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FINAL REPORT FOR Ni/ZrO₂
HIGH TEMPERATURE THERMAL
SWITCH PROGRAM

February 1971 to July 1971

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TABLE OF CONTENTS

	<u>Page</u>
NOTICE	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	v
LIST OF FIGURES	vi
I. INTRODUCTION AND SUMMARY	I-1
A. Background	I-1
B. Materials Selection	I-1
C. Process Development	I-1
D. Property Determination	I-2
II. REDIRECTION OF PROGRAM EFFORT	II-1
III. MATERIALS SELECTION	III-1
A. Metal Impregnant	III-1
B. Porous Ceramic Materials	III-3
IV. FABRICATION OF COMPOSITE MATERIALS.	IV-1
A. Process Selection	IV-1
B. Process Development	IV-1
V. PROPERTY DETERMINATION	V-1
A. Thermal Switch Test	V-1
B. Sublimation Testing	V-2
C. Compatibility Testing	V-5
D. Thermal Conductivity Testing	V-6
E. Thermal Diffusivity Testing.	V-7
F. Mechanical Property Determination	V-17
VI. NICKEL SUBLIMATION ANALYSIS	VI-1
A. Test Configuration	VI-1

TABLE OF CONTENTS (Continued)

	<u>Page</u>
B. Test Data	VI-2
C. Configuration Analysis	VI-4
D. Pellet Sublimation Analysis	VI-7
VII. REFERENCES	VII-1

LIST OF TABLES

<u>No.</u>	<u>Table</u>	<u>Page</u>
III-1	Properties of Metal Impregnants	III-2
III-2	Properties of Oxide Ceramics	III-4
IV-1	Analysis of Nickel from Hydrazine-Reduced Electroless Nickel Bath	IV-4
V-1	Sublimation Losses from Ni/ZrO ₂ at 2100°F	V-3
V-2	Thermal Conductivity of Ni/ZrO ₂ Composites	V-6
V-3	Description of Ni Impregnated, Rigidized ZrO ₂ Felt	V-7
V-4	Thermal Diffusivity of Rigidized ZrO ₂ Impregnated with Nickel	V-8
V-5	Calculated Thermal Conductivities of Rigidized ZrO ₂ Impregnated with Nickel	V-9
V-6	Thermal Diffusivity of Ni/ZrO ₂ Felt	V-11
V-7	Calculated Specific Heat (Cp) of Ni/ZrO ₂ Felt	V-12
V-8	Calculated Thermal Conductivity of Ni/ZrO ₂ Felt	V-13
V-8	Supplement Calculated Thermal Conductivity of Ni/ZrO ₂ Felt After Switching	V-14
V-9	Mechanical Properties of Ni/ZrO ₂ Composite	V-17

LIST OF FIGURES

<u>No.</u>	<u>Figure</u>	<u>Page</u>
III-1	Thermal Conductivity of ZrO_2 Foam and Felt Materials Versus Temperature	III-5
IV-1	Schematic of Impregnation Apparatus for Composite Discs	IV-5
IV-2	Schematic of Impregnation Apparatus for Composite Sleeves	IV-6
IV-3	Electroless Nickel Impregnated Zirconia Felt (Ni loading - 2.0 g/cc) 230x	IV-8
IV-4	Electroless Palladium Impregnated Zirconia Felt (Pd loading - 2.5 g/cc) 230x	IV-8
V-1	Sublimation Loss from Ni/ZrO_2 at 2100°F	V-4
V-2	Thermal Diffusivity of Ni/ZrO_2 Felt	V-15
V-3	Calculated Thermal Conductivity of Ni/ZrO_2 Felt	V-16
V-4	Deformation Under Compressive Load - Room Temperature	V-18
V-5	Deformation Under Compressive Load - 1400°F	V-19
VI-1	Experimental Weight Loss Data	VI-3

I. INTRODUCTION AND SUMMARY

A. Background

The High Temperature Metal Thermal Switch Program was originally directed to the design, development, and testing of thermal switch composite materials for radioisotope thermoelectric generator (RTG) heat sources for the Isotope-Brayton cycle system operating above 2000°F. The program was later redirected toward a lower temperature heat source requirement, i. e., the Viking RTG heat source which would operate in the 1200-1300°F range.

B. Materials Selection

Zirconia rigidized felt was selected for the high temperature thermal switch material. The selection was based on the low thermal conductivity of the felt structure and thermal and physical properties of zirconia.

The materials survey showed both nickel and palladium metals to have properties suitable for the high temperature thermal switch application. Nickel was selected for the development and testing of the thermal switch composites based on its lower melting temperature and lower density.

C. Process Development

Process development studies on impregnation of the porous zirconia rigidized felt with nickel were conducted and the electroless nickel deposition was selected for the fabrication and testing of nickel/zirconia composites. The original electroless nickel bath composition used a boro-amine reducing agent which left a low boron impurity in the electroless nickel deposit. Such materials have shown substantially depressed melting points. Subsequently, an electroless nickel composition was tested with a hydrazine reducing agent which permitted the deposition of a high purity boron- and phosphorus-free nickel with a melting point close to pure nickel (2650°F).

Process development studies were also conducted for the fabrication of palladium/zirconia felt composites by electroless plating. An electroless palladium plating solution was tested which used hydrazine for reduction and high purity palladium impregnated zirconia felt discs were prepared.

Plating fixtures were modified to enable the fabrication of nickel/zirconia felt composite discs and sleeves by the electroless plating process. The composite discs, 1 inch diameter by 1/4 inch thick, were used for development and testing; two full-sized cylindrical sleeves were also prepared.

D. Property Determination

A test program was conducted on the nickel impregnated zirconia felt composite and the results are summarized below.

1. Thermal Switch Test

The thermal switch temperature of the high purity electroless nickel impregnated zirconia was determined to be approximately 2615°F (uncorrected) or approximately 2650°F (corrected). The thermal switch effect was also demonstrated by high temperature thermal diffusivity tests performed by LASL where a sharp drop in thermal diffusivity was noted at the melting point of nickel (2650°F).

The thermal switch temperature of a high purity electroless palladium impregnated zirconia was determined to be approximately 2815°F which compares closely to the reported melting temperature of palladium.

2. Nickel Sublimation Test

The sublimation of nickel from the composite at 2100°F and $<10^{-6}$ mm pressure was effectively lowered by plasma-sprayed zirconia coatings. At 1800°F and one atmosphere argon pressure nickel sublimation from coated and uncoated Ni/ZrO₂ composites was very low and no significant difference in sublimation was found between the coated and uncoated specimens.

3. Compatibility Testing

Compatibility testing of Ni/ZrO₂ composites against Pt-20Rh, T-111 (tantalum alloy), and graphite at 2100°F showed no reaction after 2950 hours in argon. Another compatibility test at 1500°F of the same materials also showed no evidence of reaction after 1350 hours.

4. Thermal Conductivity Testing

Thermal conductivity data on the nickel/zirconia composites was determined by two techniques—cut bar comparative test and thermal diffusivity test. The data indicated conductivities of 1.5 to 2.5 Btu/hr. ft. °F for nickel loadings of 1.5 to 2.0 gm Ni/cc, respectively. The thermal diffusivity test showed a sharp drop in thermal conductivity from 1.9 to 0.1 Btu/hr. ft. °F at the thermal switch point, 2650°F, i. e., the melting temperature of the nickel phase.

5. Mechanical Property Test

Compressive testing of the nickel/zirconia composites at room temperature and at elevated temperature show a compressive deformation under loading rather than a definite compressive failure under load.

Transverse rupture testing show rupture strengths of 3000 to 5000 psi at 1400°F for composites with loadings of 1.75 to 2.0 gm Ni/cc.

6. Nickel Migration Testing

Migration testing at a hot face temperature of 1800°F and a temperature differential of 75°F indicate no measureable nickel migration after 1500 hours of testing.

II. REDIRECTION OF PROGRAM EFFORT

During the early part of the program, the technical direction of the program was based on developing and testing thermal switch materials for a high temperature, 2000-2200°F, application. The effort was later re-directed toward a lower temperature heat source requirement. Although the heat source is not defined, the operating temperature will be similar to the Pioneer RTG heat source which operated in the 1200-1300°F temperature range. Although copper/zirconia materials were shown to be attractive for the Pioneer application (Ref. 1), it was decided to concentrate on nickel/zirconia composites for the following reasons:

- There is concern over positioning a hot copper/zirconia sleeve in the vicinity of lead telluride thermoelectric materials due to the well-known poisoning effect of small amounts of copper on lead telluride thermoelectric properties. Larger amounts of nickel can be introduced into lead telluride without a poisoning effect. Also, since the vapor pressure of nickel is approximately two orders of magnitude less than copper, smaller quantities will be transferred to the thermopile.
- Previous nickel/zirconia development had indicated that relatively high thermal conductivities ($k > 2.5 \text{ Btu/ft} \cdot ^\circ\text{F} \cdot \text{hr}$) could be achieved at reasonable metal loadings (about 2.0 gm Ni/cc).
- Nickel with its melting point of 2650°F compared to copper's 1980°F melting point could enable use of nickel/zirconia composites for higher temperature applications. However, for the low temperature application, the higher melting point of nickel allows increased reentry heating prior to thermal switching which lowers the reentry protection effectiveness of the thermal switch material somewhat.

