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THERMOELECTRIC MATERIAL EVALUATION PROGRAM

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THERMOELECTRIC MATERIALS EVALUATION PROGRAM

QUARTERLY TECHNICAL TASK REPORT

NO. 43

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by
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Electro-Products Division
St. Paul, Minnesota 55101

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INTRODUCTION

This is the forty-third Technical Task Report prepared under Contract AT(11-1)-2331 with the United States Atomic Energy Commission and covers the performance period which extends from July 1, 1973 to September 30, 1973.

HIGHLIGHTS

TASK 1.0 – N-TYPE MATERIAL DEVELOPMENT

1.2 MATERIAL SYNTHESIS – GADOLINIUM-SELENIDE COMPOSITIONS

Gadolinium-selenide compositions (N-2312 through 2329) 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:

- Control Seebeck coefficient by precise control of the ratio of selenium to gadolinium.
- Elimination of macroscopic defects in fabricated elements.
- Optimization of thermoelectric composition.

Series N-2312-2317, weighed in composition of $GdSe_{1.50}$ using the RC-148 gadolinium metal, was synthesized for casting improvement process studies. The LTR cycle, identical to series N-2288-2293 and to series N-2294-2299, consisted of 72 hours at 220°C, 24 hours at 400°C, 24 hours at 600°C, 1

hour at 900°C, and 123 hours at 1015°C. In addition to the above LTR cycle, samples N-2313/2316 and N-2314/2317 were given a 42-hour soaking at 1100°C and 1150°C, respectively, and then rapidly cooled to room temperature. The purpose of this additional heat treatment was to determine the effect of a higher LTR temperature on the selenium retention during casting when using RC-148 gadolinium blocks.

These six samples were vacuum cast in the 4.8 mm diameter mold/19 mm mold support at 1800°C, cooled to 1700°C at 8°C/minute, soaked at 1700°C for one hour, and furnace cooled. These castings were designed to evaluate the modified casting procedure (modifications included a faster cooling rate and a hold at 1700°C instead of 1400°C) and to compare the selenium retention during casting of samples having LTR temperatures of 1000°C, 1100°C, and 1150°C. Table I summarizes the results of this series.

TABLE I

Summary of Weight Loss and Electrical Properties of Series N-2312-2317

Sample "N" No.	Composition After Casting (weight loss measurements)	S_{500} (μv/°C) rel. to Abs.	Remarks
2312-C	1.466	201	1000°C LTR
2313-C	1.472	214	1100°C LTR
2314-C	1.470	211	1150°C LTR
2315-C	1.465	201	1000°C LTR
2316-C	1.473	219	1100°C LTR
2317-C	1.477	225	1150°C LTR

The thermoelectric legs produced using this improved casting procedure were free of pipes in the cast leg. The selenium retention in the final product increased significantly with increase of final LTR reaction

temperature from 1000° to 1100°C. There was no consistent difference in the selenium retention when comparing the 1100°C versus the 1150°C soak, however. The white deposits of devitrified SiO_2 on the vitreous carbon LTR cricubles, previously observed for 1100°C and higher LTR reactions, were also observed in this test sequence.

Series N-2318 through N-2323 was synthesized with the objective of further delineation of the single-phase $GdSe_{1.50-x}$ region of the phase diagram. These samples were weighed out in the Labconco glove box using the Ames 31072 ultrapure gadolinium metal to the compositions $GdSe_{1.48}$, $GdSe_{1.50}$, and $GdSe_{1.52}$. The low temperature portion of the synthesis cycle consisted of 72 hours at 220°C, 24 hours at 400°C, 24 hours at 600°C, 1 hour at 900°C, and 120 hours at 1020°C. The high temperature casting of these samples followed two different cycles: the standard high temperature reaction cycle, and a rapid quench cycle with no evacuation. The process conditions and results are summarized in Table II.

These experiments indicate:

- Vitreous carbon crucibles yield material essentially free from extraneous surface side reactions (e.g. carbide formation as observed when using graphite molds).
- The rapid quenching technique on LTR 1.500 and 1.520 material produced ingots which had extensive microcracking. This same technique on the 1.480 LTR material gave a structurally sounder HTR ingot.
- The final composition for the weighed-in 1.500 and weighed-in 1.520 composition is identical; for the rapid quench casting process both initial compositions reached a final 1.496 composition, while for the standard casting process both initial compositions reached a final composition of 1.486.

From these data, it is obvious that because of the relatively high vapor pressure of the $GdSe_x$ compositions at 1800°C, where $x \geq 1.500$, bulk $GdSe_x$ compositions of $x \geq 1.500$ are not attainable via our present processing techniques. However, the glassy red regions produced via the rapid quenching technique indicate the possibility that heterogeneously distributed $GdSe_x$ regions of $x \geq 1.500$ are trapped within the bulk HTR product. Because of the minuteness of these red regions, exact stoichiometry, as determined by electrical measurements, was not possible. These red regions as well as the bulk black region were analyzed by XRD, microbar, and microprobe techniques. The XRD patterns were equivalent, having a bcc structure and an $a_o = 8.70$ Å. Microprobe analysis across sectional black-red regions indicated equivalent Gd/Se ratios. The microbar anlysis indicated a solidus temperature at 1650°C. Since the structure is the same and the stoichiometry approximately the same, it is probable that the red regions represent a local fluctuation of composition close enough to the ideal 1.500 insulator stoichiometry to be transparent.

Series N-2324-2327, weighed-in composition $GdSe_{1.50}$, was synthesized for sintering studies. These samples were weighed out in the Labconco glove box using the Ames 31072 ultrapure gadolinium metal.

Samples N-2328-2329 were synthesized to examine the effect of rare earth additions on doping of $GdSe_{1.5}$. For these samples the RC-148 gadolinium metal and UMC europium metal were used in the synthesis. The LTR cycle consisted of 72 hours at 220°C, 24 hours at 400°C, 24 hours at 600°C, 1 hour at 900°C, and 120 hours at 1020°C. The casting consisted of a rapid quench directly from the melt. The sample with weighed-in composition $(Gd_{0.67}Eu_{0.33})Se_{1.333}$ lost Se to a final composition $(Gd_{0.67}Eu_{0.33})Se_{1.298}$. If Eu^{++} were present substitutionally for the Gd^{+++} in a single-phase thorium phosphide structure, then the $(Gd_{0.67}Eu_{0.33})Se_{1.298}$ composition would be expected to have an electron carrier concentration equivalent to that of $GdSe_{1.46}$. The expected Seebeck coefficient for this case would be $S_{500} \sim 190\ \mu v/°C$. Measurement of the composition yielded a Seebeck coefficient significantly higher ($S_{500} = 331\ \mu v/°C$) than predicted,

TABLE II

High Temperature Casting - N-2318-2322
(Ames 31072 Gadolinium)

IDENTIFICATION		PROCESS VARIABLES					PROPERTIES		
Sample "N" No.	Composition Weighed-In	T, °C	t, min	Comments	Atmos.	Mold	Composition (wt. loss)	Seebeck Coefficient at 500°C	Physical Appearance
2323	1.520	1800	10	Soak	Helium	Vitreous Carbon	1.486	202	Ingot: Clean & shiny except for darkened top, ' No evidence of carbide formation.
		1800	20	Soak	Vacuum	CC-142 +			
		1800-1600	~60	Cool down backfill with He at 1600°C	Helium	graphite cover			Vitreous Carbon: As precast
		1600-1400	~ 8	–					
		1400	30	Soak					
		1400-RT	-	Furnace cool					
2320	1.500	Same as 2323			-	-	1.486	203	Same as 2323
2318	1.480	Same as 2323			-	-	1.476	179	Ingot: Cleanest of 2323-2320-2318. Vitreous Carbon: Slight matting of glassy surface at $GdSe_x$ location.
2321	1.500	1800	1	Soak	Helium	Vitreous Carbon	1.496	364	Ingot: Micro cracking all over; easily scratchable outer skin covering near top; remainder very shiny and glassy; red glassy material dispersed throughout ingot.
		1800-1600	~ 1.5	Furnace cool		CC-142 +			
		1600-1000	~ 12	Furnace cool		Vitreous Carbon			Vitreous Carbon: Very slight matting of glassy surface at $GdSe_x$ location
		1000-RT	-	Furnace cool		C-101 cover			
2322	1.520	Same as 2321			-	-	1.496	389	Same as 2321
2319	1.480	Same as 2321				-	1.480	181	Ingot Appears structurally sounder than 2321 or 2322; some micro-cracking; not glassy as 2321 or 2322; no red glassy material observed. Vitreous Carbon: More matting in $GdSe_x$ area than between 2321 and 2322.

indicating a greater complexity in the system than that contemplated above in the simple doping model, or a high level of oxygen impurity in the europium. The sample prepared at $Gd_{0.89}Eu_{0.11}Se_{1.32}$ would be expected on this substitutional model to have a carrier concentration corresponding to that of a $GdSe_{1.34}$ or $S_{500} \sim 100\ \mu v/°C$. The measured value was $113\ \mu v/°C$, which is in reasonably good agreement with Eu^{++} substitution for Gd^{3+}.

1.3 MATERIAL ANALYSES

1.3.1 Chemical Analyses

Chemical analyses are being performed on raw materials, on atmospheres for control of the synthesis process, and on element contact structures as required.

The USAEC Ames Laboratory has supplied technical and analytical support in determining the impurity levels in the gadolinium metal. As a comparison of gadolinium metal purity, the recent analyses received show the Ames metal has significantly lower impurity levels than the Research Chemicals, Inc. (RC) gadolinium metal (Table III). The high impurity levels of hydrogen, oxygen, and tantalum may be largely responsible for interfering with the control of the Gd/Se ratio.

Seebeck and resistivity measurements were performed on a routine basis to characterize batches and the recast specimens; the results of these measurements are reported in the synthesis and materials processing sections.

A sample with the nominal composition 1.511 was prepared and measured. The preparation procedure consisted of adding sufficient selenium to the cast element N-2296 to bring its composition from 1.489 to 1.520. The element and selenium were annealed for over 100 hours at 1150°C. The weight gain of the sample indicated an increase in the selenium to gadolinium ratio to a nominal 1.511.

