FINAL REPORT
FOR
Ni/ZrO₂ HIGH TEMPERATURE
THERMAL SWITCH
PROGRAM

July 1971 to December 1971

HIT-527

July 1972

Prepared Under
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

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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.

FINAL REPORT
FOR
Ni/ZrO₂ HIGH TEMPERATURE
THERMAL SWITCH
PROGRAM

July 1971 to December 1971

HIT-527

July 1972

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

HITTMAN ASSOCIATES, INC.
COLUMBIA, MARYLAND

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, expressed 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>
NOTICE	ii
TABLE OF CONTENTS	iii
I. INTRODUCTION AND SUMMARY	I-1
A. Background	I-1
B. Process Development	I-1
C. Property Determination	I-1
II. PROCESS DEVELOPMENT	II-1
A. Impregnation Studies	II-1
B. Process Specification	II-7
III. PROPERTY DETERMINATION	III-1
A. Thermal Conductivity	III-1
B. Mechanical Strength	III-1
C. Compatibility Testing	III-4
D. Sublimation Testing	III-6
E. Thermal Switch - Centrifuge Test	III-6
IV. NON-DESTRUCTIVE TESTING	IV-1
REFERENCES	R-1

I. INTRODUCTION AND SUMMARY

A. Background

The High Temperature Metal Thermal Switch Program was directed to the design, development, and testing of thermal switch composite materials for reentry protection of radioisotope thermoelectric generator (RTG) heat sources. In the previous phase of the program, the development of a nickel/zirconia composite prepared by an electroless nickel deposition technique was reported. The nickel deposited was a high purity, boron- and phosphorus-free, nickel with a melting temperature close to that of pure nickel.

This phase of the program was directed toward further development of the electroless nickel deposition-impregnation process for the fabrication nickel/zirconia composite sleeves with a uniform nickel impregnation throughout the sleeve.

B. Process Development

Process development studies on the impregnation of porous zirconia rigidized felt with nickel were conducted. The effects of the process variables such as temperature, flow rate, solution concentration and flow reversal on the impregnation uniformity were evaluated. The impregnation of full sized sleeves at the lowest temperature, and highest flow rate of the electroless nickel solution and with frequent reversal of the direction of flow of the solution through the zirconia sleeve yielded the most uniform impregnation which had an average variation of four to five percent of the average nickel content.

A process specification was prepared for the fabrication of nickel/zirconia composite sleeves.

C. Property Determination

Thermal conductivity data on nickel/zirconia composites was determined by the cut-bar comparative test. The conductivity at 500°F was determined for four nickel loadings of 1.6, 1.8, 2.0, and 2.3 grams Ni/cc and conductivities of 1.8, 2.0, 2.5, and 3.3 Btu/hr·ft·°F were measured. The thermal conductivity measurements show good agreement with data reported in the previous phase.

Mechanical property measurements show increased compressive and transverse rupture strengths over composites fabricated and tested in the previous phase. These improvements are attributed to improved impregnation processing and uniform dispersion of nickel throughout the composites.

Compatibility testing of zirconia coated Ni/ZrO₂ composites against Pt-20Rh, T-111, tantalum alloy and graphite at 1500°F in argon showed no reaction after 5100 hours at 1500°F.

Sublimation of nickel from zirconia coated and uncoated Ni/ZrO₂ composites was evaluated at 1800°F under one atmosphere argon for 5000 hours. The nickel sublimation from the coated and uncoated composite specimens was very low and no significant difference in sublimation was found between the coated and uncoated specimens.

A thermal switch-centrifuge test was performed to determine the effect of the centrifugal forces on the ability of the composite to "switch" when the composite is heated to the "switching" temperature. The test showed that the centrifugal forces had little or no effect on the ability of the composite to completely "switch."

II. PROCESS DEVELOPMENT

The objective of this phase of the program was to improve the uniformity of impregnation of the nickel/zirconia thermal switch composites and, in addition, to prepare a process specification for the high purity electroless nickel impregnation of the zirconia felt sleeves for the thermal switch application.

A. Impregnation Studies

In the previous phase of the High Temperature Thermal Switch Development Program (Ref. 1) the process for preparing a high purity nickel impregnated zirconia felt by electroless deposition was developed. The process, however, was not developed to the extent that uniform and predictable nickel impregnation of zirconia felt could be achieved and some variations were noted in the metal content of an impregnated sleeve. The thermal and mechanical properties of the thermal switch composites, i. e., thermal conductivity and thermal diffusivity, and compressive strength, transverse rupture strength, and deformation under load in the preswitch conditions are directly related to the metal loading and metal distribution in the impregnated porous ceramic.

