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Final Report, Phase I

DEVELOPMENT OF
CLAD CERAMIC FUEL PLATES BY
SPRAY-COATING TECHNIQUES

ATL Job 4010

31 October 1961

Prepared under
Contract No. AT(04-3)-250
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for the

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FOREWORD

The United States and the European Atomic Energy Community (Euratom), on May 29 and June 18, 1958, signed an agreement which provides a basis for cooperation in programs for the advancement of the peaceful applications of atomic energy. This agreement, in part, provides for the establishment of a Joint U. S. -Euratom research and development program which is aimed at reactors to be constructed in Europe under the Joint Program.

The work described in this report represents the Joint U.S. -Euratom effort which is in keeping with the spirit of cooperation in contributing to the common good by the sharing of scientific and technical information and minimizing the duplication of effort by the limited pool of technical talent available in western Europe and the United States.

This final report, prepared by Advanced Technology Laboratories for the Joint U. S. -Euratom Research and Development Board under Contract No. AT(04-3)-250, Project Agreement No. 4, covers Phase I of the experimental research program directed toward development of uranium dioxide plate-type fuel elements through appropriate oxide and/or metal spray-coating and assembly techniques. This work was conducted during the period July 1959 through October 1961.

Among those who contributed to the experimental work described in this report were Dr. H. Marchandise (Euratom representative), R. S. Kirby, and N. Holowko.

SUMMARY

An experimental investigation was conducted directed toward development of spray-coating techniques for fabricating uranium dioxide fuel plates. The initial effort was concerned with determination of the effect of spraying parameters on the characteristics of calcium-stabilized zirconia. Important parameters were then studied using uranium dioxide powders.

Uranium dioxide coatings having densities of 90% theoretical were produced. However, at conditions required for spraying fuel plates, densities of 86% theoretical appear more practical. The rate and efficiency of uranium dioxide coating deposition were also determined for various spraying conditions.

Coating adherence was good, as determined by bend tests. Gritblasting was found to provide the best surface for coating adherence. The O/U ratio of the uranium dioxide could be maintained by spraying in an argon atmosphere.

Several simulated fuel plates were sprayed to determine the feasibility of fabricating fuel plates by the spray-coating techniques developed in the first portion of the program. Zircaloy-2 was found to be the most desirable cladding material. Cladding thicknesses of 0.035 inch minimum are required if plates of 2-inch widths are to be sprayed with no distortion.

INTRODUCTION

Pellet-in-tube uranium dioxide fuel-element designs have been widely accepted for heterogeneous, partially enriched power reactors because of their proven performance and because they offer promise of long fuel lifetime. However, these designs represent a compromise at the expense of optimum reactor performance and fuel-cycle costs. The low thermal conductivity of the oxide and the lack of an integral bond at the oxide-cladding interface combine to produce a very high thermal resistance in this type of element. Thus, the centerline temperature limit of the oxide is reached at power output levels well below the potential capabilities of water and liquid-metal coolants. The high fuel-cycle cost is due chiefly to the high fabrication cost associated with the pellet-in-tube design. To partially offset the poor thermal properties of the fuel element, the assemblies must be composed of a multiplicity of small units, and close tolerances are necessary. A compromise must therefore be reached between large unit size to reduce fabrication cost and small unit size to improve thermal performance. Hence there is great incentive to develop improved oxide-type fuel elements.

Numerous modifications to the pellet-in-tube design and several alternative fabrication techniques have been suggested or are under investigation. In many of these approaches, however, the importance of both improving thermal performance and lowering fabrication costs is not recognized. Advanced Technology Laboratories, as a result of detailed analyses of reactor performance, concluded that an oxide plate-type fuel element with an integral bond between oxide and cladding would provide outstanding technical advantages over current pellet-in-tube designs, if it could be designed to meet engineering requirements and could be produced at sufficiently low cost. The use of ceramic spray-coating techniques rather than conventional ceramic fabrication practices appeared to offer the greatest promise of achieving all objectives.

The technology of spray-coating refractory oxides has undergone rapid advancement over the past few years as a result of its requirement in the aircraft and missile industry. Although most commercially available spray-coating processes are not suitable for spraying uranium dioxide, the plasma-jet spraying process is capable of producing ceramic coatings of suitable thickness and density without contamination from combustion products or from the atmosphere, and is thus applicable to the development of an oxide plate-type fuel element.

The program reported here had as its objective the development of techniques for plasma-spraying clad plate-type ceramic fuel elements. The investigation was also directed toward determining the limitations of the process as applied to fuel-element fabrication. In order to accomplish this objective, the effects of process variables on coating properties and deposition characteristics were studied, initially using calcium-stabilized zirconia rather than uranium dioxide. Data thus obtained formed the basis for a program to determine the best ranges of operating conditions for spraying uranium dioxide. Using the techniques developed during this program, uranium dioxide coatings were then evaluated for density, efficiency, rate of deposition, adherence, and chemical composition.

EQUIPMENT AND MATERIALS

A. Equipment

A complex array of equipment was assembled for the spraying of uranium dioxide. This equipment includes plasma jets, power supplies, control consoles, water systems, air-filter systems, powder feed systems, an inert-atmosphere chamber, sandblasters, and assorted ceramics laboratory equipment. This section describes in some detail the equipment utilized and gives the reader some insight into the equipment requirements for plasma-jet spraying of toxic materials.

1. Spraying System

To acquaint personnel with plasma spraying while facilities were being installed at Advanced Technology Laboratories (ATL), initial work was carried out at the Plasmakote Corporation (Los Angeles, Calif.). The equipment used during this period was considerably different from that currently in use at ATL. The plasma jet was smaller in size and constructed much differently, allowing maximum power inputs of only 12 kw. Another major difference was the mode of powder injection. The powder and the carrier gas entered a plenum chamber in the front electrode and were injected into the plasma through three holes placed 120 degrees apart around the plasma orifice. This torch produced good spray patterns but low-density coatings because of its limited capacity.

The Plasmadyne SG-1 spraying system was used throughout the major portion of the program. A sectional view showing the basic makeup of the SG-1 plasma-jet spray torch appears as Figure 1. A description of a plasma jet was presented in a recent article.¹

An arc is established between the rear electrode (cathode) and the front electrode (anode) to form a plasma. Arc gas is injected into the arc chamber tangentially to promote a vortex-like flow through the chamber. A high-voltage discharge in the arc chamber creates an ionized path for initiation of the high-current arc. The front and rear electrodes are prevented from melting by cooling water circulated through passages in the torch and by a cool insulating layer of argon adjacent to the electrode surfaces. Powder is carried into the hot core of the plasma by a gas stream through a single

1. G. M. Giannini, "The Plasma Jet," Scientific American, 197, No. 2, August 1957, p. 80.

SECTIONAL VIEW OF PLASMADYNE SG-1 PLASMA-JET SPRAY TORCH

FIGURE 1

powder-injection port. This injection port is angled back toward the arc chamber by about 5 to 7 degrees to aid penetration of the hot core of the plasma by the powder and to increase the dwell time of particles in the plasma.

This torch could be operated continuously at about 25-kw electrical power input when argon was used as the arc gas. In addition, a torch capable of 40-kw operation was studied. This torch was similar to the SG-1, but the water flow was greater, the orifice diameter was 0.437 inch rather than 0.316 inch, and the arc gap between the electrodes was slightly greater.

Power was supplied to the plasma jet by a three-phase full-wave rectifier utilizing a self-saturating reactor and selenium rectifier elements. These power supplies were capable of continuous operation at 40 kw (1000 amperes at 40 volts). Two of these units were available and could be connected in series to double the current output for use with larger torches.

The plasma jet was controlled by the operator from a console containing all controls and meters for operation of the plasma and injection of the powder. Argon was used for operation of the torch and injection of the powder and was supplied from cylinders through two-stage pressure regulators. Water was supplied by a pressurized recirculating water system.

Two powder feed systems were evaluated during this program. Initially, the hopper furnished with the Plasmadyne system was used. This hopper was an aspirator-type; i. e., gas flows through the hopper and aspirates the powder into the gas stream. Control of the powder addition rate was extremely rough, some types of powders were difficult to feed, and fine powders could not be fed at all.

Later, a Continental Coatings Corporation powder feed hopper was incorporated into the spray system. With this hopper, powder is transferred to a carburetor by an auger, and a variable-speed drive attached to the auger allows adjustment of the rate of powder addition to the carrier-gas stream. The vibrator attached to the bottom of the hopper imparts constant motion to the powder particles and packs the powder around the auger, assuring more consistent feed rates. The powder and the carrier gas are initially mixed in the carburetor and then carried into a second mixing chamber, improving the distribution of powder in the gas stream. From the second mixing chamber, the powder is carried through lines to the plasma torch.

2. Auxiliary Equipment

For spraying ZrO_2 , the gun was initially hand-held but later was mounted on a mechanized carriage. This carriage maintained the plasma torch at a constant spray distance and traversed it across the substrates at a constant rate. The traverse rate could be varied from 0 to 125 in./min. Reversing was accomplished mechanically through a transmission, while cross indexing was accomplished by a rack-and-pinion assembly mounted on the carriage. The substrates were clamped against a water-cooled chill block to prevent overheating.

Since UO_2 can be further oxidized, it was necessary to spray in an inert atmosphere. A vacuum-purged inert-atmosphere chamber was assembled for this purpose (Figure 2). This chamber is approximately 6 feet long by 3 feet in diameter and is equipped with glove ports, sight ports, light ports, and feed-through ports. One end of the chamber is a hinged door to allow access for equipment changes or maintenance. An airlock is placed through this door. This airlock can be purged of air and backfilled with inert gas to allow transfer of materials and small tools between the chamber and the room without contamination of the chamber atmosphere. The entire door end of the chamber is enclosed in an exhausted hood to comply with health-physics requirements. A glove box is placed within this hood to contain the powder hopper (upper right corner of Figure 2).

A high-vacuum pumping system is used to evacuate the chamber. An 80-cfm mechanical pump serves for evacuation to a pressure of 100 μ of mercury. A 6-inch diffusion pump serves for evacuation to pressures below 1 μ of mercury prior to backfilling with argon. The mechanical pump is equipped with a filter to remove any powder particles before they can enter the pump, and an absolute filter is attached to the exhaust to prevent any particulate uranium dioxide from entering the room atmosphere. Once the chamber has been evacuated to the predetermined pressure, the pumping system is isolated and the chamber is filled with inert gas to a slight positive pressure. Since the powder hopper is a sealed unit, it can be purged either simultaneously with the chamber or separately by an auxiliary pumping system.

Figure 3, an interior view of the chamber used for spraying UO_2 , shows the plasma torch and the mechanism for traversing the substrate beneath the torch. The water-cooled chill block is mounted on a carriage that moves the substrate in a

EXTERIOR VIEW OF INERT-ATMOSPHERE PLASMA-SPRAY CHAMBER

FIGURE 2

INTERIOR VIEW OF
INERT-ATMOSPHERE SPRAY CHAMBER

FIGURE 3

direction parallel to the axis of the chamber. A reversible motor is attached to a lead screw to drive this carriage. Cross indexing of the substrate is accomplished by a rack-and-pinion assembly that moves the chill block on tracks perpendicular to the axis of the chamber. The entire drive and indexing mechanism is controlled by a system of microswitches and timing relays to automate the entire spraying operation. The spray distance can be adjusted by driving the torch vertically by a rack and pinion.

3. Miscellaneous Support Equipment

In order to carry out the plasma-spray program, assorted ceramics laboratory equipment was required, including balances, blenders, sieves, sieve shakers, and drying ovens. The Tyler screen series was used to size powders above the 400-mesh size, using Ro-Tap sieve shakers. Gritblasting of the substrate was carried out using either a suction-type sandblaster or a pressure-type blaster. Adherence tests were performed on a Dillon 300-pound mechanical testing machine.