III. MATERIALS SELECTION

The selection of a metal impregnant and a ceramic matrix for a thermal switch composite is based on the specific normal operation and reentry protection requirements. The normal operation temperature in space generally constrains the selection of the metal impregnant since the melting temperature should be several hundred degrees Fahrenheit higher than the normal operational temperature to avoid premature switching. Since the ceramic material determines the refractoriness of the composite, the severity of reentry constrains selection of the ceramic material. For example, superorbital reentries lead to composite temperatures higher than orbital reentries and therefore more refractory ceramic matrices would be required.

The following section discusses all the factors which influence the selection of thermal switch composite materials. For purposes of this discussion, a high temperature normal operational temperature (2000°F) and a relatively severe earth orbital reentry environment (maximum composite temperature from 4500-5000°F) were assumed.

A. Metal Impregnant

The metal to be used for impregnation of the porous ceramic must have the following properties to be considered for the high temperature system application:

- (1) Melting temperature higher than the normal operating temperature of the capsule. 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 cycle.
- (2) High thermal conductivity at operating temperatures to permit effective heat transfer through the metal impregnated porous ceramic during normal operation before switching.
- (3) Compatible with the porous ceramic and will not wet the ceramic surfaces after switching.
- (4) Low vapor pressure to minimize sublimation losses of the metal.
- (5) The metal must be capable of being uniformly infiltrated into the porous ceramic.

A survey of the literature for metals and alloys which may fit the requirements listed above was made. The resultant pertinent property data is shown in Table III-1. The metals which appear most attractive as

TABLE III-1. PROPERTIES OF METAL IMPREGNANTS

Metal	Composition	Density, gm/cm ³	Melting Pt. °F	Boiling Pt. °F	Vapor Press. at 2000°F mm. Hg.	K at Rm Temp. BTU/hr. -ft. -°F	K at 2000°F	Ratio K 2000/Density	ΔF at 2000°F ⁽²⁾ kcal/mole O ₂	Symbol
Beryllium	Be	1.85	2345	4490	10 ⁻³	87	35	18.9	-230	Be
Chromium	Cr	7.19	3430	4820	10 ⁻⁵	57	36	5.0	-120	Cr
Cobalt	Co	8.90	2783	5220	10 ⁻⁶	53	22	2.5	-66	Co
Copper	Cu	8.89	1980	4700	4 x 10 ⁻³	222	185 ⁽¹⁾	20.8	-35	Cu
Iron	Fe	7.87	2795	5170	7 x 10 ⁻⁶	42	16	2.0	-85	Fe
Molybdenum	Mo	10.2	4748	5670	< 10 ⁻⁸	84	57	5.6	-60	Mo
Nickel	Ni	8.90	2651	5140	2 x 10 ⁻⁶	52	46	5.2	-60	Ni
Palladium	Pd	12.0	2825	5660	10 ⁻⁶	41	43	3.6	+5	Pd
Platinum	Pt	21.5	3256	6910	10 ⁻¹⁰	47	38	1.8	+12	Pt
Silver	Ag	10.5	1760	3920	10 ⁻²	242	207 ⁽¹⁾	19.7	+20	Ag
Silicon	Si	2.33	2600	5040	10 ⁻⁶	87	14	6.0	-149	Si
Titanium	Ti	4.51	3100	5936	5 x 10 ⁻⁸	12	6	1.3	-164	Ti
Zirconium	Zr	6.49	3380	7590	10 ⁻¹⁰	13	15	2.3	-200	Zr
430 Stainless Steel	82 Fe, 17Cr	7.75	2600-2750	—	—	12	15	1.9	—	430
304 Stainless Steel	71 Fe, 19Cr, 10Ni	7.91	2550-2650	—	—	8	17	2.2	—	304
Advance Alloy	55 Cu, 44 Ni	8.89	2355	—	—	15	35	3.9	—	Adv.
Monel	66 Ni, 30 Cu, 2 Fe	8.63	2370-2450	—	—	9	30	3.5	—	Monel
Nickel-D	93 Ni, 4Mn, 2 Fe	8.73	2500-2600	—	—	26	33	3.8	—	Ni-D
N-91	78 Ni, Co 22	8.90	2630	—	—	26	27	3.0	—	N-91

(1) K (thermal conductivity) at melting point for Ag and Cu

(2) Free energy of formation of oxides of the metals - to be compared with ΔF of Al₂O₃ = -196 kcal/mole O₂ and ΔF ZrO₂ = -200 kcal/mole O₂.

impregnants are nickel and palladium. These metals show good thermal conductivity at elevated temperature, appear to be compatible with the porous ceramic, have melting temperatures above 2100°F and have relatively low vapor pressure above 2100°F. Both of these metals may be infiltrated into the porous ceramic by the electroless deposition process.

B. Porous Ceramic Materials

The porous ceramic material must be capable of withstanding the high temperatures developed during reentry heating of the heat source and also have a low thermal conductivity at the high reentry temperatures. Additionally, the ceramic composition chosen must be capable of being formed into the selected low density porous ceramic so as to meet the low thermal conductivity requirement.

Table III-2 lists the properties of the basic refractory oxides which may be considered for this application. Based on the data shown in Table III-2, zirconium dioxide, ZrO_2 , was selected for primary consideration for this application. Zirconia has a high melting temperature and service temperature, low thermal conductivity, good thermal stability in its stabilized form and is readily available in many forms and structures.

The low density ceramic form which was used in the early phases of the high temperature thermal switch program was an open pore zirconia foam. This material was supplied by Norton Company in the form of cubes, plates, cylinders, and brick with a density of 1.4 g/cc (approximately 25 percent dense) and with pore diameters ranging from 0.015 to 0.020 inch. The foam was made by blending a presized organic burnout material with the zirconia grain, molding to size and heat treating to remove the organic pore former and to sinter the zirconia grain.

During the recent phase of this program which was directed toward the Pioneer RTG heat source (Ref. 1), a low density rigidized zirconia felt was evaluated for the thermal switch application. The low density zirconia felt was supplied by Union Carbide Corporation as 1/4-inch and 1/2-inch thick plates and as hollow cylinders 1/4- to 1/2-inch wall thickness and 4 inches diameter by 4 inches high. The felt is prepared by impregnating a polymeric fibrous precursor material, i.e., organic felt with a zirconium salt solution followed by slow drying and a controlled pyrolysis treatment. During the pyrolysis heat treatment, 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 then converts the zirconium salt to zirconium oxide and further sinters and rigidizes the resultant zirconia felt.

The zirconia felt appears to offer a number of advantages over the zirconia foam including:

- (1) Lower thermal conductivity as shown in Figure III-1
- (2) Lower bulk density, i.e., 0.8 g/cc felt versus 1.4 g/cc foam

TABLE III-2. PROPERTIES OF OXIDE CERAMICS

	<u>Density gm/cc</u>	<u>Melting Point °F</u>	<u>Thermal Stability</u>	<u>Thermal Shock Resist.</u>	<u>Availability as Porous Ceramic</u>	<u>Cost</u>
Al_2O_3	3.95	3720	Good to m. p.	Very good	Very good	Low
ZrO_2 (Stab.) ⁽¹⁾	5.75	4800	Good to m. p.	Good	Very good	Medium
BeO	3.01	4658	Phase trans- formation at 3700°F	Excellent	None	Medium- high
MgO	3.58	5160	Good to >4000°F	No data	Limited	Low
ZrSiO_4	4.68	2800	Decomp. to ZrO_2 and SiO_2 at 2800°F	Very good	Good	Low
SiO_2	2.2	3130	Phase change above 2200°F	Excellent	Very good	Low
ThO_2	10.0	5830	Good to >4000°F	Poor	None	High
HfO_2 (Stab.) ⁽¹⁾	10.0	5140	Good to >4000°F	No data	None	High

(1) Stabilized with CaO, MgO, or Y_2O_3

Figure III-1. Thermal Conductivity of ZrO₂ Foam and Felt Materials Versus Temperature

- (3) Finer pore structure, i. e., <0.001 inch versus $0.015 - 0.020$ inch which will suppress high temperature heat transfer by radiation
- (4) Improved thermal shock resistance of the fiber material over the sintered porous ceramic material due to low elastic modulus of the fibrous structure
- (5) The rigidized felt structure has shown no cracking from heat treatment due to low shrinkage of the felt

On the basis of the above, the rigidized zirconia felt was selected for the high temperature thermal switch application.

IV. FABRICATION OF COMPOSITE MATERIALS

A. Process Selection

The impregnation of the zirconia felt is being accomplished by the electroless deposition process. This process was selected after an extensive evaluation and test program was made of various impregnation methods. The methods which were evaluated included electroless deposition, slurry impregnation, fused salt impregnation, chemical vapor deposition and salt solution-vacuum impregnation. The electroless deposition method offers the following advantages over the other methods:

- (1) High impregnation efficiency, i.e., for a given amount of metal impregnant, the thermal and electrical conductivity values were considerably higher than for those samples made by fused salt impregnation.
- (2) Electroless plating impregnation processes lend themselves well to the production of quality controlled, uniformly impregnated porous ceramic structures.
- (3) The electroless plating impregnation processes are low temperature processes and can be controlled by conventional chemical methods.