TABLE III

Impurity Levels in Gadolinium Raw Materials

Purity (atomic)	Gadolinium Vendor	ppm (atomic)										
		H	C	O	N	La	Y	Ce	Ta	Fe	Ca	Mg
96.4%	RC-145	11,240	2950	12,825	460	120	320	1200	7000	100	40	5
94.4%	RC-148	31,230	2790	18,330	885	600	170	3.5	1600	200	300	100
99.85%	Ames 31072	314	250	720	33	40	10	4	1	30	0.5	< 1
99.76%	Ames 61573	1,050	420	770	55	2.5	1.7	2.8	0.6	30	0.5	< 1

The added selenium did not form a surface layer, but instead appears to be uniform throughout the leg. This conclusion is supported by the following experimental observations:

- Microscopic examination of the sectioned leg revealed only a single phase with no visible surface layer covering the sides.
- Probing across the sectioned sample gave resistances from interior to exterior which all fell in the range 2-5 kΩ. In contrast, similar measurements on a typical element, such as the undoped N-2296, would have yielded resistances in the range 1-10Ω.
- Seebeck measurements were repeated after removal of 50 mils from the surface; no decrease in the original high Seebeck values was observed. From this single preliminary experiment, it appears that the diffusion rate of selenium in Gd_2Se_3 is sufficiently high to permit effective low temperature sealed tube controlled redoping of elements.

The properties of this sample are interesting because the nominal composition puts its properties beyond the range of validity of our theoretical relations between S, ρ, and composition. This is evident in Table IV. The Seebeck coefficient no longer obeys the $S = S_o + b \ln T$ temperature dependence, but instead has a slight minimum at about 500°C. The resistivity is several orders of magnitude higher than for materials in our normal range of compositions (note that the values are Ω-cm, not mΩ-cm); furthermore, it shows a pronounced decrease with increasing temperature, indicative of an intrinsic semiconductor.

TABLE IV

Measured Electrical Properties of Nominal Composition $GdSe_{1.511}$

T(°C)	S(μv/°C, rel to Abs.)	T(°C)	ρ(Ω-cm)
124	305		
173	277	25	573
275	296	116	277
387	274	201	86
487	263	405	19
579	288	446	16
695	340	675	2
852	332		

A preliminary experimental investigation was made of possible current dependent effects in the N-type $GdSe_x$ material. An N-type element, N-2282-S-VIIa, was placed in a radiantly heated performance fixture with a gadolinium foil hot electrode. This fixture was on the four-station table, so a vacuum of $\sim 5 \times 10^{-6}$ torr was maintained during the test. The element was heated to $\sim$1000°C, and the current was switched from currents on the order of 0.2 amp to 1.5 amp with time delays up to 12 hours. No dopant drift effect was detected. Variation of Seebeck coefficient with current was observed but, since the change was small and of the wrong sign, this was interpreted as a heating effect in the electrode foil-element interface rather than a dopant drift effect. The hot junction temperature was then increased to 1150°C and the current again switched from 0.2 amp to 1.5 amp. No significant dopant drift effect was observed at this temperature either.

1.4 MATERIAL PROCESSING

The process development studies continued with the dual experimental objectives:

- Eliminate macroscopic defects in the fabricated elements.
- Reduce extraneous resistance through control of casting, annealing, and forming.

1.4.1 Casting Improvement Studies

Two samples were recast in an 8.5 mm diameter mold in a preliminary investigation of the mechanical problems in casting large diameter elements. The castings were of good quality and this experiment revealed no obvious problems. This size element was similar to that being designed in the ERTG study.

1.4.2 Pressing and Sintering

A. Studies on Elements Prepared from RC-148 Gadolinium

The sintering study, reported in Technical Task Report No. 42, page 25-27, using N-2280 HTR and N-2282 LTR cold pressed elements synthesized from RC-148 gadolinium, has been completed. The objectives of this study were to:

- Compare sintering characteristics of HTR versus LTR materials.
- Compare effect of air pressing versus argon pressing on electrical properties of sintered $GdSe_x$ material.

The procedures followed during this study are shown in Figures 1 and 2. Table V summarizes the data obtained for this study.

