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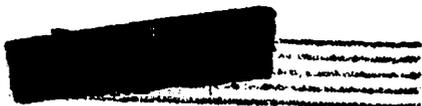
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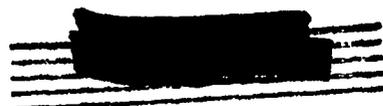
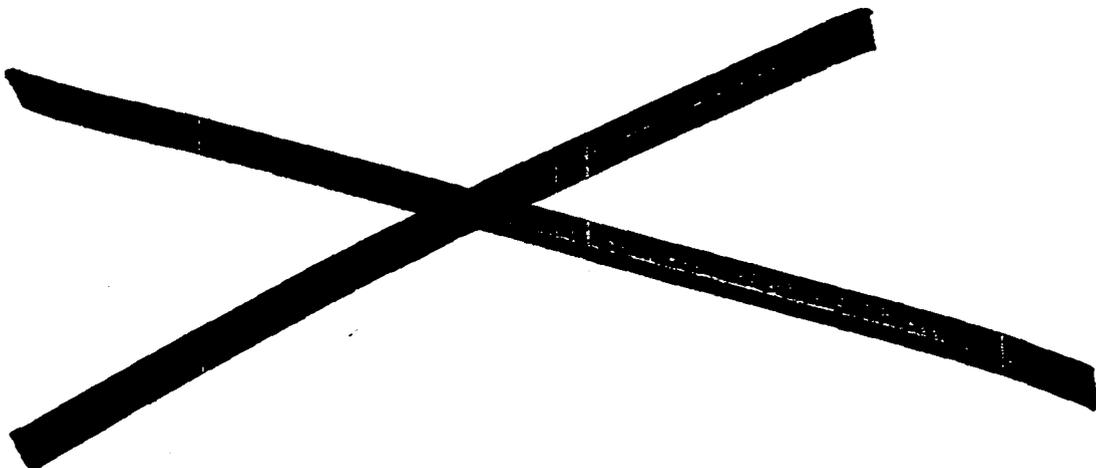
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PROTECTION OF PLUTONIUM AGAINST ATMOSPHERIC OXIDATION

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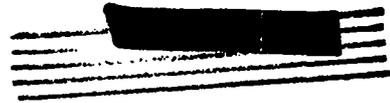
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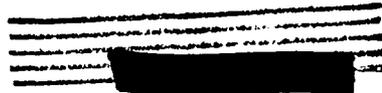
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ABSTRACT

The oxidation of alpha-phase plutonium has been investigated, and a variety of protective coatings have been studied. Organic films and evaporated metal films are unsatisfactory. A composite electroplate of silver, indium, and cadmium, heat-treated to cause diffusion, has provided excellent protection. Methods of cleaning, etching, and plating plutonium have been devised.



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PROTECTION OF PLUTONIUM AGAINST ATMOSPHERIC OXIDATION

Introduction

When plutonium metal became available in small amounts, it became apparent that it was appreciably attacked in ordinary atmospheres. When freshly cleaned, the metal is bright and similar to nickel in tone. Upon exposure at room temperature, it gradually darkens and eventually acquires a powdery surface. At slightly elevated temperatures the oxidation proceeds rapidly with the formation of green-yellow powder which has been identified as the dioxide by X-ray diffraction. Apart from considerations of loss and influence on nuclear reactions, the extremely toxic nature of the material renders it imperative that oxidation be minimized and the products contained. In addition, it is desirable that any applied coating be capable of absorbing the alpha radiation so that fabricated pieces may be handled without excessive precautions, and that such coating be unaffected by the ionization produced by the emission.

All of the work to be described has been carried out with substantially pure plutonium, i.e., the alpha phase. Recently, there have been indications that the delta phase, metastabilized by gallium, is more resistant to atmospheric oxidation. Complete confirmation is lacking at present.

Experimental

The chief obstacle to an extensive study of the protection of plutonium has been the unavailability of the material. To overcome this, much of the work has been performed with thin foils (0.002 inches), approximately one centimeter square. As might be expected, the variability is high when such small surfaces are employed, and the results should not be considered quantitative. In later work, samples of approximately the same size, but approximately five times the thickness, were used.

