INTERIM REPORT FOR Ni/ZrO₂
HIGH TEMPERATURE THERMAL
SWITCH REPORT
NOVEMBER 1970 TO JANUARY 1971

HIT-488

MARCH 1971

Prepared Under
AEC Contract No. AT(29-2)-2797

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

HITTMAN ASSOCIATES, INC.
COLUMBIA, MARYLAND

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
109

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

TABLE OF CONTENTS

	<u>Page</u>
LEGAL NOTICE	ii
TABLE OF CONTENTS	iii
LIST OF FIGURES	iv
I. INTRODUCTION AND SUMMARY	I-1
II. MATERIALS SELECTION	II-1
A. Metal Impregnant	II-1
B. Porous Ceramic Materials	II-3
III. FABRICATION OF COMPOSITE MATERIALS	III-1
A. Process Selection	III-1
B. Process Development	III-1
IV. PROPERTY DETERMINATION	IV-1
A. Thermal Switch Test	IV-1
B. Compatibility Testing	IV-1
C. Compressive Strength Testing	IV-2
D. Sublimation Testing	IV-3
E. Thermal Conductivity	IV-4
V. REFERENCES	V-1

LIST OF FIGURES

<u>Figure No.</u>	<u>Title</u>	<u>Page</u>
II-1	Thermal Conductivity of ZrO ₂ Foam and Felt Materials Versus Temperature	II-5
III-1	Electroless Deposition - Impregnation System	III-3
III-2	Nickel Impregnated ZrO ₂ Felt with 0.5 gm Ni/cc (230X Magnification)	III-6
III-3	Nickel Impregnated ZrO ₂ Felt with 1.5 gm Ni/cc (230X Magnification)	III-6
III-4	Nickel Impregnated ZrO ₂ Felt with 2.0 gm Ni/cc (230X Magnification)	III-7
III-5	Nickel Impregnated ZrO ₂ Felt with 2.4 gm Ni/cc (230X Magnification)	III-7

I. INTRODUCTION AND SUMMARY

The High Temperature Metal Thermal Switch Program was redirected back to the design, development, and testing of thermal switch materials for radioisotope thermoelectric generator heat sources operating above 2000°F. The conversion system of interest for this operating temperature is the Isotope-Brayton cycle. The major goal of this preliminary three-month effort was to fabricate thermal switch composite materials and initiate property determination testing.

The following discussion briefly summarizes the results of the three-month effort.

- Zirconia (ZrO_2) rigidized felt was selected for the high temperature thermal switch material for consideration for the Brayton cycle heat source. The selection was based on the low thermal conductivity of the rigidized felt structures and the applicable thermal and physical properties of zirconia (Section II).
- A materials survey showed both nickel and palladium metals to have properties suitable for the high temperature thermal switch application. Although nickel was selected for the original development and testing, it appears that palladium would offer some advantages in higher melting temperature, lower vapor pressure and enhanced oxidation resistance (Section II).
- 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) (Section III).
- The initial nickel/zirconia composites tested all contained nickel made with the boro-amine and hence had the boron impurity. These tests are continuing, however, additional test specimens are being prepared with a high purity electroless nickel; these materials will be tested during the next phase of the program (Section IV).

II. 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, °F, 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 Isotope-Brayton cycle application:

- (1) Melting temperature higher than the normal operating temperature of the capsule, i. e. >2000°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 cycle.
- (2) High thermal conductivity at 2100°F 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 II-1. The metals which appear most attractive as impregnants are nickel and palladium. These metals show good thermal conductivity

TABLE II-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 °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	8670	< 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	3258	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.

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 II-2 and Figure II-1 show the properties of the basic refractory oxides which may be considered for this application. Based on the data shown 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 Co. in the form of cubes, plates, cylinders, and brick with a density of 1.4 g/cc (~25 percent dense) and with pore diameters ranging from 0.015 to 0.020 inches. The foam was made by blending a pre-sized 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.