The variations in the distribution of the electroless nickel deposit in the zirconia felt may be attributed to a number of factors as non-uniform flow of the electroless plating solution through the porous zirconia felt, variations in the plating rate on the sensitized felt surfaces, density variations in the zirconia felt and a partial sealing of the surface porosity of the felt preventing a uniform flow of plating solution through the ceramic body.

A study was conducted on the effect of variations of the electroless plating conditions, i. e., plating solution flow rate, solution concentration, solution temperature, and reversal of flow of the solution through the porous ceramic on the nickel distribution in the impregnated zirconia felt.

Initial studies were conducted with zirconia felt disc samples of one inch diameter by one-quarter inch thick. The disc samples were selected for the initial studies as they are simple to impregnate and the cost of impregnation of the disc samples is considerably less than that of the full sized cylinder. In addition, the disc samples may be used for test specimens for thermal conductivity and mechanical property measurements. The following variations in the plating process for impregnating the disc samples were used:

- (1) Temperature of electroless nickel plating bath - 150, 170, and 185°F
- (2) Flow rate of solution - 500, 750, and 1000 cc/min

- (3) Solution concentration - standard concentration, i. e., 60 grams of nickel acetate per liter and 40 grams of nickel acetate per liter (see Process Specification for bath make-up)
- (4) Flow reversal of solution through the felt specimen - 1, 2, and 4 cycles per hour

The results of the study of impregnation parameters are shown in Table II-1. The variations in the nickel loading in the disc specimens were determined by machining material from the face of the disc in 0.05 inch increments and determining metal density at each thickness. The data reported in Table II-1 shows little effect on the metal variation through the specimens with any of the process variations evaluated here. The only variable that showed any specific and reproducible effect was the use of replenished plating baths instead of freshly prepared baths. The used bath is normally replenished by adding additional nickel acetate and hydrazine to replace the material depleted from the previous plating cycle. The samples prepared from the replenished baths had metal loading variations of 25 to 35 percent of the total metal loading, while samples prepared with fresh solutions in most cases had metal loading variations of 2 to 10 percent. The samples prepared from the depleted solutions had a central core that was low in metal content. This core effect could be seen with low power magnification and was soft and weak as compared to the normal impregnated specimens. The reason for the core effect resulting from the use of depleted solutions may be related to a somewhat reduced activity of the plating bath and therefore poor deposition on a surface that was not fully sensitized. A normal plating bath will deposit on partially sensitized and fully sensitized surface at much the same rate. The conclusion that may be drawn is that within the range of variations studied the temperature, flow, concentration, and flow reversals had no specific identifiable effect on the nickel uniformity in disc-type samples. The nickel variation was only evaluated in one direction, i. e., depth through the 1/4-inch section as the sample area was too small to evaluate in the other directions.

A similar study was conducted on the effect of variations of the electroless plating conditions on the nickel distribution in impregnated zirconia felt sleeves. The zirconia felt sleeve specimens, 2.5-inch outside diameter by 2.1-inch inside diameter by four inches long, were impregnated with the following variations in the process being evaluated:

- (1) Deposition temperature - in the range of 150 to 185°F
- (2) Flow rate - in the range of two to five gallons per minute flow of electroless nickel plating solution through the cylinder wall
- (3) Flow reversal - reverse direction of flow through the cylinder from zero to four times per hour of plating
- (4) Use of baffles to control flow of plating solution around and through the cylinder in the plating fixture

TABLE II-1. EFFECT OF PROCESS PARAMETERS ON NICKEL UNIFORMITY

No.	Temperature °F	Flow cc/min	Solution Concentration (gm NiAc ₂ /liter)	Flow Reversal (per hour)	Ni Loading gm Ni/cc	Ni Loading Variation	
						(gm/cc)	(percent)
13	150	750	60	2	1.73	+0.19 -0.22	+11 -13
24	150	750	60	2	2.03	+0.03 -0.05	+ 2 - 3
2R*	150	1000	60	2	2.09	+0.64 -0.53	+31 -25
16	170	500	60	2	2.81	+0.20 -0.18	+ 7 - 6
4	170	500	40	2	1.99	+0.05 -0.11	+ 3 - 6
18	170	750	40	2	2.64	+0.21 -0.25	+ 8 -10
5	170	750	60	2	2.09	+0.19 -0.29	+ 9 -13
25R*	170	750	60	2	1.98	+0.57 -0.69	+30 -35
22	170	750	60	2	2.23	+0.11 -0.09	+ 5 - 4
17	170	750	60	4	2.39	+0.13 -0.14	+ 5 - 5
20	170	750	60	4	2.01	+0.24 -0.40	+12 -20
7	170	1000	60	0	2.08	+0.12 -0.05	+ 6 - 2
10	170	1000	60	2	2.26	+0.46 -0.32	+20 -14
9	185	500	40	4	2.10	+0.08 -0.09	+ 4 - 4
23	185	750	60	2	2.27	+0.05 -0.11	+ 2 - 5
21R*	185	750	60	4	1.86	+0.58 -0.56	+31 -30
19R*	185	750	60	4	2.00	+0.39 -0.70	+20 -36
6	185	1000	60	0	2.08	+0.12 -0.05	+ 6 - 3
14	185	1000	60	1	2.55	+0.25 -0.16	+10 - 6