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Oxidation rates were determined by weighing on assay balances, and the values may be considered precise to 5 micrograms per square centimeter. Samples were contained in small platinum boats to prevent loss of oxide, and coatings were considered to have failed completely when such oxide appeared at the surface. Standard accelerated tests were performed at 65°C in laboratory air (9 mm partial pressure water vapor, approximately 5 percent relative humidity), and under these conditions the metal oxidized rapidly in 24 hours. Heating was carried out in regulated laboratory ovens, and humidity control, where necessary, achieved by the use of sulphuric acid solutions of proper concentration.

Surface Preparation:

The samples of plutonium were fabricated at first by rolling at 200°C under mineral oil and later by pressing under oil. These carried a fairly thick layer of adherent oxide which in an actual oxidation test exerted no protective action, and, therefore, had to be removed prior to coating. Unfortunately, no reagent has been found capable of dissolving the oxide chemically without dissolving metal at an appreciably greater rate. Early work on milligram quantities had indicated that the oxide could be removed and the metal simultaneously brought to a high luster electrochemically. This was subsequently confirmed with larger samples. The plutonium is made anodic in a solution of equal volumes of 85 percent orthophosphoric acid and ethylene glycol at 3 to 6 volts and approximately 0.5 ampere/sq. in. The solution is operated at room temperature, using stainless-steel cathodes. Normally, 3 to 10 minutes are sufficient for cleaning. The metal is then immersed in concentrated nitric acid for about 30 seconds to 2 minutes and is washed. It has also been found possible to substitute aqueous solutions of acetic acid, phosphates or sodium cyanide. The

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brightest luster is obtained with phosphoric acid-glycol.

Little adhesion is obtained by plating directly on the electropolished surface, hence some form of etching is required. A variety of possible etchants were investigated, and while a number of fairly suitable ones were found, the most satisfactory appears to be an aqueous solution containing 100 g/l of ammonium sulfate and 6 cc/l of concentrated sulphuric acid. An immersion of 10 minutes seems satisfactory. After etching, the metal is coated with a black film, the majority of which is removed by dipping in concentrated nitric acid for a few minutes. The remainder is removed by a very brief electropolish in the phosphoric acid-glycol solution. Following the customary nitric acid dip and washing, the plutonium may be plated.

Plating Methods

Plutonium reacts chemically with slightly acid solutions (except nitric), and is attacked by dilute sulphates and chlorides. Plating baths are, therefore, limited to alkaline electrolytes. Attempts have been made to deposit copper, cadmium, zinc, and tin directly upon plutonium, but in each case blisters develop in a short time. This difficulty can probably be overcome by a modification of the surface preparation treatment. At present, however, the only metal which can be satisfactorily deposited directly on plutonium is silver. This is plated from a bath containing 140 g/l of AgCN, 204 g/l of KCN, and 15 g/l of K_2CO_3 operated at room temperature. Current densities as high as 0.2 ampere / sq. in. may be used, but for thick deposits this quantity is halved. Other metals may, of course, then be deposited on the silver.

For the electrodeposition of tin, the solution used contained 150 g/l sodium stannate and 150 g/l potassium pyrophosphate. This bath was operated at room temperature and a current density of 0.1 ampere / sq. in., yielding a current efficiency

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of about 25 percent. Cadmium was plated from a bath containing 45 g/l of cadmium oxide, 120 g/l sodium cyanide, 0.4 g/l nickel carbonate, and 12 g/l goulac. This bath is permitted to stand for several days before filtration, and is operated at room temperature at a cathode current density of 0.1 to 0.2 amperes/sq. in., yielding a current efficiency of about 95 percent.

Indium was plated from solutions prepared by dissolving 18 grams of metallic indium in 80 cc of concentrated HCl, evaporating to dryness, and dissolving the chloride in 100 cc of water. Thirty grams of dextrose are then dissolved and the resultant solution added rapidly with stirring to one containing 160 g potassium cyanide and 40 g potassium hydroxide in 350 cc of water. The product is then diluted to one liter. Commercially available indium chloride solutions may be used in place of metal. Plating is carried out at room temperature at a current density of 0.15 amperes/sq. in., with a current efficiency of approximately 50 percent. The current efficiency is known to decrease with use and age.

