JUL 31 1961

WCAP-1820

MASTER

**THERMOELECTRIC
NUCLEAR FUEL ELEMENT
QUARTERLY PROGRESS REPORT
APRIL-JUNE, 1961**

CONTRACT AT(30-3)500

Facsimile Price \$ 4.60
Microfilm Price \$ 1.61

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

JULY 10, 1961

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THERMOELECTRIC NUCLEAR FUEL ELEMENT
QUARTERLY PROGRESS REPORT - APRIL-JUNE, 1961
CONTRACT NO. AT-(30-3)500

July 10, 1961

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SUMMARY

Two topical reports were issued in May, 1961 - WCAP-1680, "Radiation Effects on Thermoelectric Materials," and WCAP-1737, "Preliminary Core Design of a 500 KWe Thermoelectric Reactor." A proposal is being prepared for Phase III of the thermoelectric program.

Uranium-bearing thermoelectric compounds are now being regularly prepared by tantalum bomb melting and by the hydride process. Tests of devices made up from these compounds indicate that the main fabrication problems are in the areas of (a) densification of the materials, and (b) contact bonding. Data from a hot-swaged pellet and a swaged device of US_2 indicate some promise for that compound.

Further improvements in techniques of thermoelectric parameter measurements include programming of automatic test data recording at desired intervals around the clock; increased accuracy and versatility of measurements through use of a newly-constructed adjustable precision resistor; and (under investigation) a method for measuring which should lead to an experimental means for determining the thermoelectric figure of merit, Z .

Potential profile studies on PbTe pellets are yielding important information on contact resistance parameters.

Two PbTe capsules have been inserted in WTR for thermal conductivity studies. A fission-fired thermoelectric generator is being prepared for the next in-pile test.

Fabrication studies were concentrated on solving problems of densification of thermoelectric materials and bonding of the thermoelectric materials to cladding materials.

TASK 1.00 - PROJECT MANAGEMENT

Two progress letters and two topical reports were issued during the quarter, as follows:

- WCAP-1765 - Thermoelectric Nuclear Fuel Element Monthly Progress Letter for April, 1961 - May 10, 1961
- WCAP-1801 - Thermoelectric Nuclear Fuel Element Monthly Progress Letter for May, 1961 - June 10, 1961
- WCAP-1680 - Radiation Effects on Thermoelectric Materials
- WCAP-1737 - Preliminary Core Design of a 500 KWe Thermoelectric Reactor

A trip was made to the AEC New York Operations Office to finalize the work program for the six-month period April through September, 1961. The overall technical progress of the program was also reviewed.

A proposal for Phase III of the thermoelectric Nuclear Fuel Element Program (Contract AT(30-3)500) is being prepared. The proposal will present a technical program for a year's period through September, 1962.

TASK 2.00 - FISSILE THERMOELECTRIC MATERIALS STUDIES

Sub-Task 2.10 - Preparation of Materials

During this quarter, samples of US , USe , UTe , U_3Te_4 , and UTe_2 were prepared by the "hydride process." In addition, samples of USe_2 , U_3Te_4 , and UTe_2 were successfully melted in sealed tantalum bombs. Table I is a summary of all the uranium-chalcogen samples which have been prepared successfully during the period from January 1, 1960 to date.

TABLE I
SUMMARY OF URANIUM-CHALCOGEN SAMPLES PREPARED TO DATE

<u>Make-Up Composition</u>	<u>Weight (gms)</u>	<u>Preparation Method</u>	<u>Chemical Analysis</u>
US_2	29.3	A	--
US_2	29.2	A	$US_{2.23}$ 0.13 w/o Total Imp.
US_2	--	A	$US_{2.26}$ 0.067 w/o Total Imp.
US_2	28.1	A	--
US	57.2	A + E	--
US_2	36.7	F	--
US_2	58.7	F	--
U_3S_5	61.7	F	--
U_2S_3	60.5	F	--
U_2S_3	62.1	F	--
US	169.0	F	--
US_2	194.8	F	--
U_3S_5	148.2	F	--
USe_2	--	A	$USe_{2.34}$ 0.12 w/o Total Imp.
USe_2	27.5	A + C	--

