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LARGE RADIOISOTOPE HEAT SOURCE
CAPSULE PROGRAM
Topical Report No. 3
Ceramic Coating Process Development
and Evaluations

AEC Research and Development Report

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION

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LARGE RADIOISOTOPE HEAT SOURCE
CAPSULE PROGRAM
Topical Report No. 3
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By
A. K. SMALLEY

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ABSTRACT

A particular large radioisotope heat source capsule design requires a stand-off coating between the T-111* structural vessel and the Pt-10Rh oxidation-resistant cladding to prevent reaction of the two alloys for five years at 2000°F. Requirements for the coating are a dense, stable, adherent diffusion barrier. Application of the coating must not affect the T-111 substrate.

Al₂O₃ coatings from 0.5 to about 3 mils thick have been deposited on T-111 test specimens measuring 0.37" in diameter and 1" long by a chemical vapor deposition (CVD) process. The reaction employed was:

Coating temperatures ranged from 1750°F to 2200°F; the best coatings were deposited at 1950°F.

X-ray diffraction analyses show the coatings to consist predominantly (approximately 90 percent) of well-crystallized α -Al₂O₃. Metallographic examinations show the Al₂O₃ to be dense and adherent to the T-111 substrate. Microhardness indentations made in the T-111 immediately adjacent to the Al₂O₃ suggest some superficial contamination by a hardening impurity. The hardened zone usually extended only 4 or 5 mils into the substrate. Bulk chemical analyses show that all specimens were contaminated slightly with C, N₂ and H₂ during processing. The measured levels of these impurities are considered acceptable. The feasibility of applying high-quality coatings of α -Al₂O₃ to T-111 alloy has been demonstrated.

A 0.5 mil flash of tungsten, applied by CVD to the T-111 prior to coating with Al₂O₃, was not shown conclusively to prevent hardening of the T-111 during Al₂O₃ deposition. Bulk chemical analyses showed that the W-flash substrates contained approximately the same level of interstitial atoms as those specimens without the W-flash.

* Nominally Ta-8.5 W - 2.5 Hf

A few experiments to apply Al_2O_3 coatings by arc plasma spraying (APS) and sputtering did not produce coatings to meet the postulated requirements. Adherent coatings of Al_2O_3 were applied to a 1200°F T-111 substrate in an inert gas with minimal substrate contamination. The coatings were only about 20% alpha Al_2O_3 and contained some cracks. The sputtered coatings were very thin layers of amorphous Al_2O_3 .

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I. INTRODUCTION

Atomix International is developing the technology for construction of refractory-metal fuel capsules capable of operating at 2000°F for five years or more on the AEC's Large Radioisotope Heat Source (LRHS) Program.

The reference design for the LRHS capsule is shown in Figure 1. Described briefly, it consists of a series of liners which contain the fuel and a central plenum where helium accumulates. The principal structural member is a thick-walled envelope of T-111**. Its dimensions are about 1.65 inch in diameter by 7 inches long. In order to protect the T-111 from oxidation during postulated prelaunch, abort and post-reentry air exposure, it is enclosed within a Pt-10Rh shell. During a typical life-cycle of 5 to 7 years, the capsule would experience a surface temperature of 2000°F in a space vacuum.

Compatibility studies at AI⁽¹⁾ have shown that Pt reacts readily with Ta-10W at 1800°F. It is entirely reasonable to assume, then, that Pt-10Rh will react with T-111 at 2000°F. Means must be sought to prevent reaction, which could lead to the degradation of both the structural member and the oxidation-resistant cladding.

The approach to this problem was to interpose a diffusion barrier of Al_2O_3 between the T-111 pressure vessel and the Pt-10Rh sheath. Since the extent of vapor transport or surface diffusion was not known, a simple stand-off could not be considered; a continuous barrier was needed. This report describes the preliminary process development for coating the T-111 member with Al_2O_3 by chemical vapor deposition (CVD).*

Evaluation of two alternate processes - arc plasma spraying and sputtering - are described in the Appendix.

* Original Data are Contained in AI Laboratory Notebook No. B-360551.

** Nominally 8.5 w/o W, 2.5 w/o Hf balance Ta.

ISOTOPE FUEL CAPSULE

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Figure 1. LRHS Capsule Conceptual Design

II. MATERIAL AND PROCESS SELECTION

A. METAL STRUCTURES

T-111 was selected for the structural capsule material on the basis of its high-temperature strength and ductility. The oxidation resistance of Pt-10Rh and a melting point somewhat higher than that of Pt, coupled with only a modest Rh requirement, dictated the selection of Pt-10Rh.

B. DIFFUSION BARRIER

The selection of a diffusion barrier between T-111 and Pt-10Rh with a life of 5 to 7 years is not easy. The literature for materials that at 2000 to 2500°F have exhibited a negligible rate of reaction with both tantalum alloys and Pt-10Rh indicated that many of the pure single refractory oxides seem to meet this criterion. This is borne out by thermodynamic data, which indicate tantalum should be stable in the presence of the other oxides shown in Figure 2. However, the stability of refractories in contact with different materials cannot be predicted with accuracy because the amount of reaction depends upon physical factors as well as thermodynamic properties. The chief danger in using thermodynamic calculations to predict whether two substances may react lies in the possibility that some reaction may occur other than the reactions for which the calculations have been performed. A pertinent example is the reaction between Ta and Al_2O_3 . According to Figure 2, no reaction should take place between these two materials because the standard free energy of reaction, ΔG , has a large negative value at any temperature up to the melting point of Al_2O_3 . However, if Ta and Al_2O_3 are heated together in vacuo, they do react because of the formation of gaseous suboxides of aluminum.

This reaction has been described by Kohl⁽²⁾, who demonstrated in 1959 that Al_2O_3 will be reduced by Ta when heated in vacuo at temperatures of the order of 1800°F. Navias⁽³⁾ earlier showed that such a reaction takes place in the gaseous phase, beginning at 2900°F, even when Ta and Al_2O_3 are not in

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Figure 2. Free Energy of Formation of Refractory Oxides

contact with each other. Additional confirmation is found in the literature. Degussa⁽⁴⁾ literature reports that pure Al_2O_3 is not resistant to Ta above 2200°F in high vacuum. Resistance can be attained for a limited time in a reducing or inert gas up to about 2900°F. Kieffer⁽⁵⁾, reporting on the stability of furnace heating elements and construction oxides, gives ultimate temperatures for Ta that appear much too high in the light of the previous references (see Table 1).

