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THERMOELECTRIC MATERIAL EVALUATION PROGRAM

Contract AT(29-2)-2473

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Space and Defense Products
ELECTRICAL PRODUCTS GROUP
3M CENTER, ST. PAUL, MINN. 55101, PH 633-9400

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THERMOELECTRIC MATERIALS EVALUATION PROGRAM

QUARTERLY TECHNICAL TASK REPORT
NO. 39

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DATE 3/16/73

E. F. Hampl, Jr.
Program Manager

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MINNESOTA MINING AND MANUFACTURING COMPANY
Thermoelectric Systems Section
Electro-Products Division
St. Paul, Minnesota 55101

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INTRODUCTION

This is the thirty-ninth Technical Task Report prepared under Contract AT(29-2)-2473 with the United States Atomic Energy Commission and covers the performance period which extends from July 1, 1972 through September 30, 1972.

HIGHLIGHTS

TASK 1.0 - N-TYPE MATERIAL DEVELOPMENT

1.2 MATERIAL SYNTHESIS - GADOLINIUM-SELENIDE COMPOSITIONS

Gadolinium-selenide compositions (N-2214 through N-2243) were synthesized and cast into a geometry suitable for electrical (S and ρ) characterization. The synthesis technique employed followed very closely the procedure outlined in the document, "General Review of N-Type Material Developments at 3M Company for Use with TPM-217," dated November 4, 1969, page 30, and reviewed in Technical Task Report No. 33. The method consisted of placing the raw materials in a vitreous carbon crucible in a sealed vitreous quartz tube and taking it through a low temperature thermal cycle followed by a high temperature thermal cycle (without the quartz tube). The synthesis samples are related to process experiments which are in progress and have the following objectives:

- Precise control of the desired stoichiometric ratio of gadolinium.
- Elimination of microscopic defects in elements.
- Optimization of thermoelectric composition.

Improvements are continuing to be made in the synthesis of $GdSe_x$ thermoelectric alloy systems. Briefly, the synthesis scheme is outlined as shown:

* Low temperature reaction carried out in a vitreous carbon crucible and sealed in a quartz envelope.

**High temperature reaction carried out in an open vitreous carbon or graphite crucible.

All the synthesized compositions were prepared with a weighed-in composition of approximately $\text{GdSe}_{1.498}$, except for N-2238, N-2239, N-2242, and N-2243. The gadolinium metal presently being used was obtained from Research Chemical Corporation and is in the form of $1/8" \times 1/8" \times 1/16"$ blocks. This form of gadolinium has a much lower surface area than the "chips" previously used and, as a consequence, has much less surface contamination such as oxides and water. In addition, foreign material (which we have detected) that is introduced during the cutting of the blocks and chips can be separated from the blocks but cannot be separated from the chips. After the sealed tube reaction, weight loss determinations were made after each processing step. These weight losses were assumed to be due to selenium vaporization and the final compositions of the samples were calculated on this basis. The final compositions of the cast elements have been improved from $\text{GdSe}_{1.458}$ to $\text{GdSe}_{1.484}$. The improvements are consistent and have been verified by Seebeck measurements.

The synthesis of series N-2214 through N-2219 ($\text{GdSe}_{1.5}$) was completed with the objective of incorporating the synthesis and casting improvements into producing $3/16$ -inch diameter elements with maximum retention of selenium. These low temperature process

improvements, presented in Technical Task Report No. 38, included increasing the soak time to 72 hours or longer at 200°C, 24 hours at 400°C and 600°C, and approximately 96 hours at 1200°C. These improvements appear to have resulted in improved selenium retention. The extended soak at 200°C was the most beneficial. Interrelationships between the various low temperature reactions have not yet been examined. The 1350°C reaction step in an open tube was eliminated. The original purpose of this step was to obtain a more complete reaction between the reactants before proceeding to the casting step. Results have demonstrated that more selenium is retained in the final product when this step is omitted. Reducing the casting temperature from 1950° to 1800°C, increasing the heating rate from 38°C/min. to 45°C/min., and decreasing the soak time at the casting temperature from 30 minutes to 10 minutes have contributed to the reduction of selenium loss. Further modification of the low temperature reaction and the casting procedure is expected as our understanding of the system advances.

The low temperature reaction (LTR) for series N-2214-2219 did not proceed as planned in that one side of the furnace burned out while in the 1200-hour cycle. Thus, the cycles were as follows:

	<u>Planned Time</u> (Hrs)	<u>Actual Time</u> (Hrs)
200°C	118	118
400°C	24	24
600°C	24	24
900°C	8	6
1050-1200°C	-	62
1200°C	96	84

Samples N-2214 through N-2217 were heated to 1800°C in the 3/16-inch mold, cooled to 1700°C-1740°C to reduce the superheating of the melt, and then cooled at 24°C/min. to 1400°C. The samples were held at 1400°C for 10 minutes and then furnace cooled to room temperature.

An attempt was made to cast N-2218 at 1720°C but the sample did not melt. The sample was then cast at 1740°C, cooled at 24°C/min. to 1400°C, soaked for 10 minutes at 1400°C, and then furnace cooled to room temperature. The sample melted and cast. This experiment established the solidus temperature of the nominal $\text{GdSe}_{1.48}$ composition to be between 1720°C and 1740°C. N-2219 was cast at 1740°C in the same manner as N-2218.

Table I summarizes the process weight loss, Seebeck coefficient, and as-cast density measurements for each sample. The Seebeck versus temperature relations are shown in Figure 1. The results of the experiment indicate that these samples are about the same as N-2208, N-2210, and N-2212.

TABLE I

Compositions of Samples N-2214-2219 After Processing

Sample #	Weighed-In Composition GdSe _x	Calculated Composition After 1800°C 1740°C	$\bar{S}$ @ 500°C S(μv/°C rel. to Absolute)	As-Cast Density (gms/cc)
N-2214	1.498	1.484	305	
N-2215	1.498	1.482	307	7.07
N-2216	1.498	1.479	287	6.01
N-2217	1.498	1.482	295	7.17
N-2218	1.498	1.480	267	7.10
N-2219	1.498	1.482	302	7.13

The synthesis of series N-2220 through N-2231 (GdSe_{1.5}) was completed with the dual objectives of incorporation of the most improved LTR/HTR procedures to maximize selenium retention at a composition close to the calculated optimum composition and to produce 3/16-inch diameter elements. Samples from this series were used for surface film, compatibility, and proposed contacting studies. The low temperature reaction (LTR) for this series consisted of 72 hours at 220°C, 24 hours at 400°C, 24 hours at 600°C, and 96 hours at 1200°C. The samples were vacuum melted at 1800°C, cooled at 40°C/min. through the freezing range, soaked at 1400°C for 30 minutes and furnace cooled. Table II summarizes the process weight loss and Seebeck measurements for this series, and Figure 2 shows the dependence of Seebeck coefficient on temperature.

A more detailed analysis of the dependence of Seebeck coefficient on composition for the twelve samples in this series also supports the selenium doping model. Breaking the initial group of twelve into two groups of six according to whether the indicated composition is greater or less than GdSe_{1.482} gives group average compositions which differ by 0.0022 and group average Seebeck coefficients which differ by 9.9 μv/°C. The calculated Seebeck coefficient change for a 0.0022 composition difference is 9.7 μv/°C, in excellent agreement with the measured value and a strong indication that the samples differed only in the amount of Se retained during synthesis.

Figure 1. Temperature Dependence of Seebeck
Coefficient for Synthesis Series
N-2214-2219 (rel. to Abs.)

TABLE II

Compositions of Samples N-2220-2231 After Processing

Sample #	Weighed-In Composition GdSe _x	Calculated Composition After Processing	$\bar{S}$ @ 500°C S(μv/°C rel. to Absolute)	As-Cast Density (gms/cc)
N-2220	1.497	1.483	262	7.10
N-2221	1.498	1.483	266	-
N-2222	1.497	1.483	265	-
N-2223	1.497	1.481	257	7.12
N-2224	1.498	1.480	256	
N-2225	1.497	1.479	252	7.01
N-2226	1.498	1.482	260	
N-2227	1.498	1.481	247	
N-2228	1.498	1.482	255	
N-2229	1.497	1.480	246	
N-2230	1.498	1.481	246	
N-2231	1.498	1.482	252	

The synthesis of series N-2232 through N-2237 (GdSe_{1.50}) was completed with the objective of further examination of the heating rates during the casting process cycle. The low temperature reaction for this series consisted of 72 hours at 220°C, 24 hours at 400°C, 24 hours at 600°C, and 96 hours at 1190°C, and a thermal schedule the same as for series N-2220 through N-2231. The heating rate during the casting cycle was either 45°C/min., normal heating rate, or 75°C/min., the maximum heating rate for the furnace. The samples were vacuum melted at 1800°C, cooled at 4°C/min. through the freezing range, soaked at 1400°C for 30 minutes and furnace cooled. The cooling cycle was identical to the series N-2220 through N-2231. Table III summarizes the process weight loss and Seebeck measurements for this series. Figure 3 shows the dependence of Seebeck coefficient on temperature.

The elements were cast in the 3/16-inch diameter mold which incorporated the enlarged riser. Five of the six elements were solid whereas the sixth element (N-2233) exhibited holes in the casting.

The synthesis of series N-2238 through N-2243 was initiated with the objective of examining the effect of weighed-in composition on the final composition of the weighed elements. The series consisted of duplicate samples of weighed-in compositions GdSe_{1.48}, GdSe_{1.50}, and GdSe_{1.52}. For the low temperature reaction (LTR),

Figure 2. Temperature Dependence of Seebeck
Coefficient for Synthesis Series
N-2220-2237 (rel. to Abs.)

TABLE III
Compositions of Samples N-2232 Through N-2237

Sample #	Weighed-In Composition GdSe _x	Calculated Composition After Processing	Heating Rate (°C/min)	$\bar{S}$ @ 500°C S(μv/°C rel. to Absolute)	As-Cast Density (gms/cc)
N-2232	1.498	1.477	75	241	
N-2233	1.497	1.482	45	254	
N-2234	1.498	1.483	75	241	8.85
N-2235	1.498	1.479	45	243	
N-2236	1.498	1.480	45	267	
N-2237	1.498	1.481	75	254	

Figure 3. Temperature Dependence of Seebeck Coefficient for Synthesis Series N-2232-2237 (rel. to Abs.)

the reactants were sealed into the quartz tubes with a vacuum of less than 10^{-3} torr instead of the normal argon atmosphere of 20 torr pressure. This change was adopted because the procedure is simpler than backfilling with argon prior to sealing the tubes and, in addition, the introduction of impurities such as water into the system is minimized. The LTR for this series was identical to the previous series: 72 hours at 220°C, 24 hours at 400°C, 24 hours at 600°C, and 96 hours at 1200°C. The casting of these elements has not been started.