TABLE I (cont'd)

<u>Make-Up Composition</u>	<u>Weight (gms)</u>	<u>Preparation Method</u>	<u>Chemical Analysis</u>
U_2Se_3	27.7	A + D	--
USe	32.0	A	--
USe	66.3	A + E	--
U_2Se_3	67.2	F	--
USe_2	80.3	F + E	--
USe	70.1	F	--
U_3Se_4	217.0	F	--
UTe_2	--	A	$UTe_{2.31}$ 1.81 w/o Total Imp.
UTe_2	--	A	$UTe_{1.505} - UTe_{2.02}$ 0.91 w/o Total Imp.
U_3Te_4	37.2	A + C	--
UTe	79.1	A + E	--
UTe_2	123.8	F + E	--
U_3Te_4	116.1	F	--
UTe	213.8	F	--
$US_{1.1}Se_{0.9}$	17.8	A + B	--
$US_{0.8}Se_{1.5}$	36.6	A + B	$US_{0.79}Se_{1.52}$
US_xTe_y	--	A + B	--
USTe	17.0	A + B	$US_{1.1}Te_{1.04}$ 0.56 w/o Total Imp.
US_xTe_y	19.0	A + B	--
USTe	34.5	A	--
USTe	143.9	A + E	--
$USe_{1.29}Te_{0.71}$	161.1	A + E	--

- A - Intermixed uranium chips and anion powder reacted in evacuated or argon-filled quartz tube.
- B - Blending and sintering powdered binary compounds.
- C - Melting in graphite crucible pressure-sealed with platinum O-ring.
- D - Melting in molybdenum crucible pressure-sealed with platinum O-ring.
- E - Melting in welded tantalum bomb.
- F - "Hydride Process" - solid-vapor reaction between powdered uranium metal and volatile anion material in two-chamber quartz reaction tube.

Note that the last samples in each series are considerably larger than the previous ones. This is due to the recent successful construction of a vacuum-inert-gas Pyrex apparatus (shown in Figure 1) which enables the cleaning and protection of 200 grams or more of uranium shavings.

Figure 2 shows the stainless steel glove boxes in which most of the steps in preparing the above samples are carried out. An argon atmosphere is maintained in the boxes at all times, and entrance to and egress from the interior is accomplished through a vacuum-argon transfer lock.

Figures 3, 4, 5, 7, and 8 illustrate the results of thermoelectric measurements on the five most recently fabricated samples. Four of these were run as swaged devices, and one as a hot-pressed pellet. Figure 6 shows photomicrographs of the thermoelectric constituent in one of the swaged devices. Before discussing each sample, certain observations on the swaged devices in general should be presented.

First, the density of the thermoelectric materials after swaging and heat-treating is quite unsatisfactory; the best of these samples was only 79 per cent of theoretical density. Since swaging was carried out past the extrusion point, further cold reduction of the encapsulated powder is not the solution. Prior cold-pressing, prior hot-pressing, and hot swaging will all be investigated as possible means of increasing the density of the uranium compounds.

FIGURE 1 - Vacuum-Inert-Gas Pyrex Apparatus

FIGURE 2 - Stainless Steel Glove Box

FIGURE 3

THERMOELECTRIC PROPERTIES VS. TEMPERATURE FOR
 U_2Se_3 #U-Se-H-1 (SWAGED)

FIGURE 4

THERMOELECTRIC PROPERTIES VS. TEMPERATURE FOR
USTe #U-S-Te-1 (SWAGED)

FIGURE 5

FIGURE 6 - Structures of two regions in UTe swaged sample #U-S-Te-1. Magnification 100X. Note presence of one light phase and one or two dark phases.