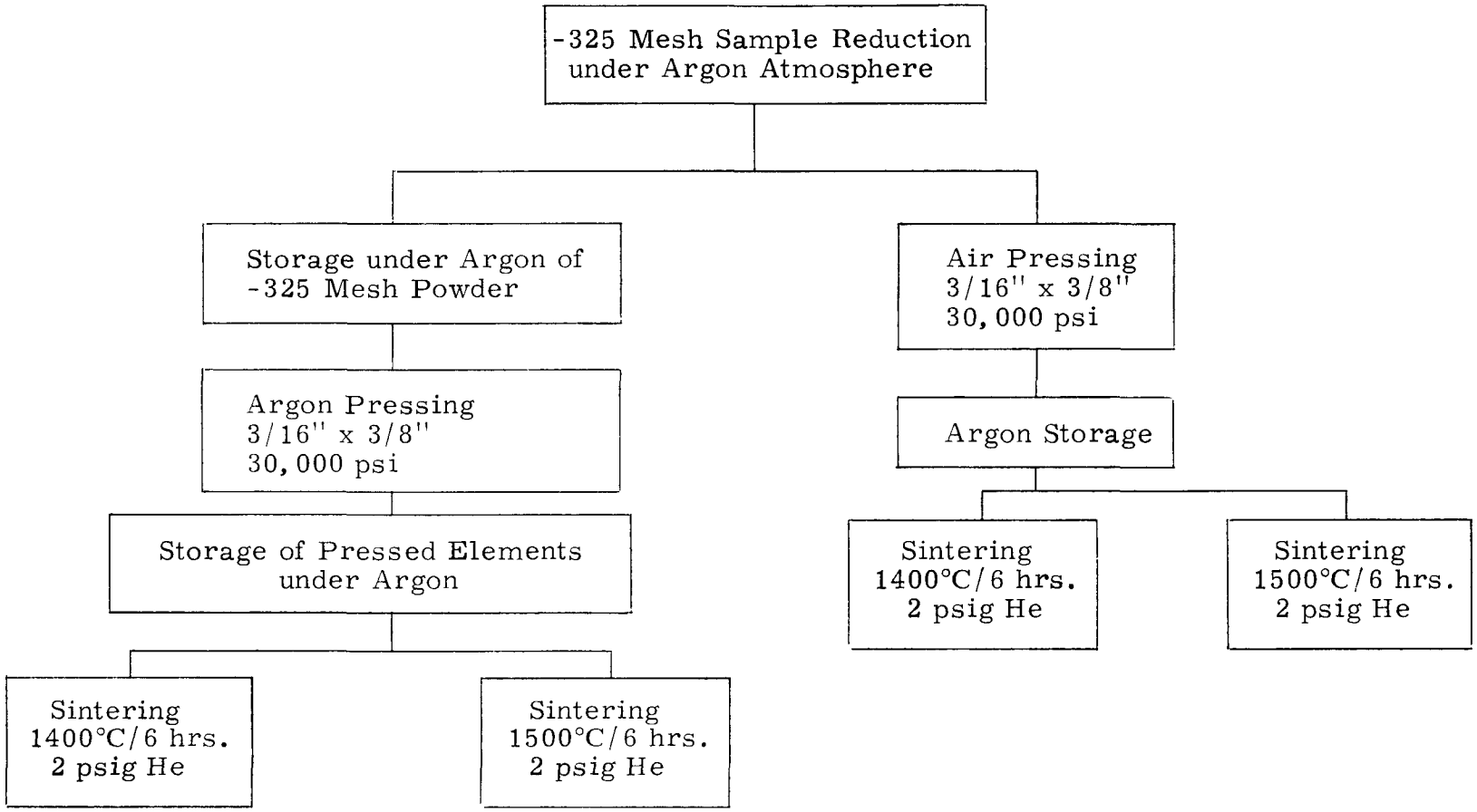


Figure 1. Flow Diagram for RC-148 N-2280 HTR Sintering Study

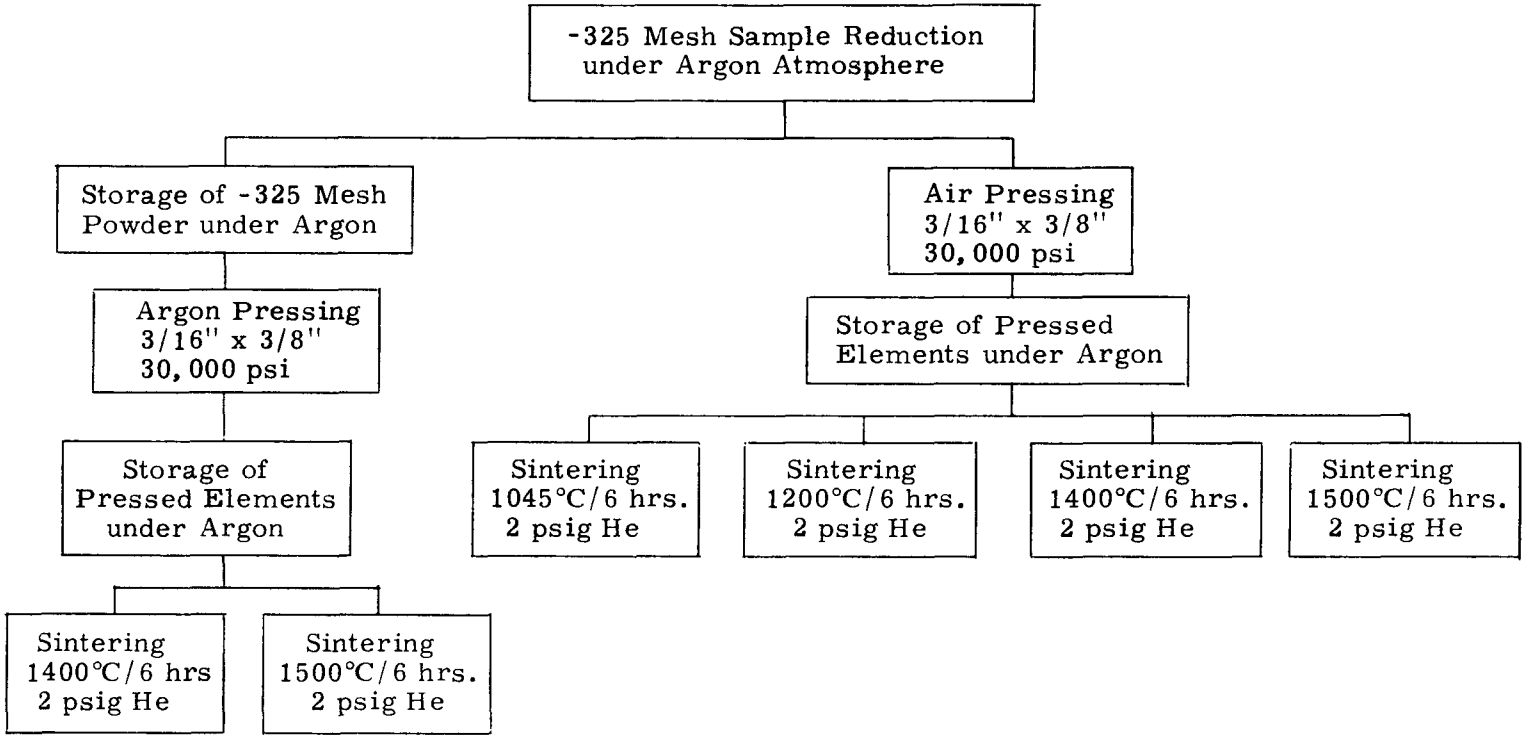


Figure 2. Flow Diagram for RC-148 N-2282 LTR Sintering Study

TABLE V

Summary of RC-148 N-2280 HTR/N-2282 Sintering Study

Sample Description		Composition after Sintering ($GdSe_x$)	Sintering Temperature, °C Time (hrs)	Density (g/cm^3)	Grain Size (microns)	S_{500} ($\mu v/°C$)	ρ_{500} ($m\Omega$-cm)
N-2282 LTR:							
S-I	Air pressed	1.467	1045/6	5.4	--	--	--
S-II	Air pressed	1.463	1200/6	5.6	--	--	--
S-IIIa	Air pressed	1.456	1400/6	6.7	--	296	59.3
S-IIIb	Air pressed	1.458	1400/6	6.8	44	299	--
S-VIIa	Argon pressed - Parawax*	1.460	1400/6	6.7	--	302	--
S-VIIb	Argon pressed - Parawax*	1.461	1400/6	6.7	--	293	--
S-V	Air pressed	1.457	1450/6	6.6	--	245	27.7
S-VIII	Argon pressed - Parawax*	1.455	1450/6	6.7	--	255	--
S-IX	Argon pressed - Parawax*	1.462	1450/2	6.7	--	301	83
S-IVa	Air pressed	1.453	1500/6	6.5	--	227	--
S-IVb	Air pressed	1.456	1500/6	6.4	102	--	22.0
S-VIa	Argon pressed - Parawax*	1.458	1500/6	6.4	--	230	--
S-VIb	Argon pressed - Parawax*	1.458	1500/6	6.5	--	--	--
N-2280 HTR							
S-Ia	Air pressed	1.458	1400/6	6.7	--	257	32
S-Ib	Air pressed	1.451	1400/6	6.9	47	--	--
S-IVa	Argon pressed - Parawax*	1.464	1400/6	6.9	--	257	--
S-IVb	Argon pressed	1.464	1400/6	6.9	--	260	--
S-III	Air pressed	1.463	1450/2	6.8	--	258	--
S-VI	Argon pressed - Parawax	1.461	1450/2	6.9	--	249	--
S-VII	Argon pressed - Parawax	1.459	1450/6	6.9	--	--	--
S-IIa	Air pressed	1.463	1500/6	6.8	--	242	23.8
S-IIb	Air pressed	1.462	1500/6	6.9	67	--	--
S-Va	Argon pressed - Parawax*	1.462	1500/6	6.8	--	239	--
S-Vb	Argon pressed	1.464	1500/6	6.8	--	--	26.1

* Die faces rubbed with wax before pressing powders.

The conclusions drawn from this study using RC-148 gadolinium are:

- Within a given sintering sequence, there is no significant variation in composition and electrical parameters between material pressed in air and that pressed in argon.

- As the sintering temperature is increased, the Seebeck coefficient decreases for both the LTR and HTR materials. However, the change is much more pronounced for the LTR materials. For example, the change in Seebeck for the LTR materials between 1400°C/6 hrs to 1450°C/6 hrs is 300 to 250 μv/°C whereas for the HTR, the change between 1400°C/6 hrs and 1450°C/2 hrs is 258 to 253 μv/°C. This suggests that the LTR material has components in addition to the two component Se to Gd ratio which affect the carrier concentration. The HTR material has presumably already expelled these impurity components and hence does not exhibit the same high Seebeck coefficient at low sintering temperatures as the LTR material.

Because of relatively high impurity levels in the RC gadolinium, the above conclusions apply only to the RC gadolinium material, and are not applicable to gadolinium-selenide material made from Ames ultrapure gadolinium.

B. Studies on Elements Prepared from Ames Ultra-Pure Gadolinium

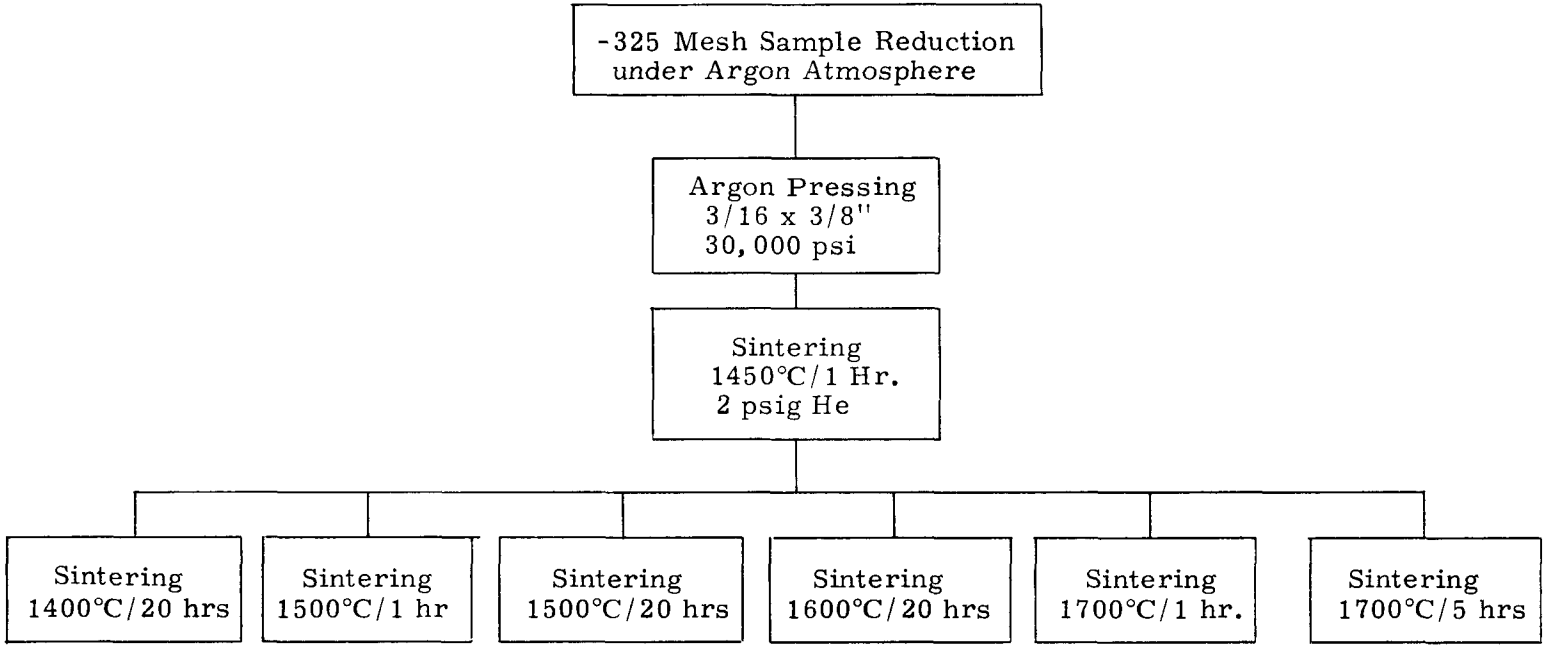
This sintering study, using samples N-2321/2322 prepared from Ames ultrapure gadolinium was completed following the experimental scheme outlined in Figure 3. Table VI summarizes the data obtained for this investigation. Figures 4 and 5 show a plot of weight loss versus 1/T and grain size and pore diameter versus sintering temperatures.

The conclusions drawn from this investigation are:

- Weight loss rate increases with increasing temperature.

- The grain size increases slightly with sintering temperature and appears to equilibrate after 5 hours at 1700°C.

- Correlations exist between weight loss rate, composition, Seebeck coefficient, and sintering times and temperatures.



After each run, measure weight loss, density, Seebeck coefficient, resistivity, and do metallography on each sample.

All sintering done under 2 psig He.

Figure 3. Flow Diagram for Ames 31072 N-2321/N-2322 Rapid Quench HTR Sintering Study

TABLE VI

Summary of Ames 31072 N-2321/N-2322 Rapid Quench HTR Sintering Study (Parent N-2321/N-2322 $GdSe_x$ = 1.496)

Description	Composition After 1450°C/1 Hr Sintering ($GdSe_x$)	Composition After Sintering ($GdSe_x$)	Sintering Temp. (°C)/ Time (hrs)	Density (g/cm^3)		Grain Size (micron)	Pore Diameter	S_{500} ($\mu v/°C$)	ρ_{500} ($m\Omega$-cm)	Weight Loss ($g/hr/cm^2$)x10^{-4}
				After 1450°C/ 1 Hr.	After Final Sint.					
SET I										
SL-4	1.488	--	--	5.7	--	--	--	300	--	
SR-5	1.488	--	--	--	--	--	--	289	--	
(Controls)										
SL-3	1.487	1.485	1400/20	5.7	6.4	23	10	268	--	0.20
SR-8	1.487	1.485	1500/1	--	--	20	5	279	--	3.40
SL-1	1.491	1.482	1500/20	6.0	6.9	45	13	212	--	0.72
SR-7	1.489	1.476	1600/20	--	--	85	17	180	9.0	1.12
SR-6	1.490	1.484	1700/1	--	--	60	13	207	16.5	11.26
SL-2	1.490	1.472	1700/5	5.8	6.8	165	21	176	--	5.66
SET II										
SR-5	1.488	1.482	1600/1	--	--	--	--	235	--	9.33
SL-2	1.490	1.463	1700/20	5.8	--	--	--	147	4.57	2.49
SL-1	1.491	1.480	1500/40	6.0	--	--	--	203	12.7	0.48
SR-8	1.487	1.481	1500/5	--	--	--	--	246	--	2.10