* Specimen plated with replenished solution; all others plated with fresh solution.

A number of cylinders were impregnated and examined under this phase of the investigation with the variations in the plating process and are summarized in Table II-2.

TABLE II-2. PLATING PARAMETERS FOR SLEEVE IMPREGNATION

<u>No.</u>	<u>Plating Temperature °F</u>	<u>Flow Rate gal/min</u>	<u>Flow Reversal times/hr</u>	<u>Baffling</u>
3	150	2.5	2	None
4	180	2.5	2	None
5	170	2.5	0	None
7	160	4.0	0	None
8	160	4.0	2	Yes
9	160	4.0	3	Yes
10	160	4.0	4	Yes

The sleeves were examined destructively for variations in the nickel loading. The destructive examination consisted of sectioning the four-inch cylinder into six rings and determining the density of each ring. Alternate rings, i. e., Ring Nos. 1, 3, and 5 were then sectioned into four, 60-degree sections approximately 3/4-inch square. The density of each section was determined by the Archimedes water immersion method. The unsectioned rings, i. e., ring numbers 2, 4, and 6 were then machined to remove material from the outside diameter and the density of the machined thin wall ring was determined.

Tables II-3 and II-4 show the results of the destructive sectioning and evaluation of two of the sleeves. The identification of the sections is as follows: the six rings are numbered 1 to 6. The sections are cut from Ring 1 and numbered 1-1, 1-2, 1-3, etc. indicating the ring number and the section number. Sections numbered 1-1, 3-1, 5-1 are in the same vertical section of the cylinder. The machined rings with reduced wall thickness are listed as Ring 2a and 2b which would be Ring Number 2 and the outer 0.1-inch thick section is 2a and the inner 0.1-inch thick section is 2b.

Sleeves 3 and 4 were impregnated using the same impregnation parameters except for the impregnation temperature. The nickel variations in the two sleeves are very similar in total variation—the variation from top to bottom of the sleeve and the variations around the sleeves. The greatest variation appears to be from the top to the bottom of the sleeve (Ring 1 is the bottom of the sleeve). This variation is probably due to gas evolving from the reaction which collected at the upper part of the plating chamber and decreased the flow of the plating solution through the upper part of the sleeve.

TABLE II-3. SECTIONING AND EVALUATION OF SLEEVE NO. 3

<u>Ring No.</u>	<u>Ni Density gm Ni/cc</u>	<u>Section No.</u>	<u>Ni Density gm Ni/cc</u>	<u>Machined Ring No.</u>	<u>Ni Density gm Ni/cc</u>	<u>Ni Variation from Cylinder Loading</u>	
						<u>gm</u>	<u>%</u>
1	2.30	---	---	---	---	+0.30	15.0
		1-1	2.20	---	---	+0.20	10.0
		1-2	2.21	---	---	+0.21	10.5
		1-3	2.32	---	--	+0.32	16.0
		1-4	2.18	---	--	+0.08	4.0
2	2.01	--	--	--	--	+0.01	0.5
		--	--	2a	1.78	-0.22	11.0
		--	--	3a	2.22	+0.22	11.0
3	2.02	--	--	--	--	+0.02	1.0
		3-1	2.13	--	--	+0.13	6.5
		3-2	2.11	--	--	+0.11	5.5
		3-3	2.00	--	--	0	0
		3-4	1.75	--	--	-0.25	12.5
4	1.68	--	--	--	--	-0.32	16.0
		--	--	4a	1.51	-0.49	24.5
		--	--	4b	1.88	-0.12	6.0

Density of Ni/ZrO₂ Sleeve = 2.89 g/cc

Nickel Density = 2.00 gm/cc

Dimensions of Cylinder = 3 in. high x $2\frac{3}{4}$ in. O.D. x $2\frac{1}{4}$ in. I.D.