THERMOELECTRIC PROPERTIES VS. TEMPERATURE FOR
 US_2 #U-S-H-2 (HOT PRESSED)

FIGURE 7

THERMOELECTRIC PROPERTIES VS. TEMPERATURE FOR
 US_2 #U-S-H-2 (SWAGED)

FIGURE 8

Second, there is considerable evidence to support the belief that large resistance drops and appreciable thermal drops exist at the hot and cold interfaces of the swaged devices. Such errors would make the measured values of Seebeck and thermal conductivity appear low, and the resistivity appear high. The overall effect would be to make Z appear low, possibly by two or three orders of magnitude. These drops are due to physical separations at the interfaces and/or severe reaction zones between the thermoelectric materials and the inner and outer claddings. It is believed that improved densification of the thermoelectric material, coupled with certain design changes in the device itself, will at least partially eliminate this problem.

Because of the large number of data points recorded on the swaged samples, the graphs are presented as curves without the actual points; the curves have been made to follow the points exactly, with no "smoothing out."

Figures 3 and 4 are data from swaged devices containing USe and U_2Se_3 respectively. The Seebeck curves for both samples indicate that they become intrinsic at relatively low temperatures; the possibility exists that proper doping and/or deviations from stoichiometry could prevent this from occurring until much higher temperatures. The thermal conductivities of both samples are quite low, and the resistivities not too high, but considerable improvement in Seebeck coefficient would be required to obtain a satisfactory value of Z .

Figure 5 shows results on a swaged device containing USTe. Again the Seebeck coefficient is the discouraging parameter; however, examination of the sample after measurements revealed a large separation and severe oxidation at the hot interface, so the results are not necessarily indicative of the potential of this composition. Figure 6 consists of two photomicrographs of different portions of the USTe bulk in this sample. These pictures indicate the presence of two (and possibly three) phases, and a considerable variation in grain size and structure.

Figures 7 and 8 are data from two US_2 samples fabricated from the same batch. Figure 7 represents a hot-pressed pellet, and Figure 8 a swaged device. The Seebeck coefficient and resistivity of the pellet are higher and lower, respectively, than those of the swaged sample. This may be attributed to an interface problem in the swaged sample; a resistance profile across the face of this sample indicated a factor of 500 resistance drop at the hot interface. The thermal conductivity in Figure 8 is satisfactorily low. Overall, this composition shows some promise; doping to achieve higher Seebecks and for lower resistivities is contemplated for the near future.

Chemical analysis for the sample of Figure 4 indicates the true composition to be $U_2Se_{2.976}$.

TASK 3.00 - THERMOELECTRIC MEASUREMENTS

Instrumentation

A variable load resistor has been constructed for use with various prototype generators. The resistance elements are a pair of thin-wall stainless steel tubes approximately 5/16 inch diameter and 3 feet long insulated from each other and mounted parallel to each other on a plywood base. Connections are made to the left end of each tube and a shorting bar connects the tubes to complete the circuit. The shorting bar can be slid along the tubes to vary the circuit length and so provide resistances from 0.1 to 100 milliohms. Water can be passed through the tubes to keep them cool.

A jig (Figure 9) has been constructed with a micrometer-adjusted probe to measure the potential profile along the radius of swaged samples. The tip of the probe has a radius of ~ 1 mil and can be inserted into a small radial hole drilled into the sample. As the probe is withdrawn in 2 mil steps, the potential and position are recorded. The resulting potential profile shows contact resistance and circumferential cracks as sudden drops in the voltage. From the size of the voltage drop, the current through the sample, and its dimensions, one can calculate the contact resistances. Typical data obtained with this equipment are shown in Figure 10. The sample was a "left-over" from a fabrication study done in early 1960. The inner conductor was mild steel, the outer conductor was stainless steel, and the thermoelectric material was N-type PbTe of unknown doping level. An examination of the curve shows that there is no noticeable potential drop at the inner conductor but that there is a discontinuity at the outer conductor. The non-linearity of the curve as it approaches the outer conductor indicates that the current flow was not radial, probably due to variations in the contact to the outer conductor.

The programmer for the digital voltmeter system has been improved so that it will turn on the printer at desired intervals (1, 2, 3, 4, 6, 8, 12, 24 hours) and manipulate sample currents and heater voltages

FIGURE 9 - Potential Profile Jig

FIGURE 10

POTENTIAL PROFILE OF TYPICAL SAMPLE

FIGURE

E. D. SK. 284870 B

to measure α , ρ , and K. It shuts off the printer between the scheduled data taking times. This permits data to be taken at regular intervals without a technician being present.