TABLE 1
STABILITY OF TA HEATING ELEMENTS IN THE
PRESENCE OF OXIDES⁽⁴⁾

Oxide	Ta Stability Range (°F)
Al_2O_3	Up to 3450
BeO	Up to 2900
MgO	Up to 3270
ZrO_2	Up to 2900
ThO_2	Up to 3450

Although an incompatibility between Al_2O_3 and Ta in vacuum is well documented, stability is expected under the LRHS operating conditions. The space between the Al_2O_3 coating and the Pt-10Rh oxidation barrier will be backfilled with helium at the time of the final closure weld. The helium overpressure should effectively retard the volatilization of aluminum oxides. Moreover, the Al_2O_3 - T-111 interface temperature is not expected to exceed 2000°F during the capsule operating lifetime.

While a reaction similar to the one between Al_2O_3 and Ta has been reported for Al_2O_3 and W⁽⁶⁾, it can be assumed to take place at higher temperature, as it was not reported under the conditions investigated by Navias⁽³⁾. Therefore, it is possible that the compatibility of Al_2O_3 with T-111 will be somewhat better than with pure Ta.

No chemical compatibility problems are expected between Al_2O_3 and the Pt-10Rh. Al_2O_3 is the standard core material for Pt-wound furnaces and for Pt Pt-10Rh thermocouple wire insulation and protection tubing, both used at higher temperatures than anticipated in the reference LRHS capsule. Also, the higher-melting pure refractory oxides are customarily used for melting Pt and Pt-rich alloys⁽⁷⁾.

Aside from compatibility, another consideration for the selection of a diffusion barrier material is that of coefficient of thermal expansion. As can be seen in Table 2, T-111 has a lower coefficient of thermal expansion than any of the pure ceramic oxides. This is advantageous, unless the mismatch becomes too great, because it tends to keep the ceramic coating under compression at temperatures above the application temperature. For a CVD coating applied at 1800-2200°F, the coating is in tension at room temperature but essentially stress free at the 2000°F operating temperature.

TABLE 2
THERMAL COEFFICIENTS OF
EXPANSION

Material	Temperature (°F)	Expansion (in/in/°F x 10 ⁶)
T-111	80 to 2000	3.9
Al_2O_3	80 to 2192	5.0
BeO	80 to 2000	5.0
Y_2O_3	80 to 2000	5.2
ThO_2	80 to 2192	5.7
HfO_2	80 to 2000	6.0
ZrO_2	80 to 2192	6.0
CaO	80 to 2192	7.6
MgO	80 to 2192	8.2

The coefficient of expansion of Al_2O_3 matches that of Ta best, followed by BeO, Y_2O_3 and ThO_2 . ZrO_2 and HfO_2 have equal thermal expansion coefficients, but both are subject to a transformation in crystal structure from monoclinic to tetragonal. ZrO_2 transforms at 1830°F with an accompanying volume decrease of 9.7%. HfO_2 transforms at a much higher temperature, between 3090° and 3270°F, with a 3.4% volume contraction. While ZrO_2 would have to be stabilized for use as a coating, use of pure HfO_2 appears feasible.

Some of the pure refractory oxides display other shortcomings. For example, CaO and the otherwise interesting MgO hydrate easily. Experience indicates that only oxides which do not tend to form suboxides are compatible with Ta. This would limit the choice of alternates essentially to HfO_2 , BeO, MgO, and Y_2O_3 . UO_2 and ZrO_2 have a tendency toward nonstoichiometry.

A dense impervious diffusion barrier is preferred to a porous one. The reason is that surface diffusion and vapor phase transport of volatilized components of the T-111 on one side and of the Pt-10Rh on the other are to be avoided. The vapor pressure of the most volatile component element at 2000°F of the elements involved (W, Ta, Hf, Al, Pt and Rh), namely Rh and Pt, can be extrapolated⁽⁸⁾ to be 10^{-9} torr for Rh and 7×10^{-11} for Pt. If this value is inserted in the Langmuir equation, and assuming that 1/10 of the surface of the Pt-10Rh is Rh and the remainder Pt, sublimation losses in ten years should amount to 0.0016 gm/cm^2 for Rh and 0.00044 gm/cm^2 for Pt. These, of course, are the maximum losses in perfect vacuum. In a He atmosphere, they would be considerably lower. Little is known about the vapor pressure of Hf. The boiling point is reported to be 9750°F⁽⁹⁾, making it one of the highest boiling elements. Using a vapor-pressure equation quoted in Reference 2, $\log p = 30,200/T - 9.46$, a vapor pressure of about 10^{-12} torr is calculated at 2000°F. A measurable sublimation of Hf may occur, but it is not regarded as serious. Surface diffusion rates along cracks in the coating cannot be

estimated. Either these rates must be determined experimentally or a crack-free coating specified.

From the above discussion, the best suited material for the diffusion barrier is Al_2O_3 . Its only disadvantage is that it may react with Ta in vacuum at the temperatures of interest. Since the atmosphere over the Al_2O_3 - Ta interface will be helium, there should be no incompatibility. To verify this and the reaction in vacuum, compatibility tests are being performed as a separate part of the LRHSC Program.

C. THE COATING PROCESS

Having selected Al_2O_3 as the candidate diffusion barrier material, certain desirable or even necessary characteristics of the coating may then be detailed. These will govern the selection of the coating process:

- 1) It should be predominantly α - Al_2O_3 .
- 2) It should be at least 99.95 percent pure Al_2O_3 .
- 3) The coating thickness should be controllable and uniform in the range of 1 to 3 mils.
- 4) Ideally, the coating will be impermeable, and not contain cracks or pin holes.
- 5) The coating process must not introduce appreciable contamination into the T-111 substrate.
- 6) The surface finish of the coatings should be as smooth as possible to aid assembly of the Pt-10Rh sleeve and to provide a maximum area for contact heat transfer.

Al_2O_3 coatings applied by various physical, chemical, or electrochemical means can be highly variable in their atomic structures. At one extreme, they may be amorphous. This form has been observed in Al_2O_3 coatings applied by a sputtering process⁽¹⁰⁾. At the other extreme is the dense, thermally stable hcp α - Al_2O_3 . Intervening are a series of metastable phases known as the

transition aluminas⁽¹¹⁾. These all have densities considerably lower than that of α - Al_2O_3 , and all can be transformed to α by heating them at 1600°F and upwards. A number of these were predominant in the vapor-deposited Al_2O_3 described by Dragoo and Diamond⁽¹²⁾. In another recent work, Ellis⁽¹³⁾ reported transparent, theoretically dense α - Al_2O_3 obtained by a chemical vapor deposition process.

The consequences of applying an amorphous or metastable Al_2O_3 diffusion barrier to an LRHS capsule are readily foreseen. At capsule operating temperature, a metastable Al_2O_3 would transform to α - Al_2O_3 , and would experience an appreciable volume decrease. This would put the coating in a stress state approaching pure tension. This, of course, is intolerable for a ceramic. Consequently, one of the criteria for selecting an Al_2O_3 coating process is that it yield a coating consisting wholly or predominantly of α - Al_2O_3 .