1.3 MATERIAL ANALYSES

1.3.1 Chemical Analyses

Raw Material Analysis:

Random inclusions of tantalum have been detected in the gadolinium blocks, used for synthesizing $GdSe_x$, when examined for impurities by electron microprobe. An attempt to purify these blocks by vacuum melting in a vitreous carbon crucible proved unsuccessful because of the formation of gadolinium carbide. The gadolinium reactivity appears to diminish the feasibility of substituting vitreous carbon crucibles for tantalum during the manufacture of gadolinium.

Surface Film Studies:

A simple experiment was run to determine the effect of water on $GdSe_x$. Water was poured over some $GdSe_x$ chips and allowed to stand for several hours. The following observations were made:

- Gas bubbles were seen on the surfaces of the $GdSe_x$ chips.
- An off-whitish along with a red solid was detected.
- Characteristic selenium odor was detected - no H_2Se , however.

This reaction most likely proceeds as follows:

This experiment points out that minimal exposure to water during storage of the $GdSe_x$ alloys is a necessity.

Preliminary experiments have been initiated to analyze various $GdSe_x$ surfaces in an attempt to identify the high resistivity film. The ion scattering spectrometer technique, capable of determining the composition of the outermost surface monolayer as well as doing a depth-profile composition analysis, will be used in these experiments.

1.3.2 Thermoelectric Properties

Seebeck Coefficient Measurements:

The Seebeck plotting routine has been modified to fit the experimental data to a theoretical curve of form

$$S = S_0 + a \ln(T/773).$$

This curve has only two free parameters, the Seebeck coefficient at 500°C (S_0) and the parameter "a", where the theoretical expression for "a" is

$$a = \frac{3}{2} \left(\frac{\partial S}{\partial \ln n} \right) \left(1 + \frac{\partial \ln m^*}{\partial \ln T} \right) \Big|_{T=773}$$

The value of $\frac{\partial S}{\partial \ln n}$ is relatively insensitive to carrier concentration, and should be about 78 $\mu\text{V}/^\circ\text{C}$ for values of S_0 from 150° to 250°C¹. The temperature dependence of the effective mass,

$$\frac{\partial \ln m^*}{\partial \ln T}$$

should also be independent of carrier concentration. Based on experience with similar semiconductors, the temperature dependence of the effective mass should be small:

$$0 \leq \frac{\partial \ln m^*}{\partial \ln T} \lesssim 0.5$$

Thus, the value of "a" should lie in the range 120-180 $\mu\text{V}/^\circ\text{C}$. Furthermore, the parameter "a" should be essentially constant, independent of variation in carrier concentration. Figures 4 and 5 display the fit of Seebeck coefficient data to the theoretical curve. The fit appears to be very good; in fact, the fit to the simple two-parameter theoretical curve appears as good as the previous fit to a four-parameter polynomial curve.

Table IV displays the values of the fitting parameters obtained for twelve elements from synthesis series N-2220-2231 fabricated for isothermal compatibility studies. The mean value of "a" determined from this series is $a = 166 \mu\text{V}/^\circ\text{C}$, with an RMS fluctuation of $\pm 4 \mu\text{V}/^\circ\text{C}$. The mean value of the Seebeck coefficient at 500°C for this series is 255 $\mu\text{V}/^\circ\text{C}$. The value of "a" should remain fairly constant with changes in composition.

¹Technical Task Report No. 35.

Figure 4. Seebeck Coefficient
Sample #N-2225

Figure 5. Seebeck Coefficient
Sample #N-2202-C2

TABLE IV
Seebeck Coefficients for Samples N-2220-2231
[$S = S_0 + a \ln(T/773)$]

Sample #	S_0 ($\mu\text{V}/^\circ\text{C}$, rel. to Abs.)	a ($\mu\text{V}/^\circ\text{C}$, rel. to Abs.)
N-2220	262	171
N-2221	266	170
N-2222	265	175
N-2223	257	162
N-2224	256	169
N-2225	252	163
N-2226	260	168
N-2227	247	162
N-2228	255	170
N-2229	246	163
N-2230	246	163
N-2231	252	161
	$\bar{S}_0 = 255$	$\bar{a} = 166$

Fitting data to a theoretical rather than an arbitrary curve has several worthwhile features which warrant the extra effort:

1. The curve fit parameters have physical significance.
2. Deviations from normal behavior are more obvious.
3. Extrapolation is better justified.
4. More information can be recovered from noisy data.

Resistivity Measurement:

A small resistivity measuring probe was constructed to obtain quantitative room temperature resistivity data on samples of irregular geometry (such as thermal diffusivity specimens, the crown produced in casting, specimens mounted for microscopic examination, and broken elements). The device consists of four collinear point probes spaced about 20 mils apart. Current is fed through the outer probes, voltage drop is measured on the inner two probes, and the measured voltage/current ratio is related to resistivity under the assumption of an infinite half plane geometry. So long as the probes are more than about 20 mils from the sample edges, and the sample is more than about 30 mils thick, the resistivity measurement should be good to about 10%.

The small collinear four-probe resistivity apparatus was used to measure the difference in resistivity between the 0.2-inch diameter cast elements and the crown produced by the residual material in the casting mold. Table V shows that there does appear to be a difference between the material in the bulk of the element and that in the crown, with the crown consistently lower in resistance. This resistivity difference may indicate a difference in carrier concentration; to check this, Seebeck coefficient measurements will be made on the crowns.

TABLE V

Comparison of Room Temperature Resistivities
for Elements and Element Crowns
(Collinear 4-Probe Measurement)

<u>Sample #</u>	<u>ρ (mΩ-cm; R.T.)</u>
N-2197-2204-C3	
Element Sides	3.7 ± 0.4
Crown	3.3 ± 0.3
N-2221	
Element Sides	8.7 ± 0.6
Crown	6.6 ± 0.3
N-2229	
Element Sides	7.0 ± 0.6
Crown	5.4 ± 0.3
N-2219-C2	
Element Sides	5.5 ± 0.3
Crown	4.2 ± 0.3

The indicated uncertainties represent the variation of the readings with probe placement.

Thermal Conductivity Measurements:

The pulsed laser diffusivity measurement currently used in the program has been described in Technical Task Report No. 37, pages 21-22. To obtain high temperature data ($>800^{\circ}\text{C}$), the equipment is being modified with a design (Figure 6) that represents an optimum combination of measurement accuracy and measurement speed.

The heart of the method is the precise measurement of the transient heat pulse on the back surface of the sample. This heat pulse is detected by a liquid nitrogen cooled indium antimonide infrared

FIGURE 6

Block Diagram of the Pulsed Laser
Thermal Diffusivity Apparatus

detector. The analogue signal from this detector is measured at 200 μ sec intervals by the high speed analogue to digital converter. The digital data are stored temporarily in the recorder, then transferred on command to the computer memory where it is subsequently analyzed to determine the thermal conductivity of the sample. In lieu of the computer disc, an alternate mode of operation can be used temporarily. The InSb detector and the amplifier components are on hand, and the Biomation 802 transient recorder (A-D converter) for use with the InSb detector is on order and scheduled for delivery about November 1972. The transient recorder will take 1000 sequential measurements during the signal pulse, store this data digitally, then either transfer the digital data directly to our computer or, in an alternate mode, reconstruct the signal at a rate compatible with x-y recorder display. The transient recorder is necessary to perform measurements on thin samples since it can operate at much higher signal frequencies than an x-y recorder; it is superior to an oscilloscope in that a hard copy is produced for signal analysis. When the disc operating system is added to our computer, the transient recorder will be controlled and interrogated directly by the computer. In the interim, it will be operated in the analogue output mode.

Dependence of Seebeck Coefficient on Composition:

For a simple parabolic band model with zero scattering parameter, the carrier concentration, n , and Seebeck coefficient, S , are formally related by the equations²

$$S = k/e \left(2 \frac{F_1(\eta)}{F_0(\eta)} - \eta \right)$$

$$n = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi k T m^*}{h^2} \right)^{3/2} F_{1/2}(\eta)$$

$$F_r(\eta) \equiv \int_0^\infty \frac{x^r dx}{1 + \exp(x-\eta)}$$

The effective mass should be essentially constant for variations in carrier concentration in a given system, so the Seebeck coefficient is a function of carrier concentration with one free parameter, the effective mass, m^* .

²T. C. Harman and J. M. Honig, Thermoelectric and Thermomagnetic Effects and Applications, McGraw-Hill, N.Y. (1967).

For the defect doping model, carrier concentration is related to composition by

$$n = (4.92 \times 10^{22}) [(1.5-x)/x] \text{ GdSe}_x$$

Combining these model predictions gives the family of curves shown in Figure 7, where each curve is labeled by its effective mass. The experimental points represent averages over several samples in a given synthesis series. The compositions were determined by the weight loss method. The experimental points show the predicted sharp rise in Seebeck coefficient as the composition $\text{GdSe}_{1.5}$ is approached, and are in fair agreement with the theoretical curve determined for an effective mass equal to six times the electron mass. This value of effective mass for GdSe_x is of the same order as the effective masses determined by independent investigators for other rare earth-chalcogenide systems. The experimentally observed variations of Seebeck coefficient with composition is taken as support of the defect doping model.

The "best points" in the statistical sense of representing the most individual elements fall rather close to the theoretical $m^* = 6 m_e$ curve, even though processing improvements increased the selenium retention from $\text{GdSe}_{1.45}$ to $\text{GdSe}_{1.48}$. The deviation of samples N-2190 and N-2191 from the standard curve is expected since these samples contain a large amount of second phase material. The deviation of the four series N-2186-2187; N-2188-2189; N-2008, 2210, 2212; and N-2214-2219 from the standard $m^* = 6m$ curve appears significant. The apparent anomaly for these four series may be nothing more than the accuracy limitation of the weight loss composition determination; however, the interesting alternative possibilities of a minor impurity dopant, loss of material other than selenium, and sample inhomogeneity are being investigated.

1.3.3 Analysis and Relationship Between Composition and Thermoelectric Properties

Definition of N-Type Material Composition with Respect to Thermoelectric Properties to Provide a Couple Efficiency of 11% when Combined with P-Type TPM-217 over the Temperature Range of 800°C to 250°C:

Table VI shows the couple efficiency for different GdSe_x compositions combined with 0.10% excess selenium P-type TPM-217. Table VII is similar to Table VI, but for the temperature interval of 800°-200°C. The second table is included since 200°C is a more realistic cold junction temperature for space applications than the 250°C cold junction of the program milestone. The

TABLE VI

Couple Efficiency Over the Temperature Interval 800°-250°C

X(Nominal Composition GdSex m*/m=6)	S($\mu\text{V}/^\circ\text{C}$ abs. at 500°C for GdSex)	η^* (% Couple Efficiency)	η^{**} (% Couple Efficiency)
1.418	140	8.9	10.1
1.438	160	9.1	10.6
1.453	180	9.2	11.0
1.463	200	9.2	11.3
1.471	220	9.1	11.5
1.477	240	9.0	11.6
1.482	260	8.7	11.6
1.486	280	8.3	11.5

* Calculated for the S versus $\ln p$ curve characteristic of recent synthesis samples (N-2187, N-2189-C2, N-2196). This is the curve for material which at the present state of the synthesis can be reproduced fairly often, Coring, porosity, and voids are still evident in this material, however, so there is a clear potential for improvement by modifying fabrication techniques.