Oxidation of Uncoated Metal

Two specimens of alpha plutonium foil have been exposed at room temperature and 40 percent relative humidity, (9 mm partial pressure of water vapor) for some time. One of these gained approximately 10 micrograms/sq. cm. after 2512 hours (105 days), while the other increased in weight by 174 micrograms/sq. cm. after 3581 hours (149 days). The large variation may be attributed to the difference in origin of the two foils, but the larger value is sufficiently small to be considered within safe limits. A test at 25°C is largely academic since massive pieces of plutonium possess sufficient internal energy to raise their temperature well above ambient. This rise may be limited by confining the metal in a suitable conducting case.

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The relative influences exerted by temperature and humidity on oxidation rates have not been investigated in detail, but some idea of their magnitude may be gleaned from Table I.

Table I
Effect of Temperature and Humidity on the
Oxidation of Alpha Plutonium

| <u>Temp. °C</u> | <u>Percent Relative Humidity</u> | <u>Time Hours</u> | <u>Weight Gain Micrograms/sq. cm.</u> |
|-----------------|----------------------------------|-------------------|---------------------------------------|
| 25 | 40 | 900 | 10 to 70 |
| 25 | 100 | 900 | 6500 |
| 50 | 7 | 900 | 4300 |
| 50 | 7 | 200 | 600 |
| 75 | 5 | 200 | 1000 |
| 65 | 0 | 200 | 15 |

It should be noted that a weight gain of approximately 6500 micrograms/sq. cm. corresponds to a loss of metal thickness of 0.001 inch assuming a metal density of 19 g/cc and the formation of plutonium dioxide. As might be expected, an increase in either humidity or temperature hastens the progress of oxidation. However, moisture appears to be essential to continuation of the process, and desiccation is indicated as an elementary method of prevention.

Organic Coatings

Although the durability of organic coatings subjected to fairly intense alpha radiation is not known, a number of such coatings were investigated to determine their protective properties. In all cases failure was almost immediate, and this line of investigation was not pursued.

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Evaporated Coatings

Group CM-6 deposited a variety of metal films on plutonium samples using the vacuum evaporation technique. These included rhodium, vanadium, manganese, and tellurium as well as gallium applied mechanically. These coatings were thin, in general being about 0.00001 inch thick. Although in a very few instances there was some evidence of delay in oxidation, failure was extremely rapid in almost all cases.

Electroplated and Diffused Coatings

It was found that even fairly thick coatings of electrodeposited silver did not provide complete protection. Fig. 1 shows a comparison between bare metal and a sample plated with about 3 mils of silver, a five-fold decrease in rate being observed over the period of test. The coating evidently fails to prevent the diffusion of oxygen and moisture to the underlying metal. In an effort to seal the pores, thinner deposits of silver were plated with alternate layers of indium and cadmium, and indium and tin, to a composite thickness of about 3 mils, and subjected to vacuum heat treatment at 97°C for about 70 hours. The result obtained is shown graphically in Fig. 1. It is evident that excellent oxidation resistance is obtainable by this method. Insufficient data are available to permit specification of minimum thickness of deposit and minimum times for heat treatment.

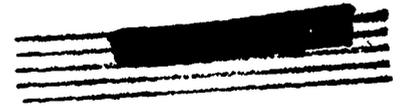
Conclusions and Recommendations

While methods of cleaning, etching, and plating plutonium have been devised, and while satisfactory protection has been realized through the use of a composite silver-indium-cadmium coating, much work remains. As indicated previously, the delta phase may prove to be considerably more oxidation-resistant than alpha, thus simplifying the problem. In any case, the study of oxidation rates as affected by temperature

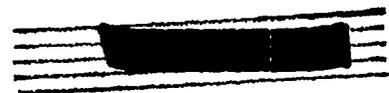
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and humidity should be extended. The minimum thickness of coating, and time and temperature of heat-treatment (if any is required) should be determined. The use of aqueous cleaning electrolytes such as the phosphates and cyanides should be investigated in greater detail, and in particular, their tolerance for the other reagents which may be carried over should be determined. It would be highly desirable to devise a method of cleaning and etching in a single step. Furthermore, a number of mechanical problems involving racking in a remote control system require immediate attention. Sufficient metal should be made available for these studies.