The coating purity requirement requires little discussion. Although Al_2O_3 is believed to be non-reactive with the capsule alloys, it must not contain impurities which might react.

The coating thickness should be small, so as not to constitute a significant thermal barrier. It also should be smooth and uniform to facilitate fit-up with the Pt-10Rh oxidation barrier. The coating should be of theoretical density and flaw-free to prevent vapor-phase transport of alloying atoms from one component to the other, and to prevent surface diffusion through coating cracks. Experience has shown, however, that perfect coatings on extended surfaces are virtually impossible to achieve and retain.

Finally, the coating process must not be such as to inherently contaminate the T-111. Appreciable amounts of embrittling impurities would be wholly intolerable, since the capsule must survive earth impact without rupturing at the end of its mission. Levels of interstitial atom contaminants generally considered by metallurgists to be acceptable are:⁽¹⁴⁾

O_2	150 ppm
C	50-60 ppm
N_2	85-95 ppm
H_2	Approximately 10 ppm

Various coating processes were considered in the light of these criteria. Of the state-of-the-art processes, chemical vapor deposition (CVD) and arc plasma spraying (APS) appeared to conform most nearly with the process selection criteria. Sputtering appeared as potentially the best method, but it is currently suitable only for thin films on simple geometry substrates.

APS coatings have never been made completely non-porous and no record of depositing an $\alpha-Al_2O_3$ coating by this process could be found. Further, during coating of actual fueled capsules, the substrate surface will be of the order of 1200°F. This would require the use of a high purity inert gas during coating to prevent substrate contamination.

CVD coatings are generally of very high density and one vendor expressed confidence that $\alpha-Al_2O_3$ coatings could be deposited. As Ellis⁽¹³⁾ stated, rather plaintively, "Although conceptually simple, the deposition of materials by this technique is in reality an extremely complex process. It requires an understanding of gas flow patterns, velocities and warm-up times, decomposition mechanisms and kinetics, accommodation coefficients and surface and bulk diffusion in the product. By specifying the deposition temperature, system pressure and deposition rate, starting materials and geometry, one can, however, fully characterize materials produced by this technique." The primary concern with the CVD process was contamination of the T-111 substrate by the reactive gases used to form the Al_2O_3 coating at 1750 to 2200°F.

Since the choice between CVD and APS processes was not clear cut but the CVD coating was potentially superior, chemical vapor deposition was selected as the reference process. As a back-up, a small effort to evaluate the arc plasma spraying process was also undertaken; this effort is described in the Appendix.

III. CHEMICAL VAPOR DEPOSITION OF Al_2O_3 ON T-111

A. INTRODUCTION

Atomics International has a well-developed capability for chemical vapor deposition of a wide variety of metals. Al_2O_3 has also been applied to a metallic substrate by vapor deposition⁽¹⁵⁾, as shown in Figure 3. However, our Al_2O_3 experience is not recent, and the equipment has been disassembled. It was therefore deemed economic to seek the services of a vendor skilled in the CVD art, with equipment and processes in being, and preferably one with a good working knowledge of tantalum alloys.

These qualifications were considered to be embodied in San Fernando Laboratories* (SFL), a Division of Fansteel Metallurgical Corporation. Negotiations for SFL to conduct preliminary coating development studies on tab-size T-111 specimens were concluded. Technical control of this program was retained by Atomics International; test specimens were coated in small lots; coating and substrate evaluations were performed by AI, and feedback of this data to SFL governed the manner in which subsequent lots were coated. Certain details of the equipment design and the processing parameters are proprietary, and cannot be disclosed to the public without the consent of SFL.

B. DESCRIPTION OF THE CVD PROCESS

The literature describing the numerous CVD processes is voluminous. A useful review is provided by S. D. Brown, et. al.⁽¹⁶⁾ of the Rocketdyne Division of North American Rockwell Corporation. A more detailed treatment is contained in the classic text of Powell⁽¹⁷⁾ and associates at Battelle Memorial Institute.

A given coating material usually may be applied by several different reactions. The equipment may take a variety of forms. Heat and flows may be generated and managed by assorted techniques. It is not the purpose of this

* 10258 Norris Avenue, Pacoima, California

Met Photo 5454-1-1

500 X

Etchant: None

Figure 3. Al₂O₃ Applied by CVD to Hastelloy N at
Atomics International

report to discuss these topics, but to describe the reaction and process employed in this phase of the LRHSC Program.

The reaction selected for these experiments was:

Chemically pure (99.5%) AlCl_3 was used. The hydrogen and the carrier gas, argon, were standard laboratory grades. The oxidant, air, was usually ambient laboratory air.

The laboratory equipment was approximately as shown in the schematic in Figure 4. A typical operating sequence consists of the following steps:

- 1) Pump down and backfill with argon several times.
- 2) Heat specimen in flowing argon to coating temperature (1750 to 2200°F) and soak for at least 10 minutes.
- 3) Start AlCl_3 heater.
- 4) Introduce hydrogen.
- 5) Introduce air.
- 6) Deposit Al_2O_3 on rotating substrate at the rate of about 1 mil per hour.
- 7) Valve off air and hydrogen in that order, and shut down AlCl_3 heater.
- 8) Cool specimen in argon.

During this sequence, the pressure in the reactor vessel is maintained at 30 torr absolute or less.

C. SUBSTRATE MATERIAL

All of the specimens employed in this program were taken from a single bar of T-111 alloy. The bar was nominally 3/8 inch in diameter and 60 inches long. Its chemical content is shown in Table 3.

A sample of the T-111 was examined metallographically, and its microstructure is shown in Figure 5.

Figure 4. Schematic of CVD Apparatus

TABLE 3
CHEMICAL ANALYSIS OF AS-RECEIVED T-111
USED FOR COATING EXPERIMENTS

Element	Amount	Units
W	8.3	w/o
Hf	2.12	w/o
Fe	100	ppm
Si	200	ppm
Zr	200	ppm
O ₂	35	ppm
N ₂	~1	ppm
H ₂	~1	ppm
C	< 50	ppm
Ta	Balance	-

Met Photo 7985-1-2 500 X
Figure 5. Microstructure of As-Received T-111, Etched
by Swabbing with a solution of 20 cc HNO₃ and 10 cc HF.

The ASTM grain size of the sample was about #9, using Chart E 112. This is equivalent to about 5μ average grain diameter. Hardness measurements, using a Tukon tester, showed it to be about Rockwell C 30.