**Calculated from the S versus $\ln p$ curve characteristic of the highest experimental S $\ln p$ data obtained in this program (Pt. A and N-2094). This may indicate the extent of improvement possible by modification of fabrication techniques to reduce sample defects.

TABLE VII

Couple Efficiency Over the Temperature Interval 800°-200°C

X(Nominal Composition GdSex m*/m=6)	S(μv/°C abs. at 500°C for GdSex)	η*(% Couple Efficiency)	η**(% Couple Efficiency)
1.423	144	9.6	11.0
1.441	164	9.9	11.5
1.455	184	10.0	12.0
1.465	204	10.0	12.3
1.473	224	9.9	12.5
1.478	244	9.7	12.6
1.483	264	9.4	12.6
1.486	284	9.0	12.5

* Calculated for the S versus $\ln p$ curve characteristic of recent synthesis samples (N-2187, N-2189-C2, N-2196). This is the curve for material which at the present state of the synthesis can be reproduced fairly often. Coring, porosity, and voids are still evident in this material, however, so there is a clear potential for improvement by modifying fabrication techniques.

**Calculated from the S versus $\ln p$ curve characteristic of the highest experimental S $\ln p$ data obtained in this program (Pt. A and N-2094). This may indicate the extent of improvement possible by modification of fabrication techniques to reduce sample defects.

efficiencies calculated in column 3 were obtained from the S versus $\ln p$ curve characteristic of recent synthesis samples (N-2187, N-2189-C2, N-2196). This represents material with S versus $\ln p$ properties which at the present state of the synthesis can be reproduced fairly often. Coring, porosity, and voids are still evident in this material, however, so there is a clear potential for improvement by modifying fabrication techniques. The efficiencies calculated in column 4 were obtained from the S versus $\ln p$ curve characteristic of the highest experimental S $\ln p$ data obtained in this program (Pt. A and N-2094). Column 4 may be interpreted as an indication of the extent of improvement possible by modification of fabrication techniques to reduce casting defects.

The maximum in the couple efficiency curve of column 3 occurs at 195 $\mu\text{v}/^\circ\text{C}$ absolute, corresponding to a nominal composition $\text{GdSe}_{1.460}$ (using $m^*/m = 6$), while the maximum in the couple efficiency curve of column 4 occurs at 250 $\mu\text{v}/^\circ\text{C}$, absolute, corresponding to a nominal composition $\text{GdSe}_{1.480}$ ($m^*/m = 6$). On this basis we conclude that the optimum GdSe_x composition for use with P-type TPM-217 in the 800°-250° $^\circ\text{C}$ temperature interval lies in the nominal composition range $\text{GdSe}_{1.460}$ to $\text{GdSe}_{1.480}$, with corresponding Seebeck coefficient at 500° $^\circ\text{C}$ of 195-250 $\mu\text{v}/^\circ\text{C}$ absolute. We further conclude that there is a reasonable probability that this optimized GdSe_x composition, when processed with improved element fabrication techniques, will satisfy the goal of an 11% efficiency couple.

The efficiencies in Tables VI and VII were calculated in the following manner. The basic equation used was

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + \bar{Z}\bar{T}} - 1}{\sqrt{1 + \bar{Z}\bar{T}} + \frac{T_c}{T_h}}$$

with

$$\bar{Z}\bar{T} = \bar{T} \frac{(|\bar{S}_n| + |\bar{S}_p|)^2}{(\sqrt{\bar{\rho}_p \bar{K}_p} + \sqrt{\bar{\rho}_n \bar{K}_n})^2}$$

The average values of S, ρ , and K for the 0.10 at.% excess P-type TPM-217 over the 800°-250° $^\circ\text{C}$ temperature interval are:

$$\bar{S}_p = 247 \mu\text{v}/^\circ\text{C}$$

$$\bar{\rho}_p = 7.68 \text{ m}\Omega\text{-cm}$$

$$\bar{K}_p = 7.24 \text{ mw/cm-}^\circ\text{C}$$

The average values for S and ρ for the N-type $GdSe_x$ compositions were calculated by integrating the measured temperature dependence of S and ρ , with the ρ curve determined by the S versus $\ln \rho$ relation at $500^\circ C$. The N-type thermal conductivity was obtained from the integration of the series 6 and 7 thermal conductivity data with electronic component adjusted to that appropriate to the resistivity determined from the S versus $\ln \rho$ relation.

1.4 MATERIAL PROCESSING

1.4.1 Casting Improvement Studies

The casting improvement study was continued with the dual objective of obtaining a more suitable geometry for testing and of improving the casting procedure to reduce or eliminate the microscopic defects in elements. Three modifications were made in the casting furnace equipment: the water cooling passages in the furnace have been cleaned, resulting in a reduced furnace wall temperature; the pumping capacity of the system was increased, resulting in a higher vacuum (~ 70 microns compared with ~ 150 microns); and the riser in the casting mold was increased in size to minimize the pipe in the cast element. Larger diameter elements, more suitable for electrical measurements, have been cast in the improved 3/16-inch diameter casting mold.

Cooling Cycle:

A series of experiments to examine the cooling cycle portion of the casting process was completed by recasting samples N-2198-C, N-2201-C, and N-2204-C ($GdSe_{1.477}$) in the 3/16-inch diameter mold. The samples were all cast from $1740^\circ C$ with the gas pressure in the furnace maintained a 1 psig. The cooling cycles of the three samples varied as follows:

- N-2198-C2: Cooled at $1^\circ C/min.$ to $1640^\circ C$, soaked at $1640^\circ C$ for 2 hours, cooled to $1400^\circ C$ at $4^\circ C/min.$, soaked at $1400^\circ C$ for 1/2 hour, and furnace cooled to room temperature.
- N-2201-C2: Cooled at $1^\circ C/min.$ to $1400^\circ C$, soaked at $1400^\circ C$ for 1/2 hour, and furnace cooled to room temperature.
- N-2204-C2: Cooled at $4^\circ C/min.$ to $1400^\circ C$, soaked at $1400^\circ C$ for 10 minutes, and furnace cooled to room temperature.

A small amount of slag was evident on the top of all three samples. N-2198-C2 and N-2201-C2 contained a small pipe whereas sample N-2204-C2 appeared solid. Weight loss during casting was about

1-2 mg from a 5-gram sample, demonstrating that the material is stable up to 1740°C. The Seebeck coefficient had dropped from 230 $\mu\text{V}/^\circ\text{C}$ to 205 $\mu\text{V}/^\circ\text{C}$ on all three samples (Table VIII). The resistivities were between 8.8 and 10.1 $\text{m}\Omega\text{-cm}$ at 500°C. The samples are substantially identical. The drop in Seebeck coefficient shows a change in composition and is probably due to rejection of an impurity during the freezing process which is also indicated by the slag on the top of the casting. Cooling rates lower than 4°C/min. apparently did not influence the properties of the element for this casting procedure, nor did soaking at 1640°C for two hours.

TABLE VIII

Summary of Cooling Cycle Experiments -
Samples N-2198-C, N-2201-C, and N-2204-C

Sample #	Starting Composition After 1st Casting GdSe_x	$\bar{S}$ @ 500°C S ($\mu\text{V}/^\circ\text{C}$ rel. to Absolute)		ρ^* @ 500°C After 2nd Casting
		After 1st Casting	After 2nd Casting	
N-2198-C2	1.477	232	205	8.8
N-2201-C2	1.477	233	206	10.0
N-2204-C2	1.477	231	203	9.5

*Sample geometry (coring, voids) and contact resistance were so high that resistance measurements were not possible after the 1st casting.

Vacuum Melting:

A series of experiments was completed to more closely determine the effect of vacuum casting on the fabricated element. In addition, the cooling rate through the freezing range was briefly examined.

Seven samples (Table IX) were recast in a 3/16-inch diameter mold, five of which were vacuum melted. The vacuum obtained in the freezing range ($\sim 1720^\circ\text{C}$ - 1750°C) was about 200 $\mu\text{-torr}$. Cooling rates through the freezing range were controlled at 1°, 4°, 8°, and 58°C/min. A 30-minute soak at 1400°C followed by furnace cooling to room temperature was incorporated to provide a uniform amount of quenched-in vacancies in the samples. The vacuum melting process was introduced because gas bubbles are continually observed to be present in the castings, indicating the presence of volatile species which could possibly be removed by vacuum

TABLE IX
Summary of Vacuum Melting Experiments

Sample #	Starting Composition After 1st Casting GdSex	Casting Process	Cooling Rate Through Freezing Range (°C/min)	$\bar{S}$ @ 500°C S($\mu\text{V}/^\circ\text{C}$ rel. to Absolute)	
				After 1st Casting	After 2nd Casting
N-2203-C2	1.475	He Atmosphere	1	236	214
N-2205-C2	1.475	He Atmosphere	8	221	209
N-2200-C2	1.478	He Atmosphere	58	234	223
N-2207-C2	1.478	Vacuum	8	242	206
N-2206-C2	1.476	Vacuum	8	228	204
N-2209-C2	1.472	Vacuum	4	222	199
N-2202-C2	1.474	Vacuum	4	224	214

melting. All of the cast samples had a slag on the top of the ingot which demonstrates that impurities are being removed during the freezing process. Metallographic examination of some of the samples revealed a single-phase material with a few random inclusions of tantalum that are predominately at the top of the casting. A large gas bubble is also in the top section of the ingot, indicating that the vacuum melting, although helpful, does not completely eliminate the volatile species so additional process experiments are necessary.

These samples had a weight loss of about 0.03%, demonstrating that the vacuum melting process does not result in further volatilization of selenium from the $\text{GdSe}_{1.475}$ composition. For these GdSe_x alloys, which had an average composition of 1.475, the Seebeck coefficient, measured at 500°C (Table IX), was reduced an average of 10% to a value of about 210 $\mu\text{V}/^\circ\text{C}$ absolute by the recasting process. The sample cooled at 58°C/min. had a Seebeck coefficient of 223 $\mu\text{V}/^\circ\text{C}$ which is about 5% higher than the slower cooling rates. In general, slower cooling rates favor the rejection of impurities from the solidifying material into the liquid. The observed reduction in Seebeck coefficient is larger than would be expected from the small weight loss if attributed only to loss of selenium with the selenium doping model. A reasonable interpretation is that the material contains some small amount of a foreign impurity dopant in addition to the selenium stoichiometry dopant. Exactly what these impurities are is not known but efforts are being made to eliminate them. Resistivity measurements have not been completed on these samples.

Four samples (Table X), N-2214-C, N-2219-C, N-2203-C, and N-2198/N-2204 combination, were recast in the 3/16-inch diameter mold prior to the introduction of the enlarged riser in the mold. The primary objective of these experiments was to minimize the hole in the element.

