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THERMAL SWITCH EFFORT
July 1970 to November 1970

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I. INTRODUCTION AND SUMMARY

A. Background

During early July 1970, the High Temperature Metal Thermal Switch Program was reoriented toward the design, development, and testing of thermal switch materials for the Pioneer radioisotope thermoelectric generator (RTG) heat source. The major goal of this three month effort was the fabrication of four quality controlled cylindrical sleeves suitable for use as the reentry protection shell for the Pioneer RTG heat source. Due to the tight Pioneer RTG schedule, it was mandatory that the sleeves be delivered to Isotopes, Inc., the Pioneer RTG contractor, no later than early November 1970. Since only limited data was available on the copper/zirconia composite materials selected for evaluation for this application, it was necessary to generate substantial information regarding the characteristics and thermophysical properties of these materials during this approximately three month period.

The Pioneer RTG heat source is described in Reference 1. The basic components of the heat source are the outer POCO graphite aeroshell (with hexagonal cross section), the pyrolytic graphite reentry protection sleeve assembly (three concentric sleeves), and the fuel capsule assembly. The fuel capsule is a hemispherically-ended cylinder loaded with PuO_2 in a cermet fuel form with tantalum-10 tungsten, T-111 (a high strength tantalum alloy) and platinum-20 rhodium containment shells. The aim of the Pioneer thermal switch effort, then, was to fabricate sleeves, with the appropriate supporting data, capable of replacing the pyrolytic graphite reentry protection sleeves. Dimensional, weight, and performance specifications were supplied to Hittman Associates by Isotopes, Inc. (Reference 2).

B. Materials Selection

Three materials were developed and evaluated for this application. They were copper/zirconia rigidized felt, copper/zirconia foam, and copper/magnesia foam. Most of the characterization effort was devoted to evaluation of the two zirconia-based materials.

Copper was selected as the impregnant material based on its impregnability, high thermal conductivity, low vapor pressure, and its attractive melting point. The melting point of 1981°F allows sufficient margin to preclude to the possibility of premature melting during normal operation prior to reentry.

Zirconia rigidized felt was selected as the ceramic matrix material. The selection was primarily based on its superior insulation properties at high temperatures. The high temperature thermal conductivity of the rigidized felt material was from 2.6 to 3.8 times lower than the foam material.

C. Sleeve Fabrication

Two methods were evaluated for the impregnation of the zirconia foam and felt materials with copper. The first method developed was based on fused salt impregnation. This method involved the impregnation of cuprous chloride into the porous zirconia, followed by a hydrogen heat treatment for reduction to metallic copper. The second impregnation technique developed utilized electroless copper deposition. This process involved sensitization of all ceramic surfaces using a palladium resinate solution, followed by pumping the electroless solution through the sensitized piece. Both impregnated techniques were compared and it was concluded that the electroless technique was the most attractive. Electroless deposition led to higher impregnation efficiencies (defined on Page III-2) and was more amenable to the production of quality-controlled, uniformly impregnated cylindrical sleeves.

A special fixture was designed and fabricated to enable electroless impregnation of the full-size cylindrical sleeves. Oversized sleeves were impregnated and then machined to the final dimensions. The deliverable sleeves were fabricated to a Hittman specification which specified dimensions, weight, porous ceramic density, metal loading, quality, and material purity. The four sleeves were successfully fabricated and passed Hittman Associates' inspection testing. These inspection tests included dimensional measurements, weight measurements, determination of porous ceramic density, metal loading determination, quality inspection (including electrical continuity testing), and purity determinations. The four inspected sleeves were delivered to Isotopes, Inc. during October and early November 1970.

D. Property Determination

A comprehensive test program was conducted on the copper impregnated porous ceramic materials based on potential application to the Pioneer RTG heat source. The following discussion summarizes the results of this testing:

1. Copper Vaporization Testing

Test results indicated that electroless impregnated zirconia materials did not vaporize measurable quantities of copper under Pioneer RTG heat source simulated test conditions. The composite was tested at 1300°F in an argon atmosphere. However, composite material made by the molten salt (cuprous chloride) impregnation technique showed significant copper vaporization. This is attributed to the vaporization of small quantities of unreduced cuprous chloride. At 1300°F, the chloride is nine orders of magnitude more volatile than elemental copper. Minimization of copper vaporization is important because minute quantities can affect the thermoelectric properties of lead telluride materials.

2. Migration

Migration testing at a hot face temperature of 1300°F with a temperature differential of 100°F indicates no measurable copper migration from the hot end to the cold end.

3. Compatibility Testing

Compatibility testing of coated Cu/ZrO₂ against graphite and Pt-20 Rh indicated no incompatibility at 1300-1500°F after 1500 hours in argon. A second compatibility rig was tested for 900 hours at 1500°F in argon; no interaction was observed between the coated Cu/ZrO₂ and MgO/ZrO₂ specimens against TZM, Pt-20 Rh, Ta felt and graphite.

4. Thermal Switch Test

Thermal switching was experimentally determined to be $1985^{\circ}\text{F} \pm 5^{\circ}\text{F}$ for both Cu/ZrO₂ felt and Cu/ZrO₂ foam specimens. The test technique utilized electrical resistance measurements followed by microscopic examination of the test specimens.

5. Mechanical Property Test

Compressive and transverse rupture strengths of the Cu/ZrO₂ composite materials were measured in the as-impregnated condition and after thermal switching.

6. Thermal Conductivity Before Switching

Three experimental techniques were utilized to determine the low temperature thermal conductivity of Cu/ZrO₂ felt and Cu/ZrO₂ foam materials. The substantial data generated indicated that copper loadings of 1.2 g/cc and 0.8 g/cc lead to a thermal conductivity of greater than 3.0 Btu/hr·ft·°F for the impregnated rigidized felt and foam materials, respectively. Based on these results, the final rigidized felt sleeves were impregnated with a minimum of 1.2 g/cc of copper.

7. Thermal Conductivity After Thermal Switching

Based on a review of potentially applicable thermal conductivity and thermal diffusivity methods, two methods were selected for the determination of high temperature thermal conductivity of the copper/zirconia materials in the switched condition. The first and primary method was thermal diffusivity testing at Los Alamos Scientific Laboratory; the second method, developed under this program, involves utilization of a plasma arc facility for thermal conductivity testing under simulated reentry conditions.

Data was obtained for both Cu/ZrO₂ felt and Cu/ZrO₂ foam materials over a temperature range of from 2000°F to about 3000°F. The test results indicated:

- (a) That both test methods give fairly consistent data
- (b) The copper/zirconia felt material is a very effective thermal insulator, with a high temperature thermal conductivity substantially lower than zirconia foam materials as well as other ceramic and graphitic insulating materials. At 4000°F, the thermal conductivity is estimated to be 0.2 But/ft·hr·°F.

