METALLURGY AND CERAMICS

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ELECTROPHORETIC PROCESSES - NUCLEAR ASPECTS

Final Report
December 1, 1956 - June 30, 1959

by

R. A. Keeler and S. J. Klach

September 30, 1959

Contract No. AT(30-1)-1996
Vitro Job 2091

Approved:

L. G. Mount, Head
Department of Chemical
Research and Development

ABSTRACT

In this research and development effort sponsored by the AEC, the feasibility of the electrophoretic (electrokinetic) coating process has been demonstrated for a number of nuclear applications. The major portion of the experimental program was directed toward work which lead to:

- A. Development of electrophoretic coatings which should be useful for the protection of graphite and graphite fuel elements against physical and chemical attack under reactor conditions. Several of these coatings also show promise for fission product retention.
- B. A technique for applying, electrophoretically, solid lubricant-metal matrix coatings for use at elevated temperatures and in high nuclear flux environments.
- C. An electrophoretic method for applying impervious aluminum oxide coatings on ceramic fuel elements for fission product retention.

Other experimental work, (special evaluation studies) of a more limited nature, was directed toward establishing the utility of the electrophoretic process for:

- A. Applying on UO_2 platelets chromium coatings to act as a diffusion barrier between the platelet and the canning material;
- B. Depositing cadmium coatings on mild steel for use as control rods and
- C. Applying coatings on graphite which would act as barriers against diffusion of fission products under special LMFRE tests.
- D. Applying thick (15-20 mil), dense molybdenum coatings on stainless steel.

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ELECTROKINETIC PROCESSES - NUCLEAR ASPECTS

FINAL REPORT

December 1, 1956 - June 30, 1959

Vitro Job 2091

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INTRODUCTION

This is the final report on AEC Research and Development Contract AT(30-1)-1996 - Electrokinetic Processes - Nuclear Aspects - and covers work performed during the period December 1, 1956 through June 30, 1959. For the purposes of internal contract control, this work is identified as Vitro Job 2091. The work reported, herein, is an extension of research conducted under AEC Research and Development Contract AT(30-1)-850 (Vitro Jobs 1099 and 2018). For a list of reports issued previously under these contracts see Bibliography (1-44).

The objectives of the investigations under this program were the development of methods for producing electrophoretic coatings on various substrates for applications of specific interest to the Atomic Energy Program. AEC sponsorship was initiated in 1953 as a result of research conducted by Vitro for Wright Air Development Center, concerning investigations of electrophoretic techniques for the preparation of solid fuel elements. A summary of the work done for WADC is presented in WADC Technical Report 53-344. (45)

A review of the electrophoretic coating process is presented in the body of this report for the benefit of those not included on the distribution lists for previous reports under the above contracts.

RESULTS AND CONCLUSIONS

I. MAJOR EXPERIMENTAL INVESTIGATIONSA. Electrophoretic Coatings for the Protection of Graphite and Graphite Fuel Elements

For the protection at elevated temperatures of graphite and graphite fuel elements against erosion or oxidation and/or for fission production retention, very hard, adherent coatings of silicon carbide, tungsten carbide, tantalum carbide and niobium carbide were obtained by depositing the metal electrophoretically and subsequently carburizing in an atmosphere of methane or propane to form the carbide, in situ. The hardness of the resultant coatings was comparable to those reported in the literature for the pure carbides. However, the applicability of the coatings was limited because of the rather porous nature of the coatings. In the case of silicon carbide, however, it has been found that the particle size of the silicon is an important factor in producing an impervious silicon carbide coating. Results, to date, indicate that silicon metal with a particle size distribution of 0.1 - 5 microns will yield an impervious silicon carbide coating by the electrophoretic process.

2/ Other coating materials investigated for protection of graphite against erosion and oxidation were alumina, fecral, and alloys of nickel-chromium-silicon and chromium-silicon-iron-aluminum. The results indicated that the nickel-chromium-silicon (75-15-10) alloy was found to wet graphite and yielded dense, well-bonded coatings with a high metallic luster. In our estimate it is believed that graphite coated with this material can be joined to ferrous and non-ferrous material by conventional brazing techniques. The other materials, alumina, fecral and chromium-silicon-iron-aluminum alloy, although satisfactorily deposited by the electrophoretic technique, exhibited poor adherence following the normal densification and sintering operations. Another aspect of the use of the electrophoretic process involved a study of nickel, molybdenum, silicon and molybdenum disilicide-nickel for protection of graphite against liquid sodium at elevated temperatures. All these coating materials were successfully deposited electrophoretically. However, after densification and sintering, the coatings either cracked or were non-adherent.

B. Solid Lubricant Coatings

Of the various solid lubricant-metal matrix mixtures studied (BN-Cu, BN-Mo, BN-Cu-Fe, BN-Cu-Ni, PbO-Cu, Fe₂O₃-Cu, MoS₂-Cu) it has been found that MoS₂-Cu, BN-Cu, BN-Cu-Ni and BN-Mo can be electrophoretically deposited and bonded to 304 stainless steel. The lubricating properties of these coatings appear promising.

C. Aluminum Oxide Coatings for Ceramic End Elements

At the request of ANP-GE and with the approval of the AEC, a program was undertaken to determine the applicability of the electrophoretic process for applying dense, well-bonded aluminum oxide coatings to tubular, ceramic fuel elements. The function of the coating would be to insure fission product retention. Studies under this program showed the electrophoretic technique to be capable of depositing uniform coatings of controlled thickness on both the inside and outside surfaces of the tubular elements. This was achieved by: (1) rendering the fuel elements conductive by developing a graphite formulation and procedure for coating the fuel elements with a thin conductive layer of graphite; (2) designing and fabricating an electrophoretic deposition apparatus which aided in obtaining the desired coating uniformity; (3) design and fabrication of a special electrode jig such that coaxial uniformity was maintained between the inner electrode and the inside surface of the element. The jig also served to support the fuel element in the deposition apparatus; (4) formulating an Al₂O₃ dispersion that yielded uniform, crack-free as-deposited coatings of the desired thickness; and (5) developed a bagging technique whereby the soft as-deposited coated fuel elements could be readily densified.

Subsequent to electrophoretic deposition, experiments were conducted to establish optimum densification pressures and presintering treatments.

Examination of the coated fuel elements after the presintering treatment revealed peripheral cracking of the coatings on the inner and outer edges of the fuel element. Our latest experimental data indicated that it should be possible to obtain crack-free coatings. Several presintered aluminum oxide coated fuel elements that were obtained crack-free were delivered to ANP-GE and are being evaluated.

II. SPECIAL EVALUATION STUDIES

A. Chromium Coatings on UO₂ Platelets

Samples of chromium coatings on UO₂ platelets were prepared at the request of Westinghouse Atomic Power Division with the approval of the Atomic Energy Commission. These coatings were designed to act as diffusion barriers between the UO₂ and a zircalloy can and could be deposited in the required thicknesses only by electrophoretic techniques. Preliminary tests at Westinghouse have yielded very encouraging results. Long-term tests are currently in progress.

B. Cadmium Coatings on Mild Steel

A brief investigation was conducted on the use of electrophoresis for the preparation of thin metallic cadmium coatings on mild steel for possible neutron absorption application. The resultant coatings exhibited excellent metallic properties and good bonding to the base metal.

C. Graphite Coatings for Use in LMFRE

At the request of Babcock and Wilcox with AEC approval, a program was carried out to examine the feasibility of the electrophoretic technique for applying impervious coatings on graphite test specimens. The coatings were to act as a barrier against diffusion of gaseous fission products into the graphite and also provide resistance to the corrosive action of the constituents of the liquid metal fuel at elevated temperatures.

Coating materials such as tantalum carbide, chromium carbide, chromium-carbide-iron, chromium carbide-chromium, tantalum-iron, tantalum-chromium, molybdenum-iron, and molybdenum-chromium were successfully deposited on the graphite substrate. The coatings, however, lacked the desired imperviousness which is required for the above application.

D. Molybdenum Coatings on Stainless Steel

Thick (15-20 mils), dense, and well-sintered, adherent molybdenum coatings on stainless steel were successfully produced by sintering at 1200°C in a high flow of activating gas (hydrogen-2 mole percent HCl) for a 2 hour period. The coating thus obtained withstood machining and polishing treatments without any visible signs of damage.