- N-2214-C2: Cycled four times through the melting point ($\sim 1730^\circ\text{C}$) under vacuum in an attempt to completely degas the melt. The result was a smaller than normal gas bubble in the riser. A total weight loss of 8.5 mg was recorded and, if all the weight loss is attributed to selenium, the sample composition changed from $\text{GdSe}_{1.485}$ to $\text{GdSe}_{1.480}$. The Seebeck coefficient (S @ 500°C) dropped from 305 $\mu\text{V}/^\circ\text{C}$ to 231 $\mu\text{V}/^\circ\text{C}$.
- N-2219-C2: Vacuum cast at 1900°C to examine the effect of higher temperature on degassing the melt. A gas bubble was evident in the riser and the total weight loss was 8.2 mg, indicating a change in sample composition from $\text{GdSe}_{1.482}$ to $\text{GdSe}_{1.477}$. The Seebeck coefficient (S @ 500°C) decreased from 302 $\mu\text{V}/^\circ\text{C}$ to 229 $\mu\text{V}/^\circ\text{C}$.

TABLE X

Summary of Casting Improvement Experiments

Sample #	Starting Composition After 1st Casting GdSe _x	Final Composition	$\bar{S}$ @ 500°C S (μV/°C rel. to Absolute)		Remarks
			Before Casting	After Casting	
N-2214-C2	1.485	1.480	305	231	Cycled through melting point under vacuum
N-2219-C2	1.482	1.477	302	229	Vacuum melted at 1900°C
N-2203-C3	1.478	--	214	209	Heated to 1950°C, furnace cooled
N-2198/ N-2204-C3	1.477	--	204	208	Combined samples, riser part of sample not in- cluded in remelt

- N-2203-C3: Recast at 1950°C in helium atmosphere and furnace cooled in a manner identical to original casting cycle. The purpose of this experiment was to determine if the Seebeck coefficient which was reduced by a slow cooling rate (N-2203-C2) would be reversible by increasing the cooling rate. It should be noted from Table X that the Seebeck coefficient (S @ 500°C) decreased further from 214 $\mu\text{V}/^\circ\text{C}$ to 209 $\mu\text{V}/^\circ\text{C}$.
- N-2198/N-2204-C2: These samples were blended and recast; however, the riser portions of the melt were not included in the recast melt. It was observed that the recast sample did not have a slag material, indicating that the slag is an impurity in the material and is not due to interaction with the mold. The Seebeck coefficient (S @ 500°C) increased slightly, from 204 $\mu\text{V}/^\circ\text{C}$ to 208 $\mu\text{V}/^\circ\text{C}$.

1.4.2 Pressing and Sintering Experiments

A pressed and sintered sample prepared for pulse diffusivity measurements was characterized by S and ρ measurements. The resistivity measurement was made using the new resistivity apparatus with four collinear point probes spaced about 20 mils apart. The room temperature resistivity measured this was was $1.8 \pm 0.3 \text{ m}\Omega\text{-cm}$. The resistivity predicted from the Seebeck measurement of 160 $\mu\text{V}/^\circ\text{C}$ at 500°C is about $1.7 \text{ m}\Omega\text{-cm}$, indicating that the pressed sample had a relatively low extraneous resistance. This quantitative resistivity measurement supports our earlier qualitative indications that the pressed material has a low resistivity. Since the mechanical uniformity and freedom from voids of the sample is evident by microscopic examination, the existence of standard S and ρ properties make this a good specimen for thermal diffusivity measurements using the new high temperature thermal diffusivity system. A pressed specimen with a lower doping level and correspondingly high Seebeck coefficient will also be prepared for thermal diffusivity measurements.

1.5 ELEMENT CONTACTING

1.5.1 Surface Studies

Preliminary experiments to identify the nature of the surface film that forms on the gadolinium-selenide thermoelements have been started using the 3M ion scattering spectrometer technique. This spectrometer is capable of determining the composition of the outermost surface monolayer as well as doing a depth-profile composition analysis. The overall sensitivity is about 1% of the monolayer and, in addition, the technique can monitor all elements of mass greater than the probe ion beam.

For the initial experiments, the thermoelement end surfaces were subjected to the following treatments followed by an analysis of the surface formed:

- a. Freshly fractured surface
- b. Ground, under kerosene, on SiC
- c. Polished with 600 grit SiC, 15 μ , 6 μ , and 1 μ diamond, and MgO, respectively.

The experiments are currently in progress.

1.5.2 Pressure Contacts

In the interim and until definitive information becomes available from the surface studies experiments, efforts continue to explore possible methods of making ohmic contact to N-type materials. Pressure engaged contacts are being used for the present ingradient experiments.

1.6 ISOTHERMAL CHEMICAL COMPATIBILITY

Isothermal chemical compatibility experiments have been initiated using single-phase GdSe_x thermoelectric elements cast from synthesis batches N-2220-2231 in direct contact with potential metallic electrode materials and in close proximity to TPM-217 materials. The test matrix is listed in Table XI.

TABLE XI

Isothermal Chemical Compatibility Test Matrix
(GdSe_x Alloys)

1. Electrode Materials	- Pt, Gd, Nb, Ta, W-25%Re
2. P-Type Thermoelectric Material	- 0.10% excess TPM-217
3. Time (Hours)	- 1000
4. Soak Temperatures, °C	- 700, 800, 900
5. Atmosphere	- Vacuum sealed @ 10 ⁻⁴ torr

The thermoelectric elements were characterized electrically prior to insertion into the test fixtures.

Chemical, metallurgical, and electrical analyses on GdSex elements from the 3200-hour 700°-800°-900°C isothermal chemical compatibility experiments have been completed. These preliminary compatibility tests were done using two-phase GdSex material characteristic of the GdSex material available when these tests were initiated. In contrast to similar experiments with P-TPM-217, the post-test electrical data on these GdSex elements did not serve as a useful parameter for compatibility evaluation. These data, even within a given test series, were scattered so that definition of trends was impossible. The post-test chemical and metallurgical data are shown in Table XII.

TABLE XII

Summary of Results of the Preliminary Isothermal
Chemical Compatibility Experiments

<u>System</u>	<u>Chemical/Metallurgical/Visual</u>
1. Gold Electrode (700°-800°-900°C)	Electrode appeared reacted in 800°-900°C tests; electrode material in 800°-900°C bulk found to be ~96% wt. Au/4% wt. Se composition.
2. Platinum Electrode (700°-800°-900°C)	No evidence of Pt within bulk GdSex.
3. Tungsten-25% Rhenium Electrode (700°-800°-900°C)	No evidence of W-25%Re within bulk GdSex.
4. GdSex Controls (700°-800°-900°C)	Polarized light phase identical in composition to rest of GdSex bulk (identical as determined by electron microprobe).
5. GdSex/TPM-217 R5 (800°-900°C)	"Quartz" spacer used to separate elements was found by emission spectroscopy to be only soda glass. This finding almost entirely negates these test results.

These experiments indicated:

- A definite polarized light effect was observed in most cases. Exactly what this is attributable to is unknown at present.
- Gold is unsuitable as a hot junction contact; however, it could be satisfactory as a cold junction contact.

- One-phase GdSe_x , as presently being synthesized, should be the focal point of isothermal chemical compatibility experiments with GdSe_x alloys.

1.7 INGRADIENT COMPATIBILITY

Test ATT 231:

ATT 231, N-type element N-2086 with silver electrodes bonded to each end and operating in a temperature interval of $800^\circ/250^\circ\text{C}$, completed 3350 hours of operation in an argon atmosphere in a TELPS performance fixture. The argon atmosphere was used instead of vacuum because the silver electrodes on this element would vaporize in vacuum at 800°C . The resistance and Seebeck coefficient increased throughout the test. The resistivity increased from $16.6 \text{ m}\Omega\text{-cm}$ at 13 hours to $90.1 \text{ m}\Omega\text{-cm}$ at 3350 hours and in the same period, the Seebeck coefficient (relative to Pt) increased from $190 \mu\text{V}/^\circ\text{C}$ to $247 \mu\text{V}/^\circ\text{C}$. This is part of a trend which has been followed through the entire test as tabulated in Table XIII.

TABLE XIII
Electrical Performance of ATT 231

Time (Hrs)	$\bar{S} (\mu\text{V}/^\circ\text{C} \text{ rel. to Pt})$	$\rho (\text{m}\Omega\text{-cm})$
0	189	15.9
13	190	16.6
400	198	23.6
1100	211	41.0
1900	226	60.4
2600	234	74.3
3350	247	90.1

Predicted at $t=0$ hours from point function data:

$$\bar{S} = 184 \mu\text{V}/^\circ\text{C} ; \rho \approx 21\text{-}23 \text{ m}\Omega\text{-cm}$$

The trend appears to be almost linear with time, indicating no apparent limiting value. Since the resistivity in this test almost reached the maximum value ($1000 \text{ m}\Omega$) readable by the computerized data acquisition system, the test was terminated for chemical and metallurgical analyses.

The following diagram illustrates the Ag- GdSe_x interface and other parts of the element/hardware arrangements and the corresponding analysis as done by the electron microprobe for this test.

ATT 231

Results:

Ag-colored coating	- Ag + minor Gd and Se
Bronze coating on GdSex T _C	- Cu + Gd, Se + trace Ag
Black coating Cu T _C insert, GdSex side	- Cu and Se
Coating on Al cold block	- Ag, Se + trace Cu

The microprobe analysis of the sectioned Ag-GdSex interface revealed no foreign or reaction phases. Metallurgical examination showed a polarized light effect at the hot junction and about one-fourth of the way toward the cold junction of this two-phase GdSex element. The rest of the element did not exhibit this effect.

This analysis indicates that silver is not suitable for hot junction electrodes at 800°C because of the appreciable vapor phase transport which occurred. The most probable source of the selenium detected is residual contamination from previous P-type life tests.

Tests ATT 256 and 259:

Tests ATT 256 and 259 were both initiated in a TELPS performance fixture to explore the utility of an electroplated nickel electrode. ATT 256 has nickel at both the hot and cold ends while

ATT 259 has nickel only at the cold junction. The resistance and average Seebeck have both increased during the test period on ATT 256 (R at $t_0 = 56.6$ to R at $t_{400} = 66.4$; S at $t_0 = 144 \mu\text{V}/^\circ\text{C}$ to S at $t_{500} = 147 \mu\text{V}/^\circ\text{C}$). Since a reaction with nickel at the hot junction was suspected to be the cause of this change, another test, ATT 259, was initiated with nickel at only the cold junction. This test has displayed increasing resistance with decreasing Seebeck coefficient (R at $t_{40} = 87.6$ to R at $t_{250} = 103.5$; S at $t_{40} = 198 \mu\text{V}/^\circ\text{C}$ to S at $t_{250} = 188 \mu\text{V}/^\circ\text{C}$). As with the silver electrode test (ATT 231) these two experiments were terminated for chemical and metallurgical analyses.

The following diagrams illustrate the element/hardware arrangements and the corresponding chemical analyses for these tests.