Although this material was quite pure chemically, it contained a fair number of microscopic inclusions, shown clearly in Figure 5. Attempts to identify them with the electron beam microanalyzer were completely unsuccessful. The precipitates, considerably smaller than the electron spot, failed to indicate a composition different from that of the bulk material.

A somewhat similar structure was described by Bourgette⁽¹⁸⁾ in a recent review article. T-111 was oxidized under controlled conditions, and a microstructure quite similar to that shown in Figure 5 developed. However, the specimens that were described contained from 165 to 420 ppm of oxygen. The precipitates were described as coherent hafnium oxide.

For ease in mounting in the coating equipment, bullet-shaped specimens were machined from the T-111 rod. The rounded ends were hemispherical, as will be the ends of the LRHS capsules. The flat ends were drilled and tapped to accept 304 stainless steel mandrels. The specimens were given a light sand-blast, to a finish of about 50μ -inch RMS and then were individually identified by vibro-engraving on the flat ends. In the ready-to-coat condition, the specimens were about 0.373 inch in diameter and 1 inch long. This is approximately 0.22 of the size of a LRHS capsule. Typically, the specimens weighed 25.5 grams. The coating samples and mandrels are shown in Figure 6.

D. SPECIMEN EVALUATIONS

The experimental evaluations of the Al_2O_3 coatings and the coating-substrate systems were planned before the coating experiments were begun. These evaluations were both destructive and nondestructive, so all tests could not be performed on each specimen.

Figure 6. T-111 Coating Samples and Stainless Steel Mandrels

The nondestructive tests were:

- 1) Weighing and measuring,
- 2) X-ray diffraction analysis,
- 3) Surface finish measurement,
- 4) Dye penetrant testing.

Micrometer measurement of the diameters of coated specimens is a rapid but rather crude means of measuring coating thickness. It has the advantage of permitting measurement of coating thickness uniformity from place to place on a specimen, but the accuracy of the method can be severely affected by surface protuberances.

The crystallographic composition of the coatings was measured by an X-ray diffraction technique. Their surface finish was measured routinely with an electromechanical profilometer.

A requirement that a CVD coating be flaw-free probably is unrealistic. Therefore, some semi-quantitative means of detecting the presence of flaws is required. Dye penetration testing was employed for each coated specimen. In this test, a specimen is immersed in a special dye for a period of time. It is removed, and its exterior is cleaned of the dye. Then it is treated with a special developer which draws dye from cracks and pores. Also, the developer spreads the dye, which serves to magnify the imperfection. Since the dye is visible and contrasts in color with the developer, the treated specimen can be photographed at various angles. Thus, a permanent, semi-quantitative record of the degree of coating imperfection becomes available.

A number of destructive tests were also planned to characterize the CVD coatings and the coating T-111 systems. Usually, specimens for destructive analysis were sectioned according to the accompanying sketch. (See following page). Metallographic techniques were employed extensively to estimate the

density, thickness, and uniformity of the Al_2O_3 coatings; to examine the Al_2O_3 - T-111 interfaces for evidence of interaction, separation, and the like; and to observe metallurgical changes within the T-111 as a result of processing. Also, microhardness indentations were made in the substrate in an attempt to establish that the T-111 had not become contaminated with hardening (embrittling) impurities during the processing. The indentations were made with a Tukon tester; the results were converted to Rockwell units, using a Tukon conversion chart. Bulk chemical analyses of stripped specimens were also performed to learn the degree to which the T-111 had gained O_2 , N_2 , H_2 , and C during coating deposition.

Finally, selected specimens were thermally cycled in a vacuum to simulate a portion of the LRHS capsule life cycle. Effects of cycling on the Al_2O_3 coating were sought by visual observation, weighing, dye penetration testing, and metallographic examination.

E. EXPLORATORY EXPERIMENTS

In general, the processing parameters by which the initial set of specimens were to be coated were left to the discretion of the CVD vendor, San Fernando Laboratories. The only constraints were that they not be ground or abraded,

that they at no time be heated hotter than 2200°F, and that extreme precautions were to be taken to prevent substrate and coating contamination during processing.

The specimens to be coated by CVD were designated C-1 through C-15. The processing parameters for the initial series of four specimens are shown in Table 4. The terms "standard," "dilute," and later "very dilute" were devised to protect the proprietary process of San Fernando Laboratories.

TABLE 4
INITIAL CVD COATING PARAMETERS

Specimen No.	Deposition Temperature* (°F)	Reactant Concentration**	Oxidant
C-1	2200	Standard	Wet Air
C-2	1950	Dilute	Room Air
C-3	1750	Standard	Room Air
C-4	1750	Dilute	Room Air

* Coating time for all samples was 60 minutes.

The appearances of the coated specimens C-1 through C-4 are shown in Figure 7. These were rather completely evaluated before additional coating runs were made at SFL. Selection of coating parameters for subsequent specimens were governed largely by these evaluations.

Figure 7. T-111 Samples Coated with 1 to 2 Mils of Al₂O₃

The property considered to be one of the more important is the crystallographic content of the coatings. Consequently, X-ray diffraction was usually the first test to be run on the coated specimens. The X-ray diffraction traces of specimens C-1 through C-4 showed no species other than Ta and $\alpha\text{-Al}_2\text{O}_3$. This probably indicates that if lower crystalline species of Al_2O_3 were present, their amounts would be no greater than 10 percent. However, an appreciable amount of amorphous Al_2O_3 probably could go undetected by this technique. The X-ray diffraction trace for specimen C-1, showing the spacings and relative intensities of the Ta and $\alpha\text{-Al}_2\text{O}_3$ peaks, is given in Figure 8.

The coating thicknesses of specimens C-1 through C-4, as measured by micrometer (pre- and post-coating), ranged from about 0.0006 to about 0.002 inch, as shown in Table 5. The surface finishes of the specimens after coating were somewhat rougher than the 50 μ -inch bare metal finish. However, the roughening was not considered severe. Bulk chemical analyses of the T-111 substrates for interstitial impurities, also shown in Table 5, indicated that C-2 and C-3 had gained substantial oxygen. When and how these specimens became contaminated is not known. With these exceptions, all of the first four specimens escaped processing contamination to a very remarkable degree.

TABLE 5
POST-COATING EVALUATIONS OF SPECIMENS C-1 THRU C-4

Specimen Number	Coating Thickness in. (1)	Surface Finish μ -in.	Chemical Analyses, ppm ⁽²⁾			
			O ₂	N ₂	H ₂	C
C-1	0.002	120	19	2	11	57
C-2	0.002	90	297	3	12	50
C-3	0.0006	60	190	7	9	57
C-4	0.0007	70	20	1	13	56

(1) By micrometer measurement.

(2) As compared with the as-received T-111 analyses of O₂ 35, N₂ ~1, H₂ ~1, and C <50 ppm.

