porosity could be reduced as before by peening and burnishing but could not be completely eliminated. The longest corrosion test lives obtained with these zirconium coatings were 80 to 100 hr for a 3-mil coating applied in two stages by magnesium reduction, each coating being peened, and 70 hr for a 7- to 10-mil-thick coating applied by zinc reduction. The 80- to 100-hr coating (3 mils thick) had a 0.47-mil-thick diffusion layer. Both specimens failed by pinhole attack.

> Since the porous zirconium coatings produced by these processes were not ideally suited for heat treatment to increase diffusion, and since a single-stage treatment process would be more practical than a two-stage, coating — heat-treating process, an attempt was made to deposit zirconium at a rate no faster than that at which it would diffuse into the base metal. This was done by packing the specimens in zirconium sponge (Bureau of Mines, Grade C) and subjecting the pack to iodine vapor at low pressure





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(0.03 to 0.3 mm mercury) in an externally heated tube. Since the displacement reaction

$$3ZrI_2 + 2U \rightarrow 2UI_3 + 3Zr$$

was to provide the chief plating action, a temperature differential between the source of ZrI_2 vapor and the plating zone was not required, and a uniform source of external heat, rather than induction heating, could be used.

Deposition was carried out in fused silica, stainless steel, and graphite-lined silica tubes. The iodine charge was placed at the bottom of the tube and surmounted by a radiation shield of glass wool or metal baffles. The zirconium pack and specimens were supported over this on a perforated molybdenum plate. An unbroken column of zirconium sponge, 4 to 8 in. in length, was used below the pack containing the specimens to convert most of the free iodine to ZrI₂ before it reached the specimen region. In operation, the iodine was outgassed at room temperature for 30 min, then cooled to minus 70 C while the pack was being heated to operating temperature. This heating was sufficiently slow that the pressure in the system did not rise above 1 micron. Most of the gas evolved from the pack came out between 250 and 350 C. With the pack at temperature, the iodine was heated to the required vaporization temperature. At the end of the run, the iodine was again chilled before cooling the pack and specimens. This cooling required from several minutes to several hours, depending upon the size of the tube and the furnace used.

The conditions of zirconizing and the results of the boiling water corrosion tests for a series of specimens are given in Table 1.

The coating action was found to be sensitive to the packing conditions. Satisfactory plating occurred when the pack was in contact with the specimen, or separated from it by not more than 2 or 3 mm. In one instance, where the pack was located at the ends of 4-cm-long wire specimens (Specimens 8258-76a, -76b, Table 1), the specimens were heavily attacked, but still received a protective coating as is indicated by the corrosion rates. The extent of corrosion of the specimen during coating was proportional to its separation from the pack.

In another instance, disc specimens were zirconized while being retained in slotted Alundum holders which separated them from the pack material by 8 to 10 mm. No attack of the specimens occurred, but neither was there any coating deposited. The specimen holders received an appreciable coating, however.

Use of a dense pack composed of a mixture of zirconium sponge and 60-mesh crystalline alumina, similar to the standard chromizing pack, resulted in severe corrosion of the specimens and no coating.



Specimen			I ₂ Temp,	Coating Time,	Coat Thickness,	Test Duration,	Average Corrosion Rate	Trend in Corrosion	
Number	Form	Spacer	С	hr	mil	hr	mg/(cm ²)(hr)	Rate	
Uncoated uranium	50-mil wire	-	-	-	0	-	2.6 to 2.9	-	
8258-73 a	Ditto	None	0 to 25	24	3.6 to 4	484	0.05	Increasing	
8258-76a		Zr at ends of speci- men	25 to 28	24	-	334	0.036	Ditto	
8258-76b		Ditto	25 to 28	24	-	334	0,134	••	
8258-87a	17	Perforated Mo sheet	25	24	5.9	> 511	0.0012 at 511 hr	Decreasing	
8258 - 87b		Ditto	25	24	5.9	349	0.0002	Specimen ac- cidentally broken	-17
8258 - 87c	••		25	24	5.9	166	0.0018	Ditto	L
8258-87d	**		25	24	5.9	> 511	0.0024 at 511 hr	Decreasing	
8258-87e	**	*	25	24	5.9	> 511	0.0017 at 511 hr	Constant	
8258 - 91a	11 .	Slotted Porcelain tube	0	6	0.6	131	0.32	Increasing	
8258 - 91b	**	Ditto	0	6	0.6	131	0.35	Ditto	
8258-91c	**	**	0	6	0.6	131	0.36	۳	
8258-91d	**	"	0	6	0.6	131	0.46	*	
8258-91e	**	"	0	6	0.6	131	0.54	"	
8258-97 a	3 x 1 x 0.125- in. sheet	None	25	24	-	186	0.016	71	
8258 - 97b	Ditto	Ditto	25	24	-	186	0,013		
8258-97c		11	25	-	-	186	0.376	Rapidly increasing	

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TABLE 1. ZIRCONIZING OF URANIUM IN ZIRCONIUM SPONGE AT 1050 C

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All of the containers used appeared to give satisfactory coatings, although the specimens coated in a stainless steel tube (Specimens 8258-87, a through e, Table 1) appeared to have slightly better coatings than specimens coated in silica, or graphite-lined silica tubes (Specimens 8258-73a, 8258-76, a and b, and 8258-97, a through c). Where specimen holders were not used, sticking of the pack to the specimens was not serious except where a stainless steel tube had been used. There may have been a slight transfer of material from the stainless steel to the specimen, but it was not sufficient to lower the melting point of the bulk of the coating below 1050 C. Direct contact of the specimen with stainless steel could not be tolerated, and unlined stainless steel tubes were heavily attacked, or fluxed away where they contacted the zirconium sponge.

These zirconized coatings appeared to consist primarily of a singlephase, well-bonded alloy layer. A possible second phase was indicated by the presence of a darker layer about 0.06 mil thick between the main coating and the base metal, as well as by numerous small islands of darker material randomly scattered throughout the main coating. Metallographic examination of a larger number of coatings has not been made to determine the effect of coating conditions, and cooling conditions and rate, upon coating structure. Coating composition has not been determined.

CONCLUSIONS

Corrosion-resistant zirconium-uranium-alloy coatings can be applied to uranium by a pack zirconizing process employing zirconium sponge and a small amount of iodine vapor in an externally heated tube. On small specimens, these coatings are essentially pore free, have corrosion rates, in boiling, distilled water, of the order of 0.001 to 0.005 mg/(cm²)(hr), and have test lives, before pinhole attack occurs, averaging about 500 hr for a coating 5 to 6 mils thick.

Other vapor-deposition methods for applying chromium, molybdenum, niobium, and zirconium, are not, at present, capable of applying consistently pore-free, uniform, and adherent coatings, and will not be capable of doing so without considerable additional development. These other methods are unable to compete with the pack zirconizing process insofar as ease of application, economy of materials, and reliability of results are concerned.

Alloy coatings of the other metals considered can probably be applied by processes similar to pack zirconizing.

Pack zirconizing is very similar to pack chromizing, which is in commercial use today for applying corrosion-resistant coatings to iron and steel. The chief difference is that pack zirconizing is carried out in a





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moderately high vacuum, although the need for this has not been well established. The chances of pack zirconizing being a commercially feasible process are considered to be good. Its development in the direction of eliminating coating porosity, determining coating composition, and coating standard fuel slugs is being continued.

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