Equipment has been set up for measuring thermoelectric parameters by the "point contact" method.

Small Area Contact Method for Measuring Thermoelectric Parameters

Experimental investigation was begun of a method for determining the figure of merit of thermoelectric materials. The technique, described by Mr. M. Cutler,* consists of applying a direct current to the material (creating in this manner a slight temperature differential), switching off the current after a short time, and rapidly connecting the sample to the input of a sensitive cathode ray oscillograph. The dissipation of the Peltier heat through the material sets up a Seebeck potential which is then measured. Reversing of the applied potential permits differentiation of Peltier and Joule heating effects. If the Seebeck coefficient is now determined by a separate measurement, the figure of merit may be calculated from the following:

$$Z = \frac{\Delta V}{VT \left(1 + \frac{V}{2\alpha T}\right)}$$

where: ΔV = Seebeck voltage produced by sample
V = Applied voltage
T = Absolute temperature
 α = Seebeck coefficient
Z = Figure of merit

The contacts used for both applying the heating voltage and measuring the thermoelectric potential are made of fine wire (10 mil diameter). The small area of contact tends to reduce heat transfer by conduction rather than by radiation. This would serve to produce more

* Journal of Applied Physics, June, 1961.

reliable data in connection with a thermal conductivity determination. The latter measurement is not directly made, however, nor is the resistivity separately measured. Since these two quantities are relatively difficult to determine experimentally, the small area contact method, which does not require them, should prove very convenient in the study of figures of merit.

Initial results with the method for lead telluride showed Z values approximating those determined by other methods. The apparatus will be refined as further experience with it is gained and it will be applied to the study of uranium semiconductors.

Testing Completed

Five cold-swaged samples of N-type PbTe (0.03 mol % PbI_2) were instrumented and their resistances measured as a function of time at various isothermal sintering temperatures (Figure 11) (one of the samples melted due to a run away furnace). In each case there was an initial drop in resistance followed by an increase in resistance as time passed. The initial decrease is due to the decreased resistance between powder particles as sintering occurs. The later increase is attributed to the shrinkage of the PbTe away from the conductors, indicating that the material was undergoing further densification. The samples were returned to Task 5.00 for metallographic examination.

Another six hot-swaged samples are being measured in a similar way.

Potential profiles of 16 mounted and polished metallographic samples were measured for Task 5.00. The samples and their history were described in WCAP-1765. In general, the contact drops at the metal-PbTe and PbTe-PbTe interfaces were large and clearly discernable. The samples may well have been damaged in cutting, mounting, or polishing. The samples and the data were returned to Task 5.00 for correlation with their fabrication procedures and their photomicrographs.

BENCH TEST 15 - PbTe - RESISTANCE Vs. SINTERING TIME

FIGURE 11

A three-inch-long 18-couple PbTe generator was tested. At a heater input of ~ 100 watts, an output of 38 watts was measured to a matched load. The data then became very erratic and the test was terminated. The erratic behavior is believed to be due to multiple intermittent shorts to the stainless steel clad.

An 18-couple, six inch long generator (fabricated in December, 1960) was tested. Figure 12 shows the output voltage and output power plotted versus the output current. The slope of the load curve indicates an internal resistance of 72.6 milliohms. The measured efficiency at matched load was 0.82 per cent. This low value was caused by the low temperatures of operation which were due to insufficient heater capacity. The generator was then given a series of daily thermal cycles. (The heater power was suddenly cut off each evening and suddenly turned on each morning.) No apparent degradation had occurred after ten such cycles. Figure 13 shows the short circuit current versus time of operation. The scatter is within the range to be expected due to fluctuation in line voltage and water pressures.