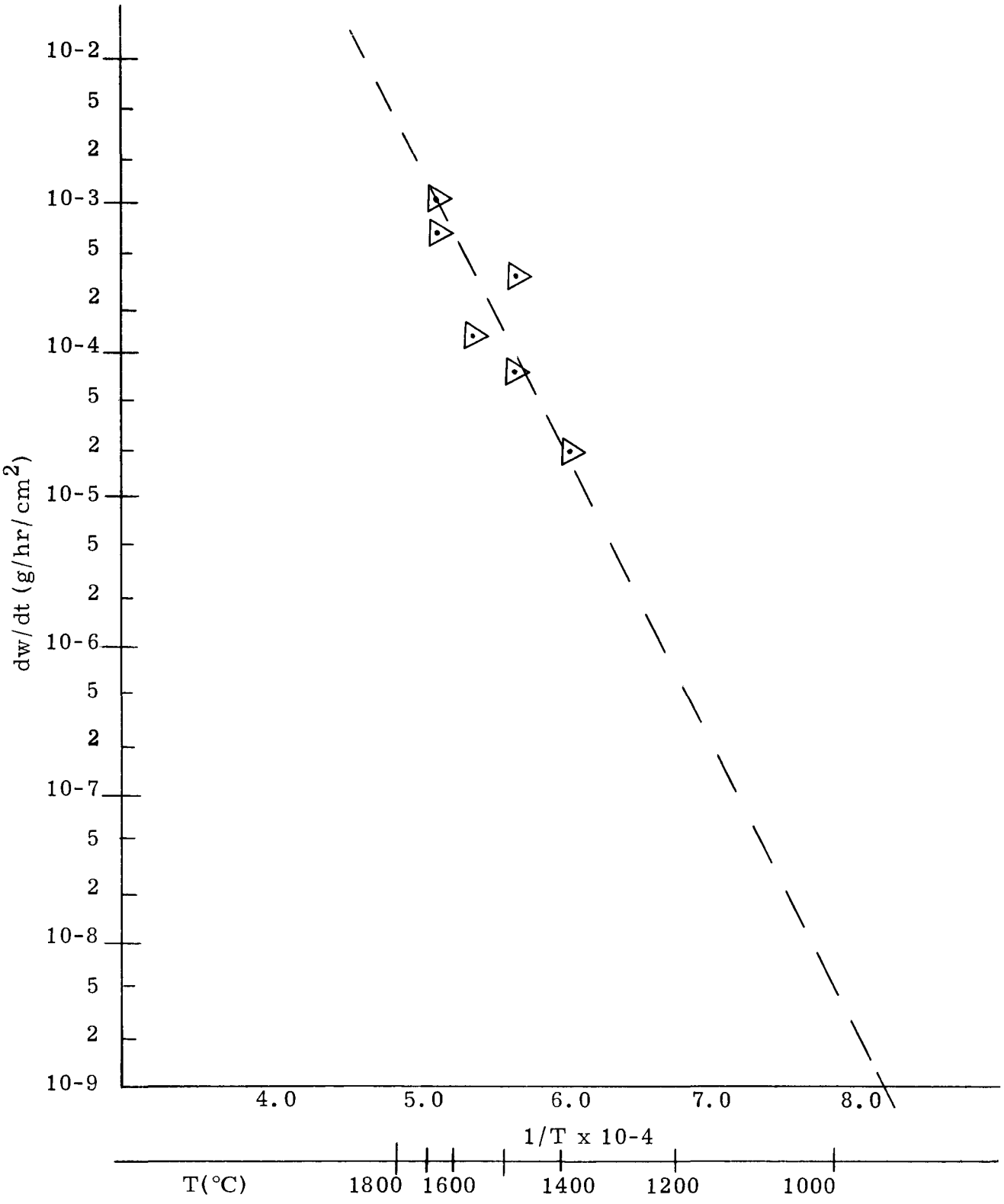


Figure 4. Weight Loss Versus Reciprocal Temperature

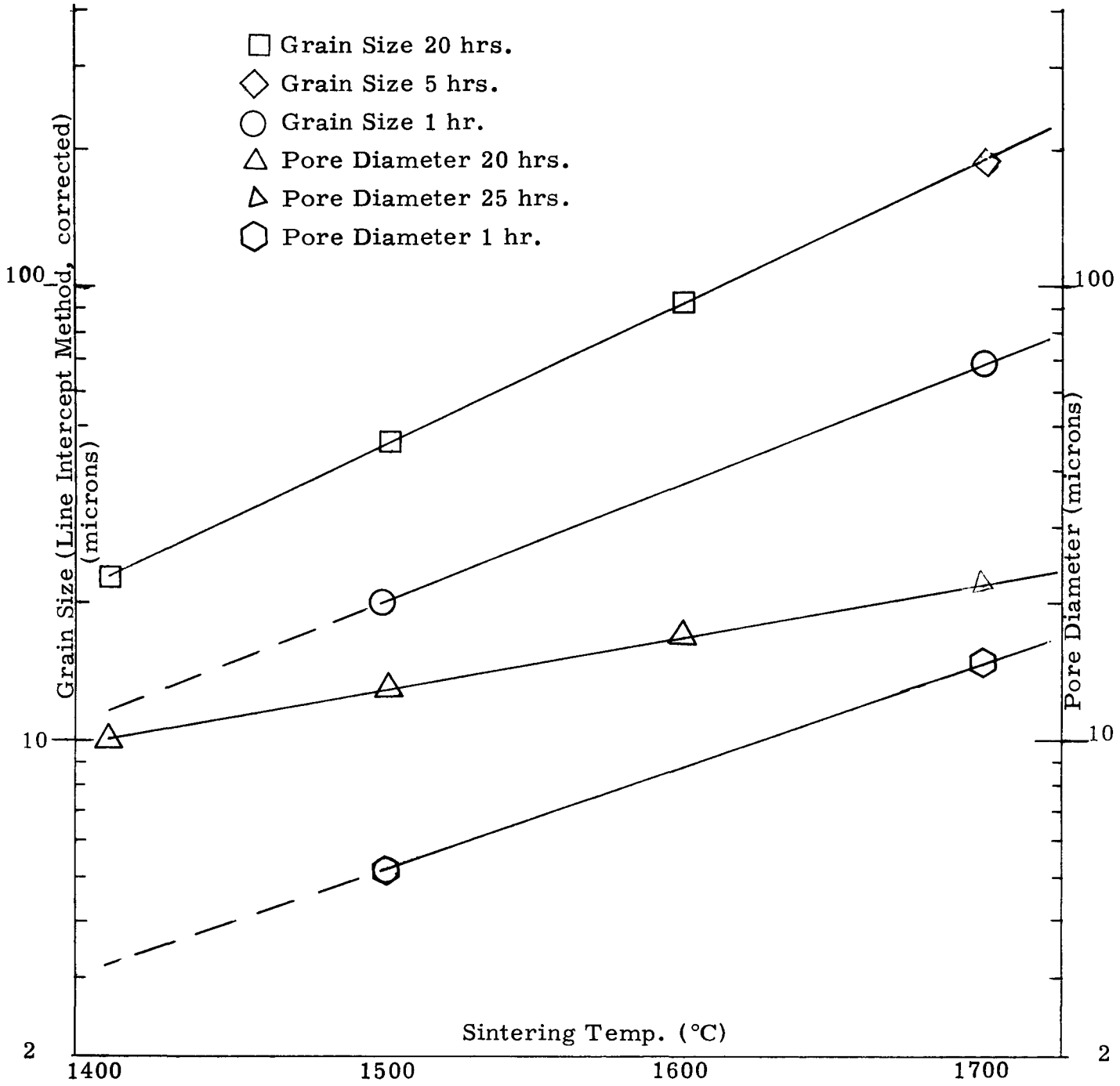


Figure 5. Grain Size/Pore Diameter Versus Sintering Temperature

The observed dependence of the Seebeck coefficient on time and temperature during sintering correlates well with a model in which sublimation of selenium plays the dominant role. The sintering experiment was sufficiently precise to permit quantitative comparison with the model calculation and to yield thermodynamic data; the model and the experimental data are discussed in section 1.8.

1.8 THERMODYNAMIC STABILITY

The variation of weight loss and Seebeck coefficient with sintering times and temperatures in the sintering experiments is in good agreement with a simple thermodynamic model for weight loss of Se by vaporization. According to the structural formula $Gd_{3-x}V_xSe$ with $x \sim 1/3$, three selenium atoms added to the lattice produce two vacancies on gadolinium sites. Since there is no evidence of an activation energy in the resistivity measurements, it may be assumed that each vacancy is triply ionized, producing three carriers in the conduction band. The addition or loss of a selenium atom to the lattice is then summarized by

$$1/2\ Se_2 \rightleftarrows 2/3\ V^{3+} - 2n^-$$

Corresponding to this equation, the difference in chemical potential between two equilibrium states at different partial pressures (P_o and P_1) of selenium is given by

$$1/2\ \Delta\mu_{Se_2} = 2/3\ \Delta\mu_{V^{3+}} - 2\mu_{n^-}$$

Using the standard relations from statistical thermodynamics,

$$\Delta\mu_{Se_2} = kT\ \ell n\ P_1/P_o$$

and

$$\Delta\mu_{n^-} = kT\ \ell n\ n_1/n_o \text{ (Boltzmann limit)}$$

and assuming $\left|\Delta\mu_{n^-}\right| >> \left|\Delta\mu_{V^{3+}}\right|$ near x = 1/3 since the vacancy concentration is much larger than the carrier concentration for $x \sim 1/3$, a power law dependence of vapor pressure on carrier concentration is obtained:

$$P_1/P_o = (n_o/n_1)^4.$$

The vapor pressure of selenium is assumed to be directly proportional to the rate of selenium loss in the sintering experiments, which is in turn directly proportional to the rate of change of carrier concentration. Thus the rate of change in carrier concentration is given by

$$\frac{d}{dt} n = A\, n^{-4}$$

Integrating this relation, the carrier concentration after a given sintering time, t, is related to the initial carrier concentration by

$$n(t) = n(t=0) \left(1 + \frac{t}{\tau}\right)^{1/5}$$

$$\tau^{-1} \cong 5 \frac{d}{dt} \ell n\, n \Big|_{t=0}$$

This equation is to be compared with measured properties in the sintering series experiments where samples were held at different temperatures for different times. The composition change was monitored in this experiment by the measured change in the Seebeck coefficient; the relation between carrier concentration and Seebeck coefficient has been determined by previous experiments to be in agreement with the theoretical form

$$S_1 = S_o + 78\ \mu v/°C\ \ell n\left(n_o/n_1\right)$$

Using this relation between composition and Seebeck coefficient, the prediction for the variation of Seebeck coefficient with sintering time reduces to

$$S_o - S(t) = \frac{78\ \mu v/°C}{5}\ \ell n\left(1 + \frac{t}{\tau}\right)$$

$$\simeq \frac{78\ \mu v/°C}{5}\ \ell n\left(\frac{t}{\tau}\right), \tau << t$$

Figure 6 is a plot of the experimental data on Seebeck coefficient as a function of time at the temperatures of 1500°, 1600°, and 1700°C. The data is fit well by three parallel lines, as predicted; the measured slope is

$$\frac{dS}{d\ell nt} \simeq 19\ \mu v/°C$$

whereas the predicted value is only slightly lower,

$$\frac{dS}{d\ell nt} = \left(\frac{78}{5}\right) \sim 16$$

This correspondence between model predictions and experiment provides evidence that our basic understanding of the origin of the property changes during annealing is correct.

