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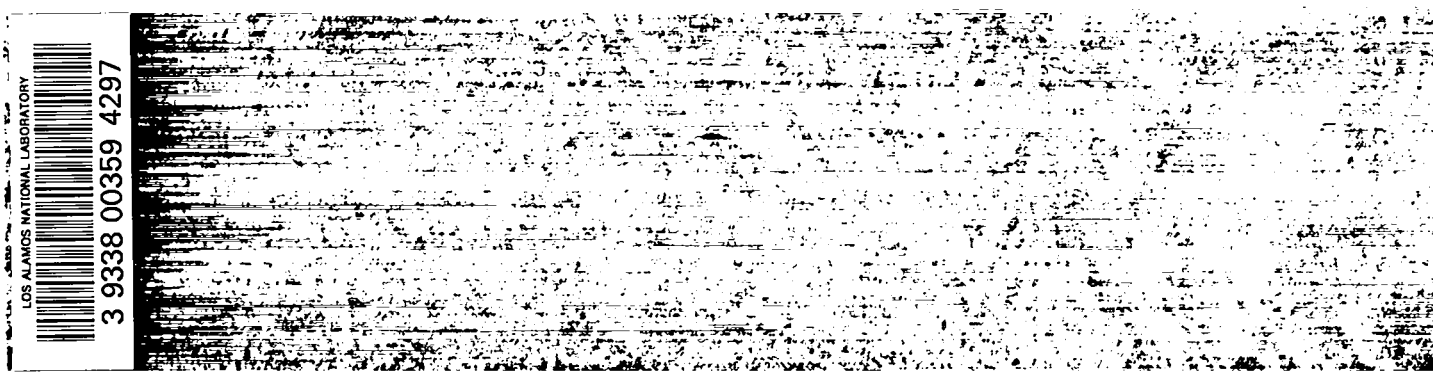
ELECTROPHORETIC DEPOSITION OF PLUTONIUM

A Feasibility Study



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ELECTROPHORETIC DEPOSITION OF PLUTONIUM

A Feasibility Study

by

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ABSTRACT

Electrophoretic deposition of plutonium hydride from suspensions in n-butyl alcohol and other organic liquids was examined for its feasibility in the preparation of thin sections of plutonium metal. Dispersions of plutonium hydride in the solvent medium were produced by wet milling. Addition of trace amounts of butyric acid prior to the milling operation was necessary for deposition of plutonium hydride on nickel or tantalum electrodes with the application of 600 to 1000 volts to suspensions of the hydride in purified n-butyl alcohol. Vacuum drying of the deposits at room temperature was followed by thermal decomposition of the hydride at 450°C. A final heating at 525°C. removed the last traces of hydrogen and sintered the deposit to produce a smooth, hard, adherent coating. Interaction of plutonium hydride and the solvent vehicle during milling leads to the formation of a mixture of metallic Pu, PuO, and Pu_2O_3 in the sintered product. The successful application of an electrophoretic process depends on the choice and availability of an inert solvent vehicle.

INTRODUCTION

Electrophoresis is identified as the movement of a charged particle under the influence of a potential gradient. Many finely divided substances dispersed in a solvent vehicle possess electric charges on their surfaces, primarily caused by the difference in surface potential of the liquid-solid interface. Application of an external voltage causes the migration of these particles, each of which consists of a large number of molecules. Electrophoretic deposition of the particles on an electrode can be accomplished without an accompanying valence change or change in physical state.

The phenomenon of electrophoresis was discovered by Reuss[1] in 1807 with the observation of the migration of clay particles in water when an external voltage was applied. One of the early commercial applications of electrophoresis was for the deposition of cellulose in 1926. Electrophoresis is employed in the application of alumina coatings to vacuum tube parts, in the manufacture of latex rubber gloves, and in the application of wax and plastic coatings to food containers.

The preparation of metallic coatings by electrophoretic deposition of oxides and subsequent reduction and sintering in purified hydrogen atmosphere has been studied.[2] The use of dilute suspensions in an organic medium makes possible the application of a high voltage with a low current density. Electrophoretic deposition offers the advantages of uniformity and control of coating thicknesses with rapid deposition on regular and irregular shapes.

An electrophoretic method for the preparation of <0.005 in. layers of plutonium was investigated using suspensions of plutonium hydride. The difficulties in the reduction of plutonium compounds limited the study to the deposition from suspensions of the metal or plutonium hydride. Plutonium hydride is obtained as a brittle powder from which the suspensions can be readily prepared. It can be thermally decomposed above 500°C., at which temperature a simultaneous sintering action to produce a thin adherent coating of plutonium metal might be expected.