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 Corp. as 1/4 inch and 1/2 inch thick plates and as hollow cylinders of 1/4 to 1/2 inch wall thickness and 4 inches diameter x 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 II-1
- (2) Lower bulk density, i. e., 0.8 g/cc felt vs. 1.4g/cc foam

TABLE II-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>	<u>Service Temp. °F</u>
Al_2O_3	3.95	3720	Good to m. p.	Very good	Very good	Low	3000
ZrO_2 (Stab.) ⁽¹⁾	5.75	4800	Good to m. p.	Good	Very good	Medium	4000
BeO	3.01	4658	Phase trans- formation at 3700°F	Excellent	None	Medium- high	3500
MgO	3.58	5160	Good to >4000°F	No data	Limited	Low	3000
ZrSiO_4	4.68	2800	Decomp. to ZrO_2 and SiO_2 at 2800°F	Very good	Good	Low	2500
SiO_2	2.2	3130	Phase change above 2200°F	Excellent	Very good	Low	2000
ThO_2	10.0	5830	Good to >4000°F	Poor	None	High	4000
HfO_2 (Stab.) ⁽¹⁾	10.0	5140	Good to >4000°F	No data	None	High	4000

(1) Stabilized with CaO , MgO , or Y_2O_3

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

- (3) Finer pore structure, i. e., <0.001 inch vs. $0.015-0.020$ inch which will suppress high temperature heat transfer by radiation
- (4) Improved thermal shock resistance by nature of the fibrous structure
- (5) Crack free felt structure

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

III. 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 impregnation processes lend themselves well to the production of quality controlled, uniformly impregnated porous ceramic structures.
- (3) The electroless impregnation processes are low temperature processes and can be controlled by conventional chemical methods.

B. Process Development

1. Surface Sensitization

Surface catalysis of non-conducting 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. The procedure used for sensitizing the zirconia felt involves the use of a dilute solution of palladium resinate in acetone which is allowed to infiltrate completely through the felt material. After impregnation and drying, the zirconia felt is heated in air to 450°F to decompose the organic palladium resinate leaving a minute amount of palladium on the felt fiber surfaces. This will readily initiate the electroless nickel deposition reaction.

2. Electroless Nickel Impregnation

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 phosphorus containing films show initial melting 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 reported for the nickel deposits.

A proprietary phosphorus-free electroless nickel deposition system was recently introduced for electronic applications. This system (Niklad-755 supplied by Allied Research Products) has a boron content of approximately 0.4 percent and the film produced has a low electrical resistivity similar to that of pure nickel. The melting temperature of the deposit was reported to be 2535°F. The eutectic composition in the nickel-boron system at 4 weight percent (18.5 atomic percent) boron has a melting temperature of 2084°F. The low-boron and zero-phosphorus content implies the use of a boron amine reducing agent in the system. This system was selected for the initial work on the electroless deposition impregnation of zirconia felt materials for the high temperature thermal switch application.

The electroless deposition-impregnation system used for the impregnation of the zirconia felt is shown in Figure III-1. The system consists of a volume of the electroless nickel plating solution heated by a thermostatically controlled hot plate and continuously pumped through the zirconia felt which is contained in the specimen holder. The zirconia piece is sealed in the specimen holder with an O-ring to ensure that all of the solution is pumped through the piece.

Initial plating work with the Niklad-755 system indicated good deposition on the surfaces of the sensitized felt materials. The electroless nickel plating appeared to uniformly deposit the nickel throughout the felt. The plating solution has a low viscosity and no problems were experienced due to closing of the pore channels or excessive pressure required to pump the liquid through the felt piece. At a pumping rate of 300-400 cc/minute, the pumping pressure was 10-15 psi when the nickel content of the impregnated felt approached 2.0 gms Ni/cc. Nickel loadings as high as 3.0 gms/cc were deposited before a significant pressure buildup was noted. The Niklad-755 electroless nickel solution was used to prepare nickel impregnated zirconia felt specimens for the following tests:

Figure III-1. Electroless Deposition -
Impregnation System

- (a) thermal switch temperature
- (b) thermal conductivity
- (c) compatibility
- (d) sublimation loss
- (e) compressive strength

In light of the results of the thermal switch temperature tests discussed in Section IV, which indicated melting points below literature values, efforts were directed toward development of an electroless process for plating a high purity, phosphorus and boron free, electroless nickel. The use of hydrazine as a reducing agent in electroless nickel plating baths was reported in the literature (Ref. 2). These early systems were not entirely successful as they were not sufficiently auto-catalytic to permit thick nickel deposits, and in some cases, the baths were unstable and decomposed. Recently, Dini and Coronado (Ref. 3) developed an electroless bath stabilized with sodium EDTA and using a hydrazine reductant capable of depositing thick, high purity nickel coatings. The electroless nickel impregnation of the sensitized zirconia felt was accomplished with the deposition-impregnation unit and initial work indicated that the hydrazine bath will readily deposit nickel on the sensitized felt at a relatively high plating rate of 1.0 gm/hr/cc of zirconia felt. The electroless nickel, as deposited, had a dark brown-black mat appearance; however, heat treatment of the nickel-impregnated foam in hydrogen yields a clean grey-metallic material. Table III-1 gives the results of a spectrographic analysis of the electroless nickel after heat treatment in hydrogen.