TABLE II-4. SECTIONING AND EVALUATION OF SLEEVE NO. 10

<u>Ring No.</u>	<u>Ni Density gm Ni/cc</u>	<u>Section No.</u>	<u>Ni Density gm Ni/cc</u>	<u>Machined Ring No.</u>	<u>Ni Density gm Ni/cc</u>	<u>Ni Variation from Cylinder Loading</u>	
						<u>gm</u>	<u>%</u>
1	2.05	--	--	--	--	+0.09	4.6
		1-1	2.21	--	--	+0.25	12.8
		1-2	2.12	--	--	+0.16	8.2
		1-3	1.95	--	--	-0.01	0.05
		1-4	1.94	--	--	-0.02	1.0
2	1.91	--	--	--	--	-0.05	2.6
		--	--	2a	1.77	-0.19	9.7
		--	--	2b	2.05	+0.09	4.6
3	1.94	--	--	--	--	-0.02	1.0
		3-1	2.06	--	--	+0.10	5.1
		3-2	1.94	--	--	-0.02	1.0
		3-3	1.92	--	--	-0.04	2.1
		3-4	1.97	--	--	+0.01	0.05
4	1.95	--	--	--	--	+0.03	1.6
		--	--	4a	1.71	-0.25	12.8
		--	--	4b	2.19	+0.23	11.8
5	1.99	--	--	--	--	+0.03	1.6
		5-1	2.01	--	--	+0.05	2.6
		5-2	2.01	--	--	+0.05	2.6
		5-3	1.96	--	--	0	0
		5-4	1.98	--	--	+0.03	1.6
6	1.94	--	--	--	--	-0.02	1.0
		--	--	6a	1.81	-0.15	7.7
		--	--	6b	2.07	-0.11	5.6

Density of Ni/ZrO₂ Sleeve = 2.82 g/cc

Ni Density = 1.96 g/cc

Dimensions = 4 in. high x 2.4 in. O.D. x 2.1 in. I.D.

The impregnation fixture was modified to allow the solution to flow out of the chamber at the top as shown in Figure II-1. In this way, the gases produced from the plating reaction were removed with the solution and the gas did not collect at any location to impede the flow of the plating solution through the sleeve being plated.

The remaining cylinders were then plated with the revised fixture according to the parameters listed in Table II-2. The evaluation of a number of the cylinders shown in Table II-5 indicate a considerable improvement in the metal impregnation uniformity over the original cylinders evaluated, i. e., 3 and 4.

The data on the average nickel variation for all the cylinders evaluated is summarized in Table II-5. The average nickel variations reported are the average of all sections for each of the cylinders examined. As seen in Table II-5, the lowest average variations are found in Cylinders 9 and 10, which were impregnated at the lowest temperature, highest flow rate, and more frequent flow reversals. The poorest uniformity, i. e., highest nickel density variation, was found in Cylinder 4 which was plated at the highest temperature studied for the electroless nickel impregnation. An improvement in the average nickel variation can also be seen over each preceding one (except Cylinder 4) which may be due to improved techniques in sensitization, solution preparation, and electroless impregnation.

B. Process Specification

The process specification for the nickel impregnation of zirconia felt sleeves is given below.

1. Materials

a. Zirconia Felt Sleeve. The rigidized zirconia felt sleeves are supplied by the Union Carbide Corporation, Tarrytown, New York to the following specification:

Density	50 $\pm$ 2 lbs/cu. ft.
Composition ($\text{ZrO}_2 + \text{HfO}_2 + \text{Y}_2\text{O}_3$)	99.6 percent
Stabilizer	7-8 percent Y_2O_3
Melting Temperature	4700°F
Fiber Diameter	4 - 10 μ

Figure II-1. Schematic of Impregnation Apparatus

TABLE II-5. NICKEL LOADING VARIATIONS OF COMPOSITE SLEEVES

<u>Sleeve No.</u>	<u>Ni Density (gm Ni/cc)</u>	<u>Average Ni Variation Found (gm Ni/cc)</u>	<u>(Percent)</u>
3	2.00	0.19	9.3
4	1.97	0.33	16.8
5	2.08	0.13	6.0
7	2.10	0.15	7.1
8	1.92	0.11	5.8
9	1.95	0.090	4.6
10	1.96	0.083	4.2

b. Palladium Resinate. The palladium resinate sensitizing solution is supplied with a palladium content of 20.0 percent.

c. Electroless Nickel Deposition Chemicals. The chemicals and the components of the electroless nickel deposition bath are listed below:

TABLE II-6. CHEMICALS FOR ELECTROLESS NICKEL BATH

<u>Chemical</u>	<u>Formula</u>	<u>Grade</u>
Nickel Acetate	$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	Certified
Glycolic Acid	CH_2OHCOOH	Purified
Hydrazine	$\text{NH}_2 \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$	High Purity
EDTA Tetrasodium Salt	$\text{C}_{10}\text{H}_{12}\text{O}_8\text{N}_2\text{Na}_4 \cdot 3\text{H}_2\text{O}$	99%
Sodium Hydroxide	NaOH	50% w/w

2. Electroless Nickel Deposition Bath

a. Bath Composition. The formulation of the electroless nickel deposition bath is the following:

Nickel Acetate	60 grams/liter
Glycolic Acid	60 grams/liter
Tetrasodium EDTA	30 grams/liter
Hydrazine	100 ml/liter

b. Bath Preparation. The bath is prepared by adding the chemicals in the following order:

- (1) EDTA salt is added to one-half the required volume of water and mixed for 10 minutes.
- (2) Glycolic acid added.
- (3) Nickel acetate added.
- (4) Mixture stirred until all chemicals are dissolved.
- (5) Hydrazine added.
- (6) Adjust to pH 11 to 11.5 with sodium hydroxide solution.

- (7) Adjust solution to final volume.
- (8) Filter.

It has been determined that a liter of the electroless nickel deposition bath will yield approximately 8.5 grams of nickel deposit on a sensitized surface. The quantity of the deposition bath will therefore be determined by the amount of nickel required.

3. Process Equipment

The electroless nickel impregnation system is shown schematically in Figure II-1 and consists of the following:

- (a) Plating solution container of polyethylene or polypropylene plastic
- (b) Glass stem immersion thermometer
- (c) Immersion heater - 500-watt Vycor or quartz sheath
- (d) Magnetic stirrer - 8 in. x 8 in. surface area
- (e) Pump - March pump Model 92101-TE with magnetic drive and plastic impeller, spindle, and magnetic housing
- (f) Plating fixture and sleeve holder as shown in Figure II-2

4. Process

- (a) Receive zirconia felt sleeve and perform visual inspection.
- (b) Weigh to 0.1 gram accuracy. Determine dimension to 0.001 inch. Calculate density.
- (c) Machine to oversize dimensions.
- (d) Air fire to 1200⁰F for two hours to clean.
- (e) Weigh.
- (f) Prepare a five percent solution of palladium resinate in acetone and add 175 cc of the five percent solution to a glass beaker containing sleeve. Allow solution to completely impregnate and saturate the sleeve.
- (g) Remove sleeve from beaker and allow to dry in air for four hours at room temperature.

Figure II-2. Plating Fixture

- (h) Place in cold furnace and heat to 500°F to decompose the palladium resinate. Hold at 500°F for two hours and cool to room temperature in furnace.
- (i) Weigh the sensitized sleeve.
- (j) Place sleeve in plating fixture and pump and outlet hose solution container (inlet hose to outside of sleeve).
- (k) Heat electroless nickel deposition bath to 160°F while stirring with magnetic stirrer.
- (l) Pump solution with valve full open through the sleeve for 15 minutes then turn sleeve over and rotate 180 degrees. Reverse hose connection, i. e., inlet hose to inside of sleeve.
- (m) Pump solution for 30 minutes .
- (n) Repeat reversal of sleeve and hose connection every 30 minutes until 2-1/2 hours of plating time is reached.
- (o) After plating, residual solution is removed from sleeve by pumping a minimum of 10 gallons of water through the sleeve.
- (p) Dry cylinder in oven at 250°F for two hours until a constant weight is obtained. Weigh and determine nickel content.
- (q) If nickel content is low, calculate the amount of nickel required and add additional batch of fresh plating solution, i. e., 8.5 grams of Ni/liter.
- (r) Repeat steps (j) through (p).
- (s) Sleeve is machined to final dimensions.
- (t) Perform final inspection of composite sleeve for weight, dimensions, defects, etc.

III. PROPERTY DETERMINATION

A test program was initiated on the nickel impregnated zirconia felt composites which were prepared by the improved impregnation process. The properties which were evaluated were thermal conductivity and mechanical strength.

The compatibility tests and sublimation tests were continued from the previous phase of the program with specimens that were prepared by the original impregnation process. A thermal switch centrifuge test was conducted with a copper impregnated zirconia composite.

A. Thermal Conductivity

The object of this test was to determine the thermal conductivity of nickel/zirconia composites which were prepared by the improved impregnation techniques.