B. Process Development

1. Surface Sensitization

Surface catalysis of nonconducting surfaces is required to initiate the nickel deposition which then proceeds auto-catalytically. Such metals as nickel, iron, tin, gold, and palladium are effective catalysts to initiate the electroless deposition. Ceramic surfaces, such as the zirconia felt fibers, must be processed to provide an active surface as catalytic sites that will accept the electroless nickel. Zirconia felt surfaces may be sensitized either by a reduction in place of a palladium salt or by thermal decomposition of an organic palladium compound. In the first method, the work is immersed in a stannous chloride solution to adsorb a layer of stannous ions on the surface. The excess stannous chloride is removed by washing and the work is then immersed in a palladium chloride activating solution which oxidizes the stannous ion to stannic with a reduction of the palladium ions to metal. The procedure used for sensitizing the zirconia felt in the present work used a palladium resinate metallizing solution which is normally used to deposit extremely thin films of precious metals on ceramic substrates for electronic and decorative applications. A very dilute solution, i.e., five percent palladium resinate in acetone, is allowed to completely infiltrate through the felt material. The felt is then air-dried to remove the acetone solvent and heated in air to 450°F to decompose the organic palladium

resinate which leaves a minute amount of palladium on the felt fiber surfaces. This palladium serves as the catalyst to the deposition of nickel in the electroless nickel plating bath. The deposition is then autocatalytic as the deposited nickel catalyzes further deposition.

2. Electroless Nickel Deposition

Electroless plating is the process by which metallic bodies may be coated with a metal as nickel, cobalt, copper through controlled auto-catalytic reduction of the cation, i.e., Ni^{++} , Co^{++} , Cu^{++} at the surface of the metallic body by means of reducing agents in an aqueous medium without the use of an external current source. Electroless plating is characterized by selective reduction of the metal ions only at the surface of the catalytic substrate immersed in the solution, and deposition will continue through the catalytic action of the deposit itself.

The deposition of electroless nickel is an oxidation-reduction reaction involving nickel complex ions and selective reducing reagents. The chemical reaction is controlled by the use of complexing agents such as citrates, acetates, tartrates, and gluconates which will control the plating rate, prevent deposition of insoluble compounds and also prevent spontaneous decomposition of the plating bath. A number of chemical reactions occur simultaneously in the oxidation-reduction process which will lead to the formation of several products. These reactions can be briefly summarized as follows, depending on the reducing agent used in the reaction:

The principal reaction is the reduction of nickel ions to nickel with the phosphide, boride, and nitride present in the nickel deposits only as a minor constituent since these products form slowly.

The majority of the commercial electroless nickel plating systems use the hypophosphite reducer which results in a nickel film containing from one to eight percent phosphorus. The nickel-phosphorus system shows a eutectic at 10 w/o phosphorus of 1620°F ; therefore low phosphorus containing films would show initial formation of a liquid phase at 1620°F and final melting at 2000 to 2500°F depending on the phosphorus content. This system was not used in the impregnation of the zirconia felt for the thermal switch application because of the low melting temperatures of the Ni-P deposits.

A proprietary phosphorus-free electroless nickel deposition system was recently introduced for application to printed circuits. The nickel deposit from this system (Niklad 755 from Allied Research Products) was reported to have a 99+ nickel content, low electrical resistivity similar to pure nickel, and a melting temperature of approximately 2500°F . The

low boron content of the deposit implies the use of a boron-amine or borohydride reducing agent. The initial work on electroless nickel impregnation of zirconia felt materials for the high temperature thermal switch was done with the Niklad 755 solution.

The plating work with the Niklad 755 electroless nickel plating solution indicated good deposition on the sensitized zirconia felt surfaces, and a uniform impregnation of nickel throughout the felt. The plating solution has a low viscosity and no problems were experienced due to closing of the pore channels. Nickel loadings as high as 3.0 grams Ni/cc of felt were deposited before a significant pressure buildup was noted. Subsequent thermal switch testing of the Ni/ZrO₂ composites containing the boron impurity showed melting at temperatures in the range of 1900 to 2000°F (see Section IV-A). The nickel-boron system shows eutectics at 4, 10, and 12 w/o boron of 2080, 2060, and 1815°F, respectively, which confirms observed melting of the nickel-boron impregnant.

Because of the undesirable effects of the boron content of the Niklad electroless nickel, efforts were directed toward the search for a high purity electroless nickel. The use of hydrazine as a reducing agent in electroless nickel plating baths was reported in 1947 by Pessel and in 1952 by Pragst (Refs. 2 and 3). In both of these reported investigations the hydrazine was effective in reducing the nickel salt to the metal, but the solutions were not autocatalytic to permit thick nickel deposits. In some cases the solutions were unstable and readily decomposed. Levy (Ref. 4) later reported autocatalytic reduction preparation of thin nickel films by hydrazine. Nickel films of 500-10,000 Å were prepared of relatively high purity and completely boron and phosphorus free. The major impurities were <2.5 percent nitrogen and <2.5 percent oxygen. Recently Dini and Coronado (Ref. 5) reported a method for producing thick, relatively pure nickel deposits by autocatalytic reduction in solutions containing nickel acetate, glycolic acid, tetrasodium ethylene diamine tetraacetic acid (EDTA), and hydrazine. Deposits of up to 10 mils thick with >99 percent purity were produced. The impurities were hydrogen, oxygen, and nitrogen which, for the purpose of this program, may be removed by heat treatment. The bath reported by Dini and Coronado consisted of the following:

Nickel Acetate	60 g/liter
Glycolic Acid	60 g/liter
Tetrasodium EDTA	25 g/liter
Hydrazine	100 ml/liter
Sodium Hydroxide (50% solution) to adjust pH	

The bath was operated at 90°C (194°F) and at a pH of 11.0.

Initial attempts were made to impregnate the zirconia felt with the above solution. The plating rate appeared to be too fast for uniform plating, possibly because of the high surface area in the zirconia felt piece. The bath was modified by replacing the tetrasodium EDTA with disodium EDTA, and increasing the EDTA as the disodium EDTA to 60 gms/liter and the hydrazine to 175 ml/liter. The bath temperature was lowered to 140-150°F. Electroless nickel impregnation of the palladium sensitized zirconia felt discs was accomplished and initial results indicated that the modified hydrazine reduced electroless nickel bath will readily deposit the nickel on the felt at a lower plating rate which permits a more uniform impregnation than the initial bath composition used. The electroless

nickel, as deposited, had a dark brown-black matte appearance; however, subsequent heat treatment of the impregnated felt in hydrogen at 1800°F resulted in a clean grey, metallic material. A wet chemical and spectrographic analysis of the electroless nickel from the hydrazine-reduced baths was conducted by Penniman and Browne, Baltimore, Md. and is reported in Table IV-1.

TABLE IV-1. ANALYSIS OF NICKEL FROM HYDRAZINE-REDUCED ELECTROLESS NICKEL BATH

<u>Metal</u>	<u>Weight Percent</u>
Nickel Assay	99.8
Copper	0.08
Cobalt	0.02
Iron	0.05
Lead	0.03
Chromium	< 0.0005
Sodium	0.04
Zinc	0.005
Aluminum	< 0.001
Beryllium	< 0.0005

The analysis confirms the reported high purity of the electroless nickel. The impurities as copper, cobalt, and iron are normally present in the nickel acetate used for preparing the bath. The sodium impurity is introduced by the sodium hydroxide used to adjust the pH. The oxygen, hydrogen, and nitrogen impurities, if originally present in the as-deposited nickel, were eliminated by the high temperature heat treatment in hydrogen.

The high purity electroless nickel from the hydrazine-reduced bath was used for all subsequent composite fabrication and testing except where noted.

The electroless nickel impregnation systems for impregnating zirconia felt discs and cylinders are shown schematically in Figures IV-1 and IV-2. A cross section of a nickel impregnated zirconia felt with a nickel loading of 2.0 gms/cc is shown in Figure IV-3.

3. Electroless Palladium Impregnation

A study was conducted to determine the feasibility of fabricating palladium impregnated zirconia felt composites for thermal switch applications by the electroless deposition method.

Figure IV-1. Schematic of Impregnation Apparatus for Composite Discs

Figure IV-2. Schematic of Impregnation Apparatus for Composite Sleeves

The electroless palladium plating solution investigated was based on work reported by Rhoda (Ref. 6) in 1959 in which he developed an electroless process which consists of the reduction of a palladium-amine with hydrazine according to the following equation:

The bath used for the electroless palladium deposition consisted of the following:

Palladium (as ammine complex)	5.4 g/liter
Ammonium hydroxide	350 g/liter
Di-sodium EDTA	34 g/liter
Hydrazine	0.3 g/liter

The bath was operated at 175°F to permit plating at 1 mil/hour. The palladium salt was a palladium ammine complex, $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$, which is prepared by converting palladium chloride solution to the tetraammine complex by reaction with ammonium hydroxide. The reducing agent used to reduce the palladium salt to the metal was hydrazine, and the di-sodium EDTA is used to inhibit spontaneous decomposition of the bath by forming a soluble complex with palladium.