1.9 INGRADIENT CHEMICAL COMPATIBILITY AND LIFE TESTING

In Technical Task Report No. 40, a review of the preliminary experimental information was reported relating to the electrode compatibility and performance of the N-type $GdSe_x$ material operating in a thermal gradient. It may be recalled that the contacting problems are related to oxygen contamination and electrode incompatibility. Two ingradient vacuum tests of N-type $GdSe_x$ elements were in operation this quarter.

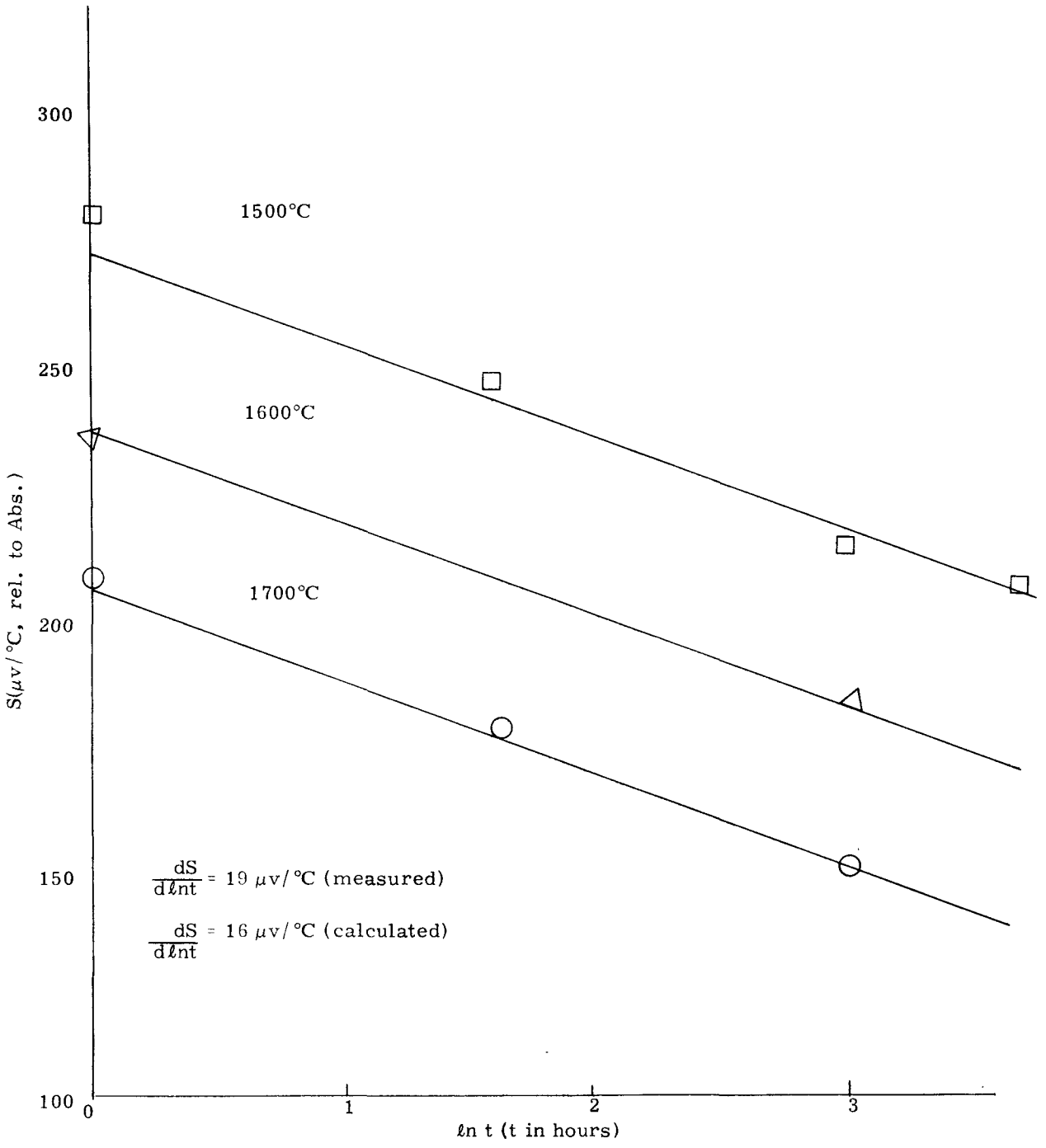


Figure 6. Dependence of Seebeck Coefficient on Sintering Time

Test ATT 281:

Test ATT 281 was operated in a performance fixture at 800°C in a 10μ vacuum. This test was terminated at 4500 hours because, when doing experiments at load current far above matched load, local heating occurred at the contacts which thermally stressed the already cracked element and resulted in complete cracking of the element. The cracked element was removed for analysis and there were no pieces large enough to put back on test. Just before the shutdown, the Seebeck coefficient was 234 μv/°C rel. to absolute and the resistance was greater than 1000 mΩ (beyond the measuring capability of the system) compared with 228 μv/°C and 992 mΩ last month. The increased resistance with time obviously was indicative of the cracked element. The performance of the test to 4500 hours is summarized in Table VII.

TABLE VII

Performance of Test ATT 281

Time (Hrs)	$\overline{S}$ (μv/°C rel. to Abs.)	R (mΩ)	$\overline{\rho}$ (mΩ-cm)
120	185	351	40.4
300	173	239	27.5
600	181	126	14.5
1000	180	126	14.5
1505	195	137	15.8
1860	202	154	17.7
2795	210	209	24.0
3275	219	243	27.9
4200	228	992	114.0
4585	234	>1000	>115.0

Test ATT 274:

Test ATT 274 has operated for 7500 hours in a nominal temperature interval of 1000°/200°C in a vacuum of 10^{-6} torr. This test is contacted with gadolinium foil pressure engaged to the element at the hot junction and carbon pressure engaged to the element at the cold junction. The overall stability of the material, measured by the performance of the average Seebeck coefficient normalized to 1000°/200°C, from the inception of the test is displayed in Figure 7 and Table VIII.

At approximately 5000 hours into the test, an experiment was performed to examine the electrical characteristics of the operating element with changes in load current. By increasing the load current from the normal operating value of 0.1 ampere to a maximum of about 1 ampere, changes in resistance with load current were observed to occur. At a load current of 1 ampere the resistance was 45 mΩ, or about one-tenth of the value at 0.1 ampere. However, the Seebeck coefficient did not change, and the resistance change occurred discontinuously at about 0.7 ampere which suggests a contact resistance problem rather than a fundamental material effect. The effect was reversible, with higher resistances occurring when the current was reduced below 0.7 ampere. The mechanism causing this change in resistance may be a high resistance coating at the element/electrode interface which is broken down under conditions of high current. When operated steadily with a current of 1 ampere the resistance remained fairly low.

The low measured resistance of 45 mΩ and the measured Seebeck coefficient of 214 μv/°C for operation in the nominal temperature interval of 1000°/200°C, together with thermal conductivity data for gadolinium-selenide derived from pulse diffusivity measurements (Technical Task Report No. 38), imply a high efficiency material. If these operating characteristics are combined with those of P-type TPM-217 in the 1000°/200°C temperature interval, the performance of this couple would be considerably above that calculated for

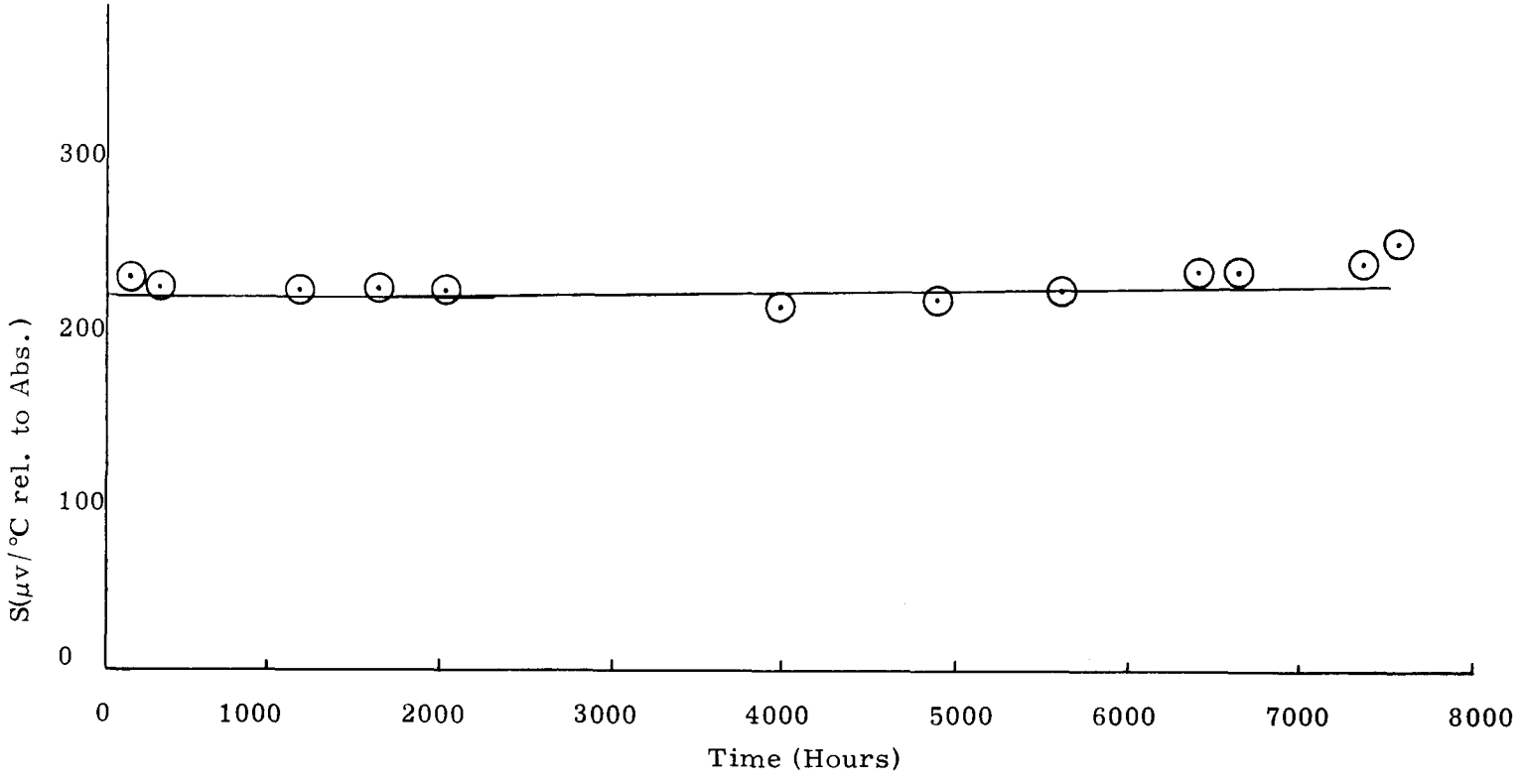


Figure 7. Seebeck Coefficient of a $GdSe_x$ Element Operating in a Temperature Interval of approximately 1000°/200°C in a Vacuum of 10^{-6} torr (ATT 274)