8. Emissivity Data

Emissivity data was generated on grafoil and ZrO₂/ThO₂ coated copper/zirconia samples. The data was obtained by NASA-Lewis, utilizing a spectral reflectivity apparatus. Above 2000°R (1540°F) both coatings exhibited a total normal emissivity between 0.5 and 0.6.

9. Superorbital Reentry Test of Copper Impregnated Porous Ceramics

A series of samples of copper impregnated porous ceramics were tested in the NASA-MSFC 1.5 MW plasma arc to determine their behavior at temperatures in excess of 5000°F for 25-second test durations. Testing indicated that uncoated and Grafoil-coated copper/zirconia rigidized felt samples exhibited only minor surface melting with no sign of thermal shock cracking or material deterioration. Similar results were obtained for the copper/zirconia foam samples, although the melting zone was somewhat greater. However, the copper/magnesia composite material exhibited substantial (and unexpected) melting. This is attributed to chemical interaction with the outer POCO graphite shroud. Also, all the samples coated with ThO₂/ZrO₂ cement showed substantial melting which is attributed to the low melting point materials which are present in the proprietary cement (Ultratemp-516) which is used as the base for the coating.

II. MATERIALS CONSIDERATION

For a given application, it is important to select the most attractive ceramic matrix material and metal impregnant for the thermal switch re-entry protection material. The ceramic material should have sufficient refractoriness for the most severe reentries and possess low values of thermal diffusivity at reentry temperatures. The metal impregnant is selected based on having a high thermal conductivity and a melting point sufficiently higher than normal space operational temperatures to prevent premature thermal switching.

A. Ceramic Materials

Zirconia was selected as the porous ceramic matrix material due to its high melting point, 4850°F. Two zirconia materials were selected for experimental evaluation. One material was zirconia foam (organic burn-out material) produced by Norton Company. The other was a rigidized felt material produced by Union Carbide. Magnesia (MgO) was also considered as a backup porous ceramic and was manufactured in the foam structure by Norton Company for the first time under this program. The potential advantage of MgO over ZrO₂ is its higher melting point (5050°F) and a higher heat capacity (0.35 versus 0.18 Btu/lb·F°). However, due to the stringent program schedule, magnesia was included only as a backup material, and only a nominal evaluation effort was planned.

The low density porous ceramic materials used for the development and fabrication of the Pioneer thermal switch composites were open pore zirconia foam and rigidized zirconia felt. The zirconia foam was supplied by Norton Company in the form of 4-1/2" cubes and 5" diameter by 4" high cylinders. The density of the ZrO₂ foam was 1.4 gm/cc (equivalent to 25 percent dense zirconia) and the pore sizes were in the range of .015" to .020". The foam is made by blending an organic burn-out material with the zirconia grain, molding to size, and heat treating to remove the organic pore former and to sinter the zirconia grain.

The low density rigidized zirconia felt was supplied by Union Carbide Corporation in 1/4" and 1/2" thick plates and in cylinders 4-3/4" long by 3-1/8" thick and 1/2" wall thickness. These materials had a nominal density of 0.8 gm/cc (equivalent to a 15 percent dense zirconia). The zirconia felt is prepared by impregnating a polymeric fibrous precursor material, i.e., organic felt, with a zirconium salt solution followed by a controlled pyrolysis treatment where the organic fiber is removed and the zirconium salt remains in the same structure as the original precursor fibrous felt structure. A high temperature heat treatment converts the zirconium salt to zirconium oxide and further sinters and rigidizes the zirconia. The zirconia fibers are 4-7 microns in diameter and the pore spaces are assumed to be slightly larger than the fiber diameter. The fiber structure of the rigidized zirconia felt is shown in Figure II-1.

Figure II-1. Rigidized ZrO₂ Felt Structure
(60X Magnification)

B. Metal Impregnant

The metal to be used for impregnation of the ceramic foam must have the following properties to be considered for the Pioneer application.

- Melting temperature must be higher than the operating temperature of the foam and capsule, i. e., greater than 1300°F. At the same time, the melting temperature of the metal impregnant should be low enough so as to effect the thermal switch during the early stages of the reentry heating.
- The metal wettability against typical porous ceramic materials, e. g., ZrO₂, should be low so that the metal can bead into discrete noncontinuous droplets subsequent to melting and effect the thermal switch.
- High thermal conductivity
- Compatible with the ceramic foam
- Low vapor pressure
- Capable of being uniformly infiltrated into the ceramic foam

The metals which best fit the above listed requirements are the group IB elements: copper, silver, and gold. Some of the properties of interest of these metals are listed below in Table II-1.

TABLE II-1. PROPERTIES OF SELECTED METALS
FOR IMPREGNATION

<u>Metal</u>	<u>Density (g/cm³)</u>	<u>Melting Temperature (°F)</u>	<u>Vapor Pressure (mm)</u>		<u>Thermal Conductivity at Room Temperature Btu/ft-hr-°F</u>
			<u>1100°F</u>	<u>1500°F</u>	
Silver	10.5	1760	10 ⁻⁸	10 ⁻⁴	236
Copper	9.0	1980	10 ⁻¹¹	10 ⁻⁷	228
Gold	19.3	1945	10 ⁻¹³	10 ⁻⁸	172

Copper was selected as the metal impregnant for the Pioneer application for the following reasons:

- The melting point of copper, 1980°F, is sufficiently higher than normal and abnormal operating temperatures to preclude the possibility of thermal switching prior to reentry.

- Copper has the best combination of thermophysical properties for this application. It has a low density, high thermal conductivity, and low vapor pressure.
- Preliminary effort had identified electroless and fused salt impregnation techniques as practicable.

III. FABRICATION OF COMPOSITE MATERIALS

A. Process Development

Two methods were evaluated for the impregnation of the zirconia foam and felt with copper.

1. Fused Salt Impregnation

Initially, copper impregnated zirconia foam specimens were prepared by a fused salt method, by which a low melting copper salt, cuprous chloride, with a melting point 422°C , was allowed to infiltrate into the zirconia foam. This was followed by a hydrogen heat treatment to reduce the cuprous chloride to metallic copper. It was found that fine pore size foam materials required high copper loadings (in the order of 1.0 gram Cu/cc foam) before a continuous film was produced on the pore surfaces. Zirconia felt specimens which were impregnated by the fused salt techniques required copper loadings as high as 1.5-1.7 grams Cu/cc before a good continuous film was produced on the felt fiber surfaces.