Initial tests with the bath composition given above were conducted with sensitized zirconia felt at temperatures ranging from 100 to 175°F. Variations in the palladium salt content and hydrazine contents were also evaluated. Initiation of the plating reaction as indicated by evolution of gas bubbles occurred at 110°F. The rate of palladium deposition increased with increasing concentrations of palladium and hydrazine and with increasing temperature. Conditions that yield the high plating rates were also conducive to spontaneous decomposition of the bath.

A number of zirconia felt discs were impregnated with palladium by pumping the electroless palladium through the zirconia felt discs at 900-1000 cc/minute. Palladium loadings of 2.0 to 2.5 gms Pd/cc were successfully prepared in approximately 2-1/2 hours at 120°F. An analysis of a heat-treated electroless palladium deposit showed a palladium metal content of >99.6 percent; the major impurities, i.e., rhodium, platinum, and other members of the platinum group were present in 100-150 ppm range.

A cross section of a palladium impregnated zirconia felt made by the above described process with a palladium loading of 2.5 gm/cc is shown in Figure IV-4.

Figure IV-3. Electroless Nickel Impregnated
Zirconia Felt (Ni loading - 2.0 g/cc) 230x

Figure IV-4. Electroless Palladium Impregnated
Zirconia Felt (Pd loading - 2.5 g/cc) 230x

V. PROPERTY DETERMINATION

A test program was initiated on the nickel impregnated zirconia felt composites for application initially to the NASA-Brayton cycle system and later tests were initiated for application of the composite to the lower temperature Pioneer Viking system. The properties which were considered for the testing program were:

- Thermal switch temperature of the nickel/zirconia felt composite
- Nickel sublimation from the nickel/zirconia composite
- Compatibility of the nickel/zirconia composite with typical heat source materials
- Thermal conductivity of the nickel/zirconia composite before switching and after switching
- Mechanical properties, i.e., compressive strength and transverse rupture strength of the nickel/zirconia composite before and after switching
- Nickel migration test

A. Thermal Switch Test

The object of this test was to verify the thermal switch temperature, i.e., the temperature at which the conducting nickel layer melts and forms discontinuous metal beads on the zirconia felt structure.

The thermal switch test was conducted by heating a 1/2 in. x 1/2 in. x 1/4 in. section of a nickel/zirconia composite under argon atmosphere in a Micro-Bar furnace. The Micro-Bar furnace is a miniature furnace used for microscopic observation of materials at elevated temperature in a controlled atmosphere. The test piece was placed on a wafer of bare zirconia felt which was placed directly on an electrically-heated molybdenum strip. A glass bell jar sealed with an O-ring isolates the sample under the controlled argon atmosphere. The top of the bell jar of optically clear glass enables microscopic examination of the specimen and also permits optical temperature measurement. During the test, the sample temperature was increased while the specimen was observed through the optical pyrometer. The temperature at which the metal phase showed first indication of melting and beading was recorded as the thermal switch temperature of the composite.

Three different metal/zirconia felt composites were tested for thermal switch temperature and the results are as follows:

- (1) High purity electroless nickel/zirconia composite switch temperature - 2615°F
- (2) Low purity Niklad electroless nickel/zirconia composite switch temperature - 2000 to 2120°F
- (3) High purity electroless palladium/zirconia composite switch temperature - 2815°F

The high purity electroless nickel and electroless palladium bath show switch temperatures close to the reported melting temperatures for the pure metals, i.e., 2615°F for electroless nickel as compared to 2650°F reported for nickel, and 2815°F for electroless palladium as compared to 2830°F reported for palladium. The temperatures reported are, in all cases, uncorrected for emissivity and for absorption through glass. If the temperature were corrected, the actual temperatures would be 15-40 degrees higher than the uncorrected values. The low purity boron containing Niklad electroless nickel showed a depression of the nickel switch temperature due to the nickel-boron eutectic which is reported to be 2080°F at four percent boron (Ref. 7).

B. Sublimation Testing

The object of this test was to determine the extent of nickel sublimation from the coated and uncoated nickel/zirconia composites at 2100°F and $<10^{-6}$ mm pressure and at 1800°F under 1 atmosphere argon.

The high temperature vacuum sublimation test was conducted for a total test time of 2800 hours in a high temperature vacuum furnace with a six-inch diameter by six-inch long heating chamber. The test specimens were 1-inch diameter by 1/4-inch thick discs of (a) uncoated composite, (b) plasma-sprayed ZrO₂ coated composite, and (c) plasma-sprayed ZrO₂ + ZrO₂ cement-coated composite. The extent of nickel sublimation was determined from periodic weight loss data taken during the test. The results of the high temperature vacuum sublimation tests are listed in Table V-1 and are also shown in Figure V-1.

The sublimation data shown in Table V-1 and Figure V-1 show the effectiveness of the plasma-spray ZrO₂ coating in nickel-suppressing sublimation from the composite. The average rate of nickel loss from the plasma-coated composite was one-twentieth of that from the uncoated composite. The weight loss from the specimen coated with plasma-sprayed zirconia and the zirconia cement was higher than that of the specimen coated only with the plasma-sprayed zirconia. It is assumed that the additional weight loss is due to sublimation of constituents in the zirconia cement.

The low temperature sublimation test at 1800°F in argon was conducted for a total test time of 1400 hours. The specimens were contained in an Inconel tube with welded closures. No intermediate weights were taken during the test.

TABLE V-1. SUBLIMATION LOSSES FROM
Ni/ZrO₂ AT 2100°F

<u>Time Hrs</u>	<u>Uncoated (%)</u>	<u>Plasma ZrO₂ Coat (%)</u>	<u>Plasma ZrO₂+ Cement Coat (%)</u>
0	0	0	0
264	1.51* (1.97)**	0.118* (0.165)**	0.268*
675	6.07 (8.58)	0.133 (0.186)	0.952
1180	7.70 (10.8)	0.279 (0.391)	1.75
1500	10.9 (15.3)	0.391 (0.540)	2.18
2300	14.0 (19.6)	0.733 (1.02)	3.49
2800	15.65 (21.9)	0.738 (1.03)	4.29
Avg. Rate (wt. loss/hr)	(7.85 x 10 ⁻³)	(3.76 x 10 ⁻⁴)	1.53 x 10 ⁻³

* percent weight loss of total pellet weight

** percent weight loss of nickel

Figure V-1. Sublimation Loss From Ni/ZrO₂ at 2100°F

The sublimation weight losses were 0.08 percent for the uncoated composite, 0.18 percent for the plasma-sprayed zirconia composite, and 0.17 percent for the plasma-coated and cement-coated specimens. These reported weight losses are significantly lower than the high temperature vacuum sublimation losses, and it is also significant that the uncoated specimen showed a lower weight loss than the coated specimens. This indicated that the weight change is probably not a nickel sublimation loss but possibly an outgassing effect and evaporation of volatiles from the coatings. A more adequate outgassing pre-treatment would have eliminated this problem.

C. Compatibility Testing

The object of this test was to determine the compatibility of the Ni/ZrO₂ composite with typical heat source materials at 2100°F and at 1500°F.

The test specimens used for the test were nickel/zirconia composites which were coated with plasma-sprayed zirconia. The compatibility of the coated nickel/zirconia composite was tested with graphite, platinum-20 rhodium, and T-111 alloy (Ta-8W-2Hf). The compatibility test materials were assembled in a vertical stack and contained in a closed Inconel alloy tube under one atmosphere argon pressure. The stack was made up in the following order:

- (1) ZrO₂ spacer
- (2) Coated Ni/ZrO₂ composite
- (3) Pt-20Rh alloy
- (4) Pt-20Rh alloy
- (5) Coated Ni/ZrO₂ composite
- (6) T-111 alloy
- (7) T-111 alloy
- (8) Coated Ni/ZrO₂ composite
- (9) Graphite
- (10) ZrO₂ spacer

The 2100°F compatibility test was conducted for a total test time of 2950 hours. The test materials were evaluated by dimensional measurements, weight change and microscopic examination. The coated Ni/ZrO₂ composites showed a weight loss of <0.1 percent, no change in dimension, and no change in appearance. The graphite showed a similar weight loss and no other change in dimension or appearance. The tantalum alloy had a weight increase of 0.5 percent, a dimensional increase of <0.001 inch and had a thin, dark grey to gold colored film which would account for the weight and dimensional change. The 1500°F compatibility test was conducted for 1400 hours. The results were very similar to the 2100°F test results in the Ni/ZrO₂ composites and the graphite showing slight weight loss of

<0.1 percent while the tantalum again had a gold colored film on the surface and a weight increase of 0.3 percent and a dimensional change of <0.001 inch. The weight change in the tantalum alloy and the graphite, and the discoloration of the tantalum alloy are probably due to a small oxygen impurity in the argon cover gas. Additional tantalum alloy and graphite samples, which were not in direct contact with the nickel/zirconia composites, both show similar weight changes and surface discoloration.

D. Thermal Conductivity Testing

The object of this test was to determine the thermal conductivity of nickel/zirconia composites during normal operations before switching.

The thermal conductivity test method used for temperatures up to 1600°F utilized a Dynatech comparative cut-bar thermal conductivity measuring system. The thermal conductivity test specimen was a one-inch diameter by one-inch high cylinder. Due to the difficulty in impregnating one-inch thick sections of the zirconia felt, the test specimens were composed of a stack of four discs of the nickel/zirconia composites one-quarter-inch thick.