ATT 256

ATT 259

Both tests had a copper block cold junction which was coated with a Cu_{2-x}Se film. As with ATT 231, the selenium was most likely residual contamination from previous P-type life tests.

As shown in Figure 8, the metallurgical examination revealed:

- The T_h gold electrode migrated into the GdSe_x element. This migration was more pronounced in ATT 259 than in ATT 256.

Figure 8
Photomicrographs of Ingradient Compatibility Tests

ATT 256
145x

ATT 259
145x

- A polarized light effect was detected about 1/7L from T_h on ATT 256 and 1/2L on ATT 259.

These analyses give further evidence that gold is unsuitable as a hot junction electrode because of its migration into the $GdSe_x$ alloy. Microprobe examination of the gold inclusions will be completed during the next quarter.

1.9 INGRADIENT LIFE TESTING

Tests ATT 267 and 268 in TELPS Performance Fixtures:

Two N-type $GdSe_{1.5-x}$ elements, ATT 267 (N-2189-C2) and ATT 268 (N-2210-C), were placed on test under vacuum in the standard TELPS performance fixture. Platinum-rhodium thermocouples are in direct contact with the elements as voltage and temperature sensing probes. A four-probe measurement of resistance is being made, thus allowing measurement of element resistance without the contribution of the electrical contacts.

The initial resistance readings on both elements were essentially those predicted by the isothermal measurements (Table XIV). The Seebeck coefficient was lower than predicted by about 10%. The tests were then operated under an argon atmosphere and the Seebeck coefficient immediately went to the value predicted from the point function data. This shift in electrical property is apparently due to improved thermal contact between the voltage probes and the element provided by the argon cover gas. Both tests remained in operation under argon until the resistance increased by a factor of about ten. This change in resistance took about 40 hours for test ATT 268 and 75-100 hours for test ATT 267. Test ATT 268 was terminated because of a heater failure and test ATT 267 was returned to vacuum operation whereupon the resistance immediately began to decrease and within 30 hours had returned to its original value. Since it appears to be necessary to operate under a cover gas atmosphere to obtain accurate Seebeck coefficient readings, test ATT 267 has been continuously operated under vacuum and momentarily backfilled with argon for electrical measurements.

Tests ATT 267 and 268 were both operating on the S- $\ln p$ trend line for those elements, indicating that good electrical and thermal contact could be made with the element. This also points out that the point function data are correlating with ingradient performance.

Test ATT 267 has operated in the standard TELPS performance fixture for over 1450 hours without any significant change in electrical properties. Table XV is a summary of the electrical performance of this test.

TABLE XIV

N-Type Ingradient Performance Tests Operating in Temperature Interval 800°/330°C
in TELPS Performance Fixtures under Vacuum

ATT #	Load Pressure (psi)	Test Time (Hrs)	$\bar{S}$ ($\mu\text{V}/^\circ\text{C}$ rel. to Abs.) Based on Integration of S vs T Data	$\bar{S}_{\text{measured}}$ ($\mu\text{V}/^\circ\text{C}$ rel to Abs.)	$\bar{\rho}$ based on Integration of ρ vs T Data ($\text{m}\Omega$)	$\bar{\rho}_{\text{measured}}$ ($\text{m}\Omega\text{-cm}$)
267	~200	165	232	226	13.2	14.7
268	~200	80*	293	310	49	43.5

*Terminated

TABLE XV

Ingradient Performance Test ATT 267 Operating
in Performance Fixture under Vacuum in Temperature
Interval 800°/330°C and Load Pressure of
Approximately 200 psi

Test Time (Hours)	$\bar{S}$ ($\mu\text{v}/^\circ\text{C}$ rel. to Abs.)	ρ ($\text{m}\Omega\text{-cm}$)
165	226	14.7
440	226	14.7
1170	218	14.7

The modified TELPS fixture in which test ATT 267 is operating has experienced heater failure twice because of vacuum operation. Apparently the ceramic insulator in the heater has caused arcing between the electrodes because of a low resistivity skin formed on the ceramic during operation. Temporary repairs, which allow several additional weeks of operation, involve shutting the test down and cleaning the ceramic. The long-term solution to this problem is to replace the heater block with a design which can operate in vacuum. Such a design is the radiant heater now used in the six-station bell jar. Four TELPS-type fixtures are being modified to accept the radiant heaters. This change will extend operation to 1000°C in vacuum. Until these fixtures are modified, short-term tests will be conducted in the TELPS fixtures. Because of heater failure, it is anticipated that the continuous tests longer than 1500 hours in a vacuum will not be possible in TELPS performance fixtures as they now exist.

Test ATT 274 in Vacuum Bell Jar:

A new test, ATT 274 (N-2218), was initiated and has operated 400 hours in a temperature interval of 1000°/220°C and in a vacuum of 10^{-6} torr. Figure 9 shows that element on test. The hot junction electrode is gadolinium foil pressure engaged to the element. The cold junction current contact is carbon. There is a platinum-rhodium thermocouple acting as a voltage and temperature probe in contact with the element at the cold end. Seat-in at the hot end contact began when the hot junction temperature reached about 850°C. This element has not exhibited creep deformation with a load pressure of approximately 600 psi. Table XVI summarizes the electrical performance of this test.

Figure 9

Gadolinium-Selenide Element (ATT 274) Operating
in Temperature Interval 1000°/220°C in Vacuum

TABLE XVI

Electrical Performance of Test ATT 274

Test Time (Hours)	$\bar{S}$ ($\mu\text{v}/^\circ\text{C}$ rel. to Abs.)	R* ($\text{m}\Omega$)
24	232	296
85	217	164
145	212	165
205	211	149
340	209	146

*For length = 0.547" and diameter = 0.194"

Four modified TELPS stations are being fabricated for N-type ingradient testing. These modified TELPS stations will feature:

- Air cooling rather than water
- A metal enclosure for vacuum or cover gas operation
- High temperature heat source (1000°C)
- Design compatible with existing performance fixture cold ends.

FIGURE 10
HIGH TEMPERATURE PERFORMANCE FIXTURE

TASK 2.0 - TPM-217 P-TYPE MATERIAL CHARACTERIZATION

2.5 ELEMENT CONTACTING

2.5.1 Cold Junction Contacting

Process control experiments using the ingradient bonding technique to bond copper electrodes to the P-type TPM-217 material continue. The copper electrode appears to have a strong bond and the electrical tests performed on the bonded elements demonstrate good electrical characteristics.

Modifications to the bonding fixture, designed to improve control of both temperature and pressure, have been submitted to the Machine Shop. The process variables to be studied when these modifications are completed include:

- Type of copper
- Effect of reverse current
- Atmosphere
- Excess selenium level
- Surface preparations
- Thermal profiles

2.5.2 Partition Bonding

The design of a mold to accommodate casting the P-TPM-217 material onto tungsten or tungsten-rhenium has been started. The process variables to be studied for the partition bonding program include:

- Materials for partition
- Surface preparation
- Excess selenium level
- Residence time in melt
- Partition geometry
- Atmosphere

2.5.3 Exploratory Bonding Experiments

An exploratory experiment to examine the feasibility of electroplating a copper electrode onto the P-type TPM-217 element was completed. The bonded element was placed on test in the temperature interval 800°/250°C in argon atmosphere to examine the compatibility of the electrode/element system. The test has completed 1048 hours of continuous operation with stable electrical properties. No unusual chemical effects have been observed to date.

2.7 COMPRESSION-CREEP STUDIES

A series of six partitioned elements continue to operate in the six-station vacuum bell jar at load pressures of 165, 225, and 300 psi, respectively, and in the temperature interval of 800°/200°C. This series of tests is designed to provide information on the dependence of creep on load pressure. Quantitative creep data are not available at present; Table XVII records the qualitative results of visual examination of the elements. It appears from visual examination of the elements loaded at 300 psi that the hot end has increased slightly in diameter and negligible changes in dimensions have taken place on the elements loaded at the lower pressures.

TABLE XVII

Arbitrary Ranking of Apparent Creep Deformation
in Elements in Order from Greatest to Least

<u>Load Pressure</u> <u>(Greatest to Least)</u>	<u>Observed Compression Creep</u> <u>During Operation</u> <u>(Greatest to Least)</u>
ATT 261 (300 psi)	ATT 262
ATT 262, 263 (225 psi)	ATT 264, 261
ATT 264, 265 (165 psi)	ATT 265, 263

There is not a one-for-one correlation between the load pressure and the apparent creep. Photographs of these elements are to be made periodically to monitor dimensional changes (if any) that may occur due to deformation processes. The microscope/camera is in the process of being procured.

2.8 ISOTHERMAL CHEMICAL COMPATIBILITY

This series of tests has been reinserted in the furnaces along with the GdSe_x test series discussed under Section 1.6. Three of the furnaces had been temporarily shut down for removal of terminated N-type samples; one furnace at 800°C was not interrupted. To review, these chemical compatibility experiments are being run at 700°-800°-900°C for the P-type TPM-217 (0.10% excess material) with combinations of the components listed below:

1. Electrodes - Tungsten, Tungsten-25% Rhenium, Molybdenum
2. Thermal Insulation - Min-K 2020, Fiberfrax
3. N-Type Thermoelectric Material - Gadolinium-Selenide

In addition, compatibility experiments with niobium and tantalum electrode materials have been initiated.

The 800°C tests that were not interrupted have been on test for 10,572 hours (includes tests reinserted after 5200 hours of previous testing) whereas the other experiments have been on test for 3200-8400 hours.

2.9 INGRADIENT COMPATIBILITY AND INGRADIENT LIFE TESTING

2.9.1 Extended Performance Life Test Series

Table XVIII summarizes the current status of the non-partitioned element extended life tests in the ingradient performance fixtures. For eleven of the twelve life tests in operation, no major changes were observed during the past quarter. The remaining test (ATT 128) is still operating but there is no measurement of Seebeck coefficient or resistance. The cause seems to be loss of contact by the thermocouple at the cold junction and the test will be temporarily shut down for fixture repair.

Three-Year Extended Life Tests at 500°, 600°, and 700°C:

The 500°, 600°, and 700°C extended life tests have been in operation for over three years. The tests continue to display that TPM-217 material has stable long-life electrical properties.

Three tests are operating at 700°C, two at 600°C, and two at 500°C; the electrical performance at 30,700 hours of a test in each of the test intervals is displayed in Figures 11-13. There is an initial increase in the Seebeck coefficient and resistance of elements in this test series because the elements were initially at 0.18% excess selenium level and the ingradient stable composition of TPM-217 is about 0.09% excess selenium level. The tests at 500°C have yet to reach the 0.09% level because the rate of change, being temperature dependent, is extremely slow at this temperature. This composition change is not a deficiency because many later tests were initiated at, and have continued to operate at, the stable composition.