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Figure 8. X-Ray Diffraction Trace for Specimen C-1.

Further evaluations showed that of the first four specimens coated, only C-4 gave a dye penetration indication of a small crack. The other specimens showed a small amount of surface porosity, as typified by the indication on C-3 in Figure 9.

Metallographically polished sections of specimens C-2 and C-3 are shown in Figure 10. No unusual features were observed in the photomicrographs. The Al_2O_3 coatings appear to be dense and of columnar grain structure. No grain boundary phases, separations, nor appreciable coating porosity were seen.

The nature of the Al_2O_3 - T-111 interface was further studied by making microhardness indentations in the T-111 in the immediate vicinity of the interface, and then progressively farther away from the interface. The Tukon indenter marks and the calculated hardness values are pictured and tabulated, respectively, in Figure 11. In all four specimens, the area immediately adjacent to the interface was substantially harder than the as-received T-111 (approximately $R_c 30$). However, as the indentations were made progressively more distant from the interface, the hardnesses dropped, usually within 4 or 5 mils, to approach that of the as-received material. Specimen C-2, the one most heavily contaminated with O_2 , had a substantially thicker hard layer than the other three specimens. Hardening was attributed to interstitial impurities superficially contaminating the specimen surfaces at the inception of the coating deposition. This is hardly surprising, since the Ta-alloy specimens were heated at up to 2200°F and then exposed to air, one of the CVD reactants. It seems, however, that the Al_2O_3 deposit almost immediately masked the surface from further incursions of O_2 and N_2 .

Still further examinations of the T-111 substrate, using etch solutions, revealed in each specimen an outer annular zone which had apparently been depleted of grain boundary precipitates. These annuli ranged in thickness from about 20 mils in specimen C-4, as shown in Figure 12, to about 40 mils in

7-05-245-31

Figure 9. Dye Penetration
Testing of Specimen C-3

Figure 10. Metallographic Sections of Al_2O_3 CVD Coatings on T-111 7-05-245-33

SPECIMEN NUMBER	HARDNESS R_c
C-1	52, 53, 36, 32, 38, 32, 30
C-2	56, 54, 58, 56, 58, 53, 50, 53, 43, 43, 42, 41, 39, 32
C-3	56, 42, 36, 31, 32, 26, 27
C-4	49, 31, 31, 27, 26, 26, 23

Note: The Hardness Values on the Left were Made in the Immediate Vicinity of the Al_2O_3 - T-111 Interface. Subsequent Values were Measured at Increments of 2 Mil Inward from the Interface

7-05-245-32

Figure 11. Microhardness Measurements of T-111 Substrates.

Met Photo 8015-4-1

75 X

Figure 12. Annular Zone in T-111 Specimen C-4 After
CVD of Al_2O_3 Coating

specimen C-2. Extensive attempts were made metallographically and with the electron beam microanalyzer again to identify the precipitates, or at least to distinguish between the compositions of the precipitate-containing and the depleted zones. These attempts were unsuccessful. Also, consultations with non-ferrous metallurgists have not led to a credible hypothesis for the development of the precipitate-free annulus.

At this point, the planned evaluations of the specimens coated in the initial CVD experiment were complete. Based on the information developed with specimens C-1 through C-4, these conclusions were formulated:

- 1) CVD is a feasible process for coating T-111 with $\alpha\text{-Al}_2\text{O}_3$.
- 2) The ranges of processing parameters selected for the initial experiment seem to have bracketed the optimum processing conditions.
- 3) Coatings of the required thickness can be deposited during an acceptably short period.
- 4) The CVD process is compatible with the purity requirement imposed by the structural shell.

Attention was then directed to verifying these conclusions and to optimizing the CVD parameters.

F. VERIFICATION, OPTIMIZATION, REPRODUCIBILITY EXPERIMENTS

After technical consultation with representatives of San Fernando Laboratories, a second CVD experiment was planned. This involved specimens C-6 through C-10*. The set of coating parameters is shown in Table 6. All coating runs at SFL were successful, and the coated parts were returned to AI for evaluations. These consisted of a battery of tests similar to those given to specimens C-1 through C-4. The tests and their results are shown in Table 7.

* Specimen C-5 was damaged during checkout and calibration of the equipment, and was not considered suited for evaluation.

TABLE 6
COATING PARAMETERS SELECTED FOR SAMPLES
C-6 THRU C-10

Specimen Number	Deposition	Reactant Concentration	Oxidant
	Temperature (°F)		
C-6	1900	Standard	Room Air
C-7	1900	Standard	Room Air
C-8	1900	Standard	Room Air
C-9	1950	Very Dilute	Room Air
C-10	1950	Very Dilute	Room Air

NOTE: "Very Dilute" = "Dilute" x 0.25

TABLE 7

EVALUATIONS OF CVD Al_2O_3 COATINGS C-6 THROUGH C-10
on T-111

Specimen Number	Coating Thick- ness, in. (1)	Surface Finish,	Dye Pene- tration Results	X-Ray Diffrac- tion, Principal Al_2O_3 Phase	T-111 Hard- ness Rc(2)	T-111 Bulk Chemical Analyses, ppm			
						O_2	N_2	H_2	C
C-6	0.0038	120	Crack	-	-	-	-	-	-
C-7	0.0029	70	OK	α	46	41	9	6	104
C-8	Variable	50	OK	-	-	-	-	-	-
C-9	0.0015	130	OK	-	57	45	15	8	197
C-10	0.0025	160	OK	α	-	-	-	-	-
C-8TC ⁽³⁾	Variable	80	Fine Cracks	α	-	35	3	3	66
C-10TC ⁽³⁾	0.0025	180	Fine Cracks	α	-	20	1	2	56

(1) By micrometer measurement

(2) In immediate vicinity of the Al_2O_3 coating. The hardness of the as-received T-111 and also of the bulk material after coating was about Rc 30.

(3) Specimens C-8 and C-10 were cycled from room temperature to 2000°F to room temperature in 4 hours in a 10^{-6} torr vacuum. Each was cycled 10 times. They then were designated C-8 TC and C-10 TC.

The coating thicknesses of these specimens ranged from about 1.5 to about 4 mils. Usually, the coating thickness variation within a single specimen was of the order of ± 0.0003 inches of the nominal, reported value. One specimen, C-8, had a variable coating thickness, as indicated by micrometer reading. It was tapered a few mils from one end to the other. The reason for this is not known. All had acceptable surface finishes, ranging from 50 to 160 μ -inch RMS. Dye penetration testing showed the coating of C-6 to contain a longitudinal crack. All of the others exhibited a small amount of superficial porosity, similar to that seen in the previous experiment. X-ray diffraction traces were made on two specimens, representing the two coating conditions employed in this experiment. α - Al_2O_3 was the only Al_2O_3 phase detected in both C-7 and C-10.