TABLE VIII

Performance of Test ATT 274

Time (Hrs)	T_h (°C)	T_c (°C)	$\bar{S}$ (μv/°C rel. to Abs.)	R (mΩ)	$\bar{\rho}$ (mΩ-cm)
24	1014	226	253	296	40.5
200	983	220	225	149	20.4
384	960	213	219	139	19.0
1120	945	210	213	142	19.4
1420	955	214	213	137	18.8
2194	965	222	213	180	24.7
3200	1006	212	209	216	29.7
3780	993	203	210	203	27.9
6400	962	222	216	46.7*	6.4*
7000	927	225	223	386	53.1
7370	924	232	224	316	43.4

*Current increased by factor of 10.

"current standard" N-type material with P-type TPM-217, as shown in Figure 8. This suggests that with processing and contacting development and improvements, superior performance to that designated "current standard" is possible.

At 7370 hours a pump failure occurred which necessitated interruption of the test to clean the fixture. The load pressure on the element was reduced during this operation, allowing cracks located near the hot junction to open. In the process of reseating the element, the top of the element broke off. The cracked pieces were removed and the top of the element was flattened. Since returning the partial element to test, it has operated for 130 hours. The new element length is approximately 0.3 inch instead of the original 0.55 inch. The last data point in Figure 7 was obtained after this operation. Since the Seebeck coefficient was increased only slightly, the test will be continued.

TASK 2.0—TPM-217 P-TYPE MATERIAL CHARACTERIZATION

2.5 ELEMENT CONTACTING

2.5.2 Exploratory Bonding Experiments

Cold Junction Bonding:

The exploratory experiment (ATT 272) to examine the feasibility of electroplating a copper electrode onto a P-type TPM-217 element continues on test. This experiment is being run in a TELPS performance fixture in the temperature interval 780°/240° and in an argon atmosphere. The test has completed 9836 hours of continuous ingradient operation with stable electrical properties. The data on life test performance is presented in Table IX. No unusual chemical effects have been observed to date.

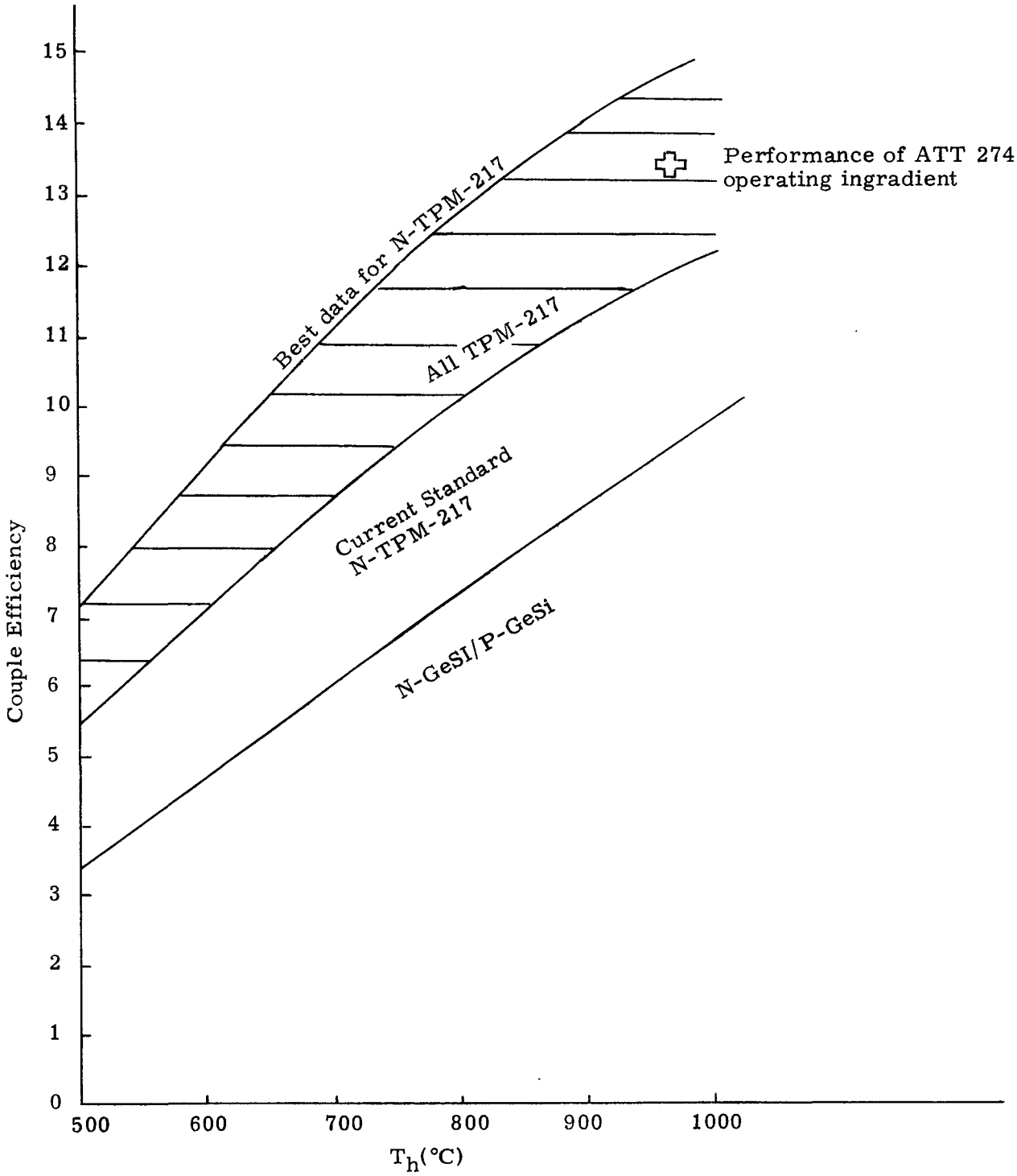


Figure 8. TPM-217 Couple Efficiency as a Function of Hot Junction Temperature and Cold Junction Temperature of T_c = 200°C.

TABLE IX

Ingradient Electrical Performance - Test ATT 272

Time (Hrs)	Temperature, °C T_h	T_c	$\overline{S}$(μv/°C rel. to Pt)	$\overline{R}$(mΩ)
308	777	235	268	33.0
349	777	235	267	32.9
499	778	237	267	32.8
1026	779	240	267	32.7
1538	776	240	268	32.7
2004	778	240	267	32.2
2578	775	239	266	32.8
3496	776	239	266	33.4
3971	774	240	267	33.5
4401	774	240	267	33.4
5000	773	242	267	33.6
5500	773	242	267	33.6
6000	772	242	268	32.7
6500	776	244	268	32.3
7000	774	247	268	32.4
7500	775	248	269	32.3
7856	778	249	269	32.4
8486	780	249	271	33.3
9006	780	251	271	33.3
9386	775	248	271	33.2
9760	776	247	272	33.2

Hot Junction Bonding:

Preliminary ingradient bonding experiments have begun in an attempt to bond a hot junction electrode to the P-TPM-217 leg. The chemically compatible, non-magnetic electrodes--tungsten, tungsten-rhenium, and molybdenum-- are being examined. The initial procedure has been to bring the temperature rapidly to slightly below the melting point of the P-material (1100°C) and cycle back to room temperature. The results have indicated that molten material is visually observed at the interface, suggesting a chemical reaction. Metallurgical examination is being done to determine the chemical and structural configuration of the interface.

A mold is being fabricated in the shop for isothermally casting TPM-217 P-material onto candidate electrode materials. These experiments are aimed at a totally bonded partitioned P-leg. The excellent performance of the bonded partitioned leg, ATT 241, with tungsten-rhenium barriers is the impetus for this work.

2.8 ISOTHERMAL CHEMICAL COMPATIBILITY

Isothermal chemical compatibility experiments at 700°, 800°, and 900°C have been on test for 9,500 - 19,100 hours. Specifically, these tests, itemized in Table X, involve electrode and thermal insulation materials in direct contact with the TPM-217 elements soaking in sealed ampoules.

2.9 INGRADIENT COMPATIBILITY AND INGRADIENT LIFE TESTING

Extended Performance Life Test Series:

Table XI summarizes the current status of the non-partitioned element extended life tests in the ingradient performance fixtures. No major changes were observed during the past quarter.