Five samples were measured for Task 2.00:

- Swaged USe assembly
- Swaged U_2Se_3 assembly
- Swaged USTe assembly
- Swaged US_2 assembly
- Hot-pressed US_2 pellet

The data on the swaged assemblies is quite sensitive to thermal and electrical contact resistance at the metal-thermoelectric interfaces. These resistances appear to be abnormally large due to the fabrication and chemical properties of the uranium compounds considered. Their effect is to give low apparent values of Seebeck coefficient and thermal conductivity and high apparent values of resistivity. As a check on these measurements, a hot-pressed pellet of US_2 was measured in the pellet apparatus for comparison with the swaged US_2 assembly made from the same batch of material. However, because of the high volatility of the anions in

FIGURE 12

OUTPUT VOLTAGE AND POWER Vs. I
FIGURE

E. D. SK. 28-4848 B

FIGURE 13

SHORT CIRCUIT CURRENT Vs. TIME AND THERMAL CYCLES

FIGURE

these compounds, there is a real possibility that the composition changed during hot-pressing and/or measurement. The point-contact method of measurement is being set up primarily to overcome the difficulties encountered in measuring swaged or hot-pressed pellets of these materials. The data on the five uranium samples were discussed under Task 2.00.

The hot-swaged PbTe couple that has been running almost continuously since July, 1960 is no longer being tested. The heater burned out in June, 1961 and the sample is being analysed in the metallographic laboratory for the long term effects of continuous operation. The results will be reported under Task 5.00.

TASK 4.00 - IRRADIATION STUDIES

Sub-Task 4.10 - Pre- Post-Irradiation Studies

As a matter of review, the fabrication, irradiation, and subsequent handling of capsule WAPD-48-1 are summarized here. The fabrication was reported in WCAP-1647, in which the capsule is described as containing five P-type and four N-type lead telluride samples. The samples were placed in the capsule alternately by type with each one spaced from its neighbors by 1/4 inch aluminum spacers. The spacers contained flux monitors of Ni foil and 0.1 w/o Co-Al wire. The capsule was irradiated in ETR for cycles 34 and 35. It was removed from the reactor on March 6, 1961, having received an integrated fast flux of approximately 1.7×10^{20} nvt. The capsule has now been disassembled in the WTR Hot Cell Facility. Numbering the pellets in sequence from the top, pellets 3, 5, 7, and 9 are in good physical condition, suffering only slight chipping of the edges; pellet 1 was cracked into two pieces about 1/4 inch from one end, pellet 4 crumbled at one end, and pellets 2, 6, and 8 were completely crumbled into pieces of about 1/8 inch or less in diameter. From the known inferior mechanical properties of P-type lead telluride, the physical conditions of the pellets suggest that the capsule contained five N-type and four P-type pellets. However, this discrepancy can easily be resolved when measurements are made on the irradiated pellets. Measurements can certainly be made on pellets 3, 5, 7, and 9; an attempt to grind an adequate contact area on pellet 4 may permit thermoelectric measurements of this pellet.

Sub-Task 4.20 - In-Pile Studies

A. Thermal Conductivity Capsules

Two instrumented capsules, identified as WTR-TE-2N and WTR-TE-3P, have been inserted in reflector positions of WTR for operation in their Cycle 15 which is scheduled for start-up on July 3, 1961.

The construction of these samples is identical except that 2N contains N-type (0.03 mol % PbI_2) lead telluride and 3P contains P-type (0.3 a/o Na); details of the samples are indicated in Figure 14. These samples were made six inches long to minimize end effects on the central plane temperature distribution. In-pile measurements of thermal conductivity, Seebeck voltage, and electrical resistivity are planned.

The results of pre-irradiation laboratory tests of these two samples are summarized in Table II. These data are all rather-low-temperature results and their principal significance is (1) the instrument leads are functioning properly and (2) the samples do not contain any abnormally large electrical or thermal resistances. This latter point may be illustrated by the comparison of the measured and calculated values of the electrical resistance and thermal conductance which is shown below. This comparison is made for the 250 watt input case so as to include the beneficial effects of thermal expansion on interface contact resistances.