TABLE III-1. ANALYSIS OF NICKEL FROM
HYDRAZINE REDUCED ELECTROLESS SYSTEM

	<u>Weight Percent</u>
Nickel assay	99.8
<u>Spectrographic Analysis</u>	
<u>Metal Impurity</u>	<u>Weight Percent</u>
Cu	0.08
Co	0.02
Fe	0.05
Pb	0.03
Cr	<0.0005
Na	0.04
Zn	0.005
Al	<0.001
Be	<0.0005

The analysis confirms the reported high purity of the electroless nickel deposit. The binary phase diagrams of nickel and the impurities listed show no eutectic temperatures for the percentages of impurities found, and only very slight depression of the melting temperature for the Pb and Be impurities. The copper, cobalt, and iron are impurities normally present in the nickel salt in the plating bath. The sodium impurity is introduced by the sodium hydroxide used to adjust pH. Any nitrogen, hydrogen, and oxygen impurities in the electroless nickel deposit would be eliminated by the high temperature treatment.

Figures III-2, III-3, III-4, and III-5 show successive structures of electroless nickel-impregnated zirconia felt material with nickel loadings of 0.5, 1.5, 2.0, and 2.4 gm/cc, respectively. The nickel deposit is completely dense and reasonably uniform in coating thickness. The nickel appears to have plated all of the exposed zirconia fibers for loadings higher than 1.5 g/cc (Figures III-4 and III-5).

3. Electroless Palladium Impregnation

A preliminary survey was made on the electroless deposition of palladium. It is planned to develop methods for impregnating the zirconia felt with palladium and to test the Pd/ZrO₂ composite for switch temperature, compatibility, sublimation, thermal conductivity, etc., in a manner similar to the tests on the Ni/ZrO₂ composite.

Figure III-2. Nickel Impregnated ZrO_2 Felt with 0.5 gm Ni/cc
(230X Magnification)

Figure III-3. Nickel Impregnated ZrO_2 Felt with 1.5 gm Ni/cc
(230X Magnification)

Figure III-4. Nickel Impregnated ZrO_2 Felt with 2.0 gm Ni/cc
(230X Magnification)

Figure III-5. Nickel Impregnated ZrO_2 Felt with 2.4 gm Ni/cc
(230X Magnification)

IV. PROPERTY DETERMINATION

A test program was initiated on the nickel-impregnated zirconia felt for application to the NASA-Isotope-Brayton cycle system. The tests that have been completed or are underway are:

- Thermal switch temperature of the nickel/zirconia felt composite
- Compatibility of the nickel/zirconia composite with typical heat source materials
- Nickel sublimation from the nickel/zirconia composite
- Thermal conductivity of the nickel/zirconia composite before switching
- Compressive strength of the nickel/zirconia composite

A. Thermal Switch Test

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

The test was conducted by heating the Ni/ZrO₂ composite in argon while continuously measuring the electrical resistance of the composite. The temperature at which the resistance changed from a low resistance (dead short) to open circuit resistance was the thermal switch temperature. It was noted during the test that a resistance increase occurred at approximately 2350°F but further heating to 2500°F did not increase the resistance nor give a dead short. It is hypothesized that the resistance change was due to a partial melting or switching of the nickel due to dissolved boron in the nickel. The low boron impurity raised the liquidus temperature above the nickel-4 w/o boron eutectic temperature of 2084°F.

A thermal switch test was performed on another nickel/zirconia specimen which was prepared in the hydrazine bath. No melting or switching was noted up to 2600°F which was the temperature limit of the furnace and for the test. Ultra-pure nickel melts at 2650°F, which implies the sample was quite high in purity.

B. Compatibility Testing

The object of this test is to determine the compatibility of the Ni/ZrO₂ composite with Brayton cycle RTG heat source materials. The test is conducted under one atmosphere argon at 2100°F.