B. Materials

Calcium-stabilized zirconia was used to determine the effects of spray variables on coating characteristics. The data thus obtained formed the basis for the program to spray uranium dioxide.

1. Zirconia

Calcium-stabilized zirconia was used in place of UO_2 during the initial portion of the program, which was devoted to an investigation of the spraying variables. About 5% calcium oxide was added to stabilize the cubic structure of zirconia and prevent phase transformation at elevated temperatures. Three types of such stabilized zirconia were used during this program: a) fused and milled; b) sintered and milled; c) sintered, milled, and chemically treated.

Zirconia fused by high-temperature firing has a high particle density. The resulting powder is very angular in appearance, as illustrated by Figure 4a. Sintered and milled zirconia (Figure 4b) is the normal mill product of lower temperature sintering. A chemical treatment that somewhat improves flowability of the sintered and milled powder is a proprietary process of Zirconium Corporation of America. Chemical treatment may remove surface static-electrical charges or dissolve the extremely fine material not removed by screening. It appears that the particle surface area is increased

a. Fused

250× (NO ETCH)

b. Sintered and Milled

250× (NO ETCH)

c. Sintered, Milled, and Chemically Treated

250× (NO ETCH)

PHOTOMICROGRAPHS OF CALCIUM-STABILIZED ZIRCONIA POWDERS

FIGURE 4

by the chemical treatment (Figure 4c), which may account for improved deposition efficiency as discussed later.

Throughout the majority of this program, -200, +325 mesh material was used.

2. Uranium Dioxide

Three types of depleted uranium dioxide powders were obtained in order to fully investigate plasma spraying of this material: a) fused and milled; b) sintered and milled; c) ceramic grade.

Prior to spraying UO_2 , a complete survey was made of all lots of powder purchased. The results were as follows:

a. The fused and milled powder in the size range -200, +325 mesh is satisfactory for plasma spraying, using current equipment and techniques.

b. The sintered and milled powder in the range from 200 to 400 mesh was improperly sized by the supplier and contained an excessive amount of fine material; it was returned to the supplier.

c. A small sample of the out-of-specification sintered and milled powder was screened at ATL to remove the fine particles. Properly sized material of this type appears to be satisfactory for plasma spraying by current techniques.

d. The +150 mesh sintered and milled powder was ball-milled to provide enough powder for evaluation.

e. Ceramic-grade powder was completely unsatisfactory for spraying.

Screen analyses of powder sprayed during this program are given in Table I; chemical analyses are given in Table II.

Powders containing a large amount of very fine particles do not flow well in the powder feed system but "cake up" in the hopper or "ball up" in the powder feed lines. This can be due to either moisture picked up by the fine particles or static-electrical charges on the particles resulting from the milling operation. It is apparent that special equipment and techniques will have to be developed to allow proper feeding of extremely fine powders before materials such as the ceramic-grade UO_2 can be sprayed.

The insufficient supply of acceptable sintered powder resulted in the investigation being carried out primarily with fused powder. The sintered powder could be expected to result in a coating of lower density.

TABLE I

SIZE ANALYSIS OF URANIUM DIOXIDE POWDERS

Powder Type	Specified Particle Size Range (mesh) and Lot No.	Screen Analysis		Remarks
		Size Range (mesh)	Percentage (wt. %)	
Fused & milled	95% within -200, +325 M-351	+200 -200, +250 -250, +325 -325	1.78 8.50 85.06 4.66	
"	95% within -200, +325 M-352	+150 -150, +200 -200, +250 -250, +325 -325	0.87 0.31 33.46 50.97 14.38	-325 mesh material must be removed for spraying.
"	95% within -200, +325 M-436	+200 -200, +270 -270, +325 -325, +400 -400	1.2 44.0 36.0 7.0 6.8	"
"	95% within -200, +325 M-437	+200 -200, +250 -250, +325 -325	15.4 46.6 35.6 2.4	+200 mesh material must be removed for spraying.
"	95% within -200, +325 M-438	+200 -200, +250 -250, +325 -325	11.7 39.3 39.8 9.2	+200 and -325 mesh material must be removed for spraying.

TABLE I
(concl.)

Powder Type	Specified Particle Size Range (mesh) and Lot. No.	Screen Analysis		Remarks
		Size Range (mesh)	Percentage (wt. %)	
Fused & milled	-325	+325	0.2	Contains some extremely fine particles which must be removed for spraying.
	M-353	-325	99.8	
Sintered & milled	95%	+ 48	26.4	Good flowability. Too large a particle size for spraying. Milled to finer size for evaluation of sintered powder.
	+150	- 48, + 65	24.35	
	M-364	- 65, +100	22.76	
		-100, +150	21.36	
		-150, +325	4.75	
		-325	0.25	

TABLE II
CHEMICAL ANALYSIS OF URANIUM DIOXIDE POWDERS

	<u>Fused Powder</u>	<u>Sintered Powder</u>
U (wt. %)	88.1-88.2	87.82
U 235 (wt. %)	0.22	0.22
Ag	<0.1	<0.1
Al	16-84	<2
B	<0.1-0.7	0.2
Bi	<3	<1
C	22-100	70
Ca	<1	39
Cd	<1	0.15
Co	<3	<5
Cr	6.95	11
Cu	13-18	24
Fe	110-350	103
Mg	4-10	8
Mn	<3	3
Mo	<1-11	<1
Ni	4-40	67
Pb	<2-15	3
Si	25-48	119
Sn	1-16	7
Ti	Not determined	<50
V	<10	<10
Zn	<10	122
O/U ratio:		
By titration	2.001-2.008	2.03
By gravimetric method	1.95	-

Note: Unless otherwise indicated, analysis is in ppm.

In practice, it is expected that the oversprayed powder would be reclaimed by simply screening. The sized powder would be blended into previously unsprayed powder with very little degradation of the product resulting. This practice of reclaiming the oversprayed product would be essential when using enriched material where fuel-cycle costs are a consideration.

Metallographic examinations of both fused and sintered grades of powder showed that both types contain some porosity within the particles, with the greatest degree of porosity being found in the sintered and milled particles (Figure 5). Slightly lower particle density was noted for the recycled powder (Figure 5c). The fused particles appear to be two-phased. X-ray diffraction studies gave no indication of the second phase and indicated the lattice parameters to be those of UO_2 . It is possible that these phases are either nitrides, carbides, or uranium metal.

3. Substrates

Substrate materials employed were Type 304 stainless steel, 1100 aluminum, mild steel, and Zircaloy-2. Stainless steel coupons $2'' \times 2'' \times 0.140''$ were used as substrates for spraying of density samples, aluminum substrates were used to determine if differences in substrate material would affect coating adherence, and mild steel coupons $16'' \times 2'' \times 125''$ were used to determine deposition efficiencies. Cold-rolled Zircaloy-2 substrates, annealed 1 hour at 800 C following gritblasting and straightening operations, were used in the study of UO_2 coating adherence and in making simulated fuel plates.

a. Fused Uranium Dioxide Powder

250× (NO ETCH)

b. Sintered Uranium Dioxide Powder

250× (NO ETCH)

c. Recycled Uranium Dioxide Powder
(Original powder fused UO_2)

250× (NO ETCH)

PHOTOMICROGRAPHS OF URANIUM DIOXIDE POWDERS

FIGURE 5

EXPERIMENTAL PROCEDURES

Several procedures were developed to prepare, spray, and evaluate coatings. Many of these procedures, although applicable primarily to the current experimental program, would apply to the production of fuel elements.

A. Preparation for Spraying

To obtain high-density adherent coatings, it was necessary to place special attention on the preparation of powders and substrates. Procedures developed were followed with little deviation, in order to obtain reproducible results.

1. Powders

Possibly the greatest variables in plasma spraying are associated with the powder. Therefore, preparation of the powder is a most important step in the procedure. The two principal factors involved are particle size and dryness of the powder. Too many fines in the powder make it difficult to feed into the plasma and can contribute to poor deposition efficiency. Moisture must be removed from the powder before spraying to prevent "caking" in the powder feed system.

All powder was first given a screen analysis to determine if it met the purchase requirements. If the material was in or near specification, it was screened to further remove small quantities of out-of-size material.

Zirconia powder was dried in an oven prior to spraying to remove any moisture. The uranium dioxide powder did not have to be dried unless it was wet-classified. When drying was required, it was carried out under infrared heat lamps. Powder thus prepared was then placed in the powder feed hopper for spraying.

Sub-sieve powders were wet-classified, using the settling rate in water to separate the various size fractions. The slimes in suspension were poured off, and the remaining particles were dried, followed by dry screening to break up any cakes or agglomerates.

2. Substrate

Adherence of plasma-sprayed ceramic coatings to metal substrates is principally by mechanical means. Anchors for the coating can be provided by gritblasting or other methods for producing roughened surfaces. Chemical milling, presprayed bond layers, and graded coatings were also studied and will be discussed more extensively later in this report.

Preparation of the substrate for spraying during this program was by gritblasting, using suction-type and pressure-type equipment. The suction-type blaster aspirates the blasting media into the compressed air stream by a venturi action, while the pressure system blows the jet of air through the media. Pressure-type blasting systems impart high particle velocity to the blasting grits and produce a rougher surface.

Silicon carbide, iron, garnet, and sand were evaluated as blasting media. Of these, silicon carbide was found preferable and was used throughout the major portion of the program. Since considerable deformation of thin substrates can be caused by the cold-working effect of gritblasting the surface, blasted sheets were straightened by passing the warped sheet through a roll straightener. A rubber sheet was inserted between the rolls and the blasted surface. Surfaces were then cleaned by scrubbing with acetone to remove any grease and loose grit embedded in the surface.

B. Spraying Procedures

To prevent oxidation of the uranium dioxide during spraying, the entire spraying operation was carried out in an argon-atmosphere chamber. The atmosphere was obtained by evacuating the chamber to a pressure of from 1 to 10 μ of mercury and back-filling with argon. Because of the size and complexity of the vacuum system, it was found necessary to conduct this operation twice in order to obtain an atmosphere of high purity.

After the inert atmosphere was obtained, the following sequence of operations was carried out.

- 1) The substrate was clamped onto the chill block.
- 2) The spray distance, traverse rate, and powder feed rate were set.
- 3) The flow of cooling water to the plasma torch and chill block was initiated.
- 4) The flow of arc gas was adjusted.
- 5) The power supplies were energized.
- 6) The plasma torch was initiated.
- 7) The arc current was adjusted.
- 8) The flow of powder carrier gas was adjusted.
- 9) Powder feed was initiated.
- 10) The carriage motion was started.
- 11) The uranium oxide was sprayed.

- 12) Powder feed was stopped.
- 13) The carriage was stopped.
- 14) The plasma torch was stopped.
- 15) After allowing a few seconds for the electrodes to cool down, the arc gas, powder gas, and cooling water to the torch were turned off.
- 16) The spray-coated specimen was removed for evaluation.

These steps were generally followed but were occasionally modified for special tests (e.g., deposition-efficiency determinations, where all spraying was carried out on one substrate coupon).

C. Evaluation Procedures

Sprayed coatings were evaluated for density, adherence, deposition efficiency and rate, and chemical composition. The structure of the coatings was determined by metallographic examination. This section describes in detail the evaluation procedures used.

1. Density

The bulk density of the coatings was determined by immersing the specimen in water after all coating surfaces were sealed with a plastic film. The plastic material was sprayed onto the ceramic coating in liquid form. The material selected would not enter pores in the coating but was in intimate contact with the coating surfaces. It dried to a waterproof, non-porous film.

The total volume of the composite specimen, consisting of substrate, coating, and plastic film, was determined by weighing it first in air and then immersed in water. This procedure results in determination of the buoyant force of the water acting on the specimen and thus the volume of water displaced.

Several steps were required to determine the coating density:

- a) Weigh the prepared and numbered substrate.
- b) Weigh the ceramic-coated substrate.
- c) Coat with plastic film.
- d) Weigh to determine weight of plastic film.
- e) Weigh the composite specimen immersed in distilled, deaerated water.