	<u>TE-2N</u>	<u>TE-3P</u>
Measured Electrical Resistance ($\text{m}\Omega$)	0.075	0.073
Calculated Electrical Resistance ($\text{m}\Omega$)	0.058	0.058
Measured Thermal Conductance ($\text{watts}/^\circ\text{C}$)	4.81	3.82
Calculated Thermal Conductance ($\text{watts}/^\circ\text{C}$)	5.82	5.09

The calculated electrical resistances shown above are, due to sample geometry and test temperature, dominated by conductor resistances and thus do not reflect differences in resistivity of the lead tellurides.

Pb Te ELEMENT FOR IN-PILE THERMAL CONDUCTIVITY TEST

FIGURE 14

E. D. SK. 284874 B

TABLE II

Laboratory Testing of In-Pile Capsules WTR-TE-2N and WTR-TE-3P

Cap- sule	Heater Input (watts)	Function Temperatures		Ave. Temp. (°C)	Resist- ance of Sample (m Ω)	Inferred Resis- tivity (m Ω cm)	Thermal Conduct- ance of Sample (watts/°C)	Inferred Conduc- tivity (watts/ cm°C)	Voltage of Sample with respect to Chromel (mv)	Inferred Seebeck coefficient with respect to Chromel (μ v/°C)
TE-2N	40	28.3	21.0	27.7	.079	18.6	5.48	.0231	1.02	---
	90	43.0	25.5	34.3	.064	15.1	5.12	.0216	2.36	134
	160	63.5	31.3	47.4	.066	15.6	4.96	.0210	4.56	141
	250	89.0	37.0	63.0	.075	17.7	4.81	.0204	7.68	147
TE-3P	40	29.5	23.3	26.4	.211	49.4	6.46	.0273	1.16	---
	90	44.3	25.3	34.8	.146	34.2	4.74	.0202	2.38	125
	160	64.8	28.0	46.4	.099	23.2	4.36	.0186	4.42	121
	250	96.8	31.3	64.2	.073	17.0	3.82	.0163	8.19	125

B. Fission-Fired Generator

The design and hazards analysis of a fission fired thermoelectric generator have been completed. Mechanical details of the generator and lead tube design are shown in Figures 15 and 16. Since this experiment will have no external means of temperature control, the selection of an irradiation position and prediction of heat generation rates for that position are matters of extreme importance. The generator has been designed for hot junction temperature of 700°C and cold junction temperature of 175°C based on the following reactor conditions:

Heat transfer coefficient - $1.7 \text{ watts/cm}^2 \text{ }^{\circ}\text{C}$

Gamma heating rate - 5.3 watts/gm

Unperturbed thermal flux - $1 \times 10^{14} \text{ n/cm}^2 \text{ sec}$

Safeguard negotiations now underway with WTR will result in final selection of operating conditions.

Under the assumed operating conditions, the thermoelectric output to matched load is estimated as 85 amps at 2.0 volts immediately after closing the circuit. For equilibrium operating conditions, Peltier heat pumping will bring about a 40°C decrease in the hot junction temperature and reduce output to 77 amps at 1.8 volts.

WAPD EXPERIMENT TE-4 FISSION
FIRED THERMOELECTRIC GENERATOR

FIGURE 15

FISSION FIRED TE GENERATOR

FIGURE 16

TASK 5.00 - DESIGN & FABRICATION OF THERMOELECTRIC NUCLEAR FUEL ELEMENT

Sub-Task 5.10 - Design & Fabrication of Prototype Elements

Fabrication work was mainly directed towards finding solutions to the densification and bonding problems outlined in WCAP-1745. Sixteen one-inch-long single-leg elements were assembled using thermally cascaded PbTe wafers. The variables included in the study were (1) the type of PbTe (0.03 mol % PbI_2 N or 0.03 a/o Na P), (2) the area of reduction (10% or 15%), (3) the temperature of swaging (room temperature or 750°C), and (4) the post-swaging heat treatment (two hours or six hours at 750°C). The PbTe-PbTe interfaces were examined for degree of metallurgical bonding, and the resistance drops across all of the interfaces (including clad-PbTe interfaces) were tested. Some of the interfaces were quite good (i.e., metallurgical bonding and very low resistance drop). See Figures 17 and 18.