The thermal conductivity data measured by the cut-bar method for Ni/ZrO₂ composites containing 1.5 and 2.0 gram Ni/cc are reported in Table V-2 below. The nickel impregnant, except where noted, is the high purity nickel derived from the hydrazine reduced electroless nickel bath.

TABLE V-2. THERMAL CONDUCTIVITY OF
Ni/ZrO₂ COMPOSITES

<u>ZrO₂ Felt Density (g/cc)</u>	<u>Ni Density (g/cc)</u>	<u>Average Temp. (°F)</u>	<u>K (Btu/hr·ft·°F)</u>
0.8	2.0	970	2.5
0.8	2.0	1350	2.3
0.8	2.0	1680	2.4
0.8	1.5	920	1.6
0.8	1.5	1400	1.5
0.8	1.5	1585	1.5
0.8	2.0*	900	2.9
0.8	2.0*	1320	2.8

* Nickel impregnant from Niklad boron-containing bath

E. Thermal Diffusivity Testing

The object of the thermal diffusivity tests was to determine high temperature thermal conductivity measurements of the nickel/zirconia composites in the preswitch and post-switch conditions.

Two series of thermal diffusivity tests were performed by Los Alamos Scientific Laboratory (LASL) on nickel/zirconia switch materials. The test reports are given in References 8 and 9 and are abstracted in the following.

1. Test No. 1 - Room Temperature Testing of Six B-Containing Specimens

Six discs of nickel impregnated rigidized zirconia felt were sent to LASL. It was intended that thermal diffusivity be measured from room temperature to well above the anticipated switching point (2650°F), however, only room temperature measurements were performed. The reason for this was that all six samples were produced by utilizing a commercially available electroless solution which leaves a slight boron impurity. As discussed in Section III, even small amounts of boron substantially reduce the melting or switching point. It was decided, therefore, that for these samples, room temperature diffusivity would be sufficient; this would give an indication of the impregnation efficiency, i.e., the effectiveness of a given amount of nickel to raise the thermal conductivity of a thermal switch composite material.

The characteristics of the six disc specimens are listed in Table V-3. The matrix of all the composites is 0.82 g/cc rigidized zirconia felt supplied by Union Carbide Corporation. The original discs were cut down from the tabulated sizes to 0.50 inch outer diameter to fit the standard sample holder.

TABLE V-3. DESCRIPTION OF Ni IMPREGNATED,
RIGIDIZED ZrO₂ FELT

<u>Sample No.</u>	<u>Thickness (inch)</u>	<u>Diameter (inch)</u>	<u>Ni Density (g/cc)</u>
PR5-2a	0.070	0.627	2.09
PR5-2b	0.070	0.627	1.98
PR5-17a	0.070	0.627	2.07
PR5-24a	0.070	0.628	1.32
PR5-24b	0.066	0.628	1.14
PR5-25b	0.060	0.625	1.23

The thermal diffusivity of each sample was measured twice in each direction by the standard laser flash technique. The data were corrected for finite pulse time and radial heat losses. All tests were conducted at room temperature in air. Reference 8 describes the tests and test results in detail.

The observed thermal diffusivities as well as the density data are listed in Table V-4. Each diffusivity (α) value is the average of four measurements. The first group of three samples, the high Ni loaded samples, had an average diffusivity of $0.0338 \text{ cm}^2/\text{sec}$. The second group of three samples were reported to contain considerably less Ni and their lower diffusivity values confirmed this fact. However, the samples numbered PR5-24a and PR5-24b averaged $0.0249 \text{ cm}^2/\text{sec}$ in diffusivity while the last sample, PR5-25b, had an α of only $0.0115 \text{ cm}^2/\text{sec}$. Macroscopic examination did not indicate any cause for this factor of two differences in α among the low Ni loaded samples. It is theorized that the explanation for this behavior is that the sample had an area with little or no nickel impregnant. If the diffusivity and temperature measurements were made in this area, one would expect a low thermal diffusivity and thermal conductivity to result.

TABLE V-4. THERMAL DIFFUSIVITY (α) OF
RIGIDIZED ZrO_2 IMPREGNATED WITH NICKEL

Sample No.	Measured ρ g/cc	Calculated ρ			α cm ² /sec
		Ni g/cc	ZrO ₂ g/cc	Ni+ZrO ₂ g/cc	
PR5-2a	3.11	2.09	0.82	2.91	0.0372
PR5-2b	2.78	1.98	0.82	2.80	0.0324
PR5-17a	2.93	2.07	0.82	2.89	0.0317
Average	2.94	2.05	0.82	2.87	0.0338
PR5-24a	2.19	1.32	0.82	2.14	0.0243
PR5-24b	2.17	1.14	0.82	1.96	0.0261
PR5-25b	2.20	1.23	0.82	2.05	0.0115
Average	2.19	1.23	0.82	2.05	0.0208

The thermal conductivity, a more useful engineering parameter, can be calculated from the thermal diffusivity by the relationship $k = C_p \alpha \rho$, where k is the thermal conductivity, C_p is the specific heat, α is the thermal diffusivity, and ρ is the density. The diffusivity and density data used in the calculation were from Table V-4. The heat capacity data was taken from the literature (Ref. 10).

The calculated conductivities in 3 units of measurement are listed in Table V-5; the values fall into the same groups as did the diffusivities. The samples with the high Ni loadings have an average k of $2.57 \text{ Btu/hr}\cdot\text{ft}\cdot^\circ\text{F}$, two of the lower Ni loaded samples have an average k of $1.43 \text{ Btu/hr}\cdot\text{ft}\cdot^\circ\text{F}$, and the third low Ni sample had a much lower k of $0.65 \text{ Btu/hr}\cdot\text{ft}\cdot^\circ\text{F}$.

TABLE V-5. CALCULATED THERMAL CONDUCTIVITIES OF
RIGIDIZED ZrO_2 IMPREGNATED WITH NICKEL*

Sample No.	C_p cal/g $^{\circ}$ K	α cm 2 /sec	ρ g/cc	k_1 cal/sec $\cdot$ cm $^{\circ}$ K	k_2 W/cm $^{\circ}$ K	k_3 Btu/hr $\cdot$ ft. $^{\circ}$ F
PR5-2a	0.107	0.0372	3.11	0.0124	0.0518	3.00
PR5-2b	0.107	0.0324	2.78	0.0096	0.0403	2.33
PR5-17a	0.107	0.0317	2.93	0.0099	0.0416	2.40
Average	0.107	0.0338	2.94	0.0106	0.0445	2.57
PR5-24a	0.107	0.0243	2.19	0.0057	0.0238	1.38
PR5-24b	0.107	0.0261	2.17	0.0061	0.0254	1.47
PR5-25b	0.107	0.0115	2.20	0.0027	0.0113	0.655
Average	0.107	0.0208	2.19	0.0049	0.0204	1.18

*At room temperature

2. Test No. 2 -

A second batch of nickel impregnated rigidized zirconia felt samples were submitted to LASL. These five samples were produced by the high purity electroless nickel impregnation system. Thermal switch testing on samples produced with this electroless system have indicated a switching point close to within the melting point of the ultra-pure nickel, 2650 $^{\circ}$ F.

Measurements on only one sample are described in this report. Reference 9 describes the test results in detail. The "as received" sample was cut down from 0.623 inch diameter to 0.500 inch to fit the standard sample holder. The measured bulk density after machining was 2.72 g/cc which is 0.28 g/cc higher than that reported by Hittman Associates. Los Alamos Scientific Laboratory's measured density and Hittman's estimate of the matrix density, 0.82 g/cc were used in subsequent calculations; the Ni density was calculated as 1.90 g/cc (0.82 g/cc subtracted from 2.72 g/cc).

Again, the standard LASL laser flash technique was used to measure the thermal diffusivity of the sample disc. Chromel-alumel thermocouple probes were utilized over the 77 to 1470 $^{\circ}$ F. The diffusivity data were corrected for finite pulse time and radial heat losses. All measurements were conducted in 0.1 atm of argon in an all-metal system (stainless steel and tantalum) to avoid carbon contamination.

According to LASL, the nickel impregnated, zirconia felt behaved differently than the copper impregnated felt in two respects: (1) the switch point was higher approximately 2650 versus 1950 $^{\circ}$ F, and (2) the molten Ni migrated to the surface of the ZrO_2 without causing extensive disruption of the ZrO_2 matrix as copper did.

The observed thermal diffusivities on Specimen No. 48-1 are listed in Table V-6. Duplicate measurements were made at 24, 402, and 699°C, and the sample cooled to room temperature for another measurement to determine if a change in diffusivity had occurred during the relatively modest heating. The room temperature diffusivity and physical dimensions were unchanged. Penetration of the sharpened thermocouples into the back of the sample was negligible.