All weighings were to the nearest 0.1 mg.

After these weights were obtained, the volume of the coating could be calculated from

$$V_c = \frac{W_{sp} + W_f + H - W_w}{\rho_w} - \frac{W_f}{\rho_f} - \frac{W_m}{\rho_m}, \quad (1)$$

and the density of the coating from

$$\rho_c = \frac{W_c}{V_c}, \quad (2)$$

where V_c, ρ_c, W_c = volume, density, and weight of the coating;

W_{sp} = weight of ceramic coating and metal substrate;

W_f, ρ_f = weight and density of the plastic film;

H = correction factor for the buoyant force acting in the specimen holder;

W_w = weight of composite specimen immersed in water;

ρ_w = density of the water, corrected for temperature;

W_m, ρ_m = weight and density of the substrate metal.

Before the coating density could be calculated, the densities of the metal substrate and of the plastic film were determined. Coating density was expressed as a percentage of the theoretical density, using values of 6.27 and 10.96 for calcium-stabilized zirconia and uranium dioxide, respectively.

The immersion method has limited sensitivity, which imparts a significant error when very thin coatings are measured. When the coating thickness was greater than 0.031 inch on a 2" x 2" coupon, the error in calculating the percent theoretical density was less than 1%.

2. Adherence

The adherence of zirconia coatings was determined using specimens of the plug-in-plate type (Figure 6). The specimens were tested with the coating-substrate bond in tension.

Coupons prepared by the following procedure were used to determine the effect of gritblasted surface roughness on bond strength of zirconia coatings.

PLUG-IN-PLATE ADHERENCE COUPON

FIGURE 6

- a) Fabricate coupons, reaming the hole in the plate (substrate) to produce a 0.002-inch radial gap between the plate and the plug. The plug was 3/4 inch in diameter.
- b) Assemble coupon and gritblast the surface.
- c) Disassemble the coupon and de-burr the plug and hole in the coupon.
- d) Reassemble with plug flush with surface, making sure that the plug is free to slide in the hole; clamp plug in place with set screw.
- e) Spray on the coating.
- f) Place in tensile testing machine and remove set screws from collar.
- g) Test to failure.

This test requires use of a thick plate to achieve equal cooling of both the plug and the plate during spraying; the heat-conductivity path through a thin substrate would be much shorter than that through the plug, thereby causing uneven heating of the specimen and erroneous adherence values. The problems of aligning the plug and plate and joining the collar to the plate are also magnified considerably when using a thin substrate. The plug-in-plate test was therefore not used for uranium dioxide coatings, since primary interest was in adherence of the uranium dioxide to thin substrates. Instead bend tests were performed on coated 0.030-inch-thick stainless steel and thin Zircaloy-2 substrates by bending the composite (substrate plus uranium dioxide coating) around a 1-inch radius. Spalling of the coating was used as a criterion for evaluation. This test did not yield absolute values of adherence but did indicate degree of adherence.

3. Efficiency and Rate of Deposition

In order to estimate the economics of the process, it is necessary to determine the efficiency and rate of deposition of the coating. This was accomplished by spraying a known amount of powder for a measured time in such a manner that all spraying took place on the substrate (mild steel in this case). The procedure followed was:

- a) Sandblast and weigh the substrate.
- b) Spray-coat the substrate at a known powder feed rate for a measured time period, always spraying on the substrate.
- c) Weigh the coated substrate and calculate the coating weight, deposition rate, and (from the known powder feed rate) deposition efficiency.

When the auger-type powder feed system was used, powder could be delivered to the plasma torch at a known rate. In order to accurately determine powder addition time and rate of addition, the hopper was instrumented with a clock timer and an electric

revolution counter to determine the revolution rate of the feed screw, thus simplifying the techniques for use in the inert-atmosphere chamber.

4. Chemical Composition

The O/U atomic ratios of the uranium dioxide coatings were determined by the gravimetric method. The uranium dioxide specimen was dried in a vacuum dessicator and weighed in an alumina boat. It was then oxidized at 800 C in a flow of oxygen for 3 to 4 hours. The increase in weight of the specimen corresponds to the reaction:

If we call W_0 the initial weight of the specimen and W_1 the weight of the specimen after oxidation, the ratio is given by:

$$\frac{\text{O}}{\text{U}} = \frac{\frac{1}{16} (W_0 - W_1) \frac{238}{280.66}}{\frac{W_1}{280.66}} \quad (4)$$

In addition, several analyses were made by a titration method as a check on the gravimetric results.

5. Metallography

Metallographic evaluation of the zirconia coatings involved essentially only examination of polished sections under the microscope. To date, the main purpose of this evaluation has been to observe the structure of the coating and its porosity.

The specimen was cut from the composite plate (substrate plus zirconia coating) by means of a silicon carbide cutoff wheel. The specimen was then mounted in a plastic material and polished. The rough polishing was performed by hand on silicon carbide paper or automatically on a Lapmaster with abrasive. Diamond abrasive on standard polishing wheels was used for the final polishing.

Metallography was performed on uranium dioxide coatings sprayed on Zircaloy-2 substrates. The composite plate was mounted in a cold-setting epoxy resin, and a small metallography specimen was cut from the plate by means of a silicon carbide cutoff wheel. The preliminary mounting step prevented separation or cracking of the coating due to the force applied during cutting. The metallography specimen was then further impregnated with epoxy resin, using a hydraulic pressure of approximately 1500 psig. Rough polishing was done by hand on silicon carbide paper and finally on a Lapmaster with Linde A abrasive. Final polishing was done with diamond abrasive on standard polishing wheels.

EXPERIMENTAL RESULTS

Calcium-stabilized zirconia was sprayed initially to evaluate the effects of process parameters on coating density, deposition efficiency, and coating adherence. Uranium dioxide coatings were then sprayed to determine the effect of selected variables on these characteristics. Uranium dioxide coatings were also studied for chemical composition. The results are divided into the following categories: a) coating density and deposition efficiency; b) adherence; c) chemical composition of uranium dioxide coatings.

Density and deposition efficiency are discussed together because both were affected similarly by the process variables. The results include data obtained in the early stages of the program when calcium-stabilized zirconia was sprayed to gain insight into the effect of process variables.

A. Effect of Process Variables on Coating Density and Deposition Efficiency

Coating density is one of the most important considerations in developing spray-coating techniques for the fabrication of oxide fuel elements. The rate and efficiency of coating deposition are also important factors, since they influence the economics of fuel-element production. As noted earlier, zirconia was used in screening process variables to determine their effect upon density and deposition. The important variables were then selected for further study with uranium dioxide.

The plasma-spray process introduces a long list of variables for study, as indicated by Table III, which includes a list of coating properties that may be evaluated. Before the study of process variables was conducted, several coupons were sprayed to determine the data spread for coatings made under the same conditions. In order to do this, five specimens were sprayed at one time and ten additional specimens were sprayed individually. The equipment was shut off and restarted for each individual sample. The results, shown in Table IV, indicate that a 90% confidence level can be placed on any differences in bulk densities of 1.2% in the graphs employed in this investigation. It must be pointed out that this confidence level does not reflect inconsistencies caused by changing electrodes or operators.

1. Variables Associated with the Plasma

The variables associated with the plasma had the greatest influence on coating density and deposition efficiency. Before discussing these variable, however, it is important to discuss some of the basic concepts of the plasma jet that are applicable to spray coating.

TABLE III

CLASSIFICATION OF PLASMA-SPRAY VARIABLES AND PERTINENT COATING PROPERTIES

A. Process Variables Listed by Category

1. Plasma a. Power input b. Type of arc gas c. Flow of arc gas d. Plasma-torch geometry	3. Powder Feed a. Type of powder feed system b. Rate of powder addition to carrier gas c. Type of carrier gas d. Flow of carrier gas e. Angle of powder entry into plasma f. Location of powder entry port	4. Spraying Procedure a. Torch-to-work distance b. Traverse rate c. Angle of torch with work d. Cover gas e. Spraying atmosphere
2. Powder a. Composition b. Physical properties c. Method of manufacture d. Powder size e. Particle-size distribution		5. Substrate a. Composition b. Surface-preparation method c. Surface roughness d. Temperature

B. Coating Properties or Characteristics Evaluated

1. Density 2. Microstructure 3. Adherence	4. Deposition efficiency and rate 5. X-ray diffraction analysis of crystal structure 6. Chemical composition

TABLE IV
DATA SPREAD FOR COATINGS MADE UNDER
IDENTICAL CONDITIONS

Powder Feed System	Powder Lot	Spray Procedure	Density (% theoretical)		
			Range	Average	Standard Deviation
Aspirator	M-332	Sprayed together	79.0-79.7	79.3	0.029
		Sprayed individually	77.6-79.3	78.5*	0.548*
Auger	M-350	Sprayed together	82.6-83.1	82.8	0.026
		Sprayed individually	81.4-83.6	82.5*	0.570*

* Calculated including average value of specimens sprayed together.

Of the plasma variables listed in Table III, power input and arc-gas flow were studied most extensively. Argon was used throughout the majority of the program as the arc-stabilizing gas. A modified electrode design was briefly studied.

The temperature in a plasma jet is dependent on the heat or energy content of the gas (enthalpy). From Figure 7, which illustrates this relationship, it can be seen that extremely high temperatures are present in a plasma jet. However, although temperature is not as important as the heat content of the gas, it does provide the driving potential for the transfer of heat to the particles. Even at low enthalpies, gas temperatures are above the melting points of most materials being sprayed. Enthalpy, as used in this report, is expressed as kilocalories per cubic foot of arc-stabilizing gas flowing through the torch.

Theoretical values of enthalpy can be calculated from the power input and the arc-gas flow rate through the torch. Actual enthalpies, however, differ greatly from the theoretical values. Calorimetric techniques were used to calculate experimental enthalpies from determinations of the power lost to the cooling water. Figure 8 illustrates the theoretical and experimental heat contents at various arc-gas flow rates and at three levels of power input. Low flow rates provide the highest heat content. The rate at which enthalpy decreases diminishes as gas flow increases. Experimental values were found to be about 50 to 80% of the theoretical values at low and high arc-gas flow rates, respectively. Enthalpy can be increased by increasing the power input, as shown in Figure 9. Curves such as those in Figures 8 and 9 permit rapid estimation of plasma enthalpies for a given combination of power input and arc-gas flow rate.

Arc-gas flow also influences the time of particle residence in the plasma (dwell time) and the velocity with which a particle is transported to, and impacts, the coating. Low gas flow rates result in high enthalpies and dwell times and low particle velocities. High gas flow rates reduce the enthalpies and dwell times and increase the particle velocities.

a. Power Input

At a given flow of arc gas, coating density and deposition efficiency increase with increasing power input, as shown in Figures 10 and 11, respectively. The major effect of increasing the electrical power input is an increase in plasma enthalpy, with

RELATIONSHIP BETWEEN PLASMA ENTHALPY AND
TEMPERATURE OF AN ARGON PLASMA
(1 ATMOSPHERE PRESSURE)

FIGURE 7

PLASMA ENTHALPY AS A FUNCTION OF ARC-GAS FLOW RATE
FOR VARIOUS POWER-INPUT LEVELS

FIGURE 8

EXPERIMENTAL PLASMA ENTHALPY AS A FUNCTION OF
POWER INPUT FOR VARIOUS ARC-GAS FLOW RATES

FIGURE 9

LEGEND	POWDER TYPE	SPRAY DISTANCE (in.)	ARC-GAS FLOW (ARGON) (cfm)	POWDER FEED RATE (gm/min)
○	ZrO ₂	5	0.68	25
●	ZrO ₂	4	0.68	25
△	UO ₂	4	0.98	60

POWDER SIZE: -200,+325 mesh
 TRAVERSE RATE: 70 in./min
 POWDER-GAS FLOW: 0.14 cfm

EFFECT OF POWER INPUT ON COATING DENSITY

FIGURE 10

LEGEND	TORCH RATING	POWDER TYPE	ARC-GAS FLOW (ARGON) (cfm)	TRAVERSE RATE (in./min)	POWDER FEED RATE (gm/min)	POWDER- GAS FLOW (ARGON) (cfm)	REMARKS
○	25	Fused UO ₂	1.00	50	29.4	0.085	-
●	25	Fused UO ₂	1.00	50	60	0.100	Estimated curve
△	40	Fused UO ₂	1.40	70	27.8	0.133	-
▲	40	Fused UO ₂	1.40	70	56.8	0.133	-
□	25	Sintered, milled, chemically treated ZrO ₂	0.68	70	25	0.085	-
■	25		1.00	70	25	0.085	Estimated curve

EFFECT OF POWER INPUT ON DEPOSITION EFFICIENCY

FIGURE 11

a minor effect on both the particle dwell time in the plasma and the velocity of impact. Figures 12 and 13 plot coating density and deposition efficiency as a function of plasma enthalpy.