2. Electroless Copper Deposition

Copper impregnation of the zirconia foam and felt by electroless deposition was evaluated at the same time as the fused salt method. The electroless copper process is based on the selective reduction and deposition of copper from a copper solution only at the surface of a catalytic substrate. The deposition will continue on the substrate through the catalytic action of the deposit itself. Electroless copper plating on properly prepared surfaces was uniform and dense and of high purity. The reducing agent in the electroless copper solution is organic and thus will not contribute any inorganic residual impurity in the copper plate.

Electroless copper deposition on non-metallic surfaces such as zirconia foam and felt may be initiated by seeding the surface with nuclei of a catalytic metal, i. e., palladium. This may be accomplished by treating the surface with a stannous chloride solution and a palladium chloride solution which will result in the deposition of palladium nuclei on the surfaces. It was found that SnCl_2 - PdCl_2 sensitizing solutions attack the zirconia foam due to their acidity. The susceptibility of the zirconias to this attack is due to the calcium oxide stabilizer in the zirconia materials which is chemically attacked by the hydrochloric acid bath in the sensitizing solution. The zirconia felt, which is stabilized by yttrium oxide, Y_2O_3 , is not attacked by the acid solutions; however, the sensitizing of the felt was non-uniform and led to a "spotty" plating on the felt in some cases. A relatively simple and reliable method for sensitizing the zirconia foam and felt surfaces was developed during this program. It involves the use of a dilute solution of palladium resinate. The palladium resinate is an organic palladium solution which will produce a metallic palladium film when painted on a glazed ceramic surface and heated to decompose and burn off the organic materials.

Palladium resinate was used in a similar manner to deposit an extremely thin film of palladium on the foam and felt surfaces to initiate the electroless copper deposition. The palladium resinate solution (which is commercially available) is diluted in acetone to reduce viscosity and is used to sensitize the porous zirconia materials. After impregnation with the solution, which consisted of allowing the porous zirconia to soak up the solution, the zirconia was air-dried and then heated in air to 450°F to decompose the organic. The palladium content of the porous zirconia after this heat treatment is less than 0.01 gm palladium/cc of zirconia.

The electroless copper plating solution used was Cuposit-70 supplied by Shipley Corporation. The Cuposit-70 system is supplied as three components: copper salt solution with complexing agents, reducing solution (formaldehyde), and an alkaline solution, sodium hydroxide. The plating is accomplished at room temperature by pumping the solution through the sensitized foam or felt piece. The final delivered pieces were cylinders approximately 3" O.D. by 4" long by 1/4" wall thickness. The copper plating solution was pumped through the porous zirconia cylinders at an initial pumping rate of approximately two gallons per minute. In order to achieve a uniform copper impregnation, it was necessary to reverse the pumping direction of the plating solution after 50 percent of the required copper had been deposited in the zirconia.

B. Selection of Impregnation Technique

The electroless technique was selected for the impregnation of the full size cylindrical sleeves. This decision was based on the following:

- The electroless technique led to higher impregnation efficiencies, i. e., for a given amount of metal impregnant, the thermal conductivity values of electroless samples were approximately twice that of the fused salt impregnated specimens.
- The electroless technique was more amenable to the production of quality-controlled, uniformly-impregnated cylindrical sleeves. This is due to the fact that the room temperature pumping of liquids through porous materials associated with electroless techniques is more controllable than fused salt impregnation.

C. Specimen and Full Size Sleeve Fabrication

The porous zirconia materials which were used for the process development and for the physical, thermal, and chemical testing were 1-1/4" diameter by 1/4" thick discs.

The final dimensions for the porous zirconia reentry shells were initially to be 2.569" length, 2.534" inner diameter, and 2.934" outer diameter. The oversized zirconia shells received from Union Carbide and Norton were machined to obtain a shell whose wall was 0.050" to 0.100" thicker and whose length was 1/4" longer than the final dimension for increased strength during handling and to permit close control of the final dimensions. However, during the latter stages of the fabrication effort, the final sleeve length requirement was changed to 3.800". Since by this time it was decided that the zirconia rigidized felt material was the best ceramic matrix material and that the oversized Union Carbide supplied shells were not long enough for this requirement, additional shells had to be procured. The dimension change made it necessary to refabricate the electroless impregnation fixture and to incorporate increased pumping capacity, to obtain the desired impregnation flow rate per area.

The fixture used for holding the final zirconia shells in the plating tank is shown in Figure III-1. The pump was connected to the inlet hole and the plating solution is continuously pumped and recycled through the zirconia shell.

Figure III-2 shows the zirconia felt sleeve in (1) the as-formed condition and (2) after copper impregnation with the electroless copper plating solution and coating with ZrO_2 cement on inner and end surfaces.

The structure of the copper impregnated zirconia felt material is shown in Figure III-3. A section of a zirconia foam after copper impregnation is shown in Figure III-4. The photomicrographs of the copper impregnated zirconia foam and the zirconia felt show, in both cases, that the copper coating is completely dense and reasonably uniform in coating thickness. The copper also appears to have plated on all exposed zirconia fiber and pore surfaces, and, in addition, the copper has plated on the coarse zirconia grains of the zirconia foam.

D. Specifications and Inspection of Sleeves for Pioneer

1. Specifications

The following were the specifications for the thermal switch composite sleeve:

(a) (1) Sleeve final dimensions (also see Figure III-5)

Length:	$3.800'' + 0''$ $- .010''$
Inner diameter:	$2.534'' + .005''$ $- .005''$
Outer diameter:	$2.931'' + .005''$ $- 0''$

A. Fixture Components

B. Assembled Fixture with Sensitized Sleeve
(Undersized in Length)

Figure III-1. Fixture for Sleeve Electroless Impregnation

Figure III-2. Unimpregnated Rigidized Felt Sleeve and
Impregnated and Coated Sleeve

Figure III-3. Copper Impregnated ZrO_2 Felt
with 1.3 gm Cu/cc
(120X Magnification)

Figure III-4. Copper Impregnated ZrO_2 Foam
with 0.8 gm Cu/cc
(60X Magnification)

- (1) Cu Impregnated Rigidized ZrO_2 Foam
 *(-1) Corresponds to nominal dimensional requirements
 (-2) Corresponds to dimensional requirement for fit into a particular POCO aeroshell
- (3) Ultratemp Zirconia Cement (516) Coating
- (4) Ultratemp Zirconia Cement (516) Coating

Figure III-5. Impregnated Sleeve Dimensions
 (Drawing No. SK-RMT102170, Rev. A)

- (2) Coating dimensions: See Figure III-5
- (b) Sleeve weight: <0.57 lb
- (c) Porous ceramic density: $55\#/ft^3 \pm 5\#/ft^3$
- (d) Metal loading: $75\#/ft^3 \pm \frac{12.5\#/ft^3}{0\#/ft^3}$
- (e) Quality: Porous ceramic sleeves will be free of visible cracks, defects, large (>.010") pores (air bubbles) and laminations.