Metallographic examinations were made on specimens C-7 and C-9. The Al_2O_3 coating and T-111 substrate structures, shown in Figure 13 were similar in all respects to those of specimens C-2 and C-3, shown in Figure 10. Microhardness indentations of the substrate showed hard layers in the immediate vicinity of the coatings of both specimens, as seen previously. The hardness a few mils away from the interface, however, was approximately that of the feed material.

Bulk chemical analyses of specimens C-7 and C-9, after removal of the coatings, showed a substantial pickup of carbon. The level may be sufficiently high to be metallurgically damaging. Concern is felt, since the source was not apparent. The O_2 , N_2 and H_2 levels of both specimens were satisfactorily low.

Specimens C-8 and C-10 were thermally cycled to study the tendency of the coatings to crack or spall as a result of this treatment. The specimens, in a 10^{-6} torr vacuum, were heated from room temperature to 2000°F and then cooled to room temperature in a 4-hour period. Each specimen was given 10 of these cycles. Coating damage was not visually apparent. Profilometer traces showed a possible superficial surface roughening after thermal cycling.

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Figure 13. Bright Field Photomicrographs of Specimens
C-7 and C-9

According to X-ray diffraction, α - Al_2O_3 was the only non-metallic phase present. Dye penetration testing of the specimens after cycling showed the coatings to contain some very fine cracks. However, the Al_2O_3 showed no tendency to spall from the specimens. The significance and consequences of these micro-cracks remain to be investigated. Metallographic examinations of the cycled specimens showed their structures to be quite similar to those of as-coated parts. As shown in Figures 14 and 15, there is no evidence of coating-substrate separation.

From the standpoint of coating thickness control and uniformity, specimens C-9 and C-10 were somewhat superior to specimens C-6, C-7 and C-8. They were also esthetically superior. On these bases, a reference CVD process, that used to coat C-9 and C-10, was selected. The reference coating temperature was $1950 \pm 25^\circ\text{F}$, and the oxidant was room air. The reference reagent concentration was "very dilute."

The reproducibility of the reference coating process was then investigated. Specimens C-11 through C-15 were each coated in a separate run under nominally identical conditions by SFL. They were given the same evaluations as the earlier C series specimens, with the results shown in Table 8.

The coating thickness of C-11 was variable, similar to that of C-8. The thicknesses of the other coatings ranged from 0.0007 to 0.0020-inch, which is considered satisfactory reproducibility at this stage of the process development. The surface finishes of specimens C-12 through C-15 ranged from 80 to 125 μ -inch RMS, also considered satisfactory. Specimen C-11, whose coating thickness was variable, had a finish of 250 μ -inch RMS. None of the five specimens showed cracks or gross porosity in the dye penetration test, and α - Al_2O_3 was the only crystalline structure detected by X-ray diffraction. Microhardness indentations on polished sections of C-11 and C-12 indicated that the hard layer observed in earlier specimens had not developed. The hardnesses of the T-111 adjacent to the Al_2O_3 coating was approximately the same as that of the feed stock.

Figure 14. Specimen C-8
After Thermal Cycling.

Met Photo 8134-1-3

250 X

Figure 15. Specimen C-10
After Thermal Cycling.

Met Photo 8134-2-3

250 X

TABLE 8
EVALUATIONS OF CVD Al_2O_3 COATINGS C-11 THRU C-15 ON T-111

Specimen Number	Coating Thickness in. ⁽¹⁾	Surface Finish μ - in.	Dye Pene- tration Results	X-Ray Diffrac- tion, Principal Al_2O_3 Phase	T-111 Hardness, R_c ⁽²⁾	T-111 Bulk Chemical Analyses, ppm			
						O_2	N_2	H_2	C
C-11	Variable	250	OK	α	27	30	51	16	150
C-12	0.0020	125	OK	α	36	53, 31	20, 76	7, 5	135, 150 ⁽³⁾
C-13	0.0014	100	OK	α	-	-	-	-	-
C-14	0.0014	90	OK	α	-	-	-	-	-
C-15	0.0007	80	OK	α	-	-	-	-	-

(1) By micrometer measurement

(2) In immediate vicinity of the Al_2O_3 coating. The hardness of the as-received T-111 and also of the bulk material after coating was about R_c 30.

(3) Specimen C-12 was sectioned longitudinally. One portion was further sectioned transversely, and bulk chemical analyses were made on the nose portion and the cylindrical portion. The first numbers in the table are the analyses of the nose portion.

Bulk chemical analyses also were run on specimens C-11 and C-12. Specimen C-11 was sectioned transversely, as has been the usual practice, and the analyses were made on the nose portion of the bullet-shaped specimen. Specimen C-12 was sectioned longitudinally, and one portion was further sectioned transversely. Analyses were made on the latter two pieces, one from the nose portion and the other from the cylindrical portion of the specimen. The purpose was to compare the compositions of substrate samples taken at two places within the specimen and to learn whether selective, geometry-controlled contamination was occurring. The results of the analyses, shown in Table 8, show apparent differences in the O_2 and N_2 contents of the two portions of specimen C-12. However, these variations are not considered significant. Both C-12 samples and also C-11 showed about the same level of carbon as C-7 and C-9, a substantial increase over that of the feed stock.

Specimens C-13 and C-14 were thermally cycled 10 times under the same conditions that were employed in the C-8 and C-10 tests (RT to 2000°F to RT in 4 hours, 10^{-6} torr). Visual examination gave no evidence of any effects in the coatings, and profilometer traces showed that no surface roughening had resulted from thermal cycling. Moreover, dye penetration testing did not yield any indication of coating damage, as contrasted with the dye penetration test results for specimens C-8 and C-10 after thermal cycling. The coatings of specimens C-13 and C-14 were considerably thinner than that of specimen C-10 (the C-8 coating thickness was variable). A thin coating probably would be more resistant to thermal cycle damage than a thick coating.

Specimen C-15 was retained as an archive.

At this point, the scheduled CVD coating experiments and the planned evaluations of the coated specimens were completed. The preliminary coating development program may be summarized in these three points:

- 1) The CVD process feasibility was demonstrated with specimens C-1 through C-4.

2) Specimens C-6 through C-10 were employed effectively to narrow the ranges of the processing variables.

3) Adequate CVD process reproducibility was demonstrated with specimens C-11 through C-15.

G. TUNGSTEN STOP-OFF COATING EXPERIMENT

Concern was felt early in the program that a CVD process which involves admitting air to a tantalum alloy at $\sim 2000^{\circ}\text{F}$ would result in massive contamination of the alloy. Consequently, it was suggested that a tungsten stop-off coating, or W flash, might effectively retard this potential contamination during application of the Al_2O_3 coating. Experiments were made to investigate the validity of the premise.