TABLE X

P-Type Isothermal Chemical Compatibility

	Test Description	Temperature, °C	Test Duration (Hrs)
1.	Tungsten-Min-K 2020-TPM-217	700-800-900	9,500
2.	Tungsten-Fiberfrax-TPM-217	700-800-900	9,500
3.	Tungsten-25% Rhenium-Min-K 2020-TPM-217	700-800-900	9,500
4.	Tungsten-25% Rhenium-Fiberfrax-TPM-217	800	9,500
5.	Moly-Min-K 2020-TPM-217	800	9,500
6.	Moly-Fiberfrax-TPM-217	800	9,500
7.	Tungsten	700-900	14,700
		800	19,100
8.	Tungsten-25% Rhenium	700-900	14,700
		800	19,100
9.	Moly	700-900	14,700
		800	19,100
10.	Min-K 2020	700	14,700
		800	19,100
11.	Fiberfrax	800	19,100
12.	Control TPM-217	700-900	14,700
		800	19,100

TABLE XI

Summary of Ingradient Performance and Compatibility Tests Currently in Progress

ATT#	Test Description Temperature, °C Hot Junction	Cold Junction	Atmos.	Hours of Operation	Test Apparatus	Purpose of Test
127**	700	280	Argon	40,400	P	Display the performance of TPM-217 at 700°, 600° and 500°C, Carbon electrodes both hot and cold junctions, except tests ATT 127 and ATT 128 which have tungsten hot junction electrodes.
128**	700	280	Argon	40,400	P	
129	700	280	Argon	40,400	P	
132	600	260	Argon	40,400	P	
133	600	260	Argon	40,400	P	
136	500	220	Argon	40,400	P	
137	500	220	Argon	40,400	P	
178	700	275	Argon	24,700	P	Molybdenum hot junction electrode ingradient compatibility. Carbon cold junction electrode.
192	700	250	Argon	20,700	P	Bonded cold junction, pressure engaged to tungsten at hot junction.
195	700	250	Argon	20,700	P	
196*	800	300	Argon	20,600	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

** Carbon electrodes at hot junction replaced with tungsten electrodes.

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

The 500°, 600°, and 700°C extended life tests have been in operation for over four 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 40,400 hours for a test in each of the test intervals is displayed in Figures 9-11. 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. The tests at 500°C reached a stable composition at about 20,000 hours as shown in Figure 11. 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. An example is the increase in standard deviation in the Seebeck coefficient of tests 128 and 132 to ± 16 and ± 14 μv/°C as compared with ± 3 μv/°C for the other tests. The probable cause is poor voltage probe contact at the junctions. The tests displaying such behavior have been periodically 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. In some cases this artifice of the experiment affects the average electrical resistance more than the average Seebeck coefficient because the resistance is geometry dependent ($R = \rho L/A$).

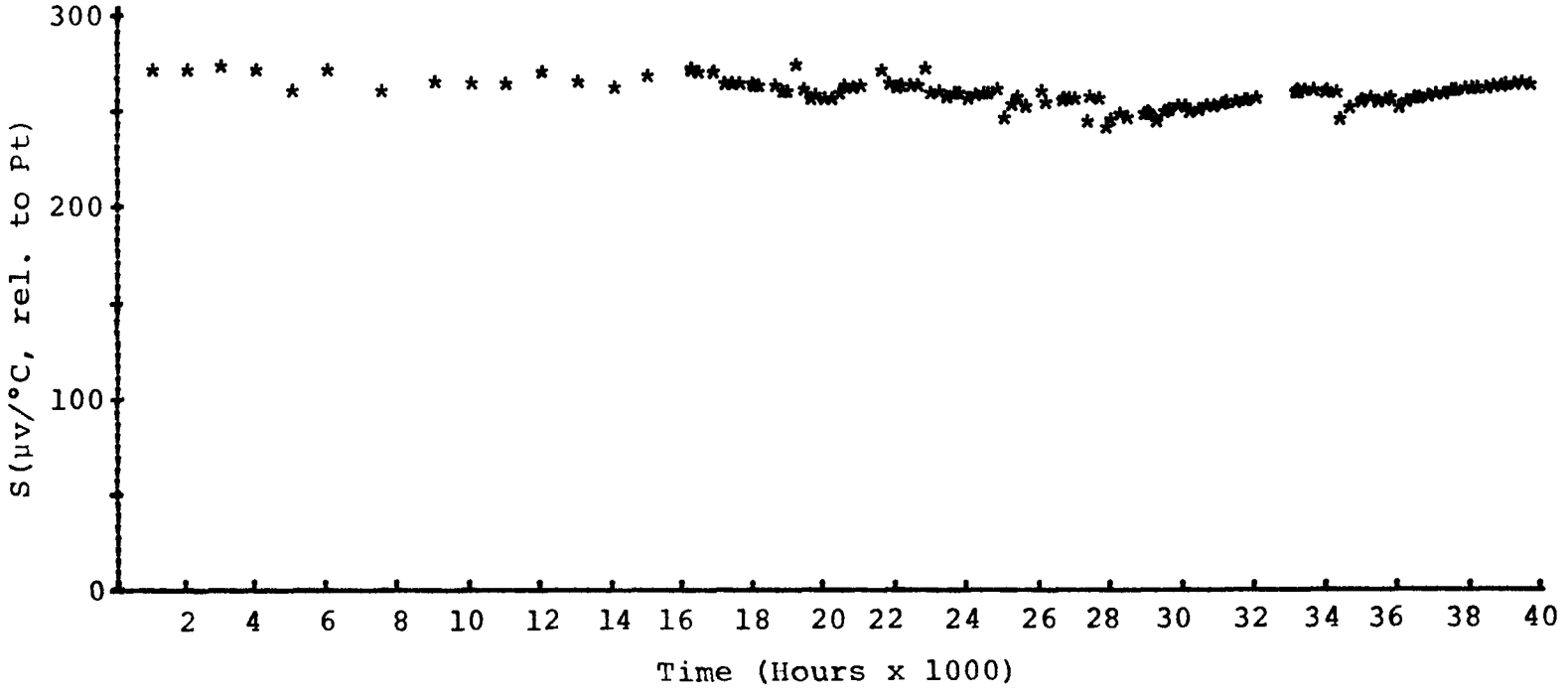


Figure 9. Average Seebeck Coefficient Versus Time for P-TPM-217 Element ATT 129 Operating in the Nominal Temperature Interval of 700°/ 280°C in an Argon Atmosphere.
$\overline{S}$ = 259 ± 6.8 μv/°C, rel. to Pt

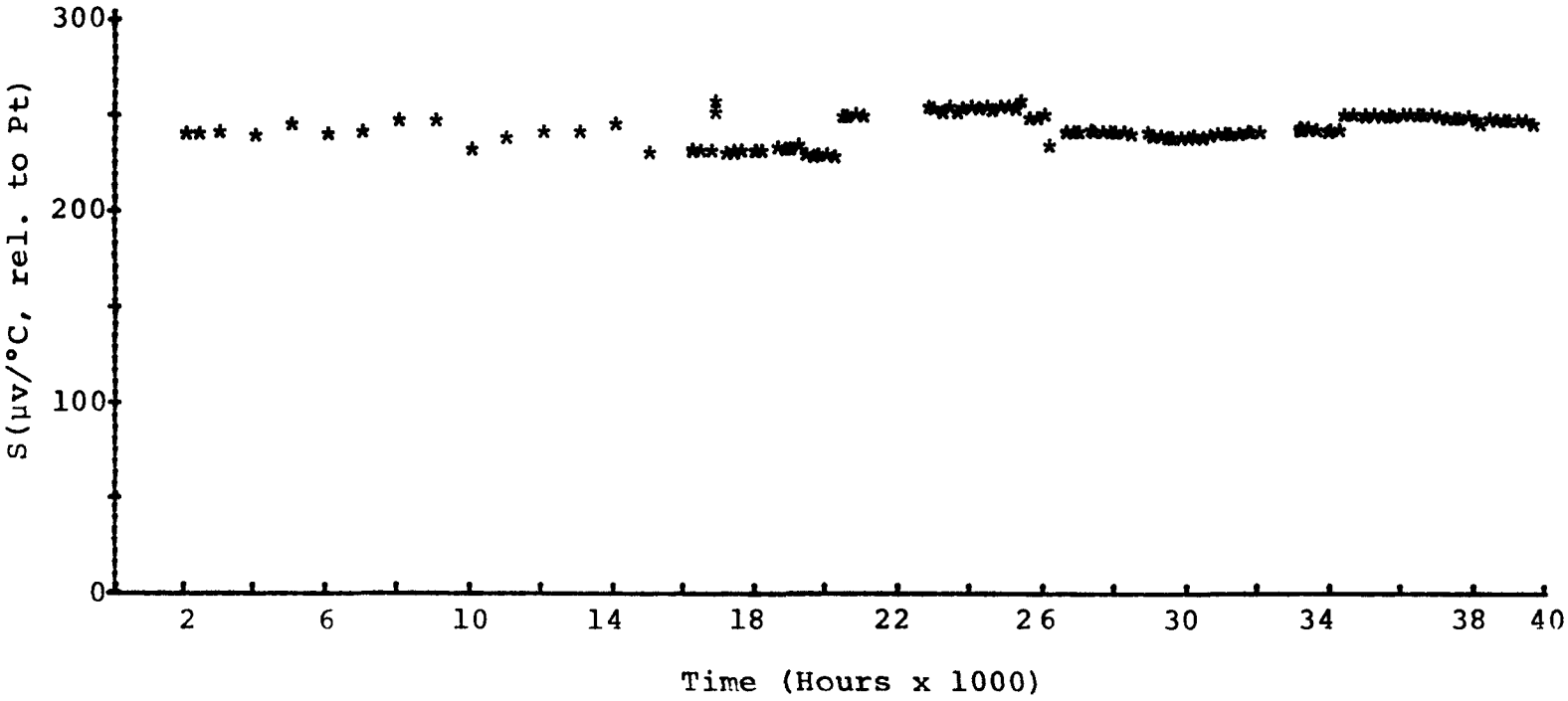


Figure 10. Average Seebeck Coefficient Versus Time for P-TPM-217 Element ATT 133 Operating in the Nominal Temperature Interval 600°/260°C in an Argon Atmosphere.
$\bar{S}$ = 243 ± 7.4 μv/°C, rel. to Pt (125 data points)