Composite materials will have no visible cracks, defects, large (>.015") pores or laminations. In addition, composite sleeves will be checked for uniformity of surface copper impregnation by means of electrical continuity testing.

- (f) Material purity: The copper purity in the as-impregnated material will be >98.5 percent copper. The palladium (sensitizer material) shall be no greater than 1.5 percent. The non-copper / palladium impurities in the as-impregnated material are <0.3 percent.

The purity of the porous ceramic sleeves ($ZrO_2 + HfO_2 + Y_2O_3$) is greater than 99 percent. The Y_2O_3 (yttria) is the crystal stabilizer material and the HfO_2 (hafnia) is ordinarily associated with all zirconia materials due to similarity of chemistry.

2. Inspection Tests

The following inspection tests were performed for each of the four thermal switch sleeves to be delivered to Teledyne Isotopes, Inc.

- (a) Dimensional Measurements: Dimension of the composite cylindrical sleeves will be taken with calibrated micrometers. At least five readings will be taken for each measurement on length, inside diameter, and outside diameter.
- (b) Weight Measurements: Weights of the composite cylindrical sleeves before and after copper impregnation will be determined with a calibrated single beam balance (Ohaus 310, Dial-O-gram balance). The balance has a capacity of 300 grams and a sensitivity of 10 mg.
- (c) Porous Ceramic Density Measurements: The volume of the ceramic foam cylinder will be determined by calculating from its dimensional measurements. The density will then be determined by the formula, density = weight/volume.

- (d) Metal Loading Measurement: The density of the metal impregnated ceramic foam cylinder will be determined from its weight and dimensional measurements. The metal density (loading) will then be calculated as the difference between the density of the metal impregnated porous ceramic sleeve and the porous ceramic foam sleeve before impregnation.
- (e) Quality Inspection:
 - (1) Visual Inspection: All porous ceramic sleeve surfaces will be visually inspected for defects such as air bubbles, cracks, and laminations.
 - (2) Electrical Continuity Testing: The uniformity of the surface copper impregnation will be checked by means of electrical continuity testing. This testing will utilize a copper foil electrode to be placed in contact with one end of the cylindrical sleeve, where a second wire bench electrode will scan all other surfaces for electrical continuity. This process will be repeated placing the foil electrode on the opposite sleeve end.
- (f) Material Purity:
 - (1) Metal: The purity of the copper deposit will be determined by wet chemical analysis. The sample will be taken from a composite cylindrical sleeve.
 - (2) Ceramic: The purity of the porous ceramic material will be that presented by Union Carbide, the material supplier.

Table III-1 presents the results of Hittman Associates' inspection testing of four thermal switch sleeves. As can be observed, all four shells were within the desired specification and were delivered to Isotopes, Inc. during October and early November 1970.

TABLE III-1. INSPECTION OF Cu/ZrO₂
THERMAL SWITCH SHELLS

	<u>Shell No. 62</u>	<u>Shell No. 63</u>	<u>Shell No. 68</u>	<u>Shell No. 69</u>
Density of Bare ZrO ₂ Shell - pcf	51.5	51.2	53.1	52.9
Copper Loading - pcf	81.3	75.9	81.3	86.1
Weight of Cu Impregnated Shell - lbs	0.48	0.46	0.53	0.50
Dimensions:				
O.D. - inches	2.930 - 2.931	2.929 - 2.931	2.930 - 2.931	2.930 - 2.931
I.D. - inches	2.529 - 2.534	2.533 - 2.534	2.531 - 2.534	2.533 - 2.536
Height - inches	3.794 - 3.798	3.796 - 3.798	3.796 - 3.798	3.794 - 3.797
Copper Purity - percent	99.5	99.5	99.5	99.5
Palladium Content - percent	0.60	0.84	0.81	0.65
Inspection for Defects	OK	OK	OK	OK
Electrical Continuity Test	OK	OK	OK	OK

IV. PROPERTY DETERMINATION

A test program was initiated on the copper impregnated zirconia foam and felt materials for application to the Pioneer radioisotope thermoelectric generator (RTG). The properties which were considered for this program were:

- Copper vaporization from the copper/zirconia composite
- Copper migration in the copper/zirconia composite
- Compatibility of the copper/zirconia composite with the Pioneer heat source materials
- Thermal switch temperature of the copper/zirconia composite
- Mechanical properties of the copper/zirconia composite before and after thermal switch. The descriptions of the tests and the test results are given below.
- Thermal conductivity testing before switching
- Thermal conductivity after testing
- Plasma arc testing
- Emissivity testing

A. Copper Vaporization Testing

The objective of this test was to determine if any copper would vaporize from the copper impregnated zirconia and to determine the magnitude of the copper vaporization under simulated Pioneer RTG heat source conditions. The test was conducted under one atmosphere of static argon at 1300°F for 500 hour and 1500 hour periods. The test specimens consisted of a 3/4" diameter by 3/4" long copper/zirconia foam cylinder containing 1.0 gm/cc of copper. The initial test sample was prepared by CuCl fused salt impregnation of the zirconia foam at 1200°F followed by reduction of the CuCl to metallic copper in hydrogen at 700°F to 1400°F. Two copper vaporization tests were initially conducted simultaneously with the following variations in the test samples:

- (1) Uncoated Cu/ZrO₂ cylinder
- (2) Cu/ZrO₂ cylinder coated with a plasma sprayed zirconia coating and an overlay of zirconia cement for final sealing

The test specimens were each contained in a separate graphite container with a 1/16" hole at one end of the graphite container to simulate the Pioneer vent hole. Each graphite contained Cu/ZrO₂ specimen was sealed in a separate stainless tube and the graphite container positioned within one inch above a water cooled condenser plate. The water-cooled condenser covered almost the entire furnace cross-sectional area so that the copper vapor would condense on the plate. The surface of the condenser was analyzed for copper deposited after the 500 hour and 1500 hour test periods. Penniman & Browne Inc. performed the analysis using spectrographic techniques. The results of the analyses of water-cooled condenser plates before and after testing are as follows:

	<u>Uncoated Cu/ZrO₂</u>	<u>Coated Cu/ZrO₂</u>
Copper deposited - 500 hours	1.50 mg	0.67 mg
Copper deposited - 1500 hours	1.70 mg	0.80 mg
Chloride deposited - 1500 hours	29 mg	25 mg

The amounts of copper which appear to have vaporized from the test specimens, while very low, are higher than expected or what may be acceptable, due to the poisoning effect of copper on lead telluride thermoelectric materials. The cuprous chloride used in the impregnation is a white powder and the film deposited on the condenser plates in all four tests, i.e., coated and uncoated specimens, 500 hour and 1500 hour tests, also had a similar whitish appearance which indicates possible presence of copper chloride. The chloride contents of the deposited films are higher than the amount which may be accounted for as copper chloride. However, it does appear that there was residual copper chloride in the specimen to permit transport of the copper to the condenser. The vapor pressure of CuCl at 1300°F is 10 mm and the vapor pressure of Cu at 1300°F is 10⁻⁸ mm. Therefore, any residual CuCl in the Cu/ZrO₂ would accelerate the vaporization of the copper by nine orders of magnitude. It appears that the copper detected in these tests was caused by residual chloride in the specimen.