Within the limits of current spraying equipment, density increases linearly with power input. If the power limitations of the equipment were extended, a point would be reached at which further increases in power would have little effect on either density or deposition efficiency. Under this set of conditions, the optimum amount of particle melting would be achieved for set values of arc-gas flow, powder feed rate, etc. Figures 12 and 13 illustrate the point that enthalpy at constant arc-gas flow is a better quantity to consider than electrical power input. Even though higher powers can be achieved when arc-gas flow is increased, no benefit is gained, since the enthalpy is not increased and particle dwell time is decreased.

Coating densities and deposition efficiencies for uranium dioxide are not directly comparable to those for zirconia, since different arc-gas flow rates and/or distances were used. Higher enthalpies were required for uranium dioxide than for zirconia to achieve equivalent densities and deposition efficiencies. The reason is not apparent from the physical properties of the two materials. Calculations based on physical-property data indicate that uranium dioxide should be more readily sprayed than would zirconia.² This discrepancy is discussed in a later section.

b. Arc-Gas Flow

As illustrated by Figure 8, arc-gas flow has a significant effect on enthalpy. In addition, particle dwell time and velocity are affected. The effect of arc-gas flow on the density of zirconia coatings is illustrated in Figure 14; it is evident that the effect is small over a wide range of flow rates; on the other hand, the density of uranium dioxide coatings is affected greatly over a very narrow range of arc-gas flow rates, as shown in Figure 15. Deposition efficiencies were influenced in the same manner, as shown in Figures 16 and 17.

Zirconia coating density and deposition efficiency go through a minimum, rise to a maximum, and then gradually decrease as arc-gas flow is increased from

2. D. R. Mash, N. E. Weare, and D. L. Walker, "Process Variables in Plasma Jet Spraying," *Journal of Metals*, 13, No. 7, July 1961, pp 473-478.

LEGEND	POWDER TYPE	SPRAY DISTANCE (in.)	ARC-GAS FLOW (ARGON) (cfm)	POWDER FEED RATE (gm/min)
○	ZrO ₂	5	0.68	25
●	ZrO ₂	4	0.68	25
△	UO ₂	4	0.98	60

POWDER SIZE: -200,+325 mesh
 TRAVERSE RATE: 70 in./min
 POWDER-GAS FLOW: 0.14 cfm

EFFECT OF EXPERIMENTAL PLASMA ENTHALPY ON
 COATING DENSITY
 (CONSTANT ARC-GAS FLOW)

FIGURE 12

LEGEND	TORCH RATING	POWDER TYPE	ARC-GAS FLOW (ARGON) (cfm)	TRAVERSE RATE (in./min)	POWDER FEED RATE (gm/min)	POWDER-GAS FLOW (ARGON) (cfm)	REMARKS
○	25	Fused UO ₂	1.00	50	29.4	0.085	-
●	25	Fused UO ₂	1.00	50	60	0.100	Estimated curve
△	40	Fused UO ₂	1.40	70	27.8	0.133	-
▲	40	Fused UO ₂	1.40	70	56.8	0.133	-
□	25	{ Sintered, milled, chemically treated ZrO ₂	0.68	70	25	0.085	-
■	25		1.00	70	25	0.085	Estimated curve

EFFECT OF EXPERIMENTAL PLASMA ENTHALPY ON
DEPOSITION EFFICIENCY
(CONSTANT ARC-GAS FLOW)

FIGURE 13

LEGEND	POWER INPUT (kw)	SPRAY DISTANCE (in.)	TRAVERSE RATE: POWDER TYPE: POWDER FEED RATE:	70 in./min Chemically treated ZrO_2 25 gm/min
○	12.0	3		
●	15.0	3		
△	20.5	3		
X	18.7	4

EFFECT OF ARC-GAS FLOW ON DENSITY OF ZIRCONIA COATINGS
(CONSTANT POWER INPUT)

FIGURE 14

LEGEND	POWER INPUT	SPRAY DISTANCE	POWDER FEED RATE	COVER-GAS FLOW (ARGON) (cfm)
	(kw)	(in.)	(gm/min)	(cfm)
○	21-27	4	60	-
●	25-26	4	30	-
△	24-25	3	30	-
□	24-27	3	60	8
+	24-26	2.5*	60	8

* First pass: 2.5"; remaining passes at greater distance.

POWDER TYPE AND SIZE: Fused UO_2 ; -200,+325 mesh
ARC CURRENT: 750 amperes

EFFECT OF ARC-GAS FLOW ON
DENSITY OF URANIUM DIOXIDE COATINGS

FIGURE 15

LEGEND

SPRAY
DISTANCE
(in.)●
○
△3
4
5POWER INPUT: 15 kw
TRAVERSE RATE: 70 in./min
POWDER TYPE: Chemically treated ZrO_2
POWDER FEED RATE: 23.4-28.1 gm/min

EFFECT OF ARC-GAS FLOW ON EFFICIENCY AND RATE OF
DEPOSITION OF ZIRCONIA COATINGS
(CONSTANT POWER INPUT)

FIGURE 16

LEGEND	POWER INPUT	ARC CURRENT	POWDER FEED RATE	POWDER-GAS FLOW (ARGON)
	(kw)	(amp)	(gm/min)	(cfm)
○	21 -25.5	750	30	0.10
●	17.5-20.8	650	30	0.085
△	21 -25.5	750	60	0.10
□	19.4-23.9	750	30	0.085
+	20	600-750	30	0.10

POWDER SIZE: -200,+325 mesh

SPRAY DISTANCE: 4 in.

EFFECT OF ARC-GAS FLOW ON
DEPOSITION EFFICIENCY OF FUSED URANIUM DIOXIDE POWDER

FIGURE 17

~0.4 to ~2.0 cfm. This phenomenon can be explained as follows. At low gas flow rates, extremely high plasma enthalpies and long particle dwell times exist. As the flow is increased, enthalpy drops rapidly until a point is reached at which enthalpy decreases slowly with arc-gas flow while particle velocity increases at about the same rate. Coating density and deposition efficiency then increase until an optimum combination of particle dwell time and velocity is reached. Above this optimum, dwell times are too short and the degree of particle melting decreases.

Since uranium dioxide coatings could not be successfully deposited at low arc-gas flow rates, they were studied for only a narrow flow range. In the range studied, the effects were more pronounced than those obtained for zirconia.

Several coatings were sprayed at constant enthalpy to determine the arc-gas flow rate at which an optimum combination exists between particle dwell time and particle velocity. The resulting data are illustrated in Figures 18 and 19. It can be seen that the optimum arc-gas flow for uranium dioxide coating density is about 1.3 cfm, while the optimum for deposition efficiency is 1.0 cfm. These optima can possibly be brought together by proper selection of particle-size range.

c. Arc-Gas Type

Several zirconia coatings were made using nitrogen as the arc gas instead of argon. Since power levels were limited by electrode design, no benefit was derived from this substitution. Recent studies at Advanced Technology Laboratories have shown that addition of 5% hydrogen to argon raises the density of tungsten coatings from 85% theoretical to above 90% theoretical. Similar additions might be used to improve spraying of uranium dioxide. Improvements are primarily due to improved heat transfer characteristics of the argon-hydrogen mixture.

d. Plasma-Torch Geometry

To permit operation of the plasma torch at power levels up to 40 kw, slight modifications were made in the electrode geometry: the rear electrode was shortened and the diameter of the plasma orifice was increased. As illustrated previously in Figures 11 and 13, no benefit was derived from the higher power level. The increased arc-gas flow rates required to maintain electrode integrity kept the enthalpy of the high-powered torch from being appreciably higher than that of the 25-kw torch.

LEGEND	POWDER TYPE	PLASMA ENTHALPY (ARGON) (kcal/ft ³)	SPRAY DISTANCE (in.)	POWDER FEED RATE (gm/min)	COVER-GAS FLOW (ARGON) (cfm)
▲	UO ₂	265	3	60	6
△	UO ₂	265	4	60	None
○	ZrO ₂	150	4	25	None

POWDER SIZE: -200,+325 mesh
TRAVERSE RATE: 70 in./min

EFFECT OF ARC-GAS FLOW ON COATING DENSITY
(CONSTANT PLASMA ENTHALPY)

FIGURE 18

LEGEND	POWDER TYPE	PLASMA ENTHALPY (ARGON) (kcal./ft ³)	TRAVERSE RATE (in./min)	POWDER FEED RATE (gm/min)
△	UO ₂	250	50	30
○	ZrO ₂	150	70	35

POWDER SIZE: -200,+250 mesh

SPRAY DISTANCE: 4 in.

EFFECT OF ARC-GAS FLOW ON DEPOSITION EFFICIENCY
(CONSTANT PLASMA ENTHALPY)

FIGURE 19

2. Variables Associated with the Powder

Probably the most difficult to analyze variables in plasma spraying are those associated with the powder being sprayed. The following paragraphs describe the results obtained during the investigation of powder composition, method of manufacture, and powder size.

a. Powder Composition

As noted earlier, zirconia powders were sprayed in the initial portion of the investigation to gain insight into the effect of spraying variables. Zirconia was found to be more easily sprayed than uranium dioxide, although calculations based on physical properties appear to indicate the opposite.² The properties and resulting calculations of maximum particle diameters are listed in Table V.

The density and deposition efficiency of uranium dioxide are affected by spray distance to a greater degree than for zirconia. This fact indicates that even though uranium dioxide may be easier to melt, because of its higher thermal diffusivity, the particles lose their heat much faster than do zirconia particles upon exit from the plasma.

b. Method of Manufacture

Three types of zirconia and two types of uranium dioxide plus recycled powder were sprayed to determine the best commercially available material. The types of zirconia were 1) fused and milled; 2) sintered and milled; 3) sintered, milled, and chemically treated. Uranium dioxide powders sprayed were 1) fused and milled; 2) sintered and milled; 3) recycled (oversprayed powder).

The results of this investigation are summarized in Table VI. Sintered powders deposited with the greatest efficiency but produced coatings of the lowest density. Fused powders produced the densest coatings but deposited with reduced efficiency. Improvements were noted in zirconia deposition efficiency when the sintered and milled powder had been chemically treated by the supplier because of the increased particle surface area. Recycled powder produced coatings with essentially the same density and deposition efficiency as the fused and milled powder.

c. Powder Size

Several sizes of uranium dioxide powders were sprayed to evaluate the effect of particle size on coating density and deposition efficiency: 1) -200,+325 mesh; 2) -200,+250 mesh; 3) -250,+325 mesh; 4) -270,+325 mesh; 5) -325 mesh (deslimed).