The cause of the erratic data in this original life test series is the extrusion of copper from the cold end of the element. The copper pushes or tilts the element from the cold base of the fixture, causing poor electrical and thermal contact. Periodically the fixtures have been interrupted and the problem with the fixtures repaired. This problem has been overly exaggerated because the thermocouple hole in the cold block causes an odd current flow in the element; the resulting high local current density accentuates the copper extrusion. The average electrical resistance

TABLE XVIII

Summary of Ingradient Performance and Compatibility Tests Currently in Progress

ATT #	Test Description		Atmos.	Hours of Operation	Test Apparatus	Purpose of Test
	Temperature, °C					
	Hot Junction	Cold Junction				
127	700	280	Argon	30,700	P	Display the performance of TPM-217 at 700°, 600°, and 500°C. Carbon electrodes both hot and cold junctions.
128	700	280	Argon	30,700	P	
129	700	280	Argon	30,700	P	
132	600	260	Argon	30,700	P	
133	600	260	Argon	30,700	P	
136	500	220	Argon	30,700	P	
137	500	220	Argon	30,700	P	
174	800	300	Argon	16,100	P	Carbon hot junction electrode as a control test. Carbon cold junction electrode.
178	700	275	Argon	15,300	P	Molybdenum hot junction electrode ingradient compatibility. Carbon cold junction electrode.
192	700	250	Argon	11,800	P	Bonded cold junction, pressure engaged to tungsten at hot junction.
195	700	250	Argon	11,800	P	
196*	800	300	Argon	11,400	P	Test the effect of a quartz sleeve seal at the hot end of the element on copper extrusion. Pressure engaged tungsten at hot junction and copper as cold junction electrode.

P = Performance fixture

*Exploratory test

Figure 11. Advanced Technology Test #128
Average Seebeck Coefficient and
Relative Resistance of TPM-217
Normalized to 700°/280°C Temperature
Interval

Figure 12. Advanced Technology Test ATT #132
Average Seebeck Coefficient and
Relative Resistance of TPM-217
Normalized to 600°/260°C Temperature
Interval

Figure 13. Advanced Technology Test #136
Average Seebeck Coefficient and
Relative Resistance of TPM-217
Normalized to 500°/210°C Temperature
Interval

is affected more by this artifact of the experiment than the average Seebeck coefficient because the resistance is geometry dependent ($R = \rho L/A$).

Two Extended Life Tests at 700°C - Bonded Elements:

Two tests, ATT 192 and 195, with tungsten hot junction electrodes and bonded eutectic cold junction electrodes have operated for 11,400 hours with stable performance, see Figures 14 and 15. The elements are operating at the selenium excess level predicted by the performance mapping current dependence work--at 0.06 and 0.07% excess selenium, respectively; the predicted level is 0.07% excess selenium. Table XIX summarizes the electrical performance of these two life tests.

Two Extended Life Tests at 800°C - Initial Composition 0.10%:

Two elements with an initial composition of 0.10% excess selenium level are currently on long-term life test at 800°/300°C (ATT 174 and 196). These two elements at 16,100 and 11,400 hours have less than 3% standard deviation in the ingradient Seebeck coefficient (Table XX).

The average Seebeck coefficient versus time for these tests at 13,000 and 8,300 hours is shown in Figures 16 and 17. The previous data reported for these tests were in error due to problems with the temperature reference. The correction of $-6 \mu\text{V}/^\circ\text{C}$ was applied to part of the old data to compensate for the fact that the tests were actually operating in a higher temperature interval than measured. These two tests will remain in operation to evaluate the long-term stability of the 0.10% excess selenium (stable composition) TPM-217 operating at 800°C hot junction temperature.

2.9.3 Six-Station Vacuum Bell Jars

Parts to build two additional six-station vacuum bell jars are being fabricated in the Machine Shop. Design modifications to reduce or eliminate some of the troublesome leak problems in the cold end manifold of the first six-station vacuum bell jar are being made and will be incorporated into these new bell jars. In addition, the internal electrical circuit will be improved to eliminate shorting which has occurred in the first six-station vacuum bell jar. The new six-station jars will feature:

- Six independent load pressure settings
- Six independent current settings
- A direct measure of the force on the element
- Gas or water fittings have been eliminated in the jars.

FIGURE 14

Ingradient Seebeck Coefficient of Test ATT 192
Operating Between 700°/250°C; Tungsten Hot/
Eutectic Bonded Cold Junction Electrodes

FIGURE 15

Ingradient Seebeck Coefficient of Test ATT 195
Operating Between 700°/250°C; Tungsten Hot/
Eutectic Bonded Cold Junction Electrodes

TABLE XIX

Summary of Performance/Compatibility Tests at 700°/250°C

ATT #	Hours of Operation	Mean Seebeck* Coefficient ($\mu\text{V}/^{\circ}\text{C}$)	% Standard Deviation of Seebeck Coefficient*	Mean Resistance* ($\text{m}\Omega$)	% Standard Deviation of Resistance*	Ingradient Composition (% excess Se)
192	11,800	283	0.8%	34.1	2%	0.06 $\pm$ 0.01
195	11,800	274	1.3%	37.3	7%	0.07 $\pm$ 0.01

*Mean and percent standard deviation of 120 data points.

TABLE XX

Summary of the Two Long-Term Tests at 800°/300°C

ATT #	Hours of Operation	Mean Seebeck Coefficient ($\mu\text{V}/^{\circ}\text{C}$ rel. Pt)	% Standard Deviation of Seebeck Coefficient	Ingradient Composition % Se Excess
174	16,100	272 $\pm$ 7	2.5%	0.09 $\pm$ 0.01
196	11,400	283 $\pm$ 8	3.0%	0.08 $\pm$ 0.01

FIGURE 16

Ingradient Seebeck Coefficient of Test ATT 174
Operating between 800°/360°C; Carbon Hot/Carbon
Cold Junction Electrodes

FIGURE 17

Ingradient Seebeck Coefficient of Test ATT 196
Operating Between 800°/300°C; Tungsten Hot/
Copper Cold Junction Electrodes

2.10 PERFORMANCE MAPPING

The copper second phase boundary of the single phase region was derived from ingradient performance mapping measurements (Technical Task Report No. 38) for the region 150°-250°C. The temperature dependence was stronger than anticipated for the 150°-250°C temperature range. This quarter, independent measurements were performed to confirm this region of the phase diagram.

The equilibrium isothermal resistivity technique was used to substantiate the ingradient phase boundary determination from 200°-250°C, and to extend the phase boundary from 250°-800°C. The technique involved measuring the ac resistivity of a copper-bonded sample in the presence of a small dc current. The dc current is essential to prevent the growth of copper at the voltage probes; this copper formation at the voltage probes has prevented use of this simple technique in the past. The preliminary results are in substantial agreement with the phase diagram as reported in Technical Task Report No. 38 and, in addition, indicate a nearly constant composition of about 0.033 at.% excess Se extending from 300°-600°C. This constancy is in agreement with the anticipated behavior. Additional analysis and experiments are necessary to separate a slight increase in indicated composition at 800°C into second-phase boundary and intrinsic excitation components.

This series of performance mapping measurements reported in Technical Task Report No. 38 has provided direct confirmation of the ability of the dopant drift model to predict element performance. In the future, measurements of average $\bar{S}$ and $\bar{\rho}$ at higher hot junction temperatures are planned to substantiate the model throughout the range of operating temperatures, but no anomalies are expected. Rather than pursuing the high temperature measurements immediately, the next step has been to modify the cold end calorimeter, thermal isolation, sample geometry, and electrode attachment in order to obtain reliable heat flux measurements at moderate temperatures.

To make these measurements, a new heat flux meter has been designed and is being fabricated for the performance mapping fixture to improve the experimental data on the variation of heat flux with current. A new series of current dependence measurements will be performed when the heat flux meter is operational.

2.11 ELEMENT PARTITION DEVELOPMENT

Nine partitioned elements are currently being tested in electrical and thermal gradients. Table XXI summarizes the status of these tests.

TABLE XXI
Status of Partitioned Tests

ATT #	Fixture	Atmos.	T _h (°C)	T _c (°C)	Load Pressure (psi)	Total Test Time (Hrs)	Number of Segments
210	Performance	Argon	800	280	150	9260	2
217	Performance	Argon	800	260	350	8820	3
241	Performance	Argon	800	250	150	3950	3*
264	Bell Jar	Vacuum	800	200	165	3500	3
265	Bell Jar	Vacuum	800	200	165	3500	3**
262	Bell Jar	Vacuum	800	200	225	3500	3***
263	Bell Jar	Vacuum	800	200	225	3500	3***
261	Bell Jar	Vacuum	800	200	300	3500	3
223	Bell Jar	Vacuum	800	200	300	6700	3

* Bonded

** Station shorted

***May have partial short in fixture

The extraneous resistance, calculated from the measured resistivity and the resistivity based on the Seebeck coefficient, has ranged from 8.3 to 53%. The highest extraneous resistance was displayed by elements recently placed on test in the six-station vacuum bell jar, apparently due to incomplete "seat-in" of the pressure contacts. The tests will be discussed in turn.

ATT 210:

Element partition test ATT 210, an R-11 element with two segments, has been operating continuously in a TELPS performance fixture at 800°/280°C in an argon atmosphere for approximately 9200 hours. A small spot of copper was observed at approximately 2700 hours--the same amount of copper than is normally observed on non-partitioned elements operating under similar conditions in 24 hours. Moderate creep deformation (8% diameter increase) has taken place; this mechanical improvement is in sharp contrast with 25-60% reduction

in element length at 5800 hours in the same temperature interval for non-partitioned elements (ATT 194 and 193, respectively). The surface of the element looks excellent except for slight discoloration and roughness.

The resistance decreased since 2000 hours, indicating seat-in at the barrier. Prior to that time, the resistance was as much as double that predicted from point function data. Table XXII summarizes the performance of this test.

TABLE XXII
Performance of Test ATT 210

Time (Hrs)	$\bar{S}$ ($\mu\text{V}/^\circ\text{C}$ rel. to Pt)	R ($\text{m}\Omega$)	$\bar{\rho}$ ($\text{m}\Omega\text{-cm}$)	$\bar{\rho}$ ($\text{m}\Omega\text{-cm}$) (Predicted from $\bar{S}$)	Extraneous Resistance %
2700	272	25.0	8.01	8.96	-11
3300	277	29.2	9.36	9.62	-2.7
3900	280	32.2	10.32	10.04	2.8
4800	281	29.8	9.55	10.18	-6
5600	278	36.2	11.6	9.76	19
6300	278	37.4	12.0	9.76	23
7090	279	37.4	12.0	9.9	21
7850	281	31.7	10.17	10.19	0
8500	284	35.6	11.42	10.63	7.4
9260	282	43.2	13.85	10.33	34

ATT 217:

Element partition test ATT 217, an R-11 element with three segments, two pressure engaged partitions, has been operating continuously in a TELPS performance fixture in the temperature interval $800^\circ/260^\circ\text{C}$ in an argon atmosphere for approximately 8800 hours. The load pressure is 350 psi. The test originally had tungsten foil barriers pressure engaged to the segments, but at 1030 hours platinum foils were added at the segment interfaces so as to be pressure engaged to the cold end of the upper segment.