ELECTROPHORETIC COATING PROCESS REVIEW

Of the many practical and theoretical methods for coating one substance with another, the phenomenon of electrophoresis offers the greatest potential with regard to the variety of materials which may be handled and the measure of process control attainable. Electroplating, vapor coating, flame coating and spraying are representative commercial methods which are highly efficient for many applications but unsatisfactory for others. By combining electrophoretic coating techniques with subsequent bonding procedures the study of coating may be extended to include nearly all solid materials, pure and composite, in films deposited to exact thickness. Figure 1 outlines the basic steps of the process and lists some of its advantages.

A. Definition of Electrophoresis and Electro-osmosis

Charged particles suspended in a liquid move under the influence of a potential gradient toward the pole of opposite charge. The term electrophoresis is used to denote this fact. When the electric potential is applied across electrodes immersed in a suspension, the charged particles migrate to and deposit upon the oppositely charge electrode.

Electro-osmosis denotes the flow of a liquid through the pores of a membrane caused by a difference in potential on the two sides. If the liquid contains suspended particles smaller than the pore openings, the porous body is impregnated by suspended particles and the voids ultimately are filled.

B. Electrophoretic Deposition

In practice, coating is obtained by connecting the article as one electrode immersed in a suspension of the coating material. Since the charge on the dispersed particle is a specific property of each system, its sign must be predetermined and the current directed to attract the dispersed phase to the proper electrode.

The electrophoretic method of deposition has several distinct advantages over other methods. Deposition rate is high and current cost relatively low. The deposit is uniform both in composition and thickness, even when coatings of composite materials are plated. The laws governing the process allow close control of thickness, density, and to some extent, adhesion.

FIGURE 1

VITRO ELECTROPHORETIC COATING PROCESS

ADVANTAGES OF VITRO PROCESS

- Excellent Uniformity Is Obtained.
- Coating Thickness Can Be Readily Controlled.
- Process Is Versatile. Alloys, Cermets, Etc. Of Controlled Composition Can Be Deposited.
- Coating Is Metallurgically Bonded And Impervious.
- Heavy Coatings Can Be Deposited Rapidly.
- Power Consumption Is Low.
- Process Is Readily Applicable To Irregularly-Shaped Articles.

1. Deposition Rate

Coating takes place rapidly. This may be attributed to the fact that each particle is large and its static charge small as compared with the ionic particles involved in the electrolytic process. As a result, deposition rates in the range of several kilograms per ampere hour may be attained and coatings 5 to 10 mils thick may be built up in 15 seconds.

The exact rate of coating has been found to depend on many factors. Distance between electrodes, dispersion concentration, voltage, particle size and particle charge, each influence the rate of deposition.

2. Coating Uniformity

Uniformity of composition is assured in electrophoretic deposition by the fact that the deposit always has the same composition as the dispersed phase even when the suspension contains several different kinds of particles. This phenomenon operates also to simplify the mechanics of maintaining a constant dispersion concentration.

Uniform thickness of coat is maintained automatically in electrophoretic deposition by virtue of an insulating effect exhibited by the deposited coating. This insulating effect is represented in Figure 2 by thickness-time curves measured at four voltage levels. The variation of current with deposition time is represented in Figure 3. As deposition progresses, any thin spots which may develop offer lower resistance causing a current shift and an increased deposition rate at these points. This effect operates to produce deposits of uniform thickness even on rough or irregular surfaces.

FIGURE 2 ELECTROPHORETIC DEPOSITION DEPOSIT THICKNESS VS. DEPOSITION TIME

FIGURE 3 ELECTROPHORETIC DEPOSITION
CURRENT VS. DEPOSITION TIME

3. Control of Thickness

In order to control the thickness of coatings deposited electrophoretically, deposition rate must be determined for each system. This cannot be calculated from stoichiometrical relations as it can for electroplating systems because the depositing unit does not have a constant charge-to-weight ratio. Instead, optimum conditions and the corresponding deposition rate must be determined for each system under consideration.

4. Control of Density and Adhesion

Variation in density and adhesion of electrophoretically deposited coatings is governed over a broad range by plating conditions. Limits imposed by characteristics of the suspension were greatly extended by techniques developed in the research program. The most marked improvements have been obtained by the substitution of nonaqueous for aqueous suspension media, discovery of new dispersion activators, and control of particle size.

One of the greatest restrictions limiting the use of electrophoretic deposition, prior to the work done by Vitro, was the evolution of gas at the electrodes with a resulting formation of very porous and weak deposits. Vitro investigated the substitution of nonaqueous suspension media and found that solvents such as isopropyl alcohol and nitropropane did not form gas at the electrodes yet performed as well as water in all other respects. Plating voltages in the range of 100 to

150 volts DC were used for most laboratory work but special tests at higher potential proved that these solvents could withstand as much as 1000 volts DC without gassing.

A long step was taken toward improving the quality of green coatings when it was discovered that certain proprietary activators, added to the dispersion, produced a marked effect on stability of dispersions and density of deposited films. These activators, furthermore, made possible the preparation of dispersions without ball-milling. In addition to simplifying the process, this permitted dispersions to be made with materials of predetermined particle size and eliminated the introduction of impurities during ball-milling.

Evaluation studies indicated these activators to be the controlling factor in determining the character of dispersions and it has been found that they can be used to impart similar plating properties to widely differing materials.

Absolute particle size and particle-size distribution have been established as important factors in obtaining dense, continuous, and adherent green coatings by electrophoretic deposition. Production of good coatings was favored in most cases by dispersions containing particles of varying size; some few problems, such as formation of solid lubricant coatings, required dispersions of uniform particle size.

In general, dispersions of particle size averaging from 1 to 50 microns perform best in the electrophoretic coating process. Larger particles make unstable dispersions and cause non-uniform deposition. Smaller particles produce films which shrink excessively and crack in drying.

Cohesion of the green coating is affected more by the activator than by particle size or coating thickness. These activators have adhesive properties which hold the green coat together through the drying and densification processes. This property provides the means for overcoming the crumbling of green coats which had heretofore been a serious stumbling block to progress in application of this process.

Activators further act to enhance the natural binding forces of the particles and substrate surface. Evidence suggests that activators impart a greater charge to dispersed particles increasing their driving force and causing them to pack more densely at the electrode.

This increases the binding energy of the Van der Waals forces holding the particles together and to the substrate.

C. Preparation of Suspension

Excellent dispersions can be prepared from commercially available powdered solids by dry mixing the powders with a small percentage of activator and stirring directly into the solvent vehicle. Ball-milling with a portion of solvent will also produce satisfactory dispersions but control of particle size is difficult, especially in a small scale operation. The ultimate study of particle size and shape will require evaluation of all practical methods for grinding and dispersing solids.

The electric charge on the particle is acquired in the process of dispersion preparation and is considered to be a surface effect caused by an unbalance of forces at the solid-liquid interface. The magnitude and sign of this charge are characteristic of the materials dispersed and the liquid media. However, when an activator is introduced, the dispersed phase often takes on characteristics peculiar to the activator and many materials of diverse suspension properties can be made to act alike by addition of such a substance. This fact suggests the possibility of using activators to classify suspensions of widely differing behavior into groups with predictable plating properties.

D. Bonding

Since the resultant electrophoretic deposits are not in themselves structural elements, the particles must be bonded together and to the substrate. In the development work performed at Vitro Laboratories several techniques have been used to accomplish densification and bonding. The methods used are usually dependent on the desired final condition of the coating.

Densification prior to bonding is accomplished by isostatic pressing. The coated item is encapsulated in a thin walled rubber bag which is then tied off, evacuated, and immersed in a suitable liquid to which the desired pressure (usually about 50,000 psi) is applied. Densification after bonding is applicable to malleable porous structures such as those resulting from reduction of an oxide coating with concurrent sintering, and is achieved by rolling or hydrostatic pressing.

Bonding of the coating is attained by sintering in controlled atmospheres at certain temperatures and times dependent on the particular material used for coating.

EXPERIMENTAL

I. MAJOR EXPERIMENTAL INVESTIGATIONSA. Electrophoretic Coatings for the Protection of Graphite and Graphite Fuel Elements

1. Silicon Carbide Coatings

Studies were conducted on the application of the electrophoretic technique to form an impervious silicon carbide coating on graphite to provide oxidation resistance and fission product retention at elevated temperatures. Such conditions as carburizing atmosphere, carburizing temperature, carburizing time, densification pressure, and particle size were investigated to determine what effect, if any, they would have for obtaining an impervious SiC coating.