The thermal conductivity test method used for the measurements utilized a Dynatech Model TCCG-Comparative Cut-Bar Thermal Conductivity Tester. The comparative standard used in the tests was a high purity aluminum oxide. The Ni/ZrO₂ composite test specimen was a one-inch diameter by one-inch high cylinder which was composed of four, one-inch diameter by one-quarter-inch thick discs of the Ni/ZrO₂ composite. The maximum variation in the nickel density of the four discs which comprise the test specimen was ± 0.1 gm/cc.

The tests were conducted at 500°F on samples containing four different nickel loadings of 1.6, 1.8, 2.0, and 2.3 gm Ni/cc and one nickel loading, i. e., 2.0 gm/cc, was then tested at 1000°F and 1500°F. The thermal conductivity data for the Ni/ZrO₂ composites are reported in Table III-1 and Figure III-1. Duplicate samples were used in the measurements in all cases.

The thermal conductivity measurements show good agreement with the data reported in the previous report (Ref. 1), although it was expected that the improved impregnation process which yielded a uniform nickel deposit dispersed through the zirconia felt structure would result in some improvement in the resultant thermal conductivity.

B. Mechanical Strength

The object of these tests was to determine the mechanical properties, i. e., compressive and flexural strengths of the Ni/ZrO₂ composites prepared by the improved impregnation process.

The compressive and flexural strengths of the composites in the "as-impregnated" condition and in the "switched" condition were measured

TABLE III-1. THERMAL CONDUCTIVITY OF Ni/ZrO₂ COMPOSITES

<u>Nickel Density</u> <u>(g/cc)</u>	<u>ZrO₂ Felt Density</u> <u>(g/cc)</u>	<u>Average Temperature</u> <u>(°F)</u>	<u>K</u> <u>(Btu/hr-ft-°F)</u>
1.6	0.8	500	1.8
1.8	0.8	500	2.0
2.0	0.8	500	2.5
2.0	0.8	1000	2.5
2.0	0.8	1500	2.7
2.3	0.8	500	3.3

Figure III-1. Thermal Conductivity of Ni/ZrO₂ Composites
vs. Nickel Loading at 500°F

at room temperature and at 1400°F. The mechanical property data are summarized in Table III-2.

The mechanical property measurements show increased compressive and transverse strengths over those composites reported previously (Ref. 1). These improvements in strength properties are attributed to the improved impregnation processing and uniform dispersion of nickel throughout the composite.

C. Compatibility Testing

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

The test was a continuation of the 1500°F compatibility test which was initiated during the previous phase of the program and conducted for 1500 hours. During this phase of the program, an additional 3600 hours of test time were accumulated to give a total test time of 5100 hours.

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 composites was tested with graphite, platinum-20 rhodium, and T-111 (Ta-8W-2Hf) alloy. 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) ZrO₂ coated Ni/ZrO₂ composite
- (3) Pt-20Rh alloy
- (4) Pt-20Rh alloy
- (5) ZrO₂ coated Ni/ZrO₂ composite
- (6) T-111 alloy
- (7) T-111 alloy
- (8) ZrO₂ coated Ni/ZrO₂ composite
- (9) Graphite
- (10) ZrO₂ spacer

After the conclusion of the test, the test materials were evaluated by dimensional measurements, weight measurements, and microscopic examination. The results were almost exactly the same as those observed

TABLE III-2. MECHANICAL PROPERTIES OF Ni/ZrO₂ COMPOSITES

<u>Ni Density (gm/cc)</u>	<u>Condition</u>	<u>Temperature (°F)</u>	<u>Compressive Strength (psi)</u>	<u>Transverse Strength (psi)</u>
2.1	unswitched	70	11,900	12,500
2.1	unswitched	1400	8,750	7,850
2.1	switched	70	700	825
2.1	switched	1400	650	850
1.5	unswitched	70	7,000	7,650
1.5	unswitched	1400	----- (1)	4,150
1.5	switched	70	750	800
1.5	switched	1400	700	785

(1) The test specimens yielded under compression load at 1400°F with no definite compression failure.

after the initial 1500-hour test period. The coated Ni/ZrO₂ composites showed a weight loss of <0.1 percent with no change in dimension and no change in appearance. The graphite again showed a very small weight loss of <0.1 percent. The tantalum alloy had the same gold colored film on the surface, a weight increase of 0.2 percent, and no further dimensional change. The weight changes 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 showed similar weight changes and surface discoloration.

D. Sublimation Testing

The object of this test was to determine the extent of nickel sublimation from coated and uncoated nickel/zirconia composites at 1800°F under one atmosphere of static argon.

This test was a continuation of the 1800°F sublimation test which was initiated in the previous phase of the program and was conducted for 1400 hours. During this phase of the program an additional 3600 hours of test time were accumulated to give a total test time of 5000 hours.