This study was greatly expanded to further study several observed trends (i.e., increased bonding with increased time at temperature). Thirty-two more one-inch-long single-leg elements were assembled with cascaded PbTe wafers. These elements, however, were vacuum degassed for two hours at room temperature and sealed. Sixteen of the elements were cold swaged to final size and sectioned. They are being heat treated. The other sixteen received an initial cold swage pass and are ready for hot swaging at 750°C.

A second study of mild steel-PbTe bonding is also underway. Six single-couple elements were assembled using segmented PbTe wafers (0.055 and 0.03 mol % PbI_2 and 1.0 and 0.3 a/o Na). In three, the mild steel hot and cold junction clads were pre-coated with PbTe; in the other three they were not. The six elements were made up to three slightly differing outer diameters - one pre-coated and one non-coated of each size. All were swaged to 0.930 inch O.D., the total reductions of area of the PbTe being approximately 10, 15, and 20 per cent respectively for the three sizes. After assembly the elements were vacuum degassed for two hours at 650°C,

FIGURE 17 - N- PbTe to N- PbTe Interface -
Cold Swaged (15% reduction) -
Heated 6 hrs. at 750°C 50X

FIGURE 18 - P- PbTe to P- PbTe Interface -
Cold Swaged (10% reduction) -
Heated 6 hrs. at 750°C 50X

swaged as noted previously, sealed in quartz, heat treated for six hours at 750°C, and machined for instrumentation. They will be tested electrically, and the results will be compared. A metallographic study will then be made.

Other fabrication work included completion of nine elements.

A three-inch-long 18-couple element was assembled around a three inch long heater. The cascaded pellets were 0.10 and 0.03 mol % PbI_2 and 1.0 and 0.3 a/o Na. Insulating members were 0.010 inch thick. The element was sealed in vacuum and hot swaged at 750°C. At a power input of 1035 watts, only 38 watts output (matched load) was measured. Since the load curve indicated that partial shorting was occurring in the generator, the test was discontinued.

A three-inch-long optimized 0.03 mol % PbI_2 N and 0.3 a/o Na P PbTe couple was hot swaged at 650°C on a solid mandrel for use as a bench test. However, due to slippage of one current-carrying clad, the element was relegated to sectioning and metallographic examination. Figures 19 and 20 show the microstructures of N- and P-type PbTe respectively.

A three-inch-long single-leg element of PbTe containing twelve thermocouples (one every quarter inch along the hot junction clad) was fabricated to determine the degree of end heat losses. The element was vacuum degassed for three hours at from room temperature to 300°C before swaging, heat treated for six hours at 750°C after swaging, and then x-rayed and sectioned. PbTe had seriously attacked all of the Aludel thermocouple leads and the AlSiMag (evidently the 60%-dense raw AlSiMag, before it is swaged to high density, is porous to PbTe).

A new element was assembled, vacuum degassed at room temperature, swaged, and heat treated for six hours at 750°C. This one is ready for sectioning.

FIGURE 19 - N-leg of Element Swaged at 650°C 50X

FIGURE 20 - P-leg of Element Swaged at 650°C 50X

A six-inch-long single-leg element of 0.3 a/o Na doped PbTe was fabricated to replace the original element designed to obtain in-pile thermal conductivity measurements. Vacuum degassing at a temperature of up to 300°C again caused PbTe attack of the AlSiMag.

A second replacement was assembled, vacuum degassed for three hours at room temperature, swaged, heat treated for six hours at 750°C, and machined for instrumentation.

The last three elements fabricated were similar three-inch-long cascaded 0.10 and 0.03 mol % PbI₂ N and 1.0 and 0.3 a/o Na P couples. Each was vacuum degassed at room temperature, swaged, and heat treated for six hours at 750°C. These elements, which are to be used as bench tests, will be ready for testing presently.

Parts 3 and 4 of the PbTe physical properties study (WCAP-1695) were continued.