T-111 specimens identical to the C series specimens were coated at AI with about 0.5 mil of tungsten by CVD. These specimens then became known as the W series. Bulk chemical analyses of one of the W flash specimens indicated that it had picked up considerable carbon of unknown origin during the W deposition. Following the W flash, seven specimens were coated with 1 to 2 mils of Al_2O_3 by the reference CVD process, and were analysed in a manner similar to the examinations of the C series. These data appear in Table 9.

Neither bulk chemical analyses nor hardness measurements showed conclusively that the W flash was effective in preventing embrittling contamination.

Some of the W series specimens differed from the C series in several important ways. For example, specimens W-5, W-6 and W-7 consisted predominantly of $\theta\text{-Al}_2\text{O}_3$, while others in the series consisted predominantly of $\alpha\text{-Al}_2\text{O}_3$. The reason for this is not known. Metallographic examinations of specimens W-4 and W-5 showed evidence of separation between the W flash and the T-111 substrate. This was not evident, however, in specimen W-1, which was etched to enhance the contrast between the T-111 and the tungsten layer, as shown in Figure 16. The Al_2O_3 coatings on all of the W series specimens appeared normal in metallographic examinations.

TABLE 9
TUNGSTEN STOP-OFF COATING EXPERIMENTS

Specimen Number	Coating Thickness in. ⁽¹⁾	Surface Finish μ -in.	Dye Pene- tration Results	X-Ray Diffrac- tion, Principal Al_2O_3 Phase	T-111 Hardness R_c ⁽²⁾	T-111 Bulk Chemical Analyses, ppm			
						O_2	N_2	H_2	C
W-1	0.0018	100	-	α	27	50	20	10	86
W-2	0.0036	100	-	α	-	-	-	-	-
W-3	W Flash coat only		-	-	-	37	5	13	393
W-4	0.0025	190	OK	α	53	54	18	11	54
W-5	0.0025	160	OK	θ	35	20	4	8	60
W-6	0.0022	110	OK	θ	-	-	-	-	-
W-7	0.0017	170	OK	θ	-	-	-	-	-
W-8	0.0028	210	OK	α	-	-	-	-	-

(1) By micrometer measurement

(2) In immediate vicinity of the Al_2O_3 coating. The hardness of the as-received T-111 and also of the bulk material after coating was about R_c 30.

Figure 16. A tungsten Stop-off Coating
Interposed Between a T-111 Substrate and
a CVD Al_2O_3 Coating

Specimen W-7 was thermally cycled, using the same sequence that was employed for the C series tests. During this treatment a portion of the Al_2O_3 coating spalled off. This provided an opportunity to analyze the Al_2O_3 , which was done by emission spectrography. The results are shown in Table 10.

TABLE 10
CHEMICAL ANALYSIS OF CVD Al_2O_3 WHICH SPALLED
FROM SPECIMEN W-7

<u>Element</u>	<u>Amount, ppm</u>
Ag	3
B	1
Ba	25
Be	1
Ca	500
Cd	1
Co	10
Cr	25
Cu	3
Fe	300
Mg	10
Mn	5
Mo	100
Ni	50
Pb	5
Si	250
Ti	250
W	1000

When the coating flaked from the substrate, it apparently took a good portion of the W flash with it. Concern is felt for the levels of Ca, Fe, Mo, Si and Ti.

The aggregate of these is 1300 ppm, or 0.13 percent. The coating vendor has been consulted on the probable sources of these contaminants, and means are being sought to eliminate them.

IV. CONCLUSIONS

This program has led to the firm conclusion that dense, adherent coatings of $\alpha\text{-Al}_2\text{O}_3$ can be applied to T-111 alloy substrates by chemical vapor deposition. The coating properties did not seem especially sensitive to the processing variables, within the limits of this investigation. The reproducibility of the process is considered adequate for a process in an early stage of development. The coating thickness was subject to some variation. However, this is expected to become more controllable as the process is further developed.

Most of the specimens were not significantly contaminated during the coating deposition. In a few cases, however, the levels of carbon and O_2 in the T-111 substrates were unacceptably high. The reasons for this have not been identified with certainty. It is thought that the equipment and/or technique could have been faulty during an individual coating run. This, of course, would be remedied as the process is refined. We have no reason to believe that substrate contamination is inherent in the CVD process.

The purity of the only Al_2O_3 coating which was analysed was considered marginal-to-unacceptable. This also is expected to yield to process development and refinement.

Potential difficulties associated with scaling up the equipment to coat full-size LRHS capsules remain to be explored.

The effectiveness of a thin tungsten stop-off layer for preventing oxidation of the T-111 prior to deposition of the Al_2O_3 was not clearly demonstrated. In fact, the CVD tungsten coating is probably deleterious for this application.

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REFERENCES

1. Radioisotope Heat Source Internal Research and Development Program, Material Research, AI-65-190, Volume 3, J. R. Miller and S. J. Veeck, January 1967, Confidential-Defense Information.
2. W. H. Kohl, Materials and Techniques for Electron Tubes, Reinhold Publishing Corporation (1960), pp 107-109.
3. L. Navias, "Comparison Between Al_2O_3 -Ta and Al_2O_3 -W Reactions above 1600°C in a Vacuum," Bull. Am. Cer. Soc. 38, pp 256-259 (May 1954).
4. Degussa Inc., "Degussit Oxide Ceramics," p 21 (1965).
5. R. Kieffer and F. Benesovsky, "Metallic Heating Element Materials for High Temperature Furnaces," Metallurgica, 58, pp 119-124 (1958).
6. A. W. Searcy, "Chemistry at High Temperatures," in Ceramics in Aerospace Technology, Ed. J. Hove, pp 45-46 (1966).
7. M. A. Schwartz, Crucible Handbook, ORNL-1354 (1953).
8. R. E. Honig, "Vapor Pressure Curves of Elements," Radio Corporation of America.
9. K. Rankama and T. C. Suhunna, "Geochemistry," p 38, Chicago University Press (1950).
10. Large Radioisotope Heat Source Capsule Program, First Quarterly Progress Report, July - September 1967, NAA-SR-12578, (October 30, 1967).
11. J. W. Newsome, et al, Alumina Properties, Technical Paper No. 10 (2nd Revision), Aluminum Company of America, Pittsburgh, Pa. (1960).
12. A. L. Dragoo and J. J. Diamond, "Transitions in Vapor-Deposited Alumina from 300° to 1200°C, J. Am. Cer. Soc., 50, No. 11, pp 568-574 (November 1967).