The sample was then heated slowly to 1661°C and the diffusivities measured at 999, 1166, 1252, 1517, and 1661°C. Between 1252 and 1517°C the diffusivity dropped from 0.0194 to 0.00387 cm²/sec—evidence that the thermal switch had occurred. The furnace was cooled to 25°C and the sample examined. Many nickel beads had coalesced on the upper surface. After these beads were removed, the sample thickness was unchanged but the density had decreased to 1.71 g/cc. The sample was returned to the furnace and the diffusivity measured at five points between 800 and 1936°C. The sample was cooled and examined; the thickness was virtually unchanged, but the density had decreased to 1.29 g/cc. Nickel from the sample had partially destroyed the sample holder so high temperature measurements were discontinued. The ZrO₂ matrix appeared to contain many small beads of nickel. The ZrO₂ felt was mechanically intact, it had not scaled and crumbled as did the ZrO₂ from the copper impregnated ZrO₂ during an earlier test phase.

The diffusivity versus temperature data were plotted on Figure V-2 and a smooth curve sketched through the points. Diffusivities at centennial temperature points were read from the curve and listed in Table V-6 as well as Table V-8 where they were used in calculating the thermal conductivity.

The thermal conductivity was calculated from the equation, $k = C_p \alpha \rho$. The specific heat of the nickel-zirconia thermal switch sample is computed by summing the products of the weight percent of each constituent in the composite multiplied by its specific heat. The C_p of 2.72 g/cc Ni/ZrO₂ is listed in Table V-7; at temperatures above the melting point of nickel, all the metal is assumed to be out of the matrix, and the C_p becomes that of only zirconia. The density of the composite is assumed to be room temperature value until the switch point, then only the room temperature value of zirconia is considered. In reality, some Ni remains in the matrix after the switch and is slowly eliminated as it migrates to the surface at a rate dependent on time and temperature. For the purposes of the thermal conductivity calculations, the nickel is considered to be absent after the thermal switch.

Tables V-8 and V-8 Supplement list the calculated thermal conductivities of the 2.72 g/cc Ni/ZrO₂ felt in three useful units, cal/sec·cm·°K, W/cm·°K, and Btu/hr·ft·°F. These data are plotted versus temperature on Figure V-3.

TABLE V-6. THERMAL DIFFUSIVITY OF Ni/ZrO₂ Felt*

Observed Data			Smoothed Data from Curve (Figure 1)		
Temperature		α cm ² /sec	Temperature		α cm ² /sec
^o K	^o C		^o K	^o F	
297	24	0.0311	300	81	0.0310
675	402	0.0189	400	261	0.0245
972	699	0.0208	500	441	0.0219
Cooled to Room Temperature			600	621	0.0200
293	20	0.0313	700	801	0.0190
1272	999	0.0167	800	981	0.0186
1439	1166	0.0190	900	1161	0.0183
1525	1252	0.0194	1000	1341	0.0181
Thermal Switch Occurred			1200	1701	0.0182
1790	1517	0.00387	1400	2061	0.0186
1934	1661	0.00428	1600	2421	0.0190
Sample Density now 1.71 g/cc			Thermal Switch Occurred		
1085	812	0.00269	1800	2781	0.0042
1468	1195	0.00344	2000	3141	0.0052
1688	1415	0.00331	2200	3501	0.0072
1899	1626	0.00468	2400	3861	off scale
2209	1936	0.00795**			

* Sample 48-1, 2.72 g/cc (0.82 g^{ZrO}₂/cc, 1.90^{Ni}/cc), Hittman Associates, March 31, 1971, High Purity Ni. All measurements in 0.1 atm argon in all metal (no graphite) system.

** Sample density 1.29 g/cc at conclusion of run.

TABLE V-7. CALCULATED SPECIFIC HEAT (Cp) of Ni/ZrO₂ FELT*

Temperature °K °F		C _p of ZrO ₂ , cal/gm-°K		C _p of Ni, cal/gm-°K		C _p of Ni/ZrO ₂ Felt cal/gm-°K ⁽⁵⁾
		ZrO ₂	Composite	Ni	Composite	
100	-279	0.038	0.011	0.057	0.040	0.051
200	- 99	0.084	0.025	0.091	0.064	0.089
300	81	0.109	0.033	0.108	0.075	0.108
400	261	0.123	0.037	0.117	0.082	0.119
500	441	0.130	0.039	0.126	0.088	0.127
600	621	0.135	0.041	0.140	0.098	0.139
700	801	0.140	0.042	0.126	0.088	0.130
800	981	0.143	0.043	0.126	0.088	0.131
900	1161	0.145	0.043	0.130	0.091	0.134
1000	1341	0.147	0.044	0.138	0.097	0.141
1200	1701	0.151	0.045	0.142	0.099	0.144
1400	2061	0.154	0.046	0.150	0.105	0.151
1600	2421	0.145	0.043	0.152	0.107	0.150
1800**	2781	0.145	0.145**	Liquid	Liquid	0.145
2000	3141	0.145	0.145	Liquid	Liquid	0.145
2200	3501	0.145	0.145	Liquid	Liquid	0.145
2400	3861	0.145	0.145	Liquid	Liquid	0.145

* Sample 48-1, 2.72 g/cc (0.82 ^{ZrO}2/cc, 1.90 g ^{Ni}/cc), Hittman Associates, March 31, 1971, High Purity Nickel.

** Thermal Switch at 1728°K (Melting Point of Nickel), Composite becomes ZrO₂ only.

TABLE V-8. CALCULATED THERMAL CONDUCTIVITY OF Ni/ZrO₂ FELT*

Temperature		C_p	α	ρ	Thermal Conductivity, k		
					1	2	3
$^{\circ}\text{K}$	$^{\circ}\text{F}$	cal/gm- $^{\circ}\text{K}$	cm ² /sec	gm/cc	cal/sec-cm- $^{\circ}\text{K}$	W/cm- $^{\circ}\text{K}$	Btu/hr-ft- $^{\circ}\text{F}$
300	81	0.108	0.031	2.72	0.0091	0.038	2.20
400	261	0.119	0.025	2.72	0.0081	0.034	1.96
500	441	0.127	0.022	2.72	0.0076	0.032	1.83
600	621	0.139	0.020	2.72	0.0076	0.032	1.83
700	801	0.130	0.019	2.72	0.0067	0.028	1.63
800	981	0.131	0.019	2.72	0.0068	0.028	1.64
900	1161	0.134	0.018	2.72	0.0065	0.027	1.59
1000	1341	0.141	0.018	2.72	0.0069	0.029	1.67
1200	1701	0.144	0.018	2.72	0.0071	0.030	1.71
1400	2061	0.151	0.019	2.72	0.0078	0.033	1.89
1600	2421	0.150	0.019	2.72	0.0078	0.032	1.88
1800**	2781	0.145	0.0042	0.82	0.00050	0.0021	0.12
2000	3141	0.145	0.0052	0.82	0.00062	0.0026	0.15
2200	3501	0.145	0.0072	0.82	0.00086	0.0036	0.21
2400	3861	0.145	---	0.82	----	---	--

* Sample 48-1, 2.72 g/cc (0.82 g ^{ZrO}2/cc, 1.90 g ^{Ni}/cc), Mittman Associates, March 31, 1971, High Purity Nickel.

TABLE V-8. SUPPLEMENT
CALCULATED THERMAL CONDUCTIVITY OF Ni/ZrO₂ FELT* AFTER THERMAL SWITCHING

Temperature		c_p	α	ρ	Thermal Conductivity, λ		
$^{\circ}\text{K}$	$^{\circ}\text{F}$				$\text{cal/sec-cm-}^{\circ}\text{K}$	$\text{W/cm-}^{\circ}\text{K}$	$\text{Btu/hr-ft-}^{\circ}\text{F}$
1000	1341	0.147	0.0025	0.82	0.00030	0.0013	0.073
1200	1701	0.151	0.0028	0.82	0.00038	0.0016	0.093
1400	2061	0.154	0.0031	0.82	0.00038	0.0016	0.092
1600	2421	0.145	0.0035	0.82	0.00042	0.0017	0.100

* Sample 48-1, 0.82 g ZrO₂/cc, Hittman Associates, March 31, 1971 after thermal switch.

Figure V-2. Thermal Diffusivity of Ni/ZrO₂ Felt

Figure V-3. Calculated Thermal Conductivity of Ni/ZrO₂ Felt

F. Mechanical Property Determination

Compressive and transverse rupture strength of the nickel/zirconia composites in the as-impregnated condition (before thermal switch) and in the switched condition were measured at room temperature and at 1400°F. Two nickel loadings, i. e., 1.75 g/cc and 2.0 gm/cc were tested.

The mechanical property data is summarized in the following table and in Figure V-4 and V-5.

TABLE V-9. MECHANICAL PROPERTIES OF Ni/ZrO₂ COMPOSITE

Ni Density (g/cc)	Temperature (°F)	Compressive Strength (psi)	Transverse Strength (psi)
1.75	80	7000	7400
1.75	1400	See Figure V-5	3000
1.75 "switched"	80	730	870
1.75 "switched"	1400	690	875
2.0	80	See Figure V-4	8000
2.0	1400	See Figure V-5	5000
2.0 "switched"	80	750	890
2.0 "switched"	1400	710	880

Figures V-4 and V-5 indicate that the high purity nickel impregnated zirconia felt composites yield under load without a distinct compressive failure at room temperature and at 1400°F. The compressive deformation at 1400°F is considerably higher than at room temperature at a given load. The compressive deformation at 1400°F appears to be elastic, i. e., will recover to original dimension up to 1300 and 2400 psi, respectively, for a 1.75 g/cc and 2.0 gm/cc nickel loading. Earlier tests made with the boron containing nickel impregnant, did not show any significant compressive deformation and a 2.0 gm/cc nickel composite had room temperature compressive strength in the range of 10,000 to 12,000 psi.