In general, silicon coatings were electrophoretically deposited on graphite from dispersions containing the metal in a 2.5 to 1 ratio of nitromethane to isopropanol using 2% zein (based on metal content) as the activator. Three typical formulations which yielded stable dispersions contained silicon particles in which the particle size distribution was either < 149 microns or < 44 microns or less than 10 microns.

However, in the preparation of silicon dispersions containing particles less than 5 microns, it was observed that upon the addition of zein (the activator), the particles tended to flocculate yielding an unstable dispersion. Coatings deposited from this type of dispersion would always develop cracks upon air drying. In order to remedy this situation, it was found that upon the addition of trace quantities of electrolyte ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) in conjunction with lower zein concentrations (0.5%) a thick (20 mils) crack-free coating could be obtained. The addition of the electrolyte helped to prevent the fine particles from flocculating and thus aided in stabilizing the dispersion.

Densified (5-50 tsi) and undensified silicon coatings were subsequently carburized at temperatures ranging from 1000° to 1450°C for time intervals of 5 minutes to 5½ hours. Carburizing atmospheres of CO, propane-argon, propane-hydrogen-HCl-argon, propane-chlorine-argon, and hydrogen-methane were employed.

a. Effect of Atmosphere

Silicon coatings fired in CO were partially carburized and contained on their surface a translucent white precipitate. Microscopic examination indicated that this white material was copious within the matrix of the coating. The material is believed to be SiO_2 , which formed as a result of the oxygen that was released during the $\text{Si} + \text{CO}$ reaction. The Diamond Pyramid Hardness values of 500 to 645 Kg/mm^2 (50 gm load) which were obtained on these coatings are much lower than the standard value of 2480 Kg/mm^2 for commercial silicon carbide.

The results of a static air oxidation test performed at 1000°C on a coated sample and two uncoated graphite panels show that although the coating gives considerable protection, it does not appear to be as good as would be expected of a dense silicon carbide coating. This consideration, in addition to the low micro hardness numbers obtained, indicate incomplete carburization.

Replacing CO with propane-argon as the carburizing medium eliminated the formation of the white deposits observed in the CO runs. These carburized coatings were adherent, crack free, and porous, varying in color from metallic grey to black. Microscopic examination of the coatings indicated that in several cases a fine layer of carbon, globular in shape, had deposited on the surface of the coating, giving a metallic appearance to the sample. DPH_{50g} values of 1064 Kg/mm^2 were obtained on individual grains of SiC from several of these coatings.

By changing the carburizing atmosphere to a propane-hydrogen-HCl-argon mixture and propane-chlorine-argon mixture, a detrimental effect was noticed in some cases on the adherence of the SiC coating to the graphite. A greenish yellow film was observed at the interface of the coating and the graphite panel.

By using a hydrogen-methane atmosphere, however, a SiC coating was obtained which was more completely sintered and more adherent to the graphite substrate than previously prepared coatings. In all cases, however, it appeared that the carburization atmosphere had no appreciable effect on the density of the SiC coating. All coatings were porous.

b. Effect of Temperature

Carburization studies at different temperatures showed that sintering and the degree of carburization varied with temperature but the porosity remained constant. Carburization temperatures below 1400°C yielded poorly sintered porous coatings having DPH_{25g} values of 500 Kg/mm², while temperatures of 1400°C yielded well sintered porous carbide coatings having DPH_{25g} values of 2145 Kg/mm². The hardness values were consistent across the thickness of the coating indicating uniform carbide formation.

Microscopic examination of coatings carburized at 1430°C showed that the silicon had liquified and flowed into the graphite substrate. It was distributed unequally to an average depth of 5 mils. Average DPH_{25g} values of 2145 Kg/mm² were obtained at the silicon-graphite interfaces indicating that extensive carbide formation had occurred at these points.

c. Effect of Carburization Time

No carburization was evident in runs of less than 30 minutes. In the runs of longer duration, the penetration of carburization into the matrix of the coating appeared to increase. Also, no appreciable effect was observed in reducing the porosity of the SiC coating by increasing the carburization time.

d. Effect of Densification

Densifying the green coatings prior to carburization with pressures up to 50 tsi had no effect in producing an impervious SiC coating. However, the pressed coatings appeared to be denser with a higher degree of sintering than the unpressed coatings.

e. Effect of Particle Size

The particle size of the silicon powder is an important factor in producing an impervious SiC coating. Results, to date, strongly indicate a degree of imperviousness can be achieved by electrophoretically depositing on graphite, silicon metal with a particle size distribution of 0-5 microns and subsequently carburizing at 1425°C for one hour in a hydrogen-methane atmosphere. Larger particles (-100 mesh and -325 mesh) failed to yield the above results. The degree of imperviousness was observed at the surface of the coating to a depth of 1 mil when examined microscopically. The interior portion of the coating (7 mils), appeared porous.

2. Tungsten Carbide Coatings

In the preparation of a tungsten carbide coating on graphite to provide erosion resistance, tungsten metal was electrophoretically deposited on graphite panels from a dispersion of the above materials in a 2.5 to 1 ratio of nitromethane to isopropanol containing 2% zein (based on solids) as the activator. Pressed (20 tsi) and unpressed coatings were heated to temperatures of 1200°-1400°C in either hydrogen or argon atmospheres and sintered in a mixed atmosphere of hydrogen-HCl for $\frac{1}{2}$ hour. The sintered coatings were subsequently carburized in a CO atmosphere at temperatures of 1000°-1400°C for one hour.

All coatings, thus prepared were unsatisfactory due to the poor adherence of the coating to the substrate. Besides having poor adherence, coatings heated in hydrogen to sintering temperatures contained fine hairline cracks throughout the coating. However, heating in the argon atmosphere resulted in a well-sintered, crack-free coating. Varying the densification pressure from 0 to 20 tsi and carburizing in an argon-chlorine-CO atmosphere at different temperatures and time intervals failed to improve the adherence of the final coating.

In another approach, densified (5-20 tsi) and undensified coatings were heated to temperatures of 1000°, 1200° and 1400°C in argon and immediately carburized using an argon-chlorine-propane atmosphere for periods of 1-2 hours. Thus, changing the carburizing medium from CO to propane resulted in well-sintered, adherent and crack free coatings at temperatures of 1000°, 1200° and 1400°C and time intervals of 1-2 hours. The carburizing temperature and time intervals did not appreciably affect the quality of the carbide coating. DPH_{10g} values ranging from 1355 Kg/mm² to 1614 Kg/mm² were obtained on these coatings.

3. Tantalum Carbide Coatings

Tantalum carbide coatings on graphite for erosion resistance were prepared by first applying a tantalum coating and then carburizing to produce the carbide. The tantalum metal coatings were electrophoretically applied to the graphite panels from a zein activated dispersion of the metal in a nitromethane-isopropanol system. The undensified coatings were carburized in a propane-hydrogen-HCl atmosphere at 1000°, 1200° and 1400°C for $\frac{1}{2}$, 1 and $1\frac{1}{2}$ hours. The specimens were subsequently cooled to room temperature in argon.

Upon microscopic examination, the coatings appeared well-sintered well-bonded and crack-free. Average DPH_{10g} values, of 591 Kg/mm^2 and 469 Kg/mm^2 were obtained on specimens carburized at 1000° and 1200°C , respectively, indicating incomplete carburization. However, specimens carburized at 1400°C at the above time intervals resulted in average DPH_{10g} values of 1930 Kg/mm^2 , whereas DPH_{10g} values of 276 Kg/mm^2 were obtained on pure tantalum powder. The time of carburization did not appear to affect carbide formation at the given temperatures.

4. Niobium Carbide Coatings

Niobium Carbide Coatings on graphite for erosion resistance were also prepared. Niobium metal was deposited electrophoretically on graphite panels from a zein activated dispersion of the metal in a nitromethane-isopropanol system. Densified (20 tsi) and undensified coatings were subsequently carburized in a propane-argon-chlorine atmosphere at 1000° , 1200° and 1400°C for 1 hour and then cooled to room temperature in argon.