EXPERIMENTAL METHODS

The feasibility of electrophoretic deposition for plutonium plating was shown in early tests to depend largely upon the choice of solvent vehicle for the plutonium hydride suspension. The viscosity and dielectric constant of the liquid influence the velocity of the particle undergoing electrophoresis. In addition, the flash point limits the selection since dry box operations are required with plutonium. For this reason, isopropyl alcohol, which is usually employed for electrophoretic operations, could not be used in the experiments with plutonium hydride.

Plutonium hydride forms a friable powder on treatment of δ-phase plutonium turnings with hydrogen. Pure hydrogen was obtained by thermal decomposition of uranium hydride. The reaction between plutonium and hydrogen is initiated by heating the turnings to approximately 100°C. The subsequent reaction is highly exothermic, making it necessary to limit the rate of addition of hydrogen in a static system. The volume increase during the conversion to plutonium dihydride gives a finely divided brittle powder. Additional hydrogen is taken into solid solution by plutonium dihydride.[3] The hydrogen-saturated product at room temperature contained 2.7 to 2.8 atoms of hydrogen per atom of plutonium.

Suspensions for the deposition experiments were obtained by wet milling the plutonium hydride in the organic liquid in a stainless steel jar half filled with a mixture of 1/8 and 1/4 in. chrome steel balls. The concentrated slurry obtained from the milling operation was transferred to a cylindrical battery jar and diluted to 750 ml. with the appropriate liquid.

The plating bath was stirred by means of a Teflon-coated magnetic stirring bar in the bottom of the cell. The electrode system consisted of a cylindrical stainless steel screen as the anode surrounding a 0.5 in. diameter nickel or tantalum tube as the cathode. The inner electrode had a surface area of 16 sq. cm. wetted by the plating bath. The electrode separation was fixed at 1 cm. A power supply was obtained to provide

d.c. voltage which could be varied from 100 to 3500 volts. The maximum current was 10 ma.

Drying and decomposition of deposits were achieved by suspending the nickel or tantalum tube horizontally in an evacuated quartz tube. The initial removal of liquid was conducted at room temperature. Slow heating released the remaining liquid prior to the beginning of the thermal decomposition of plutonium hydride at 350°C. Slightly higher temperatures required for removal of the last traces of hydrogen produced the desired sintering action.

Electrophoretic deposits of plutonium were characterized by chemical analysis and by x-ray examination. The plutonium dioxide content was estimated from the insoluble residue remaining after treatment with 6N hydrochloric acid. The metallic plutonium content was ascertained by measuring the volume of hydrogen which would react with the sintered product in re-forming plutonium hydride. The weight gain during ignition in air also served as a guide to the quality of the product.

EXPERIMENTAL RESULTS

Electrophoretic deposition as a means of preparing metallic plutonium coatings did not prove to be feasible in systems using plutonium hydride suspended in the organic liquids tested. The difficulties are attributed to interaction between plutonium hydride and the solvent vehicle. Other areas of the experimental work were developed independently of the liquid behavior. In the event a satisfactory organic medium can be obtained, a discussion of the experimental work in terms of bath preparation, deposition, drying and decomposition, sintering and analysis may be useful.

The wet-milling operation produced a satisfactory size reduction of the plutonium hydride. The desired particle size of the solid phase for electrophoretic deposition ranges from 0.1 to 20μ in diameter. Microscopic examination of plutonium hydride suspensions prepared by milling for 64 hr. showed that the solids ranged in particle size from 0.5 to

10μ with the bulk of the material present as irregularly shaped particles of 2 to 4μ. Material milled for 24 hr. consisted mainly of particles in the 4 to 8μ range, with few particles coarser than 10μ. These measurements gave assurance during the early unsuccessful tests that the solid phase was in the desired physical state.

Iron contamination of sintered deposits amounted to 1000 p.p.m. and the chromium content was 500 p.p.m. These impurities were introduced during ball milling from the chrome steel balls.

The solid phase composition of the suspension could be varied by limiting the amount of hydrogen added to the plutonium turnings and heating the powder at 350°C. for 3 to 4 hr. for a homogenizing treatment. Suspensions having a solid phase with an average composition of plutonium monohydride were too highly conducting to permit rapid deposition on the cathode. Only with compositions between that of plutonium dihydride and and that of the hydrogen-saturated state could sufficient voltage be applied to give reasonable plating times.