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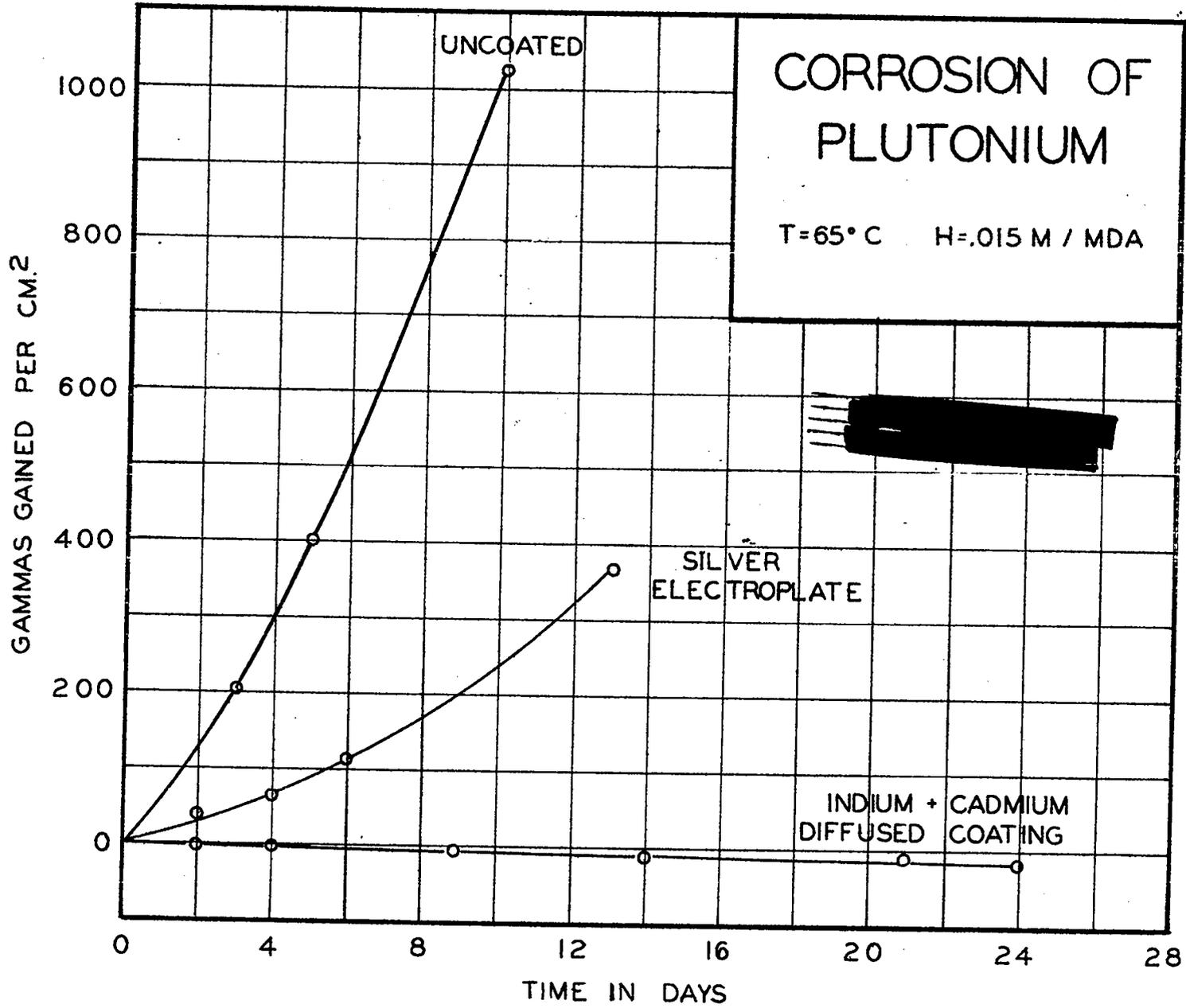


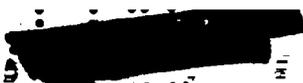
FIGURE 1.

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