Part 3 - Four of the one-inch-long single-leg elements of PbTe were tested for resistivity as a function of time at the constant temperatures of 600, 700, 750, and 800°C. A slight temperature gradient was maintained across each element during testing. A fifth element, which was to be maintained at 650°C, melted when a temperature controller failed. Test data are given under Task 3.00. The initial decrease in resistivity with time is explained by sintering of the swaged PbTe. The increasing resistivity might be explained by the sintering of PbTe away from the conductors, or by the formation of a high resistance compound at the metal-PbTe interface, or by the loss of some doping material. The desired curve would show an initial decrease in resistivity, followed by constant resistivity. Further work will be done until the desired results are approached.

Part 4 - Four elements, each containing two one-inch-long single legs of PbTe, were hot swaged (one at 650°C, one at 750°C, and two at 850°C) (Note: elements had been previously hot swaged at both 650°C and 750°C).

Microstructures of PbTe swaged at 650°C (Figure 21), 750°C (Figure 22), and 850°C* were obtained.

Testing similar to Part 3 above is in progress; results will be reported when testing is completed.

The study of the compatibility of PbTe with potential cladding and insulating materials was continued.

A series of beryllium-PbTe samples was fabricated, encapsulated, heat treated, and metallographically examined. No reaction occurred at 650°C -- 200 hours (Figure 23) or at 750°C -- 100 hours (Figure 24).

A series, Supramica 620, Al_2O_3 , Mica tape, and Armco-iron-PbTe samples were also fabricated, encapsulated, heat treated, and prepared for metallographic examination. The examination is not complete.

A sub-contract has been placed with the Nuclear Materials & Equipment Corporation of Apollo, Pennsylvania to investigate the feasibility of coating iron conductors with high density Al_2O_3 in thicknesses in the range one to 20 mils (0.0001 in. to 0.020 in). To date several processes appear promising. Two samples were slowly cycled from room temperature to 750°C and back ten times. One exhibited no apparent spalling or cracking; the other exhibited a slight circumferential crack through the Al_2O_3 . Three more thermal cycles, consisting of soaking at 750°C and water quenching, produced no further defects.

Sub-Task 5.20 - Evaluation of Prototype Elements

The original hot-swaged single-couple element of N and P PbTe exceeded 7000 hours of operation. Even though the element had undergone

* The PbTe swaged at 850°C is not shown because of its inconsistency with other results at 850°C and with the results at 750°C. The microstructure is being obtained from the other specimens.

FIGURE 21 - PbTe Structure As-swaged at 650°C 50X

FIGURE 22 - PbTe Structure As-swaged at 750°C 50X

FIGURE 23 - Be-PbTe Interface After 200 hrs at 650°C/250X

FIGURE 24 - Be-PbTe Interface After 100 hrs at 700°C/250X

several thermal cycles (due to shut-downs of equipment) the total Seebeck coefficient, total resistance, and thermal conductance remained at approximately $460 \mu\text{v}/^{\circ}\text{C}$, 1.2×10^{-3} ohms, and $1.8 \text{ watts}/^{\circ}\text{K}$ respectively ($T_H \sim 565^{\circ}\text{C}$ and $\Delta T \sim 500^{\circ}\text{C}$) until the electrical resistance heater failed.

The element was sectioned through both the N- and P- legs to metallographically examine the integrity of the PbTe (Figures 25 and 26) and the depth of interface reaction (Figures 27 and 28). Both the N- and P-types of PbTe showed circumferential cracking, the P-type exhibiting more, as usual. The depth of the interface reactions were extremely small, being ≤ 0.002 inch at the P PbTe-to-hot junction-clad interface and ≤ 0.001 inch at the N PbTe-to-hot junction-clad interface.

FIGURE 26 - N- PbTe Leg of Hot Swaged Element After
7000 hrs. of Operation 25X

FIGURE 25 - P- PbTe Leg of Hot Swaged Element After
7000 hrs. of Operation 50X

FIGURE 27 - P- PbTe to Hot Junction Clad Interface After
7000 hrs. of Operation 200X

FIGURE 28 - N- PbTe to Hot Junction Clad Interface After
7000 hrs. of Operation 200X