Figure V-4. Deformation Under Compressive Load - Room Temperature

Figure V-5. Deformation Under Compressive Load - 1400°F

VI. NICKEL SUBLIMATION ANALYSIS

The sublimation experiments yielded data pertaining to the loss of weight as a function of time for several samples of Ni impregnated ceramic. Both uncoated and coated samples were evaluated. The configuration selected for test was similar to a flight configuration in that the samples were surrounded by a graphite container with small holes to simulate the gaps that might exist in a flight configuration. The graphite container then was placed within a vacuum furnace to provide the desired test environment.

Several analyses are necessary to evaluate the test data. First, one is interested in the effect of the imperfect vacuum in the furnace on the experiment. Therefore, the pressure inside of the container must be calculated and compared to the experimentally determined pressure outside of the container (within the vacuum furnace) to see if the back pressure has any effect on the evaporation rate. Next, the probable effect of the container walls on the evaporation rate of nickel needs to be considered to assess the effect of the container on the experiments. A comparison of the experimental rates with rates that would be found with pure nickel in a vacuum under similar conditions also will yield a useful comparison. Finally, when an understanding of the experimental conditions has been developed, one can hope to generate a model that will describe the evaporation of nickel from the porous ceramic in a vacuum or near vacuum conditions, or in an inert gas environment. The initial steps of the model development should be straightforward so that an understanding of the processes is developed before attempting to generate a highly accurate model.

A. Test Configuration

The test fixture has approximately the following configuration:

This graphite structure is placed in a vacuum furnace that is maintained at approximately 2100°F and approximately 2×10^{-7} torr.

Three one-inch diameter samples are contained inside the graphite. These have the following characteristics:

<u>Sample No.</u>	<u>1</u>	<u>2</u>	<u>3</u>
Basic Composition	Ni/ZrO ₂	Ni/ZrO ₂	Ni/ZrO ₂
Thickness (in.)	0.261	0.274	0.276
Surface Treatment	Bare	Plasma-Sprayed Coating	Plasma-Sprayed Coating Plus Cement
Ni Loading (gm/cm ³)	1.10	1.20	1.05
Sample Mass (gms) (after coating)	6.79	8.58	10.73

The base ZrO₂ is a felt material of about 20 percent theoretical density (~ 5.5 gm/cm³). The plasma-sprayed ZrO₂ is about 10 to 15 mils thick and approximately 80 percent dense. The precise cement composition is unknown, but is basically a ZrO₂ base with silicates added for binder. Experimental study has established a substantial initial outgassing rate from this coating, which is brush applied. Cement thickness is estimated as 10 to 18 mils.

The three samples are placed within the graphite structure with spacers separating them so that essentially all surfaces are exposed.

B. Test Data

The test data for each of the three samples are summarized in Figure VI-1. Note the overall behavior. The bare sample weight decrease is much more rapid than the coated samples, results one would expect. The bare sample data correlate by a curved line of decreasing slope with increasing time; the coated samples show straight line behavior with time. The former data are characteristic of a process in which the supply of evaporating material is limited. The straight line behavior is expected for a process in which the evaporating material is available in an unlimited supply. Several processes may be postulated. In the bare sample, the nickel close to the exposed surface may become depleted with increasing time. Then the source of subliming nickel becomes further and further within the ceramic structure, thus yielding a classic shape of decreasing evaporation rate with time. In the coated samples, the coating acts as a

Figure VI-1. Experimental Weight Loss Data

resistance to the passage of nickel. Apparently, the partial pressure of nickel on the inside remains constant and the loss rate is determined by the rate at which nickel atoms make their way through the coating.

This does not explain why the loss rate of the sample with two coatings is greater than the rate with one coating. One would expect the opposite. The investigators suspect that the cement coat is outgassing and evaporating, thus contributing to the weight loss. The plasma-sprayed coating is believed to be more stable. For this reason, the basic conclusion that may be drawn is that coating results in a significant nickel evaporation rate decrease. Quantitative values may be obtained for the plasma-sprayed sample, but no quantitative conclusions are warranted for the double-coated sample.

C. Configuration Analysis

The major experimental concern is whether the test configuration has an effect upon the test results. The potential interrelationship is one in which the nickel pressure within the graphite structure, and hence in the vicinity of the samples, is substantially different from the measured pressure in the vacuum furnace system. Next, one must be concerned with the return of nickel from the graphite walls to the samples and from one sample to another. If these effects may shown not to be of concern, then one may concentrate on analysis of sample behavior.

Figure VI-1 shows a weight loss of 16.1, 4.5, and 0.8 percent for samples 1, 3, and 2, respectively, at a test time of 3000 hours.* If this loss is assumed to be nickel (and this already has been stated to be incorrect for Sample No. 3), then the total nickel released during the 3000 hours was $1.09 + 0.30 + 0.05 = 1.44$ gms. The mean release rate was $1.44/3000 = 4.80 \times 10^{-4}$ gms/hr. Nickel's atomic weight is 58.7. The atom release rate therefore is $(4.80 \times 10^{-4} \text{ gms/hr}) / (58.7 \text{ gms/mole}) (6.02 \times 10^{23} \text{ atom/mole}) = 4.93 \times 10^{18}$ atoms/hr. These atoms will be assumed to flow out of the two holes located at the ends of the graphite container. Any leaks between the side wall and the end cap and porosity of the graphite will be neglected.

The initial behavior will be based upon a free molecule flow assumption; that is, only collisions with the walls will be allowed. There will be no collisions between atoms. The validity of this assumption may be checked after the pressure inside the graphite container has been determined. With this assumption, Lee (Ref.11) has shown that the number of atoms that cross a small area (from either side) is:

$$n = \frac{\bar{p}\bar{v}}{4} \quad (1)$$

*The total weight was assumed to be the same for each of the samples in arriving at these values from the experimental data. Therefore the plotted data are approximations. The actual data may be obtained by noting that the uncoated pellet mass was 6.79 grams, the value used for computing all weight loss values.

where:

$$\begin{aligned} n &= \text{atoms per unit area per unit time} \\ \rho &= \text{atom density} \\ \bar{v} &= \text{atom mean velocity} \end{aligned}$$

The mean velocity is (Ref. 9):

$$\bar{v} = \left(\frac{8kT}{\pi m} \right)^{1/2} \quad (2)$$

where:

$$\begin{aligned} k &= \text{Boltzmann constant} \\ T &= \text{temperature} \\ m &= \text{mass of an atom} \end{aligned}$$

Substitution of Equation (2) into (1) yields:

$$n = \frac{\rho}{4} \left(\frac{8kT}{\pi m} \right)^{1/2} \quad (3)$$

For the test conditions ($2100^{\circ}\text{F} = 1422^{\circ}\text{K}$):

$$\bar{v} = \left(\frac{8kT}{\pi m} \right)^{1/2} = \left[\frac{(8)(1.381)(10^{-16})(1422)(6.02)(10^{23})}{(\pi)(58.7)} \right]^{1/2} =$$

$$\bar{v} = 7.17 \times 10^4 \text{ cm/sec}$$

The flow rate has been found experimentally to be $(4.93)(10)^{18}/2/3600 = 6.85 \times 10^{14}$ atom/sec through each hole. The area of a hole is $(\pi)(0.031)^2 (2.54)^2 = 1.944 \times 10^{-2} \text{ cm}^2$. Therefore:

$$n = 6.85 \times 10^{14} / 1.944 \times 10^{-2} = 3.52 \times 10^{16} \text{ atoms/cm}^2 \text{ sec}$$

Now Equation (3) yields:

$$\rho = \frac{(4)(3.52 \times 10^{16})}{7.17 \times 10^4} = 1.962 \times 10^{12} \text{ atoms/cm}^3$$

One mole of an ideal gas contains 6.02×10^{23} atoms and occupies $22,400 \text{ cm}^3$ of volume at STP. The atom density is $(6.02 \times 10^{23} / 22,400)(530/2560) = 5.56 \times 10^{18} \text{ atom/cm}^3$. The pressure within the graphite container if the outside pressure is zero (so that no atoms return) is $1.962 \times 10^{12} / 5.56 \times 10^{18} = 3.53 \times 10^{-7} \text{ atm}$, or $(3.53)(10^{-7})(760) = 2.68 \times 10^{-4} \text{ mm Hg}$. Clearly, the pressure inside the graphite container is significantly above the $2 \times 10^{-7} \text{ mm Hg}$ determined at the vacuum station. (Chamber pressure in this system probably is within

a factor of two or so of the pressure at the measurement point.) Further, the effect of the test chamber pressure upon the inside of the graphite container will be negligible. Equation (3) shows that the atom flow rate is a direct function of the density, and the density outside the container is a factor of about 1000 below that inside the container. The vacuum system, if reasonably uncontaminated, will have no effect on the sample behavior.