Under visual and microscopic examination the coatings appeared well-sintered, well-bonded, and crack-free. DPH_{10g} values of 235, 551, and 1715 Kg/mm^2 were obtained on specimens carburized at the above respective temperatures.

A control test on pure niobium metal yielded a DPH_{10g} value of 153 Kg/mm^2 , while commercial niobium carbide gave a DPH_{10g} value of 1930 Kg/mm^2 . Densification did not affect the degree of carburization at a given temperature; however, the porosity of the coating was reduced as would be expected.

One experiment was made at a carburization temperature of 1400°C in a propane-argon-chlorine atmosphere for 3 hours. Microscopic examination of a cross-section of the sintered coating showed continuity at the surface which would indicate imperviousness. However, the inner portion of the coating appeared porous.

5. Ni-Cr-Si Alloy Coatings

A nickel-chromium-silicon (75-15-10 weight percent) dispersion was used to electrophoretically coat graphite to provide erosion and oxidation protection. Pressed and unpressed specimens were sintered in argon at 1100° , 1200° and 1300°C .

Well-bonded coatings with high metallic luster were obtained at 1200°C and 1300°C. At 1300°C there was an apparent flow of molten metal to the lower area of the graphite samples. It was noted that this alloy has a strong wetting action upon graphite and may be useful for joining graphite components to ferrous and non-ferrous materials. Microscopic examination of these sintered coatings indicated that both pressed and unpressed coatings had low porosity and were strongly bonded to the graphite surface.

6. Fecral Coatings

Fecral, an alloy containing iron, chromium, and aluminum (70.3-23.7-6 weight percent), has been reported in literature to have high-temperature oxidation resistance superior to 80-20 Nichrome. A zein activated dispersion containing iron, chromium, and nickel powders in the ratio specified above was used to deposit coatings upon graphite. The coatings were pressed at 20 tsi and samples were fired in either of two atmospheres, purified hydrogen or argon, at 1100°C-1400°C.

Coatings fired below 1400°C were not sintered. Coatings fired at 1400°C in argon for 2 hours were well-sintered and bonded. However, there was a tendency toward the formation of metallic beads upon the coated surface indicating poor wetting of the graphite surface by the alloy.

7. Alumina Coatings

Three different alumina formulations were electrophoretically deposited on graphite. One dispersion contained 96% levigated alumina, 2.0% cupric oxide powder, and 2.0% titanium dioxide powder. The second dispersion contained 96% alumina, 2.0% titanium dioxide, and 2.0% manganese oxide. The third dispersion contained 98% alumina, 0.5% bentonite, and 1.5% Kentucky No. 4 ball clay. Excellent "green" coatings were obtained. After isostatic pressing, the coated specimens were fired in purified argon at 1400°C.

The final coatings were not well-sintered. However, results indicate that this technique plus a slightly higher sintering temperature could produce dense well-sintered alumina coatings on graphite. Such coatings should be useable for the protection of graphite against oxidation at elevated temperatures.

8. Cr-Si-Al-Fe Alloy

A Cr-Si-Al-Fe alloy was investigated as a possible oxidation resistant coating. Graphite specimens were coated electrophoretically from a dispersion containing chromium powder, silicon, aluminum, and iron powder (56.8-41.5-0.4-1.3 weight percent). The coated specimens were pressed isostatically, and fired in purified argon at 1350°C. The coatings were poorly sintered, and poorly bonded to the graphite substrate.

9. The electrophoretic technique was investigated as a possible method for applying various coatings such as nickel, molybdenum, silicon, and molybdenum disilicide to graphite to provide resistance against corrosion by liquid sodium at elevated temperatures.

a. Nickel Coatings

Prior to the nickel deposition, it was necessary to deposit electrophoretically a thin intermediate layer of iron fired at 1070°C for $\frac{1}{2}$ hour to act as a bonding layer for the nickel. Iron was chosen as the bonding layer because graphite and iron are known to react and to form solid solutions at elevated temperatures.

The nickel coating was deposited (either the metal or oxide) on a series of iron coated graphite panels from a dispersion containing the metal or oxide in a nitromethane-isopropanol (90-10 by volume) system containing 2% zein (based on solids) as the activator. The as-deposited coating was isostatically densified at 20 tsi and fired at 1070°C for $\frac{1}{2}$ hour in purified hydrogen. Samples of undensified nickel coatings were also prepared.

All coatings were well sintered and appeared to be adherent. In every case, however, cracks developed in the nickel coating during the sintering operation.

b. Molybdenum Coatings

Molybdenum coatings (15-20 mils thick) were electrophoretically deposited on graphite panels from a dispersion of the metal in a nitromethane-isopropanol solution (volume ratio of 2.5 to 1) containing 2% zein (based on weight of solids) as the activator. The green coatings were isostatically pressed at 20 tsi and fired in a mixed hydrogen-HCl (2 mole percent HCl) atmosphere at 1200°C for $\frac{1}{2}$ hour. The resultant coatings were non-adherent and only partially sintered.

c. Silicon Coatings

Silicon metal was electrophoretically deposited on graphite from a nitromethane-isopropanol dispersion of the metal using zein as the activator. The coatings were isostatically pressed at 20 tsi and fired in either argon, or hydrogen or mixed hydrogen-HCl atmospheres at temperatures up to 1400°C. The fired coatings were crack-free but were non-metallic in character and showed no evidence of sintering.

Another approach was attempted in which silicon and carbon were codeposited from zein activated dispersions in stoichiometric proportions to form silicon carbide. This reaction occurs at temperatures from 1200°C to 1400°C. Pressed (25 tsi) and unpressed coatings were fired at 1200°C in hydrogen or at 1400°C in argon for 1 hour. In general, the coatings were soft and powdery and showed no sintering and little adherence to the graphite.

d. Molybdenum Disilicide Coatings

Attempts were also made to prepare cermet coatings containing 94% MoSi₂ and 6% nickel (by weight). The coatings were deposited from zein activated dispersions of molybdenum metal, silicon, and metallic nickel in the proportions required to yield the desired cermet composition. Both pressed and unpressed electrophoretically deposited coatings were fired at 1200°C in hydrogen or at 1400°C in argon. Here again, the final coatings were unsintered and showed no appreciable adherence to the graphite.

A series of experiments was also conducted in which various combinations of MoSi₂ and nickel were codeposited on graphite and subjected to a final firing operation at 1200°C in hydrogen or at 1400°C in argon. Coatings containing 6%, 50% and 80% nickel (by weight) were electrophoretically deposited from zein activated dispersions.

The coatings containing 6% and 50% nickel adhered to the graphite and were well sintered. However, as expected, the coatings containing 50% nickel were more adherent and better sintered. Coatings containing 80% nickel showed evidence of melting on the surface of the graphite. All coatings appeared to develop hair-line cracks on cooling. In general, the samples pressed at 20-25 tsi had a higher metallic luster than the unpressed specimens.

B. Solid Lubricant Coatings

Studies were conducted on the development of solid-film lubricants for use in environments of high nuclear flux. In general, the coatings studied consisted of potentially suitable lubricants incorporated in a metal matrix, deposited electrophoretically on a substrate of 304 stainless steel, and the matrix diffusion-bonded to the metal substrate. The quality of the finished coat was studied by physical inspection and microscopic examination.

1. Boron Nitride-Copper Coatings

Several dispersions (seven in number) were evaluated in an attempt to achieve a coating which would possess both high mechanical strength and excellent lubricating properties. The dispersions evaluated are shown in Table I, designated as dispersions A, B, C, D, E, F, and G.

TABLE I
DISPERSION COMPOSITIONS

DISPERSION	A	B	C	D	E	F	G
BN (Norton Co.)	4.0 g	10.8 g	1.8 g	1.3 g	0.9 g	1.9 g	1.9 g
Cu ₂ O (Baker Reagent)	-	49.3 g	8.2 g	8.7 g	9.1 g	4.3 g	4.3 g
Cu (Baker)	16.0 g	-	-	-	-	3.8 g	3.8 g
Zein	0.6 g	1.8 g	0.3 g	0.3 g	0.3 g	0.3 g	0.3 g
Nitromethane	248 ml	135 ml	274 ml	274 ml	274 ml	274 ml	274 ml
Isopropanol	152 ml	135 ml	96 ml	96 ml	96 ml	96 ml	96 ml

All coatings were electrophoretically deposited on 304 stainless steel rods. Coatings obtained were 5-20 mils. thick. The coating mixtures which contained Cu₂O as a matrix material were first reduced in purified hydrogen at 400°C. All coatings with the exception of coatings from dispersion G were densified at 25 tsi and sintered in pure hydrogen at 1000°C for 2 hours. Coatings from dispersion G were prepared as follows:

1. Rods which had been diffusion coated with copper were lightly sand blasted and cleaned in acetone.
2. A coating seven mils thick was electrophoretically deposited from dispersion G.
3. Densified isostatically at 25 tsi.