13. R. C. Ellis, "An Investigation for Fabricating and Evaluating the Properties of Chemically Vapor Deposited Alumina and Magnesia," AMRA-CR-67-08, Raytheon Company Research Division, Waltham, Mass. (April 1967).
14. P. B. Ferry, Atomics International, personal communication.
15. K. Langrod, "Formation of an Adherent Alumina Coating on Hastalloy N," NAA-SR-Memo-10268, August 8, 1964, Confidential-Restricted Data.
16. S. D. Brown, et al, "Critical Evaluation of Ceramic Processing at Sub-conventional Temperatures," AFML-TR-67-194, June 1967.
17. C. F. Powell, J. H. Oxley, and J. M. Blocher, Jr., Vapor Deposition, J. Wiley and Sons, New York, 1966.
18. D. T. Bourgette, "Materials in Vacuum Environment," J. Metals, 19 (12) 50, December, 1967.

APPENDIX

A. ALTERNATE COATING METHODS

1. Arc Plasma Spraying

Although chemical vapor deposition was considered the prime candidate process for applying the LRHSC Al_2O_3 coating, a backup process was also investigated. This was arc plasma spraying of Al_2O_3 onto T-111 substrates.

The arc plasma spraying process can be much simpler than the CVD process. Feed material in a carrier gas is fed into a spray gun, an integral part of which is a system of electrodes. An arc is struck across the electrodes. The carrier gas is ionized, and the feed material is melted, accelerated, and directed onto a substrate. Considerable operator skill is required to deposit controlled, uniform, and reproducible thicknesses of coating material, and there are several operating parameters which must be controlled. Although these coatings are generally permeable and of lower density than CVD coatings, the likelihood of contaminating the substrate is lower, and the process is usually easier to control.

Two requirements of the LRHSC Program make arc plasma spraying of Al_2O_3 coatings somewhat more complex than normal. One is that the T-111 must be protected from oxygen and nitrogen during the time that it is hot. The second is that the specimens must be preheated prior to coating to simulate the condition of a fueled LRHS capsule. These two requirements dictate that the coating operation be performed in an inert-atmosphere glove box. The specimens were to be preheated to between 1200° and 1700°F with a small removable furnace. Some design problems with the glove box were encountered, since there were large quantities of heat to control and dissipate.

This work was performed for AI by a coating vendor, using the equipment shown in Figure A-1.

GLOVE BOX SETUP

GLOVE BOX WITH HEAT EXCHANGER

INTERNAL FURNACE AND GUN

SPECIAL PLASMA SPRAY GUN

Figure A-1.

Al_2O_3 PLASMA SPRAY DEVELOPMENT EQUIPMENT

The specimens used in the arc plasma spraying experiments, designated the A series, were identical to those used in the CVD studies. They were placed in the glove box, and the system was pumped out and backfilled several times with high-purity argon. The specimens were preheated to about 1700°F, removed from the furnace and mounted in a rotating chuck, and immediately arc plasma sprayed with Al_2O_3 with a special miniature plasma gun. The feed material was Norton Company grade 183-TR Al_2O_3 .

The coated specimens were returned to AI for evaluation, and these data are shown in Table A-1.

Specimens A-1, A-4, and A-7 had badly spalled and excessively thick coatings. They showed evidence of rework. No tests were run on them.

The remaining A series specimens had light gray coatings which were not of uniform thickness. The thicknesses given in Table A-1 are "average" values. The coating texture was somewhat rougher than that of the CVD coatings, but the texture was relatively uniform from specimen to specimen. Dye penetration testing showed the coatings to contain considerable open porosity, which was expected. X-ray diffraction traces indicated that in all of the A series specimens tested $\gamma\text{-Al}_2\text{O}_3$ was the predominant phase. Some indications of $\alpha\text{-Al}_2\text{O}_3$ were usually seen, but the amount of α was generally about 20 percent. Hardness measurements did not show a hard layer in the T-111 immediately adjacent to the Al_2O_3 coating in the only specimen so tested. Bulk chemical analysis of the same substrate showed that contamination during processing was extremely small, if real. The microstructure of an arc plasma sprayed Al_2O_3 coating is shown in Figure A-2.

The A series coatings were found not to meet two of the criteria of the LRHSC Al_2O_3 coating requirement. They contained appreciable open porosity, and they consisted primarily of the metastable $\gamma\text{-Al}_2\text{O}_3$. Consequently, and in view of the apparent success of the CVD process, further development of the arc plasma spraying process has been terminated.

TABLE A-1
EVALUATION OF ARC PLASMA SPRAYED Al_2O_3 COATINGS ON T-111 SPECIMENS

Specimen Number	Coating Thickness in. ⁽¹⁾	Surface Finish, μ - in.	Dye Pene- tration, Results	X-Ray Diffrac- tion, Principal Al ₂ O ₃ Phase	T-111 Hardness, R _B	T-111 Bulk Chemical Analyses, ppm			
						O ₂	N ₂	H ₂	C
A-1	UNSUITED FOR ANALYSIS								
A-2	0.0047	320	Pores	γ	R _B 94	24	8	3	69
A-3	0.006	230	-	γ	-	-	-	-	-
A-4	UNSUITED FOR ANALYSIS								
A-5	0.0085	260	Pores	γ	-	-	-	-	-
A-6	0.010	230	-	γ	-	-	-	-	-
A-7	UNSUITED FOR ANALYSIS								
A-8	0.0077	325	Pores	γ	-	-	-	-	-
A-9	0.015	330	-	γ	-	-	-	-	-
A-10	0.0085	330	Pores	γ	-	-	-	-	-

(1) By micrometer measurement

Met Photo 8134-5-1

500 X

Figure A-2. Typical Arc Plasma Sprayed Coating of Al_2O_3 on T-111

2. Sputtering

A second alternate coated method was also examined briefly. This was the process of sputtering. Sputtering is physical deposition accomplished by creating molecular vapors of a material by electron bombardment of a target in a vacuum, whereupon some of the molecules impinge on and adhere to a heated substrate. Since the process is carried out in a high vacuum, it has an excellent chance of depositing high density coatings with minimal substrate contamination.

For a preliminary experiment, small disks of T-111 measuring 0.25-inch in diameter by 0.050-inch thick were submitted to a coating vendor for sputter-coating with Al_2O_3 . They were coated with about 0.5 mil of Al_2O_3 , and returned for evaluation. The coatings, shown in Figure A-3, were almost entirely amorphous, but contained 5 to 10 percent each of α and γ - Al_2O_3 .

It appeared that considerable equipment modification and development work would be required to produce satisfactory coatings. Therefore, further evaluation of this process was not pursued.

7-05-245-41

10 X

Figure A-3. Sputtered Al₂O₃ Coating
on a T-111 Substrate