The calculations have been based upon no atom-atom collisions. Now that the atom density and pressure have been calculated, this assumption can be checked. Typical atomic radii are about 2×10^{-8} cm. The collision cross section therefore is $\sigma = 4\pi [2 \times 10^{-8}]^2 = 5 \times 10^{-15}$ cm². Lee (Ref. 11) gives, for a Maxwellian velocity distribution, the following equation for mean free path:

$$\lambda = \frac{0.707}{\sigma \rho} \quad (4)$$

At an atom density corresponding to conditions inside the graphite container, the mean free path is roughly:

$$\lambda \approx \frac{0.7}{(5)(10^{-15})(2)(10^{12})} \approx 70 \text{ cm}$$

This is large in comparison to the size of the container; the free molecular behavior assumption is justified.

Next, the behavior of the nickel atoms in the vicinity of the samples must be considered to determine if the "ambient" nickel atmosphere will affect the behavior of the sample. The collision rate of nickel atoms within the container with the container (and sample) surfaces has been found to be 3.52×10^{16} atoms/cm² sec. This is the "incoming" flux of nickel that will be "seen" by the sample surface. Past experience would indicate that a sizeable fraction of these atoms would stick and then reevaporate, or, given favorable conditions, diffuse into a porous wall. There are two potential problems:

- (1) Nickel can coat surfaces, thereby perturbing the results
- (2) The high incoming flux of nickel atoms will negate the experimental results

Each potential problem will be considered in the following paragraphs.

The vapor pressure of nickel at 2100°F is about 10^{-5} mm Hg (Ref. 12). The rate at which nickel will evaporate from a surface, assuming there are no surface-nickel attraction effects other than a nickel-nickel attraction, is (Ref. 13):

$$\Gamma = \frac{P}{\sqrt{2\pi m k T}} \quad (5)$$

where:

p = vapor pressure

At 2100°F, one finds:

$$\Gamma = \frac{(10^{-5})(1333)}{[(2\pi)(58.7/6.02)(10^{-23})(1.381)(10^{-16})(1422)]^{1/2}}$$

$$\approx 1.2 \times 10^{15} \text{ atoms/cm}^2 \text{ sec}$$

This far below the previously calculated atom-wall collision rate of 3.5×10^{16} atoms/cm² sec. Either the nickel does not stick to the graphite container walls, or these walls are accumulating nickel. If the latter, then the pressure within the graphite container is significantly below the previously calculated 2.7×10^{-4} mm Hg.

The surface area of a sample pellet is $[2\pi(0.5)^2 + (\pi)(1)(0.27)](2.54)^2 = 15.6 \text{ cm}^2$. Most of the nickel comes from one pellet. If, for the moment, all is assumed to come from one pellet, then the flow rate out of the pellet has to be $(6.85 \times 10^{14})(2)/15.6 = 8.79 \times 10^{13}$ atoms/cm² sec. This is significantly below the rate at which nickel would leave a surface due to evaporation, and even further below the rate at which the calculations have indicated that nickel is returned to the samples.

There must be a net loss of nickel from the samples (unless some other unrecognized phenomena are taking place); either the graphite is adsorbing and/or absorbing significant quantities of nickel or the porous structure of the zirconia is acting as a significantly extended area for nickel evaporation. But, the latter does not make sense for a free molecule flow situation. Therefore the former must be the case and/or the nickel atom concentration within the pores is so high that a significant atom-atom collision rate is taking place. In any event, the possibility of the graphite container inhibiting the flow of nickel from the samples appears to be a real one. Therefore, the experimental data must be interpreted in this light.

D. Pellet Sublimation Analysis

A precise analysis of the sample behavior is not feasible for this study. Such an analysis would require consideration of the geometry within the sample pellets, something that has not been established with any precision. For example, the pore and channel dimensions and configurations on the average and the deviations from those data would have to be established. Since this information is not available, there is little to be gained by attempting a highly sophisticated analysis that would be inconsistent with the approximate information that has been established.

The area of the curved surface on each of the samples is about $(\pi)(0.27)(1.0) = 0.847 \text{ in.}^2$ and the area of the flat ends is $(\pi)(0.5)^2(2) = 1.570 \text{ in.}^2$. Clearly, the side surface area may not be neglected in comparison to the end area. This unfortunately complicates the mathematical treatment somewhat.

Consider a pellet section:

To a good approximation, one may assume the volume contained within the dotted lines to be of uniform composition provided the thickness (distance between dotted lines) is taken sufficiently small (Of course, the corner sections will become depleted of nickel more rapidly than will the other portions, but this will be neglected for the initial analysis.) Next, the assumption will be made that flow of nickel vapor occurs only in a direction perpendicular to the dashed lines. (This follows from the previous assumption pertaining to the nickel concentration. There would be no driving force to cause nickel to flow in any other manner if the initial assumption is satisfied.) Next, the pellet will be assumed to be homogeneous, an assumption necessary if a straightforward mathematical treatment is to be attempted. Finally, flow of nickel within the pellet will be assumed to occur according to the diffusion equation, and the diffusion coefficient will be assumed independent of the nickel concentration. The former assumption probably will be realistic if the voids are relatively small and passages between voids also are small. The latter assumption will require that the nickel not act as a seal within the zirconia or, if it does, that the sealing characteristics not change over the concentration range of interest to this analysis. In addition, one requires that the collision characteristics of the nickel atoms not change considerably over the concentration range for which an analysis is to be attempted.

These assumptions would allow one to set up a classical diffusion equation with the variables r and t (x may be related to r , thus eliminating one of the position variations and greatly simplifying the potential analysis). But, the source term for production of nickel "gas" within the felt has not been considered. One interesting aspect of the experimental evaporation rates and the theoretical evaporation of pure nickel is that in all cases the rate at which nickel apparently left the felt samples was far less than would have been the case with pure nickel. One explanation for this behavior may be the high nickel return rates due to reflection or reevaporation of nickel from the surrounding surfaces. Another possibility is a restriction to flow of nickel from the interior of the sample to the surface since there is plenty of nickel spread over an extended surface within the foam which can replenish external surface losses. The postulate will be made that the interior of the felt is saturated with gaseous nickel as long as any remains on the interior surfaces. Consistent with this postulate is the assumption that as long as a coating of nickel remains on an interior surface, there can be no concentration gradient from the part of the felt inward to the center of the sample. From that point outward to the external surface, a concentration gradient is possible and all of the nickel that was readily available to interconnected pores would have been depleted in that region. Further, a portion of the nickel that was not available to interconnected pores also may have been depleted due to diffusion to "open" pores. For analysis purposes, the assumption will be made that there is no layer of nickel on pores that are not connected in some way to the outside surface. (One may pose the question, "How could the nickel get into a closed pore in the first place?" Viewed in this manner, the assumption appears to be realistic, although all doubts have not been removed.)

Next, consider the quantity of nickel that exists in gaseous form as compared to that existing in "condensed" form. The former obviously is very small. An additional assumption will be made that there is no accumulation (or depletion) of the "gaseous" form within the foam since the quantity is so small. This will greatly simplify the analysis.

This model was applied to the development of a mathematical description of the events which take place during the evaporation process. With a length to diameter ratio of 0.5, solution resulted identical to the one that would be obtained for a spherical geometry. Obviously, this is not a mathematically correct description of the events, although it might serve to give an indication of what takes place. The concern is that such a description is too approximate to be useful. One of the major areas for concern is the use of a cylindrical description for the isoconcentration plane. This should be eliminated, which correct a portion of the model inaccuracy. Therefore, the recommendation is made that a more precise model be utilized for further investigation of this problem. The presented model, for this reason, is not applied to the determination of numerical results.

VII. REFERENCES

1. HIT-480 Final Report - Pioneer Thermal Switch Effort (January 1971).
2. Pessel, L., U.S. Patent 2,430,581 (November 1947).
3. Progst, W., German Patent 717,547 (February 1952).
4. Levy, D., "Thin Nickel Films by Hydrazine Autocatalytic Reduction" *Electrochem. Technology Journal*, 1, (1-2) 38-42 (1963).
5. SCL-DC-66-22, Dini, J. and Coronado, P., "Thick Nickel Deposits of High Purity by Electroless Methods" (June 1966).
6. Rhoda, R., "Electroless Palladium Plating" *Trans. Inst. Metal Finishing*, 36, 82-85 (1958-1959).
7. Hansen, M., Constitution of Binary Alloys, McGraw-Hill, New York, New York, 1958.
8. Memorandum, Morrison and Sturgess, N-1, Thermal Diffusivity-Conductivity of Nickel Impregnated Rigidized Zirconia Felt, N-1-2732, February 26, 1971.
9. Memorandum, Morrison and Sturgess, N-7, Thermal Diffusivity-Conductivity of Pure Nickel Impregnated Rigidized Zirconia Felt, N-7-954, April 26, 1971.
10. Goldsmith, et al, Handbook of Thermophysical Properties of Solid Materials, Vol. III Ceramics, Macmillan, New York, New York, 1961.
11. Lee, J.F., et al, Statistical Thermodynamics, Addison-Wesley, Reading, Mass., 1963.
12. Weast, R. C., and Selby, S. M., Handbook of Chemistry and Physics, forty-eighth edition, Chemical Rubber, Cleveland, Ohio, 1967.
13. Lyon, W. C., "Thruster Exhaust Effects Upon Spacecraft," NASA-TM-X-65427, X-460-70-401, Hittman Associates, Columbia, Md., Oct. 1970.