TABLE V
COMPARISON OF PROPERTIES OF ZIRCONIA AND URANIUM DIOXIDE

Material	Melting Point	Density, ρ , at 20°C	Specific Heat, C_p , at 20°C	Thermal Conductivity, k , at 20°C	Thermal Diffusivity, α^*	Thermal Expansion at 20°C	$d_{\max}$ **	Available Powder Quality
	(°C)	(gm/cm ³)	(cal/gm-°C)	(cgs)	(cm ² /sec)	(10 ⁻⁶ /°C)	(micron)	
Zirconia	2690	6.27	0.16	0.005	0.005	8.7	26	Good
Uranium dioxide	2880	10.96	0.075	0.020	0.025	10	58	Fair

* $\alpha = k/\rho C_p$.

** Calculated maximum particle diameter for reaching a center temperature of 0.9 melting point in 100 microseconds dwell time in the plasma jet (see reference 2).

TABLE VI

DENSITY AND DEPOSITION EFFICIENCY OF COATINGS SPRAYED FROM
VARIOUS TYPES OF ZIRCONIA AND URANIUM DIOXIDE POWDERS
(Traverse Rate = 70 in. /min)

Powder Type	Powder Size (mesh)	Power Input (kw)	Arc-Gas Flow (Argon) (cfm)	Plasma Enthalpy (kcal/ft ³)	Spray Distance (in.)	Powder Feed Rate (gm/min)	Cover-Gas Flow (Helium) (cfm)	Density (% theor.)	Deposition Efficiency (%)
<u>Zirconia</u>									
Fused and milled	-200,+325	18	0.68	255	5	25	None	81.0-82.6	31
Sintered and milled	-200,+325	18	0.68	255	5	25	None	79.0	49
Sintered, milled, and chemically treated	-200,+325	18	0.68	255	5	25	None	79.4	38
<u>Uranium Dioxide</u>									
Fused and milled	-200,+250	25.6*	1.42	230	3	22.5	6.67	80.2	22.5
Sintered and milled	-200,+250	27.2*	1.60	220	3	22.5	6.67	69.8-72.0	
	-200,+250	25.6*	1.46	230	3	28.4	6.67		44.3
Recycled**	-200,+250	23.2	1.17	240	3	22.5	6.67	82.2	20.6

* 40-kw torch configuration.

** Powder that was previously oversprayed and did not form part of a coating.

It must be pointed out that these were the size ranges placed in the powder hopper. The uranium dioxide powders broke down further in the feed system, so that finer particles actually were fed to the torch. The screen analyses for some uranium dioxide powders as fed to the torch are given in Table VII. The results of these investigations are given in Table VIII.

Good coating densities and deposition efficiencies can be obtained using any of the above particle-size ranges. Very little difference was noted when spraying any of the sizes falling within the -200,+325 mesh range. Sub-sieve powders (-325 mesh) required drastic changes in spraying conditions; much lower enthalpies (obtained by increased arc-gas flow) were necessary when spraying this material. The chamber atmosphere became very "foggy" when sub-sieve powders were sprayed, because of increased vaporization of the powders.

Narrow ranges of particle sizes appear best for plasma spraying, permitting conditions to be adjusted so that each particle is treated nearly the same. The choice of particle size may be dictated to some extent by economics, since very narrow size ranges increase the material costs considerably.

3. Variables Associated with Spraying Procedure

Several process variables are associated with the spraying procedure, including a) spray distance, b) traverse rate, c) powder feed rate, d) angle of torch to substrate, and e) use of cover gas.

a. Spray Distance

Density and deposition efficiency increase with decreasing spray distance, as illustrated in Figures 20 and 21. It can be seen that greater spray distances can be used for spraying zirconia than for spraying uranium dioxide; this finding can be accounted for by the differences in thermal diffusivity: $0.005 \text{ cm}^2/\text{sec}$ for zirconia, and $0.025 \text{ cm}^2/\text{sec}$ for uranium dioxide. The uranium dioxide loses heat rapidly upon leaving the plasma and must therefore be sprayed at closer distances.

Close spray distances result in higher thermal gradients within the coatings. Those made at 3 inches or less generally crack or lift off the substrate unless cover gas is used. Spraying distance must therefore be the closest possible without causing cracking or loss of coating adherence.

TABLE VII

SCREEN ANALYSIS OF VARIOUS TYPES AND SIZES OF
URANIUM DIOXIDE POWDER AS FED TO THE PLASMA TORCH

Powder Type	Screen Size Powder Placed in Hopper (mesh)	Powder Fed to Torch (wt. %)		
		<u>-200,+250</u>	<u>-250,+325</u>	<u>-325</u>
Sintered	95 wt. % -200,+250	71.5	25.1	3.4
Fused	95 wt. % -200,+250	53.0	44.5	2.5
Fused	95 wt. % -250,+325	-	91.0	9.0
Recycled	95 wt. % -200,+250	18.8	72.6	8.6

TABLE VIII

OPTIMUM CONDITIONS FOR SPRAYING VARIOUS PARTICLE-SIZE RANGES
OF URANIUM DIOXIDE POWDER
(Traverse Rate = 70 in. /min)

Powder Size (mesh)	Plasma [*] Enthalpy (kcal/ft ³)	Power [*] Input (kw)	Arc-Gas [*] Flow (Argon) (cfm)	Spray Distance (in.)	Powder Feed Rate (gm/min)	Cover- Gas Flow (cfm)	Cover- Gas Type	Best Coating Density (% theor.)	Best Deposition Efficiency (%)
-200,+325	255	25.5	1.26	4	60	-	-	88.7	-
	265	25.5	1.29	3	60	8	Argon	90.2	-
	250	23.2	0.99	4	30	-	-	-	45.4
	270	24.0	0.98	4	60	-	-	-	32.8
-200,+250	240	22.4	1.07	3	22.5	6.67	Helium	81.2	-
	255	22.4	0.96	3	22.5	6.67	Helium	-	31.6
-250,+325	235	23.2	1.22	3	22.5	6.67	Helium	80.3	-
	<250	<21.6	>0.96	3	22.5	6.67	Helium	-	30.2
-270,+325	225	24.75	1.42	4	30	-	-	88.1-91.6	-
	270	24	1.01	4	30	-	-	-	39.0
-325	<170	<27.0	>1.98	3	45	8	Argon	85.4	-
	<190	<26.2	>1.81	3	30	8	Argon	-	31.2

* Optimum plasma conditions.

LEGEND	POWDER TYPE	POWER INPUT (kw)	ARC-GAS FLOW (ARGON) (cfm)	POWDER FEED RATE (gm/min)	REMARKS
○	ZrO ₂	18.2	0.68	25	-
●	ZrO ₂	12.6	0.84	25	-
△	UO ₂	23-25	1.26	60	-
▲	UO ₂	24	1.29	60	8 cfm of argon cover gas used at 3-inch distance

POWDER SIZE: -200,+325 mesh
TRAVERSE RATE: 70 in./min

EFFECT OF SPRAY DISTANCE ON
COATING DENSITY

FIGURE 20

LEGEND	POWDER TYPE	POWER INPUT	ARC-GAS FLOW (ARGON)	POWDER FEED RATE	TRAVERSE RATE
		(kw)	(cfm)	(gm/min)	(in./min)
○	ZrO ₂	17.5	0.68	25	70
●	ZrO ₂	15	0.79	25	70
△	UO ₂	20-23	0.98	30	50

POWDER SIZE: -200,+325 mesh

EFFECT OF SPRAY DISTANCE ON
DEPOSITION EFFICIENCY

FIGURE 21

b. Traverse Rate

Traverse rate was found to have little effect on coating density or deposition efficiency in the ranges studied. Increasing the traverse rate aids in decreasing the thermal gradients in the coating, resulting in reduced cracking and improved adherence.

c. Powder Feed Rate

The rate of powder addition to the plasma had no effect on coating density. Deposition efficiency decreased and deposition rate increased with increasing powder feed rate, as shown in Figure 22; that is, at increased powder feed rates, deposition rates increased but the available heat melted a smaller percentage of the particles. Figure 23 illustrates the plasma enthalpy at constant arc-gas flow required to achieve specific deposition efficiencies for zirconia. It is obvious that enthalpies must be increased to compensate for increased powder feed rates. To achieve the most economical operation, a balance must be established between high deposition efficiencies and high deposition rates with increased amounts of recycled materials.

d. Powder-Gas Flow

Powder-gas flow was not extensively studied. This flow determines the velocity at which the powder particles enter the plasma. Excessive flow rates propel the powder through the plasma, causing it to exit at an improper angle. Very low flow rates will not carry the powder effectively and may not provide enough velocity to permit the particles to penetrate to the hot core of the plasma. Powder-gas flow rates just high enough to carry the uranium dioxide to the plasma torch resulted in the best spray patterns.

e. Angle of Torch to Substrate

The angle of the torch with the substrate could be decreased from 90 to 60 degrees before the density or deposition efficiency of zirconia was decreased; further decrease in angle resulted in drastic lowering of density and deposition efficiency. Torch angle may be important if geometries other than flat plates are sprayed.

f. Use of Cover Gas

Cover gas was used to lower the thermal gradient within the coating to prevent cracking and loss of adherence when close spray distances were used. Both argon and helium were studied as cover gases. Helium is superior to argon, having substantially higher specific heat and thermal conductivity.

EFFECT OF POWDER FEED RATE ON DEPOSITION EFFICIENCY AND RATE

FIGURE 22

EXPERIMENTAL PLASMA ENTHALPY REQUIRED TO
ACHIEVE SPECIFIC DEPOSITION EFFICIENCIES

FIGURE 23

Coating density and deposition efficiency were unaffected when argon was used as a cover gas; however, lifting of the coating occurred frequently. Cracking and lifting of coatings were generally avoided by use of a helium flow across the coating surface. Density and deposition efficiency were slightly lowered by use of the helium at the required high flow rates.

B. Effect of Process Variables on Coating Adherence

An integral bond between the uranium dioxide coating and the substrate is probably the most important technical advantage of a plasma-sprayed fuel element. Therefore, the adherence of the sprayed coatings is extremely important.

As discussed in the Experimental Procedures section, pages 21-23, the plug-in-plate type specimen was of no assistance in evaluating the adherence of uranium dioxide coatings to stainless steel and Zircaloy-2 coupons of fuel-element-cladding thickness. Bend and torsion tests were investigated, and the bend test was chosen as a basis for evaluating coating adherence.

Uranium dioxide adherence was studied as a function of 1) substrate surface preparation, and 2) spraying procedure.

1. Substrate Surface Preparation

Surface-preparation methods studied included a) gritblasting, b) chemical milling, and c) sprayed bond coatings.

a. Gritblasted Substrate Surfaces

Four blasting media (silicon carbide, iron, garnet, and sand) and two types of blasting equipment (suction and pressure) were used during this study; the surface finishes produced on stainless steel and Zircaloy-2 are listed in Table IX. Finer sizes of each media were also available but produced finer surface finishes.

Tensile adherence was studied for zirconia coatings, using the plug-in-plate samples. The results are shown graphically in Figure 24 as a function of the substrate surface finish. Surfaces were prepared by gritblasting with pressure equipment.

Surfaces of similar roughness for a given substrate metal showed slightly greater adherence when silicon carbide rather than steel grit was used as a blasting medium. Although stereoscopic examination revealed no noticeable differences in the depth, breadth or spacing of the craters caused by the impacts of the two grits, a higher degree of superimposed fine jagged edges was noted throughout the entire surface of specimens blasted with silicon carbide. This extensive secondary roughness would

TABLE IX

ROUGHNESS OF STAINLESS STEEL AND ZIRCALOY-2 SURFACES PRODUCED BY
GRITBLASTING WITH VARIOUS MEDIA AND BLASTING EQUIPMENT

Blasting Media	Surface Roughness (microinch)			
	Suction Blasting*		Pressure Blasting*	
	<u>Stainless Steel</u>	<u>Zircaloy-2</u>	<u>Stainless Steel</u>	<u>Zircaloy-2</u>
No. 16 Silicon carbide	200	225	400	500
No. 18 Iron	150	200	450	450
No. 16 Garnet	175	150	400	500
No. 16 Sand	100	100	175	300

* Blasting conditions: air pressure = 100 psi; blasting distance = 6 inches.