The Seebeck coefficient has been low from the time the platinum foils were added at the interfaces. It is suspected that the element may have been oxidized during test start-up. The resistance was also low (close to that appropriate for Seebeck) as

evidenced by Table XXIII. The test was shut down, but no obvious fixture-related problems were found. The highest resistance interface was at the upper end of the second segment. Following restart of the test, the resistance returned to its original value. The relative stability of the data indicates that no substantial chemical or physical changes are taking place.

At approximately 8800 hours, this test displayed an increase in Seebeck coefficient and resistivity to approximately what would be expected for this material. It was felt that this fixture was causing low Seebeck and resistivity readings but the source of the problem could not be found. It appears that the problem may have disappeared.

TABLE XXIII
Performance of Test ATT 217

Time (Hrs)	$\bar{S}$ ($\mu\text{V}/^\circ\text{C}$ rel. to Pt)	R ($\text{m}\Omega$)	$\bar{\rho}$ ($\text{m}\Omega\text{-cm}$)	$\bar{\rho}$ ($\text{m}\Omega\text{-cm}$) (Predicted from $\bar{S}$)	Extraneous Resistance %
2200	227	24.9	7.74	4.40	76
2800	227	26.8	8.33	4.40	89
3500	224	18.8	5.84	4.22	38
4400	226	17.6	5.47	4.34	26
5900	227	18.2	5.66	4.40	29
6630	232	19.2	5.97	4.72	26
7390	231	19.3	6.00	4.65	29
8050	232	20.0	6.22	4.72	32
8820	280	30.5	9.40	9.33	1.7

ATT 241:

Test ATT 241 was initiated to determine the performance of a three-segment element with bonded tungsten-rhenium barriers and a eutectic cold end bond. The Seebeck and resistance indicated that the composition had changed significantly during the bonding process. The initial composition was 0.10% excess selenium and after bonding the Seebeck indicated 0.054% excess selenium and resistivity 0.043% excess selenium. This apparently is due to the distribution of copper throughout the element during the bonding process. The initial Seebeck coefficient was $300 \mu\text{V}/^\circ\text{C}$ and after 300 hours was $302 \mu\text{V}/^\circ\text{C}$ and the initial resistance was $56.4 \text{ m}\Omega$ and after 300

hours was 59.4 mΩ. The closeness of the resistance to that calculated (48 mΩ for $\bar{S} = 300 \mu\text{v}/^\circ\text{C}$) and the apparent lack of seat-in appears to indicate a low initial bond resistance.

The resistance and Seebeck coefficient of ATT 241 remained constant during the first 750 hours and then began dropping. Investigation into the cause of the change in properties will be deferred until this test is terminated. One possible explanation for such changes in electrical properties is the formation of a bypass of TPM-217 material around the W-Re barrier disc. This could occur if TPM-217 material is deposited on the barrier edge and the electrical and thermal gradients across the barriers drive copper into lower segments. If this occurred, a possible solution would be to extend the barrier beyond the diameter of the element. Another possible reason for changes in electrical properties is the high current density which would result from voids in TPM-217 near the barriers. Such voids were seen at the barriers in test ATT 238. At approximately 1000 hours ATT 241 stabilized at $\bar{S} = 287 \mu\text{v}/^\circ\text{C}$ and $R = 41.5 \text{ m}\Omega$. This resistance indicates a resistivity within 10% of that predicted from $\bar{S}$.

Test ATT 241 continues to exhibit very stable electrical and mechanical operation as shown in Table XXIV. There is no significant creep deformation and the small quantity of copper at the cold end apparently is that which was trapped in the element during the process of bonding the cold end electrode. The increase in extraneous resistance exhibited by ATT 241 around 3800 hours appears to be due to noise in the measurement, probably connected with random fixture fluctuation. ATT 241 exhibited two cycles from 38.0 to 41.6 mΩ during the test period 3100-3900 hours as shown in Figure 18. A possible reason for this may be variation in thermocouple (voltage probe) contact.

TABLE XXIV
Performance of Test ATT 241

Time (Hrs)	$\bar{S}(\mu\text{v}/^\circ\text{C})$ rel. to Pt)	R (mΩ)	$\bar{\rho}$ (mΩ-cm)	$\bar{\rho}(\text{m}\Omega\text{-cm})$ (Predicted from $\bar{S}$)	Extraneous Resistance %
300	302	59.4	17.95	13.70	31
1000	290	41.3	12.48	11.56	-8
1750	289	41.7	12.6	11.4	11
2509	289	40.9	12.35	11.4	8.3
3150	289	39.7	11.99	11.4	5.2
3950	290	41.6	12.56	11.56	8.7

FIGURE 18

ATT 241

ATT 261-265 and 223 - Vacuum Bell Jar Tests:

The partitioned elements in the six-station vacuum bell jar continue to operate at three different load pressures and at a hot junction temperature of 800°C. These tests consist of:

One element from single-station bell jar (ATT 223)

Five partitioned elements from batch R11 made with three pressure engaged segments with the approximate dimensions:

overall diameter $\approx$ 0.25 inch
overall length $\approx$ 0.40 inch

length of each active segment (not including bond) $\approx$ 0.133 inch.

The cold end of the five new elements is bonded with CuAg eutectic and the hot end is pressure engaged to tungsten. The barriers are 0.005-inch thick platinum foil over 0.006-inch thick tungsten foil (refer to Technical Task Report No. 36, page 54).

The primary objective of this test series is to study the mechanical behavior of partitioned elements; therefore, three stations in the fixture which had possible shorts have been repaired. The tests are uninsulated to allow photography, by means of a close-up camera, of the dimensional changes if any occur. The 200°C versus 250°C cold junction was chosen to be more in line with anticipated space system applications.

These partitioned elements have experienced partial seat-in during the first 400 hours of operation. Although the seat-in was not complete, the load pressures were readjusted to those to be used during the test. This was done to insure that there would be no significant deformation due to the excessively high load pressures (400 psi) applied during the seat-in period. It was anticipated that seat-in would continue at a reduced rate.

All of these tests have displayed significant seat-in since the inception of the tests. It does not appear that there is a correlation between the time necessary to seat-in and the load pressure. The seat-in process may be more dependent on the random mating of the various barrier/element interfaces than the load pressures. The six elements have not exhibited any copper extrusion.

The Seebeck coefficient observed on partitioned elements 261-265 initially varied over a wide range. Several possible explanations are offered for this behavior:

1. The middle segment may be progressing to its steady state composition at different rates in the five elements.
2. The temperature profiles of the legs may differ markedly because of poor thermal contact between segments.
3. The distribution of dopant in each of the segments may not be uniform. This may be due to poor electrical contact leading to high local current densities.
4. Fixture wiring difficulties.

The bell jar was shut down briefly to determine why there have been apparent difficulties associated with obtaining electrical data. Several shorts were found in the 8-wire lead throughs located under the main mounting plate for the test stations. These apparently occurred when the wires were moved after the mechanical assembly was done. Improved wire routing will be incorporated into the new jars now being designed. Apparently the shorts affected all of the data which were generated. The Seebeck coefficients and resistances are now fairly close in the five tests which were initiated at the same time (Table XXV). The Seebecks are $251 \pm 6 \mu\text{V}/^\circ\text{C}$ and the resistances are $39 \pm 3 \text{ m}\Omega$. The calculated extraneous resistances are generally lower than they were, due in part to the elimination of shorts in the fixture. The extraneous resistance of three of the elements is still above 20% and does not appear to be a function of load pressure.

The Seebeck coefficient is typical of 0.108% excess selenium and the resistivity of 0.089% excess selenium. These excess levels are greater than expected from other performance information obtained thus far. An excess level of 0.05% to 0.06% excess selenium would be predicted from the operating mechanisms which are thought to be in effect. A possible reason for this discrepancy in composition is contamination by oxidation due to minor air leaks in the system. It was thought originally that a pressure of 10^{-5} torr would be adequate; however, recent considerations indicate that a flow of air through the bell jar at these pressures could cause element contamination. The same problem will not exist in the new jars since the redesign has eliminated the causes for the leaks. The effect of oxygen would be to reduce the average Seebeck coefficient and resistivity and increase the average carrier concentration. Additionally, the oxygen as a dopant may act analogous to selenium to increase creep deformation.

TABLE XXV

Performance of Five Partitioned Tests in Vacuum Bell Jar

ATT #	Load Pressure (psi)	Time (Hrs)	Number of Segments	$\bar{S}$ ($\mu\text{V}/^\circ\text{C}$ rel. to Pt)	R ($\text{m}\Omega$)	$\bar{\rho}$ ($\text{m}\Omega\text{-cm}$)	$\bar{\rho}$ ($\text{m}\Omega\text{-cm}$) (Predicted from $\bar{S}$)	Extraneous Resistance %
264	165	3,500	3	257	28.4	8.13	7.69	6
265	165	3,500	3	245	28.2	8.07	6.54	23
262	225	3,500	3	244	31.1	8.73	6.50	34
263	225	3,500	3	246	29.5	8.25	6.58	25
261	300	3,500	3	251	27.1	7.64	7.04	9

Test ATT 223 has three segments pressure engaged to a tungsten partition at 300 psi load pressure, operating in the temperature interval of approximately 800°/250°C in a vacuum bell jar apparatus. This test was used in the early stages to test couple hardware. For example, at approximately 2100 hours, the test had noticeably tipped from the vertical due to the bellows load pressure system biasing the elements. The test was shut down and guides were added to the hardware system to keep the cold block in alignment without adding friction to the system. The modifications for this test were subsequently incorporated into the six-station vacuum bell jar.

To date, test ATT 223 has been on test over 6700 hours with relatively stable performance as evidenced by the following summary of data:

<u>Time</u> <u>(Hrs)</u>	<u>$\bar{S}$ ($\mu\text{V}/^\circ\text{C}$)</u> <u>rel. to Pt)</u>	<u>R</u> <u>(mΩ)</u>
2100	269	27.0
6700	272	27.1

The test continues to operate in the six-station vacuum bell jar.

TASK 3.0 - COUPLE DEVELOPMENT

3.4 DESIGN AND DEVELOPMENT OF TPM-217/N-PbTe COUPLE

3.4.1 Ball-Socket Hardware

A P-type TPM-217/N-PbTe couple, utilizing the couple technology that employs ball-socket cold end (U.S. 3,075,030) and the pivoting hot end (U.S. 3,496,028) hardware that was similar to or residual from the SNAP-27 thermoelectric generator program, was assembled and placed on test. The objective of the couple test is to clearly demonstrate that it is possible to design and construct a TPM-217/PbTe couple that will perform in a predictable way. Figure 19 is a configuration drawing of this one-couple test with the unique hot and cold end hardware features.