The formation of a 0.005 in. coating of plutonium hydride was completed in 1 to 2 min. from a bath containing 40 g. of plutonium hydride per liter. By milling only enough plutonium hydride for a single deposit, complete removal of the solid phase gave a control of the coating thickness. Deposition was not rapid with the dilute suspensions; the formation of a 0.005 in. coating on the nickel or tantalum electrode required 20 to 60 min. before all of the solid phase was deposited. Slow stirring of the bath gave uniform thickness of the deposit over the length of the electrode. Stirring was also necessary for exhaustion of the bath of its plutonium hydride content.

The plating operation was usually carried out with 600 to 1000 volts. The higher conductivity of baths in which the liquid and plutonium hydride had been in contact for more than one day limited the potential gradient on account of the upper limit of current. As deposition was continued the conductivity decreased, possibly as a result of the insulating qualities of the plutonium hydride deposit.

Deposits obtained from the less volatile organic liquids, such as n-butyl alcohol and 1-nitropropane, could be vacuum dried at room temperature without flaking. Thin sections of 0.001 to 0.003 in. thickness showed no further gas evolution until decomposition was initiated in the vicinity of 350°C. Coatings of 0.003 to 0.005 in. thickness required 3 to 4 hr. at 100°C. to complete the removal of the organic liquid. Completion of the drying treatment was indicated by the restoration of the vacuum on the system to 0.1 to 0.5μ .

Decomposition of the plutonium hydride began at 350°C. but the rate of liberation of hydrogen was too slow. A temperature of 450°C. gave a rate of hydride decomposition which allowed completion of the operation in 3 to 4 hr. Samples which had been vacuum dried at room temperature were stable in air; those which had been heated were highly pyrophoric, even after cooling to room temperature. A final treatment at 525°C. for 1 hr. completed the hydride decomposition and produced a sintered deposit which could be transferred in air.

The sintering treatment caused alloying of the plutonium with the nickel substrate. Samples of these coatings showed 1 to 2 per cent nickel in the plutonium. The substitution of a tantalum electrode for the nickel eliminated the alloying problem. Phase transformations during cooling of sintered deposits were a matter of concern in that volume changes might affect the adherence of the deposit. The use of δ-phase plutonium successfully avoided this difficulty.

A number of solvents were tested for the preparation of plating baths containing plutonium hydride. A comparison of the physical properties of these organic liquids with those of isopropyl alcohol, from which it was assumed plutonium hydride could be deposited, indicated that the surface tension was another factor in addition to the viscosity, dielectric constant, and flash point to be considered in the selection of the dispersing medium.

Nitrobenzene gave a stable suspension in which reaction between plutonium hydride and the liquid phase was not evident. Deposition on a

nickel electrode could not be achieved with voltages as high as 2500 volts. There was an apparent inability of nitrobenzene to wet the electrode. Tests with dibutyl ether as the dispersing medium were also fruitless in yielding a plutonium hydride deposit. These suspensions had a very low conductivity, allowing use of the full potential of 3500 volts.

Electrophoretic deposition of plutonium hydride was achieved using n-butyl alcohol as the dispersing medium. Interaction between plutonium hydride and n-butyl alcohol was indicated by the increasing conductivity of the bath with contact time. Purification of the n-butyl alcohol by distillation from a suspension containing uranium hydride gave a product from which plutonium hydride could no longer be deposited. Small additions of butyric acid as a stabilizing agent restored the plating behavior of n-butyl alcohol systems. Stable suspensions were obtained by adding a small amount of a 5 per cent solution of butyric acid in n-butyl alcohol prior to milling. If deposition was too slow from such a bath, small additions of the dilute butyric acid solution to the bath could be made.

The effectiveness of butyric acid additions in the preparation of suspensions was observed in a number of solvent systems. Exceptions were suspension of plutonium hydride in nitrobenzene, carbon tetrachloride, and n-tributyl phosphate, since these solvents did not wet the electrode.

Most of the experimental studies were devoted to deposition from the n-butyl alcohol solvent medium. X-ray and microscopic examination of plutonium hydride coatings vacuum dried at room temperature identified the deposits as plutonium hydride. Some volatile component was also retained, since ignition of plutonium dioxide showed that the dried deposit contained only 94.0 per cent plutonium hydride. X-ray examination of the sintered product from this dried material showed that the major constituent was the monoxide, PuO. Similar deposits from this plating bath contained, in addition to plutonium hydride, 5.3 per cent plutonium dioxide after vacuum drying at room temperature; after drying at 250°C. the plutonium dioxide content had increased to 7.8 per cent.