TENSILE ADHERENCE OF ZIRCONIA COATINGS TO ALUMINUM AND STAINLESS STEEL SUBSTRATES AS A FUNCTION OF SURFACE ROUGHNESS

FIGURE 24

appear to provide for a greater degree of mechanical adherence of the coating. This effect is probably due to the high friability of silicon carbide as compared to steel grit. Silicon carbide grit shatters upon impact, providing sharp angular secondary abrasions, as well as primary roughness due to the initial impact. Steel grit does not shatter and eventually becomes rounded if reused a number of times.

Adherence values were appreciably higher for aluminum substrates than for stainless steel substrates of similar roughness and prepared with the same type of grit. Examination of the blasted surfaces revealed that the only noticeable difference was the presence of a greater degree of the secondary roughness on the surface of the aluminum. The effect of any shattering of the grit would be expected to be larger with the aluminum due to its lower hardness. There is also a possibility of slight surface reaction between the zirconia and the aluminum substrate.

Stainless steel and Zircaloy-2 substrates 0.031 to 0.034 inch thick with uranium dioxide coatings 0.050 to 0.060 inch thick were bent around a 1-inch radius, and the deflection of the specimen was measured. Figure 25 shows four bend-tested coupons for uranium dioxide coatings 0.047 to 0.054 inch thick on 0.031-inch-thick stainless steel. It can be seen that the coatings deposited on surfaces blasted with iron, garnet, and silicon carbide cracked after bending but remained tightly adherent, whereas the coating lifted from the surface blasted with sand. Iron, garnet, and silicon carbide produced equivalent degrees of surface roughness (400 to 450 microinches), while sand produced a smoother surface (200 microinches). It is evident that good adherence results only when a gritblasted surface of greater than 200 microinches is used. Figure 26 shows a 0.050-inch-thick uranium dioxide coating on Zircaloy-2 as deposited, and after bending around a 1-inch radius.

b. Chemically Milled Substrate Surfaces

Chemical milling was investigated as a method of substrate surface preparation. Unlike gritblasting, this technique would not result in deformation of the specimen. The Kodak Photo-Etch Process was used. A light-sensitive emulsion was sprayed on the substrate surface, dried, and then exposed to a pattern, using a carbon-arc lamp. Following exposure, the emulsion was developed and the unexposed portion washed away. The substrate was then baked, leaving an acid-resistant coating over the areas that had been exposed to light.

No. 18
IRON

No. 16
GARNET

No. 16
SiC

No. 16
SAND

BLASTING MEDIA

Spraying Conditions

Powder Type:	Fused UO_2	Traverse Rate:	70 in./min
Powder Size:	-200, +250 mesh	Powder Feed Rate:	52 gm/min
Power Input:	25 kw	Powder-Gas Flow:	0.1 cfm (argon)
Arc-Gas Flow:	1.46 cfm (argon)	Cover-Gas Flow:	6.67 cfm (helium)
Spray Distance:	3 inches		

Substrate Thickness: 0.031 inch

Coating Thickness: 0.047-0.054 inch

BEND-TESTED COUPONS OF URANIUM DIOXIDE ON STAINLESS STEEL SUBSTRATES

FIGURE 25

- a. 0.050-inch-thick Uranium Dioxide Coating on
0.031-inch-thick Zircaloy-2 Substrate (Zircaloy
surface prepared by pressure-blasting with No. 16
silicon carbide)

- b. Above Coating after Bending around 1-inch
Radius (2-inch Deflection)

URANIUM DIOXIDE COATING ON ZIRCALLOY-2 SUBSTRATE
BEFORE AND AFTER BENDING

FIGURE 26

Throughout this program, specimens were exposed to grid patterns having 35 lines to the inch and allowing either the lines or the spaces between the lines to be etched. The most satisfactory etchants found were a 3:1 solution of H_2O and HCl (electrolytic etch) for stainless steel and a 9:1 solution of H_2O and HF for Zircaloy-2.

It was extremely difficult to obtain a consistent degree of protection over the entire surface of the specimens. In many cases, the protective emulsion was destroyed by the great amount of gas evolution during the etching procedure. For these reasons, chemical milling experiments were discontinued. It did not appear that the surfaces produced would have been as satisfactory as those prepared by gritblasting, since no undercutting for mechanical adherence was noted.

c. Sprayed Bond Coatings

Another method of preparing the surface involves the spraying of a bond coating on the substrate. Molybdenum, which has been successfully used in the preparation of steel shafts for metallizing, was plasma-sprayed on both stainless steel and Zircaloy-2 substrates. The spraying conditions are shown in Table X.

Molybdenum coatings sprayed on both Zircaloy-2 and stainless steel substrates (with no previous surface preparation) formed a strong metallurgical bond as illustrated in Figure 27. Initial gritblasting of the substrate surface greatly enhanced the bond by providing some mechanical adherence and an increased surface area for metallurgical bonding. When -150,+200 mesh molybdenum powder was sprayed, the roughness of the resulting surface was approximately equivalent to surfaces prepared by blasting No. 16 sand (200 microinches). Uranium dioxide coatings sprayed onto the molybdenum layers were fairly adherent, requiring 0.6 to 1.6 inches bend deflection around a 1-inch radius before any lifting was noted. Two tested coatings are shown in Figure 28.

The sprayed bond coating may therefore be used in lieu of gritblasting for preparing the substrates, but adherence is not as great as that to surfaces gritblasted by No. 16 silicon carbide. In fuel-element fabrication, columbium could possibly be substituted for molybdenum.

TABLE X

SPRAYING CONDITIONS FOR
MOLYBDENUM, STAINLESS STEEL, AND GRADATED COATINGS

Powder:	<u>Molybdenum</u>	<u>Stainless Steel</u>	<u>50 wt. % Molybdenum- 50 wt. % Uranium Dioxide</u>	<u>28 wt. % Stainless Steel- 72 wt. % Uranium Dioxide</u>
Powder size (mesh)	-150,+200	-150,+200	(Mo) -200,+325 (UO ₂)-200,+250	(SS) -150,+250 (UO ₂)-200,+250
Power input (kw)	19	11	21	21
Arc-gas flow (cfm argon)	0.96	1.17	1.07	1.07
Plasma enthalpy (kcal/ft ³)	215	115	230	230
Spray distance (in.)	3	3½	3	3
Traverse rate (in./min)	70	70	70	70
Powder feed rate (gm/min)	22.5	22.5	22.5	22.5
Powder-gas flow (cfm argon)	0.08	0.08	0.08	0.08
Cover-gas flow (cfm helium)	None	None	6.67	6.67

- a. Molybdenum Bond Layer on Unblasted Stainless Steel Substrate

250×

Etchant: Murakami's Reagent

- b. Molybdenum Bond Layer on Unblasted Zircaloy-2 Substrate

250× (NO ETCH)

MOLYBDENUM BOND LAYERS SPRAYED ON
STAINLESS STEEL AND ZIRCALOY-2 SUBSTRATES
(NO PREVIOUS SURFACE PREPARATION)

FIGURE 27

- a. 0.057-inch-thick Uranium Dioxide Coating on
Molybdenum Bond Layer, Stainless Steel Substrate
(Bend Deflection at Failure: 0.72 inch)

- b. 0.040-inch-thick Uranium Dioxide Coating on
Molybdenum Bond Layer, Zircaloy-2 Substrate
(Bend Deflection at Failure: 0.66 inch)

BEND-TESTED SAMPLES OF URANIUM DIOXIDE COATINGS
DEPOSITED ON SPRAYED MOLYBDENUM BOND LAYERS

FIGURE 28

Several coatings were sprayed with the following gradations:

1) Stainless steel or Zircaloy-2 substrate	Mo, Mo + UO_2 , and UO_2
2) Stainless steel or Zircaloy-2 substrate	Mo + UO_2 , and UO_2
3) Stainless steel substrate	Stainless steel, and stainless steel + UO_2
4) Stainless steel substrate	Stainless steel + UO_2 , and UO_2

The spraying conditions are given in Table X. The gradated coatings appear to be strong and adherent. Figure 29 shows the metallurgical bond between stainless steel coating and substrate, and gradated layers are shown in Figure 30. Bend-tested gradated coatings are shown in Figures 31 and 32.

Gradated coatings have been used quite successfully with rocket nozzles and may be superior to a simple coating when a thermal gradient is imposed across the coating.

2. Effect of Spraying Procedure on Residual Stresses and Coating Adherence

The procedure used during spraying has a great influence on coating adherence. A portion of the program was devoted to determining the relative amount of stress remaining in a sprayed composite.

Residual stresses in the sprayed composite are due to differences in thermal expansion between the coating and the substrate material. These stresses result in deformation of each component and impose a combination of shear and tensile stresses on the coating-substrate interface.

A study was made to determine the effect of various spraying conditions on the deflection of composites due to thermal stresses. Substrate and coating temperatures were measured by thermocouples welded to the substrate and positioned so that they were in the coating during spraying, as shown by Figure 33. Additional strips 1" x 12" x 0.031" thick were sprayed without thermocouples for comparison. Figures 34, 35, and 36 show the thermal histories of composites (stainless steel substrate, uranium dioxide coating) sprayed at traverse rates of 24, 48, and 71 in./min, respectively. Increasing the traverse rate decreases the coating and substrate temperatures (Figure 37), the degree of thermal cycles experienced by the composite, and the temperature differential between the coating and the substrate. Also, decreasing the spray distance increases the temperature during spraying (Figure 38).

250×

Etchant: Ferric Chloride Solution

STAINLESS STEEL LAYER DEPOSITED ON
STAINLESS STEEL SUBSTRATE

FIGURE 29

a. Molybdenum + Uranium Dioxide Gradated Layer on Zircaloy-2 Substrate

b. Stainless Steel + Uranium Dioxide Gradated Layer (separated from substrate during cutting and mounting)

GRADATED LAYERS OF MOLYBDENUM +
URANIUM DIOXIDE AND STAINLESS STEEL + URANIUM DIOXIDE

FIGURE 30

Gradated Coating: 0.008 in. Mo, 0.024 in. Mo + UO_2 ,
0.027 in. UO_2

Failure at UO_2 - Mo + UO_2 Interface

BEND TEST OF GRADATED COATING ON
UNBLASTED ZIRCALOY-2 SUBSTRATE

FIGURE 31

- a. Gradated Coating: 0.007 in. SS, 0.029 in.
SS + UO_2 , 0.023 in. UO_2

Bend Deflection at Failure: 0.65 in.
Failure at Substrate-SS Interface

- b. Gradated Coating: 0.024 in. SS + UO_2 ,
0.029 in. UO_2

Bend Deflection at Failure: 0.6 in.
Failure at Substrate- UO_2 + SS Interface

BEND TESTS OF GRADATED COATINGS ON
STAINLESS STEEL SUBSTRATES

FIGURE 32

SUBSTRATE INSTRUMENTED FOR DETERMINATION OF
TEMPERATURE DURING SPRAYING

FIGURE 33

THERMAL CYCLES DURING DEPOSITION OF
URANIUM DIOXIDE COATING ON STAINLESS STEEL SUBSTRATE
TRAVERSE RATE = 24 IN./MIN

FIGURE 34

THERMAL CYCLES DURING DEPOSITION OF
URANIUM DIOXIDE COATING ON STAINLESS STEEL SUBSTRATE
TRAVERSE RATE = 48 IN./MIN

FIGURE 35

THERMAL CYCLES DURING DEPOSITION OF
URANIUM DIOXIDE COATING ON STAINLESS STEEL SUBSTRATE
TRAVERSE RATE = 71 IN. /MIN

FIGURE 36

LEGEND		SPRAY DISTANCE (in.)	COVER-GAS FLOW (ARGON) (cfm)	POWDER TYPE:	
COATING	SUBSTRATE			POWDER SIZE:	Fused UO ₂
○	●	4	0	POWER INPUT:	-200,+325 mesh
▽	▼	3	0	ARC-GAS FLOW (ARGON):	25-26 kw
□	■	3	7	POWDER FEED RATE:	1.25 cfm
				POWDER-GAS FLOW (ARGON):	30 gm/min
					0.085 cfm

EFFECT OF TRAVERSE RATE ON
COATING AND SUBSTRATE TEMPERATURES DURING SPRAYING

FIGURE 37

LEGEND		COVER-GAS FLOW (ARGON) (cfm)	POWDER TYPE:	
COATING	SUBSTRATE		POWDER SIZE:	Fused UO ₂
○	●	0	POWER INPUT:	25-26 kw
△	▲	7	ARC-GAS FLOW (ARGON):	1.25 cfm
			TRAVERSE RATE:	71 in./min
			POWDER FEED RATE:	30 gm/min
			POWDER-GAS FLOW (ARCON):	0.085 cfm

EFFECT OF SPRAY DISTANCE ON COATING AND
SUBSTRATE TEMPERATURES DURING SPRAYING

FIGURE 38

Deflection of the coated specimens due to residual stresses was measured after they were sprayed and cooled to room temperature. Positive deflection was assigned to those composites in which the coating surface was convex, and negative deflection to concave surfaces (see Figure 39). Table XI summarizes the data obtained from this investigation.