This couple has operated in a temperature interval of 565°/200°C (1050/392°F) in an argon atmosphere for 1600 hours with stable electrical performance. The test was cycled at 250 hours to replace an electrical heater that failed. The power output of the couple is stable at 0.275 watt with an extraneous resistance factor of 1.03 (3% over expected theoretical performance) since the heater repair. Figure 20 displays the power as a function of

FIGURE 19

Configuration of One-Couple Test with Ball Socket Hardware

FIGURE 20

Power Out of TPM-217/3N-PbTe Couple (ATT 266)
with Ball-Socket Hardware Operating in a
Temperature Interval 565°/200°C (1050°/392°F)
in Argon Atmosphere.

Cycle 1 - replaced hot block heater.

time for this test. Figure 20 also displays that prior to heater failure, the couple was operating stably and with a negligible extraneous resistance factor. The close agreement between predicted and measured electrical performance of this couple prior to the heater failure is given in Table XXVI. Although care was taken so as not to disturb the test when the heater was replaced, the extraneous resistance increased. The mathematical model and experimental data obtained from the performance mapping experiments (Task 2.10), involving the current dependence on electrical properties of P-TPM-217, were used to predict the performance of the couple. To facilitate construction of the couple, the 3N-PbTe geometry was held constant and the P-TPM-217 geometry was tailored to obtain maximum power output of the couple. The detailed calculations are as follows:

First, determine the length of the P leg for maximum efficiency and power:

$$L_P = I_N \frac{A_P}{A_N} \sqrt{\frac{\rho_P K_P}{\rho_N K_N}} \quad (1)$$

$$= 0.571 \text{ cm} \leftrightarrow 0.225 \text{ in.}$$

Then calculate the matched load current at maximum power, with junction temperatures at 565°/200°C and extraneous resistance factor of 1.10:

$$i = \frac{(\bar{S}_P + \bar{S}_N) \Delta T}{(1.10) 2 \left(\frac{L_N}{A_N} \rho_N + \frac{L_P}{A_P} \rho_P \right)} \quad (2)$$

$$= 3.65 \text{ amperes}$$

From the performance mapping work, the ingradient stable composition of TPM-217 can now be determined.

$$\bar{n} = n_O + i L/A 0.0055 (T_M/773)^{2/3} \quad (3)$$

using $n_O = 0.05$

$$\bar{n} = 0.081$$

The average Seebeck coefficient and resistivity can then be determined from:

$$\bar{S} = \bar{S}_{0.10} + 70 \ln 0.10/\bar{n} \quad (4)$$

$$\bar{\rho} = \bar{\rho}_{0.10} \bar{n}/0.10 \quad (5)$$

TABLE XXVI

Measured Versus Predicted Operating Characteristics
of a TPM-217/3N-PbTe Couple Employing
Ball-Socket Hardware

Temperature: $T_h = 565^\circ\text{C}$ (1050°F), $T_c = 200^\circ\text{C}$ (392°F)

TPM-217 Operating Composition: 0.077% excess selenium

	TPM-217		3N/PbTe	
	Predicted	Measured	Predicted	Measured
$\bar{S}$ ($\mu\text{V}/^\circ\text{C}$ relative to absolute)	228.8	227.0	204.5	205.1
ρ ($\text{m}\Omega\text{-cm}$)	6.92	6.92	2.22	2.14
Resistance - m-ohms no extraneous factor	11.7	11.7	10.4	10.0
Length - in.	0.202		0.400	
Diameter - in.	0.245		0.207	
L/A cm^{-1}	1.69		4.68	
L/A in^{-1}	4.29		11.87	
K ($\text{mwatt}/\text{cm-}^\circ\text{C}$)	6.94		16.98	

Matched load current - 3.25 amps

Predicted couple power out (extraneous factor 1.10) - 0.257 watts

Predicted couple power out (extraneous factor 1.0) - 0.282 watts

Measured couple power out (extraneous factor 1.0) - 0.283 watts

Predicted couple efficiency (rel. to absolute) - 7.43%

[In these equations (derived in Technical Task Report No. 35), $\bar{S}_{0.10}$ and $\bar{\rho}_{0.10}$ are the average Seebeck coefficient and resistivity obtained by integrating the standard S and ρ curves for 0.10% excess selenium material in the same temperature interval.]

The calculation process is reiterated by placing the new $\bar{S}$ and $\bar{\rho}$ values into equations 1 and 2 to find the length of the P leg and the matched load current of the couple. Equation 3 is again used to determine the stable ingradient composition. By continuing this iteration process, a unique set of operating parameters are determined. Table XXVI is a summary of the predicted operating parameters of the ball-socket TPM-217/PbTe couple compared with the measured operating parameters in the early stages of the test. The agreement is excellent; furthermore, the extraneous resistance is essentially zero.

For purposes of couple design comparisons, calculations of couple performance as a function of hot junction temperature for given cold junction temperatures was made to determine how the P-TPM-217/3N-PbTe couple compared with the state-of-the-art thermoelectric couples. These calculations were made from point function data given in the references cited³. Couple efficiency is calculated as follows:

$$\eta = \frac{T_h - T_c}{T_h} \left[\frac{\sqrt{1 + \bar{Z} \bar{T}} - 1}{\sqrt{1 + \bar{Z} \bar{T}} + \frac{T_c}{T_h}} \right]$$

where

$$\bar{Z} = \frac{(S_p + S_n)^2}{(\sqrt{\rho_p K_p} + \sqrt{\rho_n K_n})^2}$$

It should be evident from Figure 21 that on an absolute couple basis, the performance of a P-TPM-217/3N-PbTe couple is as good or better than competitive couple combinations. Furthermore, the performance of the couple on test, including the 3% extraneous resistance factor, is 7.01% and falls very close to the predicted couple performance line (Point A) in Figure 21.

3.4.2 Rigid Hardware Configurations

The P-TPM-217/N-PbTe couple test (ATT 258), described in Technical Task Report No. 38, employing a eutectic bond at the cold end of the P element, molybdenum hot junction electrodes, and low L/A

³TAGS data from BMI, 4/18/69, J. J. Mueller and J. F. Lagedrost.

FIGURE 21

SPACE ISOTOPE APPLICATIONS

geometry elements (Figure 22) was placed on test last quarter. The test operated continuously in an argon atmosphere for 630 hours before being terminated because of air leakage into the bell jar. The test was stably producing 1.02 watt of power (77 mv, 12 ampere) in the temperature interval 540°/140°C (1000°/285°F) prior to shut down. The power output of this couple was stable (Figure 23) and was performing as predicted with an extraneous resistance factor of 1.15 (15% for total couple configuration). An attempt to resume the test after the leak was repaired was abandoned because the hot junction electrode was severely oxidized, causing a 15-25% increase in extraneous resistance of the couple. The hot end hardware was replaced and a new test (ATT 273) was initiated under similar conditions.

Semi-Rigid Hardware:

A P-TPM-217/N-PbTe couple (ATT 273) with low L/A geometry elements and modified rigid hardware was placed on test. The couple has operated for 300 hours in a temperature interval of 540°/140°C (1000°/285°C) in an argon atmosphere. The power out is stable at 1.02 watts per couple; the predicted power out for this couple is 1.14 watts. This couple is operating with an extraneous resistance factor of 11% compared with 15% for the last rigid hardware couple that was on test. This test replaced the couple (ATT 258) with rigid hardware that was terminated due to air leakage into the bell jar. Attempts to resume the test (ATT 258) were abandoned because the hot end hardware became severely oxidized.

The hardware changes introduced into this couple to minimize the extraneous couple resistance consist of the following (refer to Figure 24):

- The rigid molybdenum hot junction electrode was replaced by hot end hardware similar to test ATT 266.
- An interface was removed in the TPM-217 leg by bonding the element directly to the copper spacer at the cold end.

Figure 25 displays the power out as a function of time for this test.

3.5 INGRADIENT COMPATIBILITY

Ingradient compatibility experiments involving N-type PbTe and P-type TPM-217 couples have been on test in the soak fixture section of the TELPS facility. The objective of these experiments is to quantitatively define the material transport and resultant compatibility problems associated with a PbTe/TPM-217 couple. The tests are operating under the following conditions:

FIGURE 22

Configuration of One-Couple Test with Rigid Hardware

Elements operating between 540°/140°C (1000°/285°F)

Power out - 1.0 watt

Voltage - 77 mv

Amperes - 13.0

FIGURE 23

Power as a Function of Time for TPM-217/3N-PbTe Couple
(ATT 258) with Rigid Hardware Operating in the Temperature
Interval 540°/140°C (1000°/285°C) in Argon Atmosphere

FIGURE 24

Configuration of Couple Test with Semi-Rigid Hardware
Elements Operating between 540°/140°C (1000°/285°F)

L/A:

N-PbTe = 2.85 in^{-1} (1.12 cm^{-1})

P-TPM-217 = 1.90 in^{-1} (0.747 cm^{-1})

FIGURE 25

Power Out of TPM-217/3N-4N PbTe Couple (ATT 273)
with Rigid Hardware Operating in Temperature
Interval 540°/140°C (1000°/285°F).

- Atmosphere - argon
- Insulation - none
- Hot Junction Electrode - molybdenum
- Cold Junction Electrode - eutectic for P leg
carbon for N leg
- Hot Junction Temperature - 520°C
- Cold Junction Temperature - 220°C
- Current - open circuit and matched load

In accordance with the Technical Program Plan, samples were examined after 2000 hours of continuous testing for chemical compatibility between the two thermoelectric materials. Metallurgical examination of the TPM-217 elements from the TELPS open circuit and 2-1/2 amp 2000-25000 hour N-PbTe/P-TPM-217 couple compatibility experiments showed no evidence of PbSe second phase inclusions within the bulk P-TPM-217 element. Open circuit voltage measurements on the N-PbTe/P-TPM-217 compatibility couples (5800-7800 hours on test) continue to indicate the bonded TPM-217 elements are performing without degradation. There has not been any visual appearance change for >3000 hours.

Originally, the test schedule called for PbTe/TPM-217 couples to be run for 1000, 2500, 5000, and 10,000 hours with analyses after each time cycle. At this stage of the testing schedule, it has been recommended and the Technical Plan revised so that the post-5000 hour analyses be omitted and, instead, the time cycle be extended to at least 10,000 hours. By following this recommendation, there would be duplicate couples at equal times in excess of 5000 hours for each set of experimental parameters.

TASK 5.0 - PROGRAM MANAGEMENT

Work under this task included technical direction and overall coordination of activities associated with the program and liaison with the AEC. The following reports were published during this period:

- Milestone Report No. MMM-2473-0338, dated June 30, 1972
- Top Summary Report No. 52, dated July 6, 1972
- Technical Task Report No. MMM-2473-0337, dated July 18, 1972
- Top Summary Report No. 53, dated August 7, 1972
- Top Summary Report No. 54, dated September 7, 1972

An invited paper was presented at the 7th Intersociety Energy Conversion Engineering Conference held in San Diego, California, September 25-29, 1972.

TASK 6.0 - LIAISON WITH JPL

Consultation was provided regarding measurements of P-type TPM-217 elements being conducted under Contract AT(29-2)-2853.