The test specimens used for the test were nickel/zirconia composites (a) uncoated, (b) coated with a plasma-sprayed ZrO₂ layer of approximately 0.020 inch thick, and (c) coated with 0.020 inch plasma-sprayed ZrO₂ plus a 0.010 thick layer of a ZrO₂ cement. The sublimation test specimens were contained in an Inconel alloy tube with welded closures. No intermediate weights were taken during the test.

The sublimation weight losses for the test specimens were extremely low, i. e., less than 0.01 percent for all specimens. The same test specimens with initial 1400-hour test period showed sublimation weight losses of 0.08 percent for the uncoated composite, 0.18 percent for the plasma-sprayed ZrO₂ composite, and 0.17 percent for the plasma-coated and cement-coated specimens. As stated in the previous report, the weight changes were probably due to outgassing and evaporation of volatiles from the coatings rather than nickel sublimation from the composites. The extremely low weight losses noted in this test support this theory as the samples were well outgassed during the previous test period.

E. Thermal Switch - Centrifuge Test

The object of this test was to determine the effect of centrifugal forces on the ability of the metal impregnated ceramic felt to "switch" when the composite is heated above the melting temperature of the metal impregnant.

The thermal switch-centrifuge test was conducted at the NASA-Goddard Centrifuge Facility. The test assembly is shown in cross-section in Figure III-2.

Figure III-2. Thermal Switch Centrifuge Test Assembly

The assembly consisted of a copper impregnated zirconia felt sleeve which was heated by an internal platinum wound resistance heater. The heater and test sleeve assembly were insulated with Min-K 2000 (Johns-Mansville). The entire assembly was contained in a seamless aluminum box with provisions for evacuating the chamber, purging with argon and conducting the test under a static argon atmosphere. The test specimen was, as noted above, a copper impregnated zirconia felt sleeve which was prepared by a copper electroless deposition technique similar to that used for the nickel impregnation. The copper impregnated sleeve was tested in place of the nickel impregnated composite because of the lower temperature required for melting of the metal impregnant. The melting temperature of the copper, 1980°F , may be attained with normal heater materials and efficient insulation materials for operation at 2000°F are readily available. Heaters and thermocouple materials for operation at 2700 to 3000°F are less reliable and an efficient insulation material similar to Min-K 2000 for operation at temperature in the 2700 to 3000°F range is not available. It was felt that the thermal switch effect in the centrifuge could be demonstrated as well with copper as with nickel.

The test was conducted by heating the composite contained under protective argon atmosphere to $>2000^{\circ}\text{F}$ in the closed aluminum container. The entire assembly was first mounted on the centrifuge arm as shown in Figure III-3. The initial heatup was accomplished with no rotation of the centrifuge arm. When 1700°F temperature was reached, the centrifuge was started and the assembly was rotated at 20 rpm or 4 g's centrifugal force until the temperature of the test sleeve indicated 1930°F at which time the rotational speed was increased to 101 rpm or 13 g's centrifugal force. Power to the heater was increased until the temperature on the outside diameter surface was 2020°F and the inner diameter surface was 2400°F . At this point, the entire specimen was heated above the thermal switch temperature (melting temperature) of the copper impregnant. The power to the heater was turned off and the entire assembly allowed to cool. Figure III-4 shows the time-temperature plot and the g loading of the Cu/ZrO₂ sleeve during the thermal switch-centrifuge test.

After cooling, the specimen was examined for copper switching or beading and for flow of the molten copper in the zirconia felt sleeve and from the zirconia felt sleeve due to centrifugal force. The examination of the sectioned felt sleeve showed a uniform dispersion of fine copper beads throughout the sleeve and also showed no apparent flow of molten copper in the zirconia sleeve. The only effect of the centrifugal force appeared to be on the copper at the surface of the sleeve which showed some flow on the surface to the side opposite the centrifuge center of rotation. The copper retained in the zirconia sleeve was approximately 90 percent of the total copper in the sleeve. The 10 percent of the copper lost from the sleeve appeared as large loose beads on the surface of the thermal insulation surrounding the test sleeve.

A static thermal switch test was conducted in the same manner as the centrifuge test with the only difference being that the test assembly was not rotated during the heating of the assembly. Post-test examination of the sleeve showed essentially no difference in the uniformity of the dispersion

Figure III-2 Thermal Switch Centrifuge Test
Assembly

Figure III-3. Thermal Switch Centrifuge Test Assembly

Figure III-4. Thermal Switch Centrifuge Test

of the switched copper beads in the static test sleeve when compared to the sleeve tested in the centrifuge. The static test sleeve retained approximately 80 percent of the total copper in the sleeve. It is believed that the difference in copper retention noted in the two tests is due to a less uniform copper dispersion in the static test sleeve and a high concentration of copper at the outer surface of the sleeve.