A similar vaporization test was conducted with an electroless copper impregnated zirconia foam specimen. The test was again conducted at 1300°F under static argon; however, the test time was only 350 hours due to limited time available for the test. The water-cooled stainless steel condenser plate after the test was examined prior to chemical analysis for copper deposit. The surface of the plate was clean and showed no white deposit as noted in the previous test. Also, no copper-colored deposit was observed. The surface of the condenser was analyzed for copper by an independent test laboratory and a copper deposit of 0.62 mg was reported. As before, a blank stainless steel plate was also analyzed for copper. The copper content of the surface was reported to be 0.22 mg. The area of the condenser surface was approximately 3-4 times that of the stainless steel blank. On the basis of copper-surface area ratio, no copper was deposited on the condenser plate during the 250 hour vaporization test.

B. Copper Migration Test

The object of this test was to determine the extent of any copper migration across the copper impregnated zirconia foam due to a temperature differential through the Cu/ZrO₂ foam in a simulated Pioneer RTG heat source environment.

The test specimens in this test consisted of three discs, 3/4" diameter by .083" thick, of the copper impregnated zirconia foam with no coating on the outer surfaces. The three Cu/ZrO₂ discs with a bare ZrO₂ foam disc at each end were assembled and sealed in a stainless steel container under one atmosphere argon pressure at 1300°F. A temperature differential was imposed across the three Cu/ZrO₂ discs by controlling the furnace heater and the water flow rate at the cool end of the stack. Water input temperature was about 60°F. Thermocouple No. 1 was controlled at 1300°F, and the temperature at thermocouple No. 2 was controlled by the water cooling at 1200°F. This simulated approximately the 100°F temperature drop across a Pioneer composite reentry protection shell.

A 1500 hour migration test of the Cu/ZrO₂ composite at 1300°F with a temperature gradient of 100°F was completed and the test specimens were examined. The three Cu/ZrO₂ test pieces show extremely small weight changes of less than 0.02 percent. Each of the three specimens showed approximately the same weight loss, indicating no copper diffusion across the temperature gradient. The weight loss of the three specimens is attributed to outgassing and baking out of the test pieces.

C. Compatibility Testing

The object of this test was to determine the compatibility of the Cu/ZrO₂ composite with Pioneer RTG heat source materials. The total test time was 1800 hours (1000 hours at 1300°F and 800 hours at 1500°F).

The test specimens used for the test were copper impregnated zirconia cylinders, 3/4" diameter by 1/4" high, containing 1.0 gm/cc copper. The specimens were prepared by the CuCl fused salt impregnation process and were coated with flame sprayed ZrO₂ and a ZrO₂ cement. The materials tested are summarized below:

- (1) Graphite versus ZrO₂ foam
- (2) Graphite versus ZrO₂ coated Cu/ZrO₂ composite
- (3) Pt-20Rh versus ZrO₂ foam
- (4) Pt-20Rh versus ZrO₂ coated Cu/ZrO₂ composite

The zirconia foam, the copper-zirconia foam composites, and the system materials (i. e., graphite and platinum alloy) were evaluated after test by dimensional measurement, weight change, and microscopic examination. In every case, the weight changes were extremely small (less than

0.2 percent). No measurable changes in dimensions were observed. Microscopic examination of the surfaces of the materials in contact with each other and examination of the cross-section of the test material did not show any change or reaction.

A second set of compatibility test materials was tested for 900 hours at 1500°F in argon. The test was completed and the materials were examined. The materials tested are:

- (1) TZM versus $\text{ThO}_2\text{-ZrO}_2$ coated Cu/ ZrO_2
- (2) Ta felt versus $\text{ThO}_2\text{-ZrO}_2$ coated Cu/ ZrO_2
- (3) Graphite versus $\text{ThO}_2\text{-ZrO}_2$ coated Cu/MgO
- (4) Pt-20Rh versus $\text{ThO}_2\text{-ZrO}_2$ coated Cu/Mgo
- (5) TZM versus $\text{ThO}_2\text{-ZrO}_2$ coated Cu/Mgo
- (6) Ta felt versus $\text{ThO}_2\text{-ZrO}_2$ coated Cu/MgO

Weight and dimensional measurements of the test materials again show very small or no changes with the exception of the tantalum felt which compressed and had a permanent set under the load placed on the sample. The tantalum felt also appeared more brittle and some weight loss was noted which appeared to be due to breakage and falling-out of the felt fibers on handling. The $\text{ThO}_2\text{-ZrO}_2$ coatings appear to have degraded during the long term heating and the coatings were flaky and soft. This resulted in some weight loss of the coated specimens and a change in the length of the specimens.

Microscopic examination of the surfaces of the materials in contact with each other shows no sign of reaction or incompatibility.

D. Thermal Switch Test

The object of this test was to verify the thermal switch temperature, i. e., the temperature at which the conducting copper layer would melt and form discontinuous beads in the porous zirconia structure.

The test was conducted by heating the Cu/ ZrO_2 composite pieces in an argon atmosphere while continuously measuring the electrical resistance of the composite. The temperature at which the resistance changed from essentially dead short (low resistance) to open circuit resistance was the thermal switch temperature. The thermal switch effect was also confirmed by microscopic examination of the composite after the heat treatment.

The thermal switch temperature of both Cu/ ZrO_2 felt and Cu/ ZrO_2 foam was determined to be $1985^\circ\text{F} \pm 5^\circ\text{F}$. The melting point of copper, as reported in the literature, is 1981°F . The Cu/ ZrO_2 composites after the thermal switch test showed complete melting and beading of the copper in the porous zirconia structure.