The test specimens are nickel-impregnated zirconia felt pieces one inch diameter by 1/4 inch high. The specimens currently under test were prepared with the boro-amine nickel plating system and therefore contain the boron impurity. The nickel-impregnated zirconia specimens were coated with plasma sprayed ZrO_2 and heat treated in hydrogen at 1700°F before testing. The compatibility of the Ni/ZrO_2 is being tested against graphite and Pt-20 Rh alloy. The compatibility test materials are assembled in a stack and are contained in a closed stainless steel tube under one atmosphere argon pressure. The stack is made up of the following materials

- (1) ZrO_2 spacer - 1/8 inch thick
- (2) Ni/ZrO_2 composite - 1/4 inch thick
- (3) Pt-20 Rh Alloy - 0.010 inch thick
- (4) Pt-20 Rh alloy - 0.010 inch thick
- (5) Ni/ZrO_2 composite - 1/4 inch thick
- (6) T-111 alloy - 0.030 inch thick
- (7) T-111 alloy - 0.030 inch thick
- (8) Ni/ZrO_2 composite - 1/4 inch thick
- (9) Graphite - 1/8 inch thick
- (10) ZrO_2 spacer - 1/8 inch thick

Another test capsule assembly similar to that listed above is being prepared. The nickel/zirconia composite samples in this assembly were prepared with the hydrazine reduced electroless nickel. As previously discussed, this nickel is of high purity which should have improved compatibility with the test materials.

C. Compressive Strength Testing

Compressive strengths of the nickel/zirconia composite were initially determined at room temperature. The compressive strengths of two Ni/ZrO_2 composites are 8,200 psi and 12,400 psi for nickel loadings of 1.6 gm Ni/cc and 2.3 gm Ni/cc; then, composites were made with the boro-amine reduced electroless nickel. The resultant boron impurity will tend to lower the ductility of the nickel and therefore would tend to increase the compressive strength of the composite.

Additional samples made with the high purity nickel are being prepared and will be tested. The higher purity, ductile nickel will probably give lower compressive strengths than those determined above. It should be noted that the compressive data reported above indicates these materials are the highest strength thermal switch composites we have produced.

D. Sublimation Testing

The object of this test is to determine the extent of nickel sublimation from the nickel/zirconia composite at 2100°F and $<10^{-6}$ mm pressure.

The test specimens are nickel-impregnated zirconia felt which were prepared with the boro-amine nickel plating bath. The specimens under test are both uncoated Ni/ZrO₂ composite pieces one inch diameter by 1/4 inch high and composite pieces coated with plasma sprayed zirconia. The test is being conducted in a high temperature vacuum furnace with a six-inch diameter by six-inch high chamber.

The extent of any nickel sublimation will be determined from weight loss data of the composite specimens and examination of the composite sections after the completion of the test. Due to the low melting point of this material it is questionable whether we can obtain careful data from this test due to premature melting.

Another set of composite specimens is being prepared for sublimation tests which will contain the high purity nickel from the hydrazine bath. These specimens will be placed on test with the original specimens, and will be tested concurrently.

E. Thermal Conductivity

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

The thermal conductivity test specimen is a one inch diameter by one inch high cylinder which is made by stacking four discs of the nickel/zirconia one inch diameter by 1/4 inch high. The nickel loading of the nickel/zirconia composite was 2.0 grams of nickel/cc felt. The thermal conductivity of the composite was determined utilizing a Dynatech comparative cut-bar unit and the thermal conductivity (K) for the nickel/zirconia composite with a 2.0 gm/cc nickel loading was determined to be 2.9 Btu/hr ft °F at 1030°F and 2.8 Btu/hr ft °F at 1320°F.

Additional thermal conductivity measurements will be made on specimens with the high purity nickel impregnant from the hydrazine-reduced electroless nickel. These specimens will be tested up to 1800°F.

V. REFERENCES

1. Hittman Associates, Inc., Final Report for Pioneer Thermal Switch Effort, HIT-480, January 1971.
2. Levy, D. J., Thin Nickel Films by Hydrazine Auto-catalytic Reduction, Electrochemical Technology Journal, Vol. 1, pp. 38-42, Jan. 1963.
3. Dini, J. W., and Coronado, P. R., "Thick Nickel Deposits of High Purity by Electroless Methods," SCL-DC-66-22, June 1966.