IV. NON-DESTRUCTIVE TESTING

The objective of this task was to evaluate non-destructive test procedures that may be used to determine uniformity of distribution of the metal impregnant in the zirconia felt sleeves.

The non-destructive test techniques which were used for evaluation of the nickel/zirconia composites were x-ray radiography and a thermal mapping test. The radiographic evaluation was accomplished by placing the x-ray film in the form of a cylinder at the inside diameter of the sleeve. The sleeve was attached to a low speed motor drive and the sleeve was rotated at 10 rpm under the x-ray beam. The x-ray film was then developed and examined for density variations. It was found in all cases that the rotation of the sleeve and film while being x-rayed resulted in a "washing out" of the film and the resultant film showed a uniform density over the entire composite sleeve. The x-ray examination method was dropped as it did not indicate the density variations in the impregnated sleeve. It is felt, however, that with proper equipment and further work, the x-ray method can be used to qualitatively evaluate the uniformity of nickel impregnation in the zirconia felt.

The second method used was a thermal mapping of an internally heated sleeve. The thermal mapping test appears to best fit this application as it is based on the required property of the composite, i. e., conduction of heat uniformly through the wall of the composite sleeve. The test is based on the variation of the thermal conductivity of the metal impregnated zirconia with the metal content in the composite. The thermal mapping test unit is shown in Figure IV-1. The heater, a cartridge type 6 inches long by 5/8 inch in diameter, was encased in a heavy wall copper sleeve to increase the diameter and surface of the heater. The aluminum powder fill on the inside of the Ni/ZrO₂ sleeve and the aluminum oxide fill on the outside of the Ni/ZrO₂ were necessary to eliminate any convective nonuniform heating effects. The test was conducted by applying 400 watts to the heater and allowing the assembly to come to thermal equilibrium in approximately 1-1/2 hours. Temperature measurements were taken on the outer surface of the sleeve at 32 locations with thermocouples located around the sleeve at 90-degree intervals and at one-half-inch intervals along the length. The temperature variations found in the sleeves tested are given in Table IV-1 and the temperature distribution of a single sleeve (No. 10) is shown in Table IV-2. The temperature variations determined in the thermal mapping test do not relate closely to the nickel density variations determined by destructive testing. This is probably due to the fact that the thermal test measurement is taken at the point at which the thermocouple makes contact on the sleeve whereas the destructive test section is approximately a one-inch square.

The thermal mapping test does show that the temperature on the outer surface of the sleeve is relatively uniform and does indicate a relatively uniform distribution of the nickel conductive phase throughout the nickel/zirconia composite sleeve.

Figure IV-1. Thermal Mapping Test Unit

TABLE IV-1. THERMAL MAPPING TEST

<u>Sleeve No.</u>	<u>Nickel Loading gm Ni/cc</u>	<u>Power Input, watts</u>	<u>Average Temperature °F</u>	<u>Maximum Variation from Average Temperature, °F</u>
5	2.08	400	365	+50 -35
7	2.10	400	365	+65 -85
8	1.92	400	330	+60 -60
9	1.95	400	300	+30 -55
10	1.96	400	315	+65 -40

TABLE IV-2. THERMAL MAPPING TEST FOR NO. 10 SLEEVE

<u>Thermocouple Number</u>	<u>Thermocouple Location</u>	<u>Temperature (°F)</u>	<u>Temperature Variation (°F) from Average Temperature</u>
1	0°	340	+25
2	0°	310	-15
3	0°	290	-25
4	0°	315	0
5	0°	360	+45
6	0°	340	+25
7	0°	350	+35
8	0°	330	+15
9	90°	340	+25
10	90°	300	+15
11	90°	280	-25
12	90°	350	+35
13	90°	380	+65
14	90°	350	+35
15	90°	330	+15
16	90°	305	-10
17	180°	300	-15
18	180°	320	+ 5
19	180°	275	-40
20	180°	275	-40
21	180°	275	-40
22	180°	300	-15
23	180°	275	-40
24	180°	330	+15
25	270°	345	+30
26	270°	310	- 5
27	270°	275	-40
28	270°	300	-15
29	270°	330	+15
30	270°	305	+10
31	270°	375	+60
32	270°	375	+20

REFERENCES

HIT-503, Final Report for Ni/ZrO₂ High Temperature Thermal
Switch Program, August 1971.