E. Mechanical Property Test

Compressive and transverse rupture strengths of the Cu/ZrO₂ composite materials in the as-impregnated (before thermal switching) and after thermal switching conditions were measured. The mechanical property data is summarized in the following table:

TABLE IV-1. STRENGTH OF Cu/ZrO₂
THERMAL SWITCH COMPOSITES

<u>Material</u>	<u>Compressive Strength (PSI) at 1300°F</u>	<u>Transverse Strength (PSI) at 1300°F</u>
ZrO ₂ foam + 0.8 g/cc copper	2550	2200
ZrO ₂ foam + 0.9 g/cc copper	-- --	3080 5100(1)
ZrO ₂ foam + 1.4 g/cc copper	3440 5000(1)	4150 --
ZrO ₂ foam + 0.8 g/cc copper (switched)	1500	630
ZrO ₂ felt + 1.3 g/cc copper	2140	2000
ZrO ₂ felt + 1.2 g/cc copper (switched)	400	480

F. Thermal Conductivity Before Switching

Basically, three experimental methods have been utilized. They are a low temperature (<700°F) thermal conductivity method utilizing the Dynatech comparative cut-bar rig, a high temperature (>1000°F) thermal conductivity technique utilizing a modified and more accurate Dynatech comparative cut-bar rig, and a thermal diffusivity technique performed by Los Alamos Scientific Laboratory (LASL) and capable of generating thermal conductivity data well beyond the composite switch temperature (1985°F).

Tables IV-2 and IV-3 present all the data generated on Cu/ZrO₂ rigidized felt and Cu/ZrO₂ foam materials, respectively.

(1) 80°F data

TABLE IV-2. THERMAL CONDUCTIVITY OF
Cu/ZrO₂ FELT BEFORE SWITCHING

<u>ZrO₂ Density (g/cc)</u>	<u>Cu Density (g/cc)</u>	<u>Average Temperature (°F)</u>	<u>Method</u>	<u>k (Btu/hr·ft·°F)</u>
0.8	1.2	600	Low temperature cut-bar	3.3
0.8	1.2	1110	High temperature cut-bar	4.3
0.8	1.2	1320	High temperature cut-bar	2.9
0.8	1.2	1450	High temperature cut-bar	2.4
0.8	1.4	600	Low temperature cut-bar	4.8
0.8	1.4	1100	High temperature cut-bar	6.9
0.8	1.4	1350	High temperature cut-bar	4.5
0.8	1.4	1430	High temperature cut-bar	4.3
0.68	1.58	440-1980	Diffusivity (Ref. 3)	5.2

TABLE IV-3. THERMAL CONDUCTIVITY OF
Cu/ZrO₂ FOAM BEFORE SWITCHING

<u>ZrO₂ Density (g/cc)</u>	<u>Cu Density (g/cc)</u>	<u>Average Temperature (°F)</u>	<u>Method</u>	<u>k (Btu/hr·ft·°F)</u>
1.4	0.5	600	Low temperature cut-bar	2.0
1.4	0.6	600	Low temperature cut-bar	2.1
1.4	0.9	600	Low temperature cut-bar	4.2
1.4	0.95	600	Low temperature cut-bar	4.5
1.4	1.1	600	Low temperature cut-bar	5.2
1.4	0.60	1341	Diffusivity (Ref. 3)	4.3

Based on the above data, optimum copper loadings of 1.2 g/cc and 0.8 g/cc were selected as the optimized levels for the rigidized felt and foam zirconia materials, respectively. This selection was based on the requirement set by Isotopes, Inc. of a minimum pre-switched thermal conductivity of 3.0 Btu/ft·hr·°F for the Pioneer RTG heat source (Ref. 2).

G. Thermal Conductivity After Switching

Two methods were selected for determination of high temperature thermal conductivity of the copper/zirconia materials in the switched condition. The first and primary method selected was thermal diffusivity testing utilizing the laser unit at Los Alamos Scientific Laboratory; the second method involves utilization of a plasma arc facility for thermal conductivity testing under simulated reentry conditions.

Prior to selection of the two aforementioned methods, a review of potentially applicable thermal conductivity and thermal diffusivity test rigs was made. Very few conductivity or diffusivity test rigs could be utilized due to the rather stringent test requirements. The following were the most severe test requirements:

- (1) Data was desired in the 2000 to 4000°F temperature range.
- (2) It was not practicable to supply large test specimens, such as those required by radial-in-flow devices.
- (3) It was desirable to obtain high temperature data with the copper droplets still present in the porous ceramic structure. Methods requiring long test times under vacuum conditions would lead to copper sublimation during testing. This problem is inherent in large thermal conductivity test rigs, such as radial in-flow set ups, which require a long time to reach thermal equilibrium during a test run.

The two test methods utilized were generally capable of meeting the above requirements. The LASL diffusivity technique is considered the primary source of data due to the success of this method in measuring high temperature diffusivities of various graphitic and ceramic materials. The plasma arc technique is a novel method innovated under this program. Although this technique has the distinct advantage of measuring thermal conductivity under simulated reentry conditions, it must be remembered that there is no prior experience utilizing this method. The following briefly describes the test techniques and presents the experimental data for the two zirconia materials.

1. LASL Thermal Diffusivity Testing

The diffusivity testing was performed by Dr. Bruce Morrison at LASL during August and September 1970. Both copper/zirconia rigidized felt and copper/zirconia foam materials were tested.

The oversized copper/zirconia discs were ground down to 0.070 inch while the diameter remained at 0.500 inch. Both sides of the discs were sprayed with a thin layer of dry film graphite (d'g) to darken the zirconia so that the laser light pulse could be absorbed on the front face ("as received" ZrO₂ is transparent to 1.04μ laser radiation). The complete laser pulse technique has been described previously (Ref. 4). Briefly, it consists of instantaneously heating one face of a thin sample by a laser pulse and measuring the transient time-temperature response of the opposite face. These data are corrected for finite pulse time and radial heat losses and then converted to thermal diffusivity by the equation:

$$\alpha = \frac{w \ell^2}{t \frac{1}{2}}$$

where:

- α = the thermal diffusivity in cm²/sec
- w = the "Cowan" heat loss correction factor
- ℓ = the sample thickness in cm
- $t \frac{1}{2}$ = the half time to maximum back face temperature after heating by the laser pulse

The individual zirconia discs were heated to the test temperature in vacuum which supported in a graphite holder inside a graphite heating element. The samples were fulgurated several times at each test temperature and the data averaged.

Since it takes from ten minutes to one-half hour to heat the specimens up to the high temperatures required, it has been observed that an appreciable amount of the copper has sublimed prior to initiation of the laser pulse. This implies that the data generally represents the thermal diffusivity of porous zirconia materials with only a small amount of copper.