Considerable scatter was noted in the data, making analysis extremely difficult. Deflection was influenced by coating thickness, number of passes, and small inconsistencies in spraying procedure. However, certain definite conclusions were reached:

a) To obtain adherent coatings with minimum distortion from residual stresses, coating temperature should be held below 870 C, while stainless steel substrate temperatures should be held below 450 C. Lower temperatures can result from increased traverse rate or spray distance, and from the use of cover gas to lower the thermal gradient in the coating.

b) The substrate must be annealed after the gritblasting and straightening operations. Initial studies were made on unannealed substrates, resulting in severe and extremely inconsistent deflection.

Several 0.020-inch-thick Zircaloy-2 substrates were also sprayed and the deflection measured. Deflections were smaller (-0.11 to -0.58 inch over a 12-inch span) than with the stainless steel, and adherence was good.

Several 2" x 12" stainless steel sheets were sprayed. When cover gas was not used, the composites were deformed in a wavy manner. Relatively flat samples were prepared by using a flow of helium cover gas to cool the coating.

Experience gained during this portion of the investigation indicates that power input, spray distance, traverse rate, and powder feed rate must be controlled to produce adherent coatings. High power levels, or low gas-flow rates, result in high-enthalpy plasmas. These plasmas transmit considerable heat to the coating and cause cracking or loss of adherence unless a cover gas is used. Close spraying distances also result in loss of adherence; however, a flow of cover gas reduces the thermal gradients. Adherent coatings were difficult to make at a 3-inch spray distance without cover gas. With cover gas, adherent coatings could be made consistently. Traverse rates below 70 in./min result in poor coating adherence. High traverse rates lower

a. Positive Deflection

b. Negative Deflection

TERMINOLOGY USED IN STUDY OF RESIDUAL STRESSES

FIGURE 39

TABLE XI

SUMMARY OF RESIDUAL-STRESS DATA
(See third page of table for spraying conditions)

Power Input (kw)	Arc-Gas Flow, (Argon) (cfm)	Plasma Enthalpy (kcal/ft ³)	Spray Distance (in.)	Traverse Rate (in./min)	Cover- Gas Flow (Argon) (cfm)	Coating Temp. (°C)		Substrate Temp. (°C)		Coating Thickness (mil)	Longitudinal Deflection (in.)	Relative Adherence
						Max.	Min.	Max.	Min.			
23-25	1.23	230	2.5	71	None	Thermocouple broken				6, 9, 24	+0.03, ^a +0.03, +0.03	Good
23.6	"	"	"	48	"	-	-	-	-	10	-0.43	Poor ^b
22	0.92	255	"	71	"	940	440	440	240	12, 11	+0.03, ^{a, b} -0.23	Poor ^b
"	"	"	"	48	"	-	-	-	-	10	-0.65	Poor ^b
25-26	1.24	230	3	71	"	915	515	520	350	19, 22	+0.03, ^a +0.10	Poor
25	"	"	"	"	"	-	-	-	-	21, 27	-0.30, -0.31 ^c	Good
"	1.21	255	"	48	"	-	-	-	-	19	+0.03 ^c	Poor
20-24	0.92	230-280	"	71	"	930	520	515	230	18, 38, 26	+0.04, ^a +0.02, 0 ^b	Poor
23	"	270	"	"	"	860	440	340	180	29	+0.05 ^a	Good

a. Instrumented specimen.

b. Poor spraying atmosphere, resulting in slight oxidation of the coating, contributed in part to poor adherence.

c. Deflection concentrated at one end of sample.

TABLE XI
(cont.)

Power Input (kw)	Arc-Gas Flow, (Argon) (cfm)	Plasma Enthalpy (kcal/ft ³)	Spray Distance (in.)	Traverse Rate (in./min)	Cover- Gas Flow (Argon) (cfm)	Coating Temp. (°C)		Substrate Temp. (°C)		Coating Thickness (mil)	Longitudinal Deflection (in.)	Relative Adherence
						Max.	Min.	Max.	Min.			
23-24	0.92	270-280	3	36	None	1060	420	670	300	21, 21	-0.15, +0.03	Poor
26	1.24	260	4	71	"	850	525	490	370	31, 21	-0.05, ^a +0.05	Good
"	"	"	"	48	"	850	390	470	250	29, 32	+0.18, ^a +0.05	Good
"	"	"	"	24	"	1260	440	780	290	24, 24	-0.40, ^a -0.33	Poor
22-23	0.95	260-265	"	"	"	860	240	435	130	33, 28, 21	+0.03, ^a -0.21, -0.37	Good
24	0.96	275	"	"	"	-	-	-	-	10	-0.43	Poor
24-25	1.26	240-245	2.5	71	7	940	260	450	205	49, 13	+0.05, ^a -0.47	Good
"	"	"	"	48	"	1040	250	530	185	16, 18, 19	-0.16, -0.60, -0.45 ^a	Good to Poor
22-25	1.00	250-280	"	71	"	830	180	400	185	32, 35	-0.20, ^a +0.08	Fair
24-25	"	270-280	"	48	"	1100	230	480	220	19, 30	-0.52, ^a 0	Fair

a. Instrumented specimen.

TABLE XI
(concl.)

Power Input	Arc-Gas Flow (Argon)	Plasma Enthalpy	Spray Distance	Traverse Rate	Cover- Gas Flow (Argon)	Coating Temp. (°C)		Substrate Temp. (°C)		Coating Thickness	Longitudinal Deflection	Relative Adherence
(kw)	(cfm)	(kcal/ft ³)	(in.)	(in./min)	(cfm)	Max.	Min.	Max.	Min.	(mil)	(in.)	
25	1.26	245	3	71	7	700	300	350	165	16, 16	+0.29, ^a -0.02	Good
"	"	"	"	48	"	960	330	465	210	34, 31, 39	+0.25, ^a -0.12, +0.06	Good
"	"	"	"	24	"	885	300	535	230	43, 41	-0.17, ^a -0.57	Poor
22-24	0.96	255-280	"	71	"	640	320	410	250	31, 32	+0.15, +0.22 ^a	Good
22-25	0.95	255-290	"	48	"	630	220	345	165	45, 23, 10, 40	+0.11, ^a -0.16, -0.21, +0.04	Good
23-24	"	265-275	"	24	"	770	230	470	140	110, 54	-0.63, ^a -0.07	Good to Fair

Constant Spraying Condition

Powder Type: Fused UO₂ Powder-Gas Flow: 0.085 cfm (argon)
 Powder Size: -200, +325 mesh Substrate: 0.031-in.-thick stainless steel
 Powder Feed Rate: 30 gm/min

a. Instrumented specimen.

thermal gradients in the coating, and thus the stresses imposed on the interface. At powder feed rates of 30 gm/min or less, a fairly diffused deposition pattern exists. At 55 to 60 gm/min, a fairly hot area occasionally exists in the center of the pattern. In addition, more heat is carried to the coating by the greater mass of material. In general, more adherent coatings could be produced at the lower powder feed rates.

C. Chemical Composition of Uranium Dioxide Coatings

Several uranium dioxide coatings were analyzed to determine the oxygen-to-uranium ratio. The results of these analyses, given in Table XII, indicate that with proper preparation of the spraying atmosphere the stoichiometry of uranium dioxide can be maintained.

TABLE XII
OXYGEN-TO-URANIUM RATIO OF AS-RECEIVED POWDER AND
COATINGS SPRAYED UNDER VARIOUS ATMOSPHERES

Spraying Atmosphere	Color	O/U Ratio	
		Gravimetric	Volumetric
As-received powder*	Dark brown	1.95	
Air	Light green	2.34	
		2.42	
Argon - slight contamination with air	Light-green tint	2.05	
		2.08	
Argon - double purge	Brown	1.93	
		1.98	2.009
		1.98	2.075
		1.98	
		2.00	
		2.00	
		2.01	2.014
		2.05	2.009

* Arc-fused and ground uranium dioxide.

SPRAYING OF SIMULATED FUEL PLATES

Several simulated plates of the configuration and dimensions shown in Figure 40 were sprayed, using a combination of spraying conditions that would provide the best coating density and adherence. It had been determined, as a result of the work discussed in the preceding section, that the following spraying conditions would give the desired results:

Fuel	Fused or recycled UO_2 powder
Powder size	-200,+325 or -200,+250 mesh
Power input	22 to 23 kw
Arc-gas flow (argon)	Varying (from 1.27 to 1.50 cfm)
Spray distance	3 in.
Traverse rate	70 in./min
Powder feed rate	22.5 gm/min
Powder-gas flow (argon)	0.07 cfm
Cover-gas flow (helium)	6.67 cfm

Selection of the above conditions was checked by spraying 0.040-inch-thick Zircaloy-2 substrates to determine coating density and 0.125-inch-thick mild steel substrates to determine deposition efficiency. Results are shown in Table XIII. Densities and deposition efficiencies were lowered by use of the helium cover gas.

During the spraying of the initial fuel-plate mockups, it was noted that the cladding buckled transverse to the long axis (as shown by Figure 41). The coating width that could be deposited with no transverse buckling was then determined for various sheet thicknesses of Zircaloy-2. Figure 42 illustrates the results. It can be seen that cladding thicknesses of 0.035 inch or better must be used if fuel elements of reasonable width (~2 inches) are to be fabricated by plasma spraying. Longitudinal deflection was not a problem.

Stainless steel (0.031 inch thick) buckled transversely when a 1.75-inch-wide coating was applied. Since the thickness of a stainless steel plate that could be sprayed with no buckling would probably be prohibitive for reactor applications, most of the simulated-plate spraying was conducted on Zircaloy-2.