4. Sintered at 800°C for 1 hour in a hydrogen atmosphere.
5. Vacuum impregnated with BN, followed by electrophoretically coating with BN.
6. Densified isostatically at 50 tsi.
7. Sintered at 1000°C for 2 hours in a hydrogen atmosphere.

Coatings containing copper as the initial ingredient (dispersion A) did not form an acceptable bond with the stainless steel even though the coating mixture itself had developed high strength. It formed only a shell which could be separated easily from the substrate.

Coatings prepared from dispersion B, although well-bonded to the substrate, formed a soft mixture which could be easily scraped off. This softness is typical of boron nitride (Mohs hardness = 2). Obviously the proportion of BN was on the high side and possibly a decrease would improve strength.

Decreasing the BN content as in dispersions C, D, and E, resulted in an increase in coating strength. However, lubricating properties of the decreased BN in the coating were not very satisfactory.

Coatings prepared from dispersion F, containing coarse copper particles, definitely established the value of matrix particle size control as a factor in the promotion of good strength. The appearance of the coating insofar as BN content is concerned was not quite satisfactory.

Coatings produced from dispersion G exhibited rough surfaces. The penetration of the BN into the pore structure of the copper was poor, probably because the copper was too dense before impregnation. This method shows promise if the copper coating can be made porous and malleable before application of the BN lubricant so that a large volume percent of BN can be introduced and trapped in the porous structure.

2. Boron Nitride-Molybdenum Coatings

In an effort to explore this system quickly for preliminary evaluation, a limited number of BN-Mo coatings containing 30-50% BN by volume were electrophoretically deposited from a dispersion of the BN-Mo in a 2.5 to 1 ratio of nitromethane to isopropanol containing 0.40 g zein as the activator. The coatings were isostatically pressed at 25 tsi and sintered in a mixed atmosphere of hydrogen - 2 mole percent HCl for 20 minutes at temperatures of 1175°C to 1250°C.

The resultant coatings showed a definite reaction with the steel substrate indicating the possible formation of a eutectic composition. Little visual evidence of lubrication by the BN could be found although portions of the surface were smooth and hard enough to form a suitable bearing surface. Although the sintering or alloying reaction has not been studied extensively, it seems unlikely that a molybdenum-boron eutectic compound was formed since the lowest known eutectic of these materials occurs at 2120°C. However, eutectic formation is more likely in a Mo-Cr-Ni or a Mo-Cr-Fe system (46).

3. Lead Oxide-Copper Coatings

Several dispersions were prepared using 50-50% and 75-25% by volume of (a) lead oxide and metallic copper (b) lead oxide and copper precipitated from an acid CuSO_4 solution, and (c) lead oxide and copper which had been reduced from Cu_2O at 300°C. Stainless steel (304) rods were coated with the above PbO -Cu mixtures by electrophoretic deposition. The as-deposited coatings were sintered at 800°C in purified argon for 2 hours.

All coatings formed metallic lead globules in the copper matrix. In some instances, yellow crystals of PbO and red crystals of Pb_3O_4 were observed. It is interesting to note that the steel substrate in every case had been oxidized. The source of oxygen probably being the PbO .

4. Iron Oxide-Copper Coatings

Red iron oxide (Fe_2O_3) does not plate as readily as some of the other oxides or metals. However, several dispersions were made and tested for plating characteristics; of these, the three shown below in Table II were found to be exceptionally smooth plating.

TABLE II

Fe_2O_3 (Vitro Mfg.)-325 mesh	7.4 gm	12.8 gm	6.1 gm
Cu (Baker Reagent)	12.6	7.3	-
Cu_2O (Baker Reagent)	-	-	3.9
Zein	0.6	0.6	0.3
Nitromethane	246	246	234
Isopropanol	214	214	196

After the standardized electrophoretic plating, the coatings were densified at 25 tsi and sintered in argon at 1000°C for 2 hours. In the case of coatings prepared from dispersion C a reduction step was performed in hydrogen at 300°C for 1 hour prior to sintering.

The coatings were well-sintered. They were not, however, diffusion bonded to the steel substrate but merely "clad on". The Fe_2O_3 was reduced to the lower oxide of iron and/or to metallic iron. A reaction similar to that found in system No. 3 had occurred; i.e., reduction of the oxide coating and an oxidation of the steel substrate.

5. Molybdenum Disulfide-Copper Coatings

Dispersions containing 50 and 75% (by volume) of MoS_2 were prepared as shown below in Table III.

TABLE III

MoS_2 (The Alpha Corp.) Type 2 - 325 mesh	7.0 gms	6.2 gms	5.9 gms
Cu (Baker Reagent)	13.0	-	-
Cu (precipitated from acid CuSO_4 solution)	-	3.8	-
Cu_2O (Baker Reagent)	-	-	4.1
Zein	0.6	0.3	0.3
Nitromethane	268 ml	286 ml	274 ml
Isopropanol	132 ml	114 ml	96 ml

Stainless steel (304) rods were electrophoretically coated from the above dispersions, densified at 25 tsi and sintered in argon for 1-2 hours at 1000°C. Coatings containing Cu_2O were first reduced in hydrogen at 300°C for one hour prior to sintering.

This system has shown the most promise for low friction, strong and hard diffusion bonded coatings. Coatings containing larger particles of copper (dispersion A) exhibited fair bonding with limited diffusion. A uniform mixture of MoS_2 and copper, slippery to the touch, was also developed.

Coatings containing 75% by volume of MoS_2 and finely divided copper (dispersions B and C) were dense and hard. Bonding to the steel substrate, and finished surface characteristics were both excellent. The coatings also exhibited low frictional characteristics. A higher proportion of MoS_2 can probably be introduced to further reduce friction coefficient without too great a sacrifice of strength and bonding properties.

6. Boron Nitride-Copper-Iron Coatings

It has been reported (47) that copper-iron alloys are used for heavy duty bearing applications. With this fact in mind, the following composition was made:

BN	1.2 gms
Cu ₂ O	5.1 gms
Fe ₂ O ₃	3.8 gms
Zein	0.3 gms
Nitromethane	400 ml

Copper coated stainless steel (304) rods were coated electrophoretically from the above dispersion, reduced in hydrogen at 400°C for one hour, densified at 25 tsi and finally sintered in hydrogen at 1000°C for 3 hours.

Microscopic examination of the final coatings indicated that a preferential plating had taken place. The coating could be removed by peeling. Evidently the BN and iron had plated first and the copper last. After removal of the loose and semi-loose cladding material, the remaining coating exhibited fair bonding and good slip characteristics. The thickness, however, was only $\frac{1}{2}$ mil.

7. Boron Nitride-Copper-Nickel Coatings

Copper-nickel alloys are reputedly of good strength (48) and experimental compositions in this field were investigated. Two variations were made, Table IV, characterized by high and low nickel increments:

TABLE IV

	A	B
BN	0.9 g	1.8 g
Cu ₂ O	4.0 g	7.3 g
NiO	5.0 g	0.9 g
Zein	0.3 g	0.3 g
Nitromethane	400 ml	400 ml

The electrophoretically applied coatings on 304 stainless steel rods were reduced in hydrogen at 350°C for one hour. Two different densifications and sinterings were made:

	<u>Ex -A</u>	<u>Ex -B</u>
Isostatic Densification:	25 tsi	-
	49 tsi	49 tsi
Sintering:	1000°C, 3 hours	-
(hydrogen atmosphere)	1050°C, 2 hours	1050°C, 2 hours

The Ex-B coating was soft and non-adherent and the coefficient of friction could not be estimated. The Ex-A coating looked and felt good. It was characterized by a gray surface, indicative of the high nickel content. Diffusion bonding to the substrate was fair to good. The feel of the coating indicated a low friction surface. The general appearance and properties were similar for both densifications and sintering trials but densification at 49 tsi and sintering at 1050°C yielded somewhat better results.