Thermal conductivity has been derived from the output thermal diffusivity data using the following equation:

$$k = \alpha C \rho$$

where:

- k = thermal conductivity Btu/ft·hr·°F
- α = diffusivity ft²/hr
- C_p = heat capacity, Btu/lb·°F
- ρ = density, lb/ft³

2. Plasma Arc Thermal Conductivity Testing

Three thermal conductivity models were tested in the NASA-MSFC 1.5 MW plasma arc facility on September 22-23, 1970. The purpose of the test series was to determine high temperature thermal conductivity of metal switch composite materials.

The general characteristics of the models used for the plasma arc tests are shown in Figure IV-1. Each model used the same sting support and each was instrumented with three Pt/Pt-13Rh thermocouples. Each copper impregnated porous ceramic conductivity specimen was in a switched condition, switching having been accomplished prior to assembly of the models. This was done to assure attainment of a thermal equilibrium condition during testing within a reasonable period of time.

The basic data obtained from the test are shown in Table IV-4. These data consist of three thermocouple readings, one pyrometer reading, and the convective heat flux applied to the specimen by the plasma stream. The data were taken at close to equilibrium conditions; the temperatures were relatively constant with test time. Generally, it required about two minutes to reach equilibrium at each new arc setting. The pyrometer reading has been corrected to account for an assumed emissivity of the specimen surface.

Each specimen was measured before and after the test. The basic dimensions of importance to a thermal conductivity estimate are shown in Figure IV-2. In general, a specimen consists of cylindrical disc samples with the temperature measurements taken at the front and rear face via a pyrometer and thermocouples, respectively. Thermal conductivity of the specimens has been calculated by using the equation:

$$k_b = \frac{1_b \sigma \epsilon_E (T_2'^4 - T_1'^4) k_a k_d}{(k_a k_d) (T_0 - T_2) - \sigma \epsilon_E (T_2'^4 - T_1'^4) (1_a k_d + 1_d k_a)}$$

The variables in the above equation are defined in Table IV-4 and Figure IV-2 with the exception of ϵ_E , T_1' and T_2' . T_1' and T_2' are the absolute temperature versions of T_1 and T_2 . The effective emissivity, ϵ_E , applies for the gap between the sample rear face surface and the sink surface. The emissivity of each of these surfaces has been estimated to be 0.85 and remains relatively constant over the temperature ranges encountered during the test. Therefore, considering the radiation transfer between two parallel surfaces, an effective emissivity value of $\epsilon_E = 0.74$ has been used in the equations. As can be noted from the above equation, k_b is a strong function of this assumed gap emittance.

Heat transfer from the specimen rear face to the heat sink is assumed to occur by radiation only. Estimates of conduction heat transfer have been made for this path using an estimated nitrogen pressure in the gap. At the reduced gas pressure during the runs, conduction is generally less than five percent.

Figure IV-1. Thermal Conductivity Plasma Arc Model

TABLE IV-4. PLASMA ARC CONDUCTIVITY
TEST DATA

Model	Cold Wall Heat Flux to Front Face (Btu/ft ² -sec)	Corrected (1) Pyrometer Temperature, T ₀ (°F)	Specimen Rear Face Temperature, T ₂ (°F)	Sink Temperature, T ₁ (°F)
No. 1-4 ZrO ₂ felt	48	2030	1202	630
	92	2310	1490	1202
	190	2800	2015	1895
	249	3660	2470	2327
	265	4020	2560	2405
	190	3490	2290	2170
No. 2-4a ZrO ₂ foam	48	1980	1393	670
	92	2300	1632	1091
	190	2800	2120	1502
	249	3640	2535	1961
	265	3770	2587	2027
	190	3220	2275	1855

(1) Corrections are made according to the following assumption:

Temperature, °F	Total ϵ
0	0.40
1000	0.37
2000	0.32
3000	0.60
4000	0.77
5000	0.80

Model	Dimension			
	l_b *	l_c *	l_a **	l_d **
1-4, ZrO ₂ Felt	0.105	0.130	.013	.012
2-4a, ZrO ₂ Foam	0.113	0.134	.010	.011

* Measured
 ** Estimated

Figure IV-2. Plasma Arc Conductivity Specimen Characteristics Used for Data Reduction

3. Summary of Plasma Arc Data, LASL Data, and Literature Data for Cu/ZrO₂ Materials

All pertinent high temperature thermal conductivity data on Cu/ZrO₂ and porous ZrO₂ materials are presented in Figures IV-3 and IV-4. These figures present thermal conductivity data based on:

- (a) The plasma arc tests previously described
- (b) Thermal diffusivity testing at LASL
- (c) Literature data on the bare (unimpregnated) porous zirconia

Figure IV-3 presents thermal conductivity data for Cu/ZrO₂ rigidized felt and ZrO₂ rigidized felt materials; Figure IV-4 presents data for Cu/ZrO₂ foam and ZrO₂ foam materials. A description of the materials whose data is presented in Figures IV-3 and IV-4 is delineated on the figures' legend.

Based on these data, the following is concluded:

- (a) The diffusivity, plasma arc, and literature data are in good agreement. This implies that the copper/zirconia felt and foam composites after switching have approximately the same thermal conductivity as the same unimpregnated porous ceramic.
- (b) The copper/rigidized zirconia felt composite is a much better insulator than the copper/zirconia foam material. For example, at 3000°F the foam-based composite has a thermal conductivity of 2.6 times that of the felt-based composite. At 4000°F, this factor is estimated to be 3.8. This lower conductivity is believed to be due to the vastly different structures of the two materials. The rigidized felt has a weakly-joined fibrous structure with an effective pore size in the micron range, while the foam has a continuous matrix, burn-out structure with a pore size of approximately 15 mils. A discussion of porous ceramic structure and its effect on thermal conductivity is presented in Reference 5.
- (c) The solid lines on the two figures, corresponding to literature data for the bare zirconias, are considered reasonable estimates for copper/zirconia conductivity and are recommended for reentry thermal calculations.

H. Emissivity Data

Emissivity data has been obtained on three coated Cu/ZrO₂ samples. Two of the samples (3-1 and 3-2) had coatings of ZrO₂/ThO₂, while sample 4-1 utilized a 5 mil sheet of Grafoil. Grafoil is a flexible laminated pure

Figure IV-3. Thermal Conductivity of Cu/ZrO₂ and ZrO₂ Rigidized Felt Materials Versus Temperature

Figure IV-4. Thermal Conductivity of Cu/ZrO₂ and ZrO₂ Foam Materials Versus Temperature

graphite product produced by Union Carbide exhibiting anisotropic properties similar to pyrolytic graphite. For the Pioneer heat source, the Grafoil could be applied by layers bonded with a graphite cement.