IDENTIFICATION NO.	DIMENSIONS (in.)						ANGLE θ (degrees)
	A	B	C	D	E	F	
I	12	2	11-1/2	1-1/2	0.020	0.040	90
II	11-3/4	1-1/2	11-1/4	1	0.035	0.050	90
III	11-3/4	2	11-1/4	1-1/2	0.040	0.050	75
IV	11-1/2	2-1/2	11	2	0.040	0.050	75
V	6	2	5-1/2	1-1/2	0.035	0.050	90
VI	6	2	5-1/2	1-1/2	0.040	0.050	75
VII	6	2-1/2	5-1/2	2	0.040	0.050	75

DIMENSIONS OF SIMULATED FUEL PLATES

FIGURE 40

TABLE XIII
DENSITY AND DEPOSITION EFFICIENCY AT CONDITIONS USED
TO SPRAY SIMULATED FUEL PLATES

Powder Type	Powder Size (mesh)	Power Input (kw)	Arc-Gas Flow (Argon) (cfm)	Coating Density (% theor.)	Deposition Efficiency (%)
Recycled UO_2	-200,+250	22.8	1.38	82.0	-
			1.46	83.1	-
			1.27	78.4	-
Fused UO_2	-200,+325	22.8	1.42	{ 85.7, 85.2, 83.3, 84.6	20.0, 23.8
			1.50	-	13.5
			1.34	-	24.6

ILLUSTRATION OF TRANSVERSE BUCKLING
DURING SPRAYING OF SIMULATED FUEL-PLATE MOCKUP

FIGURE 41

POWDER TYPE:	Recycled UO ₂
POWDER SIZE:	-200,+250 mesh
POWER INPUT:	22.8 kw
ARC-GAS FLOW (ARGON):	1.3-1.38 cfm
SPRAY DISTANCE:	3 in.
TRAVERSE RATE:	70 in./min
POWDER FEED RATE:	22.5 gm/min
POWDER-GAS FLOW (ARGON):	0.075 cfm
COVER-GAS FLOW (HELIUM):	6.67 cfm

EFFECT OF THE THICKNESS OF ANNEALED ZIRCALOY-2 CLADDING
ON THE WIDTH OF COATING THAT CAN BE DEPOSITED
WITHOUT TRANSVERSE BUCKLING

FIGURE 42

Several fuel-plate mockups were then prepared, using 0.040-inch-thick Zircaloy-2 cladding and 0.050-inch-thick Zircaloy-2 frames, as shown in Figure 43. The tendency of coatings deposited on flat surfaces to lift along the edges and at the corners was prevented by dovetailing the frame joints. The fuel plates were fabricated as follows:

- 1) Gritblast Zircaloy-2 sheet, straighten, anneal for 1 hour at 800 C, and shear.
- 2) Cut the Zircaloy-2 frames to size and weld at the corners.
- 3) Etch the frames.
- 4) Braze the frames to the cladding (vacuum-furnace-braze at 900 C, using 78 wt. % Ag-22 wt. % Cu alloy).
- 5) Spray uranium dioxide to a thickness of 0.050 inch.

A section through such a plate, showing the bond area between the Zircaloy-2 and the UO_2 , is presented in Figure 44. This photomicrograph also illustrates the factors that influence coating density: 1) interlayer cracking, 2) interlayer porosity, 3) trans-layer cracking, and 4) porosity within layers.

When the fuel plates were fabricated as indicated above, no lifting of the coatings was noted; however, in some cases, three types of cracking were observed, as shown in Figure 45:

- 1) Edge cracking, probably caused by overheating of the frame at the edge of the coating.
- 2) Thermal cracking, caused by a high thermal gradient during a deposition pass. Occasional transient conditions sometimes cause a "hot spot" on the deposition pattern, followed by a crack.
- 3) Checking on thermal cracking, caused by general overheating of the coating.

The conditions that led to these types of coating failure were generally associated with poor cooling, excessive arc power, excessive powder feed rates, or impingement of the plasma flame on the coating surface. These conditions resulted in localized or general overheating of the specimen, which caused the types of cracking noted above. By proper control of spraying conditions, cracking was avoided.

The results of these studies indicate that fabricating plate-type fuel elements by spray-coating techniques is feasible. The sequence of steps involved in fabricating a fuel element by plasma spraying would include:

a. Edge Cracking

b. Thermal Cracking

c. Flaking

FIGURE 1
TYPES OF CRACKING OBSERVED ON
SPRAY-DRIED FUEL PLATE

FIGURE 1

TRANSVERSE SECTION

POROSITY WITHIN
LAYERS

INTERLAYER
CORROSION

LAYER

LAYER

INTERLAYER
CORROSION

THE TRANSVERSE SECTION
COATING POROSITY - 30% OF THEORETICAL
Note: The coating of the large void areas was removed
by "pickling" during polishing.

SECTION OF GRAPHITE LINING COATING ON SINGAPORE-2 SUBSTRATE
ILLUSTRATING FACTORS THAT INFLUENCE COATING DENSITY

FIGURE 4

11/10/60

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- 1) Gritblast Zircaloy-2 sheet, masking off the areas where the frames are bonded to the cladding.
- 2) Straighten the sheet, shear or slit to size, and vacuum-anneal.
- 3) Prepare the frames by welding at the corners, milling the bevel, and milling the closure-weld preparation.
- 4) Diffusion- or eutectic-bond the frame to the clad.
- 5) Spray the uranium dioxide into the recess and inspect.
- 6) Tungsten-arc-weld two mated sprayed plates together.

CONCLUSIONS

Results of the investigation to date indicate that uranium dioxide coatings of 88 to 90% theoretical density can be produced by plasma-jet techniques under a given set of conditions. However, it appears more practical to fabricate fuel plates under conditions that produce coatings of 86% theoretical density. When conditions are altered to produce 88 to 90% dense coatings over a large area, adherence is poor, overheating and buckling of the substrate become a major problem, and severe cracking of the coating results. It must be pointed out that the 86% density refers to the fuel density of the entire cavity within the fuel element, as contrasted with pellet density.

Several factors limit the density of plasma-sprayed uranium dioxide coatings, as illustrated by Figure 44. These are: 1) porosity within the deposited layers; 2) porosity between the layers and at the coating-substrate interface; 3) interlayer cracking or delamination; 4) translayer cracking.

Porosity within the layers is caused by incomplete melting and fusing of a percentage of the powder particles. This can be reduced only by allowing longer dwell times in the plasma for complete melting, followed by transfer of the particles to the coating before substantial freezing of the molten particles takes place. Uranium dioxide loses considerable heat during the transfer time, thus requiring high particle velocities and close spray distances.

A great deal of porosity occurs between the layers and may be due to rapid quenching of the particles as they strike the cooler material of the previous layer. However, if the particles in the spray pattern were well fused, they would spread out upon impact and reduce this interlayer porosity. Examination of the particles at varying radial distance from the center of the plasma indicates a much smaller percentage of particle melting as the radial distance increases. These particles would deposit just ahead of and following the deposition of the "hotter" particles in the center of the spray beam. Thus, less dense coatings might be deposited on the surfaces of the layers. Attempts to spray thick single-layer zirconia coatings were unsuccessful, since all were non-adherent. However, single-layer coatings were extremely dense (90% theoretical or better), with cracking being the major factor in lowering bulk density.

Some degree of porosity occurs at the interface between the coating and the substrate because of rapid quenching of the particles by the cold substrate. To some extent, this interfacial porosity may also be attributed to the "colder" particles surrounding the hot central core of the spray beam. Close spray distance alleviates this problem somewhat. Poor coating quality at the metal-ceramic interface can lead to both low density and poor adherence.

Cracking also contributes to lowering of the density. Interlayer cracking is caused by thermal stresses built up during deposition of each new layer. This type of cracking may be reduced by eliminating the continuous network of interlayer porosity. Translayer cracking occurs across the layers normal to the substrate surface. These cracks indicate tensile stresses in the coating and are possibly due to shrinkage in the coating as the fused particles freeze.

The same factors that contribute to the porosity also affect the deposition efficiency. Good density and deposition efficiency require a high degree of fusion of all the particles fed into the plasma. Such fusion can be obtained by proper adjustment of spraying conditions to provide: 1) adequate plasma temperature and heat content; 2) adequate dwell time for the particles in the hot core of the plasma to allow time for complete fusion; 3) transfer of the molten particles to the substrate rapidly enough or across a minimum distance to prevent their cooling to too low a temperature before being deposited. The best spraying conditions as determined by this investigation are summarized in Table XIV.

It was difficult to reproduce conditions with current equipment. Slight variations in torch geometry due to electrode wear or change of electrodes resulted in changes in spraying conditions. However, with improved control of parameters, better reproducibility may be possible. Slight variations had little effect on zirconia coating density but had significant effects on uranium dioxide coating density.

Adherence of a ceramic coating to a metal substrate is by mechanical means.³ Hence, an adequate anchor must be provided for the coating. The best surface preparation found during this investigation was gritblasting. Although coating adherence was directly

3. "Basic Studies of Particle-Impact Processes for Applying Ceramic and Cermet Coatings," National Bureau of Standards, Progress Report No. 4, WADC Contract No.. AF(33-616) 58-19, April 1, 1959 to June 30, 1959, AD 219 844.

TABLE XIV

BEST SPRAYING CONDITIONS DETERMINED FOR
URANIUM DIOXIDE COATING DENSITY, DEPOSITION, ADHERENCE, AND COMPOSITION
(Plasmadyne SG-1 Spray System)

	For Coating Density	For Deposition Efficiency	For Deposition Rate	For Adherence	For Composition
Power input (kw)	25	25	25	*	-
Arc-gas flow (argon)(cfm)	1.3	1.0	1.0	1.3	-
Plasma enthalpy (kcal/ft ³)	240	280	280	-	-
Spray distance (in.)	3	4	4	3	-
Traverse rate (in./min)	-	50-70	50-70	>70	-
Powder type	Fused or recycled	Sintered	Sintered	-	-
Powder size (mesh)	-200,+325	-200,+325	-200,+325	-	-
Powder feed rate (gm/min)	**	<10	>60	<60	-
Powder-gas flow (argon)(cfm)	0.08	0.08	0.08	-	-
Cover-gas flow (helium)(cfm)	6.67	None	None	6.67	-
Spraying atmosphere	Argon	Argon	Argon	Argon	Argon
Substrate type	-	-	-	Zircaloy-2	-
Substrate condition	-	-	-	Annealed	-
Surface preparation	-	-	-	Gritblasting	-
Surface finish (microinches)	-	-	-	>400	-
Substrate temperature (°C)	-	-	-	<450 [†]	-
Coating temperature (°C)	-	-	-	<870 [†]	-

* High power levels result in lower adherence and cracking of the coating.

** Did not affect coating density.

† Peak temperatures.

proportional to the roughness of the surface, the coating adherence obtained on Zircaloy-2 substrates was probably aided by good matching of thermal-expansion coefficients.

Spraying procedure also affects coating adherence. If the substrate or the deposited coating is heated excessively during spraying, adherence will be poor. These requirements place limitations on spray distance, power input, and traverse rate. Effective temperature control is accomplished by a flow of cover gas over the coating to remove heat and reduce the thermal gradient. This procedure generally results in a limit on the density of the coating. For uranium dioxide, this limit is in the range of 86 to 88% theoretical at conditions required for spraying fuel-element-cladding thicknesses of Zircaloy-2.

The oxygen-to-uranium ratio can be controlled by proper preparation of the spraying atmosphere. Coatings having the same O/U ratios as the powder fed into the system were made.

Several simulated fuel plates were sprayed to demonstrate the feasibility of fabrication by spray-coating techniques. It was determined that the Zircaloy-2 cladding thickness must increase as the fuel width is increased to prevent buckling of the cladding during spraying. For a fuel width of 2 inches, the cladding must be 0.035 inch thick. Transverse buckling of 0.031-inch-thick stainless steel was severe, indicating that an excessive thickness of stainless steel would be required in fabricating a fuel plate of reasonable width.

RECOMMENDATIONS

Results of this investigation indicate that uranium dioxide fuel plates having fuel densities of 86% theoretical, good adherence, and an O/U ratio equivalent to that of the powder being sprayed can be obtained by spray-coating techniques. However, improvements must be made in both equipment and techniques in order to permit fabrication of fuel plates on an economically competitive basis with current fuel-element designs. This investigation has laid the groundwork for a continuing effort to make such improvements.

At the current stage of development, the next logical step is to determine the behavior of sprayed plates under irradiation. This phase of the program would determine the ability of the coatings to withstand thermal gradients similar to those experienced in a reactor. In-pile tests will permit evaluation of the stability of the oxide coating and fission gas release, and allow a value to be placed on the burnup expected from elements fabricated with sprayed uranium dioxide.

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