C. Aluminum Oxide Coatings on Ceramic Fuel Elements

At the request of ANP-GE with AEC approval a program was undertaken to investigate the feasibility of applying aluminum oxide coatings to ceramic fuel elements by the electrophoretic process. During this study the following areas relative to the coating process were investigated, namely, (1) preparation of conductive specimens, (2) preparation of dispersion, (3) special electrode jig, (4) bagging operation, and (5) pre-sintering of coating.

1. Preparation of Conductive Specimens

In the electrophoretic process, the article to be coated acts as one of the electrodes and therefore must be capable of carrying an electric charge. Since the fuel elements supplied by ANP-GE were found to be non-conductive, an investigation was conducted to select a material and develop a procedure for imparting the desired conductivity to the elements. The material chosen would have to be such that it could be readily removed during some step in the electrophoretic process without causing damage to the final Al_2O_3 coating. The material selected was carbon in such forms as carbon black and graphite, since this material could be easily removed by oxidation at elevated temperatures.

For applying the carbon undercoat to the fuel element, two principal methods were investigated, namely: (a) subjecting the non-conductive fuel elements to a carbonaceous atmosphere (cracked methane) at elevated temperature, and (b) dipping the fuel element into various colloidal dispersions of graphite and carbon black. For this report the former method will be referred to as the cracked-methane method while the latter method will be designated as the carbon dispersion method.

a. Cracked-Methane Method

The non-conductive nuclear fuel elements were subjected to a carbonaceous atmosphere (cracked methane) at elevated temperatures. The elements were carburized at temperatures ranging from 800° - 1200°C for time intervals of 1-2.5 hours.

All the carbon coatings produced under these varying conditions were very conductive and adherent. However, they were repeatedly more conductive on the inside surface of the fuel element which always resulted in heavier electrophoretically deposited coatings on the said surface.

In one experiment, the outside surface of a fuel element was slightly roughened, in the belief that a heavier carbon deposit would result on the roughened surface and thereby render the overall conductivity uniform. This however, failed to materialize. Results were similar to those obtained in previous experiments.

b. Carbon Dispersion Method

A number of colloidal graphite dispersions¹ (Aqua Dag, Oil Dag, and Dag 154) and colloidal furnace carbon black dispersions² were investigated as possible materials for imparting thin carbon coatings of uniform conductivity to the nuclear fuel elements. In general, a carbon coating was applied by dipping half of the fuel element into a given dispersion and slowly withdrawing the element from the dispersion. This allowed for most of the excess liquid to drain off before the element was completely withdrawn. The last drop which accumulates is then shaken off to

¹Acheson Colloids Co., Port Huron, Michigan

²Carbon Dispersions, Inc., Newark, New Jersey

prevent an edge build-up. After air drying, the uncoated portion of the element is dipped in the same manner and allowed to air dry. The technique assures a uniform coating and eliminates edge build-up of the coating.

The results are tabulated below:

<u>Dispersion</u>	<u>Result</u>
Oil Dag	Difficult to apply, and exhibited non-uniform conductivity.
Dag #154	Coating washed off when immersed in Al_2O_3 dispersion using isopropanol as the dispersing medium.
Furnace Carbon Black	Poor conductivity and poor adherence. Comes off on handling.
Aqua Dag	Firm, well-bonded, thin film exhibiting good and uniform conductivity. On ignition leaves small residue.

To date, the best method found for making the fuel elements uniformly conductive is to coat them by dipping in a water-acetone dispersion of aqua dag. Acetone was added to the Aqua Dag dispersion to speed up drying and minimize end build-up due to drainage. The resin in the aqua dag is set by baking for 1 hour at 250-300°C. By this procedure hard, well-bonded, thin uniformly conductive coatings (about 0.001 in. thick) can be easily and rapidly applied. However, this coating, on ignition, leaves a small residue.

2. Preparation of Dispersion and Coating Apparatus Modification

Three basic dispersion formulations were studied in efforts to electrophoretically deposit a uniform, crack-free coating on nuclear fuel elements. The dispersions investigated had the following compositions:

<u>Dispersion #1</u>	<u>Dispersion #2</u>	<u>Dispersion #3</u>
20 gm Al_2O_3 (Alcoa A-2)	40 gms Al_2O_3 (Alcoa A-2)	40 gms Al_2O_3 (Alcoa A-3)
250 ml nitromethane	400 ml isopropanol	230 ml isopropanol
100 ml isopropanol	1% Zein (based on solids)	106 ml nitromethane
1.5% Zein (based on solids)	Trace Al $(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	3% Zein (based on solids)
Trace Al $(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$		Trace Al $(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

In initial experiments, the inside surface of several tubular fuel elements were coated electrophoretically with Al_2O_3 from dispersion #1. The dispersion was constantly circulated through a 4" I. D. plating cell in a clockwise direction. The as-deposited coatings thus obtained appeared uniform. However, in attempts to coat the entire fuel element (inside and outside surface) excessive edge build-up of the coating had occurred.

In efforts to reduce or eliminate this edge build-up of the coating, such conditions as plating voltage, plating time, solids concentration and solvent ratio were varied over a wide range. These adjustments had no effect in eliminating or reducing the edge build-up.

In other experiments, such modifications as: (1) reversing the flow of the dispersion through the plating cell, and (2) directing the flow of the dispersion toward the top and bottom of the specimen also failed to minimize the edge build-up. The results from these experiments did indicate however that the dispersion was not flowing through the fuel element at the same steady flow rate as through the rest of the cell. This was mainly due to the small bore (3/16") of the fuel element.

In order to increase the flow of the dispersion through the fuel element, a narrow electrophoretic cell (2" I. D.) was fabricated. The design was such that the narrow cell tapered into a funnel shape at the bottom. This narrow cell design was instrumental in reducing edge build-up of the coating by allowing for a constant flow rate of the dispersion through the fuel element as through the rest of the plating cell. However, it did not reduce it to the extent where it would fall within the imposed coating tolerance limits of 4 mils $\pm$ 1 mil.

In coating the fuel elements from dispersion #2 and using the modified plating cell (2" I. D.) coatings were obtained exhibiting a very slight edge build-up. This improved coating uniformity was chiefly due to the attainment of a more homogeneous dispersion resulting from the

increase in viscosity of the dispersing medium and to the geometry of the modified plating cell. It should be noted, however, that some difficulty was encountered in keeping this dispersion active. After several depositions, the dispersion failed to plate properly. Adding more zein and/or more electrolyte failed in each case to reactivate the dispersion. Also after several depositions, some of the coatings developed microscopic cracks upon air drying.

In depositing coatings from dispersion #3 using the 2" I.D. cell, all coatings deposited uniformly and remained crack-free after drying. In using this 60-40 weight % ratio of isopropanol to nitromethane, a higher zein concentration could be tolerated without fear of flocculating the solids. This resulted in as-deposited coatings possessing excellent green strength which greatly reduced coating losses during the bagging and pressing operation.

3. Special Electrode Jig

Although the results obtained above yielded coatings approaching the desired thickness tolerance limits, it was found necessary to modify the electrode assembly.

The electrode assembly consisted of an electrode jig as shown in Fig. 4. The design of the electrode jig was such that it gave rigidity to the inner electrode (anode), and it also served as a means of supporting the fuel element (cathode) in the dispersion. Moreover, it allowed for a constant flow of dispersion through the hollow fuel element which is essential for achieving coating uniformity.

4. Bagging Technique

To isostatically densify the as-deposited Al_2O_3 coated fuel elements it is necessary to protect the coated specimen from coming in contact with the densifying medium, in this case, glycerin. Heretofore, a coated specimen having a simple geometric shape was wrapped with a thin (1 mil) teflon film and inserted into a thin-walled rubber tube which was then evacuated and sealed. This standard procedure however is not entirely applicable for a geometric shape such as the tubular type fuel element for the simple reason that the rubber envelope would be punctured at the hollow portion of the element when pressure is applied, exposing the coating to the glycerin.