The emissivity data has been generated by NASA-Lewis utilizing spectral reflectivity apparatus. The basic system components consist of a heated hohlraum (cavity), a water-cooled sample, and an optical system. The hohlraum has two openings with the water-cooled sample inserted in one opening and is so arranged that radiation from either the sample or the hohlraum can pass through the second opening and be directed into the monochromator. For a given wavelength setting of the monochromator, the energy reflected from the sample is compared to the energy emitted by the ideal radiator. The ratio of the net deflections of the recording system is a direct measure of the spectral reflectance.

Figure IV-5 presents spectral emittance for the three coated composite samples. This data has been used to obtain emissivity versus temperature data by integrating the spectral data in conjunction with Planckian distributions. Figure IV-6 presents this data. Due to the lack of data in the low wavelength regime, it became necessary to extrapolate the spectral data to these lower wavelengths. This extrapolation does introduce some inaccuracy, particularly at the higher temperatures where low wavelength radiation predominates.

It should be noted that coatings for this application were considered to perform the following possible functions:

- (1) A coating on the external sleeve surface could increase the refractoriness of the zirconia. By using a coating thickness in excess of ten mils of either Grafoil or $\text{ZrO}_2/\text{ThO}_2$, the effective melting point of zirconia could be raised in excess of 150°F during superorbital reentries. Such an external coating would also act as an emissivity coating to lower the normal operational radiation temperature drop in the event of a gap between the outer sleeve surface and the inner POCO graphite surface.
- (2) A coating on the inside of the sleeve would act as a compatibility barrier to protect the Pt-Rh alloy clad refractory fuel capsule from any interdiffusion with the copper impregnant. This coating would also act as an emissivity coating.

During the course of this Pioneer sleeve development effort, it was deemed unnecessary to coat the outer surface since plasma arc tests indicated that the zirconia felt material did not require additional refractoriness and the overall Pioneer heat source design required a zero or negative (interference) fit between the sleeve and the POCO graphite sleeve, eliminating the need for an emissivity coating.

However, it was decided to include a coating on the inside sleeve surface to act as a diffusion barrier. Compatibility tests utilizing a ZrO_2 based cement indicated the effectiveness of the material in prohibiting any copper/platinum-rhodium interdiffusion. The emissivity data for the ZrO_2 coating should be similar to that of the $\text{ZrO}_2/\text{ThO}_2$ coating shown in Figure IV-5.

Figure IV-5. Normal Spectral Emittance for
ZrO₂/ThO₂ and Grafoil
(Data Measured at NASA-LRC, September 1970)

Figure IV-6. Derived Total Emissivity for $\text{ZrO}_2/\text{ThO}_2$ and Grafoil

I. Superorbital Reentry Plasma Test of Copper Impregnated Porous Ceramics

A series of samples of copper impregnated ceramic foam and rigidized felt materials were tested in the NASA-MSFC 1.5 MW plasma arc to determine their behavior at temperatures in excess of 5000°F for short periods of time. The superorbital reentry heating rate history was calculated to approximate heat source outer surface temperatures for a -6°, 36,000 ft/sec superorbital reentry. Table IV-5 summarizes typical test conditions for these models.

TABLE IV-5. TYPICAL SUPERORBITAL TEST CONDITIONS

<u>Step Number</u>	<u>Time Duration of Step (sec)</u>	<u>Btu/ft²·sec (cold wall)</u>	<u>Measured Maximum POCO Graphite Temperature (°F)</u>
1	45	82	2140
2	25	410	4460
3	25	688	5210
4	35	410	4510
5	90	82	3060

Figure IV-7 shows the plasma arc model. Table IV-6 summarizes the specimens tested in the plasma arc and the results of the test.

Post-test examination of the samples showed complete switching and melting of the copper impregnant in the ceramic foam or rigidized felt. The uncoated zirconia felt and the zirconia felt with the Grafoil layer showed the least effect of the high temperature plasma arc. A thin (~10 mils) fused layer was evident on both specimens which when analyzed by X-ray diffraction was found to be a pure zirconia glass; no free metallic zirconium was found in the system. The specimens coated with the ThO₂/ZrO₂ cement all showed some reaction and melting which was probably due to low melting materials such as sodium or potassium silicates which are present in the proprietary cement, Ultratemp-516 (Aremco Company), used as the base for the ThO₂/ZrO₂ coating. These acted as fluxing agents and lowered the melting temperature of the coated samples.

The magnesia foam samples showed a high degree of melting which was probably due to some reduction of the MgO by carbon to magnesium metal and also some reaction of the SiO₂ foam insulation material in the specimen holder. The uncoated zirconia foam showed little effects of the plasma arc other than surface melting. However, the glassy penetration zone was thicker (~20 mils) than the uncoated zirconia rigidized felt.

Figure IV-7. Plasma Arc Superorbital Test Model

TABLE IV-6 . PLASMA ARC TESTING OF
COPPER IMPREGNATED CERAMICS

<u>Specimen No.</u>	<u>Material</u>	<u>Coating</u>	<u>Test Results</u>
2-11	Cu/ZrO ₂ Felt	Grafoil + ThO ₂ /ZrO ₂ Cement	Reaction and partial melting
3-2	Cu/ZrO ₂ Felt	ThO ₂ /ZrO ₂ Cement	Reaction and partial melting
4-2	Cu/ZrO ₂ Foam	ThO ₂ /ZrO ₂ Cement	Reaction and partial melting
12-5	Cu/MgO Foam	ThO ₂ /ZrO ₂ Cement	Reaction and complete melting of MgO
1-7A	Cu/ZrO ₂ Felt	Grafoil layer	Surface melting of ZrO ₂ felt
1-7B	Cu/ZrO ₂ Felt	None	Surface melting of ZrO ₂ felt
11-2	Cu/MgO Foam	None	Reaction and melting of MgO foam
25-2	Cu/ZrO ₂ Foam	None	Surface melting and some penetration of melt into ZrO ₂ foam

V. REFERENCES

1. Isotopes, Inc., "Pioneer RTG Semi-Annual Report," INSD-2873-44, January 1971.
2. Isotopes, Inc., "Preliminary Specification for a Thermal Switch Insulating Sleeve for the SNAP-19 Pioneer Heat Source," 30856, August 3, 1970.
3. Morrison, B. H., L. L. Sturgess, "Thermal Diffusivity-Conductivity of Thermal Switch Materials," N-1-2707, January 7, 1971.
4. Morrison, B. H., "Thermal Diffusivity of ATJ-S Graphite 100° to 3000°K," CONF-691002, USAEC, March 1970.
5. Hittman Associates, Inc., "High Temperature Metal Thermal Switch Development Program - Fourth Quarterly Report," HIT-468, August 1970.