More complete purification of the n-butyl alcohol by distillation from uranium hydride improved the chemical character of the coating. On the basis of the volume of hydrogen which would react with the sintered product, the metallic plutonium content was increased to 33 to 40 per cent. X-ray examination of these sintered samples identified the main constituents as metallic Pu, PuO, and Pu_2O_3, present in nearly equal quantities. Analysis for plutonium dioxide gave 1.3 per cent in the material as the insoluble residue from treatment with dilute hydrochloric acid.

In an effort to isolate the phase of operations in which oxide contamination of the plutonium was introduced, the role of milling time was re-examined for its effect on the chemical composition of the sintered product. Carbon contamination of electrophoretic deposits after sintering was directly dependent on the time of contact between plutonium hydride and n-butyl alcohol in the ball mill. Carbon contents of 0.44, 0.61, 0.75, and 0.87 per cent were reported after 16, 20, 24, and 44 hr. milling, respectively. Following the deposition from the bath containing plutonium hydride milled for 44 hr., the remaining solids were left in contact with the n-butyl alcohol for an additional 24 hr. before deposition. The sintered product from the deposition contained 1.23 per cent carbon.

The metallic content of sintered electrophoretic deposits was closely related to the carbon contamination introduced during milling and contact. Contact periods during ball-milling operations of 5, 47 and 238 hr. gave 78.6, 37.4 and 6.6 per cent metallic plutonium, respectively, in the sintered deposits obtained from the suspensions in n-butyl alcohol.

The results obtained as a function of contact time are seemingly not consistent with the x-ray and microscopic observations that the deposit on the electrode is plutonium hydride. However, the amount of oxygen necessary to convert a significant fraction of the deposit to plutonium monoxide during heating is small. The formation of a small amount of an oxygen-containing impurity during the milling operation could easily escape detection.

Deposits from dibutyl ether and kerosene (Gulf Solvent BT) were obtained after additions of butyric acid had been made. These deposits were quite voluminous and tended to flake from the electrode during drying in air. Bromobenzene was considered as a dispersing medium containing no oxygen. The deposit from bromobenzene suspensions containing a trace of butyric acid is rapidly flaked from the electrode during vacuum drying at room temperature. The sintered electrophoretic deposit from a suspension milled for 5 hr. with practical grade 1-nitropropane contained 42.5 per cent plutonium metal. Supplies of this liquid were not available in sufficient quantity to allow a prior purification by distillation from uranium hydride.

On the basis of the observations made in this study, it is believed that the successful application of an electrophoretic process for the deposition of plutonium hydride remains with the choice of the solvent vehicle. The other phases of the deposit treatment do not appear to present serious problems.

SUMMARY

Electrophoretic deposition of plutonium hydride from suspensions in n-butyl alcohol and other organic liquids was examined for its possible application in the preparation of thin sections of plutonium metal. Dispersions of plutonium hydride in the solvent medium, which had been purified by distillation from a suspension containing uranium hydride, were produced by wet milling. Additions of trace amounts of butyric acid prior to the milling operation imparted the necessary plating properties to the solid phase in most of the liquids tested. Deposition of plutonium hydride on nickel or tantalum electrodes was obtained with the application of 600 to 1000 volts to the suspensions of the hydride in n-butyl alcohol. After the deposits were vacuum dried at room temperature, thermal decomposition of the plutonium hydride was accomplished by heating at 450°C. Final traces of hydrogen were removed by heating at 525°C., at which temperature a simultaneous sintering action produced a smooth, hard, adherent coating.

Interaction of the n-butyl alcohol and plutonium hydride was shown by an increase in conductivity of the plating bath. This was confirmed by the increase in the carbon and oxygen content of the sintered product with increased milling or contact time. The sintered product contained metallic Pu, PuO, and Pu_2O_3, present in nearly equal proportions.

The use of other organic liquids did not yield encouraging results. Deposition was not possible from nitrobenzene, n-tributyl phosphate, or carbon tetrachloride. Electrophoretic deposition from dibutyl ether and bromobenzene containing traces of butyric acid gave voluminous deposits which tended to flake from the electrode during the initial drying stages. The use of 1-nitropropane was encouraging, but could not be pursued.

The application of an electrophoretic process for plutonium coating is limited by the reactivity of plutonium hydride. Since the other phases of the process do not present serious problems, emphasis should be placed on the procurement of an inert solvent vehicle for preparation of the suspensions.

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