FIGURE 4

ELECTRODE JIG FOR ELECTROPHORETIC DEPOSITION OF Al_2O_3
COATING ON INNER SURFACE OF TUBULAR FUEL ELEMENT

During this program several methods of bagging were investigated in order to solve this problem. One method investigated consisted of placing the coated specimen in a rubber tube containing enough mercury to cover the specimen. The rubber tube was then sealed below the mercury level to insure the expulsion of entrapped air. The bagged specimen was subsequently densified at 50 tsi. Visual examination of the coating revealed a satisfactory dense coating. However, when the coating was viewed microscopically, the mercury was observed to have penetrated the coating. In another method, a 1/4" O.D. glycerine filled rubber tube was inserted into the coated fuel element. This unit was then placed in a rubber bag which was then evacuated and sealed. The enveloped specimen was subsequently densified at 50 tsi. A well densified coating resulted utilizing this technique.

This technique of bagging, however, does have a number of disadvantages attached to it, namely: (1) it is a cumbersome method, (2) extreme care must be exercised during insertion and removal of the inner glycerine-filled capsule so as not to damage the green coating, and (3) occasionally, some of the coatings were damaged as a result of the outer rubber tube rupturing during densification. This permitted the glycerine to penetrate and damage the coating. Rupturing of the outer rubber tube always resulted from a pinching action which occurred at a point between the inner rubber capsule and the sharp inside edge of the fuel element.

A more satisfactory technique for bagging the coated fuel elements was achieved by replacing the inner glycerine filled capsule with a 1/4" rubber tube open at both ends. This permitted the densifying medium (glycerine) to freely enter the inner rubber tube during densification. This bagging technique is shown schematically in Fig. 5.

Also, it should be noted, that some coatings were damaged when attempts were made to remove the teflon film surrounding the densified coating. Parts of the coating would strongly adhere to the teflon film. This was remedied by wrapping an ashless tissue around the coating in place of the teflon film. After densification of the coating, the ashless tissue is not manually removed as was the case with the teflon but instead is burned off during the oxidation of the graphite undercoat.

FIGURE 5 BAGGING TECHNIQUE FOR ISOSTATIC PRESSING

5. Pre-sintering of Al_2O_3 Coatings

In preliminary experiments, as-deposited Al_2O_3 coated fuel elements were first fired at 1000°C in air for 1 hour (to eliminate the graphite undercoat) and then pre-sintered at 1400°C in hydrogen for 1 hour. Coatings so obtained were non-adherent to the substrate and exhibited severe longitudinal cracking along the entire length of the fuel element.

In view of this early result, a series of experiments was conducted to determine the effect of densification pressure, pre-sintering atmosphere and particle size distribution on the application of pre-sintered, crack-free coatings on the fuel elements.

a. Effect of Densification Pressure

A series of as-deposited Al_2O_3 coated fuel elements were subjected to densification pressures ranging from 0 to 50 tsi: The densified and undensified coatings were all fired in air at 1400°C for 1 hour. Results from these experiments were inconsistent and not reproducible. Cracked and crack-free presintered coatings were obtained at each densification pressure investigated. Moreover, most of the cracked coatings exhibited only peripheral cracks at the inside or outside edge of the fuel element.

In view of this, the sharp edges of several fuel elements were rounded off, then the fuel elements were coated and fired at 1400°C in air for one hour. No improvement was observed in the resultant coatings. Two out of the three coatings fired developed cracks at the modified edges of the fuel elements. This procedure did, however, eliminate slight edge imperfections of the conductive undercoat and the as-deposited Al_2O_3 coating which heretofore could not be remedied.

b. Effect of Firing Atmosphere

Electrophoretically deposited Al_2O_3 coatings on nuclear fuel elements were first fired in air at 1000°C to eliminate the graphite undercoat and then heated to 1400°C in such atmospheres as hydrogen, argon and carbon monoxide for one hour. All the coatings fired under these conditions exhibited the same peripheral cracks at the inside or outside edge of the fuel element as experienced in previous experiments.

The choice of CO as one of the firing atmospheres was made primarily for its reducing value since any U_3O_8 formed during the oxidation step of the firing cycle could be converted to UO_2 according to the equation:

However, specimens fired in this atmosphere were contaminated with carbon which was produced from the decomposition of CO.

$$> 800^\circ C$$

c. Effect of Particle Size Distribution

A series of nuclear fuel elements were electrophoretically coated with Al_2O_3 from a dispersion containing Alcoa A-2 levigated Al_2O_3 and increments of coarser 16 hr. ballmilled Norton Al_2O_3 (-325 mesh). The solids were dispersed in a 60-40 by weight ratio of isopropanol to nitromethane and activated by zein (3% based on solids) and a trace quantity of $Al(NO_3)_3$. All the coatings deposited uniformly and remained crack-free upon air drying.

The densified (~ 50 tsi) and undensified coated fuel elements were subsequently presintered in such atmospheres as air, argon, and hydrogen at temperatures ranging from $1400^\circ C$ to $1485^\circ C$ for approximately 1 hour. Results indicate that the particle size distribution of the Al_2O_3 had no affect in preventing the coatings from cracking. Most of the coatings contained the familiar peripheral cracks observed in previous experiments. Coatings pressed at 50 tsi and fired in argon at $1485^\circ C$ resulted in crack-free translucent coatings containing small metallic beads protruding from the coating. Analysis of this material was not made but it is believed to be uranium.

II. SPECIAL EVALUATION STUDIES

A. Chromium Coatings On UO₂ Plates

Interest has been expressed by the Westinghouse Atomic Power Division in coating uranium oxide plates (approx. 5/8" x 5/8" x 1/32") with a refractory metal, such as chromium, over which a thin layer of graphite would be deposited. This composite coating would serve as a diffusion barrier between the uranium oxide plate and the can encasing the plate. In view of this interest, a program was undertaken by Vitro with AEC approval to coat 12 uranium oxide plates, supplied by Westinghouse, with a chromium coating 0.5 mil and 1 mil in thickness.

Preliminary coating studies were conducted using inconel panels as the base material. The chromium coatings were deposited from a dispersion containing 20 grams of finely divided chromium metal powder (-325 mesh), 250 ml nitromethane, 100 ml isopropanol, and 2% zein (based on solids) as the activator. No attempt was made at this time to control the thickness of the coatings. Instead, emphasis was placed on determining the required plating and sintering conditions.

The as-deposited coatings were densified at 50 tsi and sintered in a hydrogen atmosphere for 2 hours at 1200°C. The coatings appeared well sintered and impervious upon microscopic examination.

Using conditions established by preliminary results, two uranium oxide plates were coated with chromium metal powder from the above dispersion, densified at 50 tsi and fired in hydrogen at 1200°C for 2 hours. The two coatings were 0.5 mil and 1 mil thick respectively, and appeared well sintered and adherent. However, upon microscopic examination, the coatings did not appear to completely cover the uranium oxide plates. Shrinkage during sintering, and the high percentage of coarse chromium particles with limited contact area could account for the incomplete coverages of the uranium oxide plates. These chromium coated uranium oxide plates, nevertheless, were delivered to Westinghouse for compatibility studies.

In the next series of experiments, to achieve maximum contact area, chromium oxide was deposited on inconel panels from a dispersion containing 20 grams chromium oxide, 150 ml nitromethane, 150 ml isopropanol and 2% zein (based on solids) as the activator. This dispersion plated satisfactorily, but the green coatings developed cracks upon drying. The

addition of binders to the dispersion did not appreciably aid in obtaining a crack-free green coating. Also, spraying the green coating with Krylon showed no significant improvement. However, reducing the solids concentration to 2% did result in producing a thick crack-free green coating.

Using this modified chromium oxide dispersion, two uranium oxide plates were coated, densified at 50 tsi, reduced with hydrogen at 900°C for one hour and finally sintered at 1200°C for one hour. The two resultant coatings were 0.3 mils and 0.5 mils thick, and appeared well sintered, adherent, and impervious upon microscopic examination. Complete coverage of the base material was also achieved by using the oxide in place of the metal. The two chromium coated uranium oxide plates also were delivered to Westinghouse for further evaluation.

It should be noted that to reduce the oxide at the above temperature, the reaction products must be rapidly removed. It was found that this can be accomplished by maintaining a high flow of hydrogen during the reduction step.

B. Cadmium Coatings On Mild Steel

A brief investigation was conducted on the preparation of thin metallic cadmium coatings on mild steel for possible neutron absorption studies. All experiments were conducted with metallic cadmium dispersions since previous work (13) had shown that the reduction of the cadmium oxide was not a practical method for coating preparation.

All dispersions were prepared from -325 mesh cadmium metal which was ball-milled for 20 hours in acetone to reduce its particle size. A typical cadmium dispersion contained 25 grams of the metal in 200 ml of nitromethane containing 2% zein (based on the solids) as the activator.

Coatings were electrophoretically deposited which possessed good green strength and appeared to be uniform in thickness. After isostatically pressing at approximately 20 tsi, the coatings showed excellent metallic properties and good bonding to the base metal. Sintering was accomplished in a purified argon atmosphere at 300°-310°C for 1 hour. The final coatings, averaging 0.1 to 0.5 mil thick, were far superior to those previously prepared by sintering in a purified hydrogen atmosphere. The coatings showed no tendency to flake off in simple bending tests.

C. Coatings for Graphite for Use in LMFRE Tests

The feasibility of the electrophoretic technique was also examined for the application of impervious coatings on graphite to act as a barrier against diffusion of gaseous fission products such as Xe^{135} and I^{135} into the graphite. The coatings were also to offer corrosion resistance against the constituents of the liquid metal fuel (bismuth containing magnesium and zirconium) at elevated temperatures. The materials investigated as possible protective coatings for graphite were tantalum carbide, chromium carbide, chromium carbide - 6% chromium, tantalum - (6 and 10%) iron, chromium carbide - 6% iron, tantalum - (6) chromium, molybdenum - 6% iron, and molybdenum - 6% chromium.

1. Tantalum Carbide Coatings on Graphite

Tantalum metal (-10 microns) was electrophoretically deposited on graphite test panels from a dispersion of the metal in 200 ml isopropanol and 50 ml nitromethane. The dispersion also contained 1% zein (based on solids) as the activator and a trace of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as the stabilizer. Densified (50 tsi) and undensified coatings were subsequently carburized in an argon-methane atmosphere at 1450°C for one hour.

The resultant coatings were well-sintered, crack-free, and adherent to the graphite substrate. However, microscopic examination of a cross-section of the coatings revealed a porous structure.

2. Chromium Carbide Coatings on Graphite

Coatings of chromium carbide, chromium carbide-6% iron, and chromium carbide-6% chromium were electrophoretically deposited on graphite panels from dispersions of the metal in a 2.5 to 1 ratio of nitromethane to isopropanol, containing 2% zein as the activator. The chromium carbide (-100 mesh) used in the dispersion was initially ball-milled for 24 hours to reduce the particle size to 10 microns. Pressed (10 tsi-20 tsi) and unpressed chromium carbide coatings were subsequently fired in an argon atmosphere for one hour at temperatures of 1400° and 1450°C .

The final coatings were well-sintered and adherent to the substrate but shrinkage cracks were observed throughout the coating.

Densified (10 tsi) chromium carbide coatings containing either 6% iron or 6% chromium as binders were fired in hydrogen at temperatures of 1100°C and 1300°C for one hour. These materials yielded poorly sintered and non-adherent coatings on the graphite.

3. Molybdenum Coatings on Graphite

Molybdenum-6% iron and molybdenum-6% chromium were electro-phoretically deposited on graphite panels from dispersions of the same general composition as those previously discussed. The as-deposited coatings were densified at 20 tsi and fired in a hydrogen atmosphere at 1100°C and 1300°C for one hour.

The final coatings fired at the higher temperature were well-sintered and crack-free. However, the coating did not adhere to the graphite substrate. Coatings fired at the lower temperatures were partially sintered, cracked, and non-adherent.

Increasing the binder content (chromium and iron) of the coatings to 10% and using such sintering atmospheres as hydrogen, argon, and mixed gas (H_2 + 2 mole percent HCl) up to temperatures of 1400°C also failed to yield the desired coating. Although the coatings were well-sintered and adherent, shrinkage cracks were present throughout the surface.

4. Tantalum Coatings on Graphite

Dispersions containing tantalum-6% iron and tantalum-6% chromium in a nitromethane-isopropanol system (2.5 to 1 ratio) activated by 2% zein (based on solids) were used to electrophoretically deposit the above tantalum compositions on graphite panels. The as-deposited coatings were densified at about 10 tsi-20 tsi and subsequently fired in argon at 1200°C, 1300°C and 1400°C for one hour.

The resultant coatings of both compositions were only partially sintered at the lower temperatures (1200° and 1300°C). At the higher temperature (1400°C) and densification pressure (~ 20 tsi) the coatings appeared to be better sintered but non-adherent.

Increasing the binder content of the tantalum-iron coatings from 6% to 10% and firing in argon at 1400°C for one hour resulted in a coating that formed a melt with good adherence to the graphite. The melt, however, did not distribute itself evenly over the graphite surface. Some areas of the graphite panel were exposed.

On the basis of the above result, a series of experiments was conducted to study the effect of sintering temperature, densification pressure and coating thickness, on the application of impervious and adherent tantalum-10% iron coatings on graphite.

The tantalum-10% iron coatings 5 mils and 20 mils thick were applied to graphite panels electrophoretically from a dispersion having the following composition:

20 gms tantalum	} ball-milled for 2 hours
2 gms iron	
250 ml nitromethane	
100 ml isopropanol	
2% zein (based on solids)	

Densified (10 and 20 tsi) and undensified coatings were then fired in an argon atmosphere at temperatures ranging from 1200° to 1400°C for time intervals of 1 hour at the lower temperatures and 10 minutes at the higher temperature.

The resultant coatings fired below 1400°C showed no sintering and little adherence to the graphite. Coatings fired at 1400°C exhibited the same phenomenon observed in previous experiments, that is, the formation of a melt indicating that a eutectic occurred.

Unpressed coatings (5 mils and 20 mils thick) formed blisters during the firing cycle. However, specimens densified at ~ 10 tsi exhibited blistering to a lesser extent while coatings densified at ~ 20 tsi were devoid of blisters.

In general, all coatings fired at 1400°C in argon exhibited the familiar microscopic pin holes observed in previous experiments. Moreover, complete coating coverage (neglecting the pin holes) of the graphite panel was achieved by increasing the coating thickness from 5 mils to 20 mils.

D. Molybdenum Coatings on Stainless Steel

It has been observed in previous work that thick molybdenum coatings (15-20 mils) in which sintering is effected partially by chemical reaction were unsatisfactory. These coatings tend to be soft and very porous at the surface of the substrate. For example, thin coatings (5 mils) of molybdenum

on stainless steel, that are sintered in a hydrogen atmosphere containing 2 mol % HCl at 1200°C are dense, hard and impervious, while thicker coatings (15 mils) treated in the same manner are hard and dense at the surface of the coating but soft and porous near the substrate metal. This is probably due to the formation of a well-sintered, impervious layer of molybdenum at the outer surface preventing access of the mixed reactant gas to the metal below.

To confirm this theory a series of scoping experiments were conducted on 15-20 mil thick molybdenum coatings on stainless steel panels. Varying quantities of the mixed gas were used in the hope of obtaining complete diffusion through the pressed coating before the outer surface reaction occurs.

A number of stainless steel panels were electrophoretically coated with molybdenum and subsequently densified isostatically at about 20 tsi. The thickness of the densified coatings was from 15-20 mils. The specimens were then fired at 1200°C in a hydrogen atmosphere containing 2 mole percent HCl at varied flow rates for time intervals of $\frac{1}{2}$ hour to 2 hours. The flow rate of the mixed gas was qualitatively measured by observing the height of the flame at the exit end of the furnace tube. The results are given in the table below.

Run	Sintering		Result
	Time	H ₂ -HCl Gas Flow Rate	
1	$\frac{1}{2}$ hr.	Low flow, 1 " flame	Poorly sintered, porous coating
2	1 hr.	Low flow, 1 " flame	Poorly sintered, porous coating
3	$1\frac{1}{2}$ hr.	Low flow, 1 " flame	Poorly sintered, porous coating
4	2 hr.	High flow, 6 " flame	Well-sintered, dense coating
5	1 hr.	High flow, 6 " flame	Poorly sintered, porous coating

All coatings obtained from the above experiments were tested for ease of machinability and polishing. Coatings obtained from runs 1, 2, 3, and 5 crumbled upon machining, and chipped during the polishing step, while the coating obtained in run 4 withstood machining and polishing without any visible signs of damage indicating a well-sintered coating. Moreover, the coating appeared dense when examined microscopically.

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