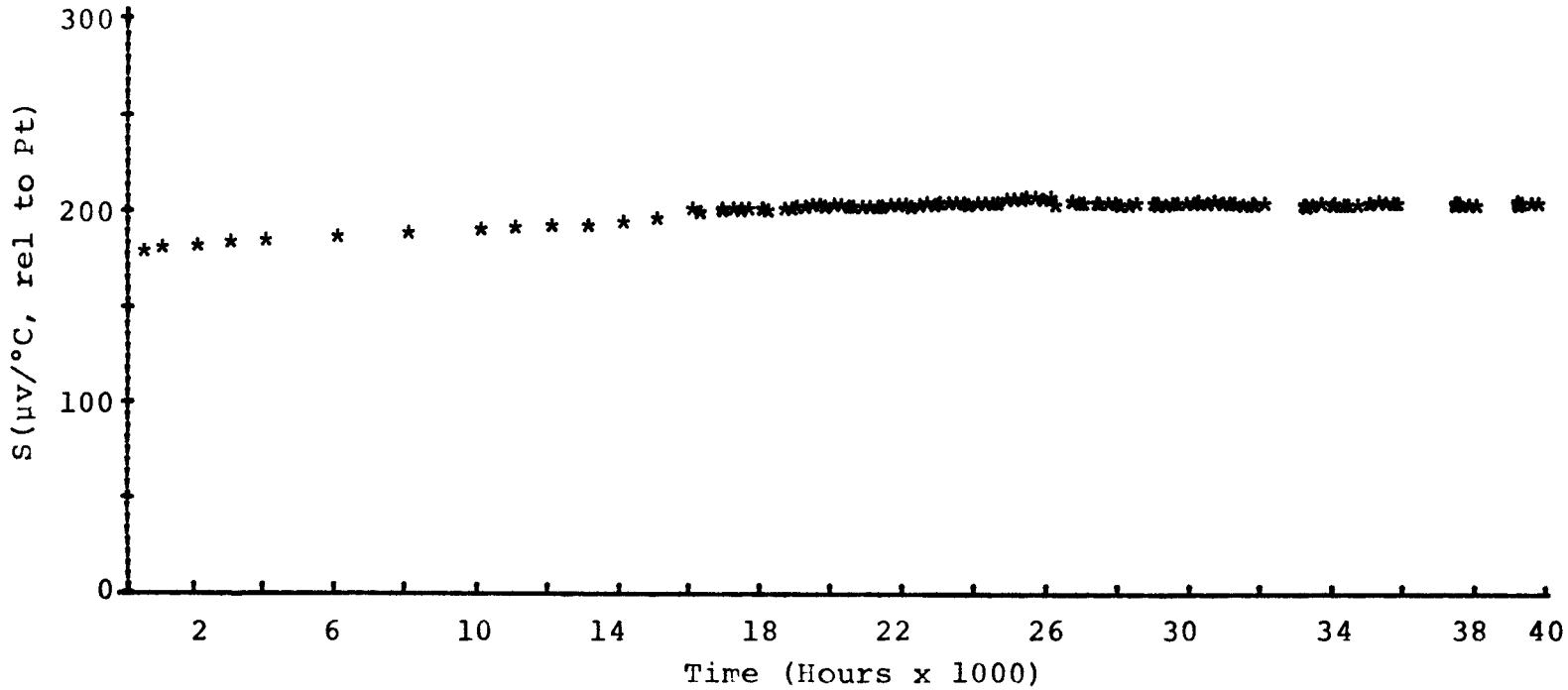


Figure 11. Average Seebeck Coefficient Versus Time for P-TPM-217 Element ATT 137 Operating in the Nominal Temperature Interval of 500°/220°C in an Argon Atmosphere.

$\overline{S}$ = 203 ± 5.3 μv/°C, rel. to Pt

Of the three long-term tests operating in the temperature interval 700°/280°C, two have the tungsten discs at the hot junction. The third test and the two long-term 600°/260°C tests should also have tungsten discs at the hot junction electrode to eliminate the problems associated with the hole.

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 18,300 hours with stable performance (see Figures 12 and 13). 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 XII summarizes the electrical performance of these two life tests.

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

Test ATT 196, an element with an initial composition of 0.10% excess selenium level, and a quartz sleeve around the hot end continues on long-term life test at 800°/300°C and at 20,600 hours has less than 3% standard deviation in the ingradient Seebeck coefficient (Table XIII).

The average Seebeck coefficient versus time for this test at 20,600 hours is shown in Figure 14. The previous data reported for this test was in error due to problems with the temperature reference. The correction of -6μv/°C was applied to part of the old data to compensate for the fact that this test was actually operating in a higher temperature interval than measured. The necessary correction to the reference junction has been accomplished, so this data correction is no longer necessary. This test 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.

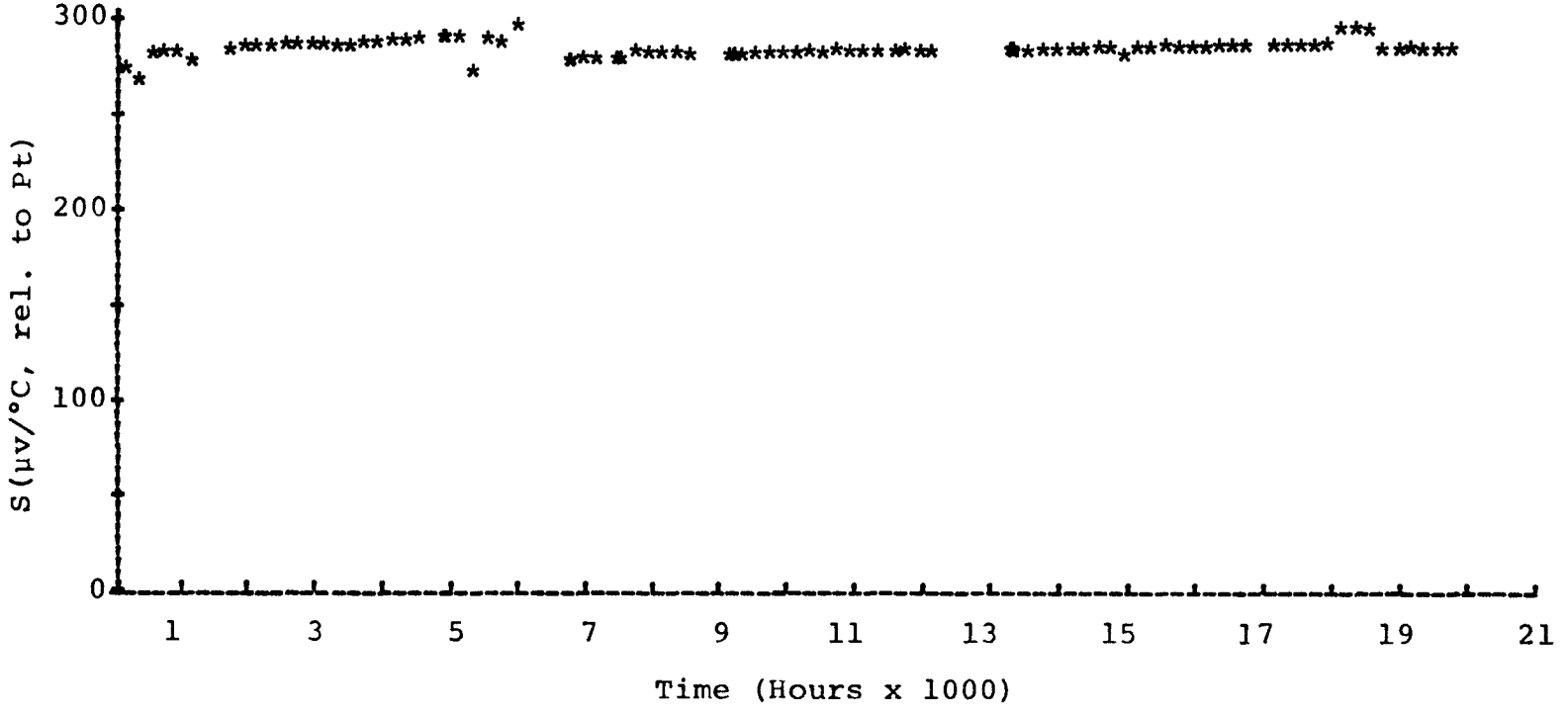


Figure 12. Average Seebeck Coefficient versus Time for P-TPM-217 Element ATT 192 Operating in the Nominal Temperature Interval of 700°/250°C in an Argon Atmosphere.

$\overline{S} = 285 \pm 4.2\ \mu v/°C$, rel. to Pt (93 data points)

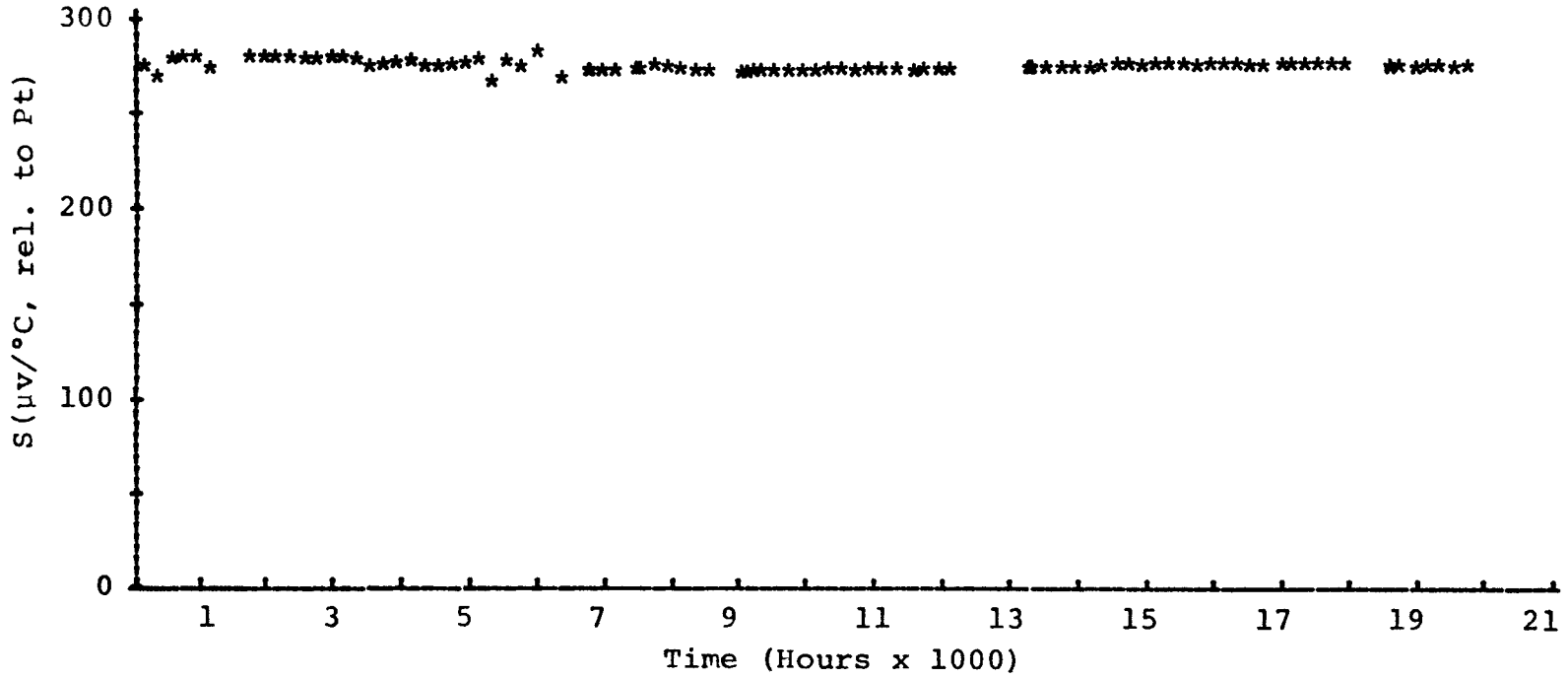


Figure 13. Average Seebeck Coefficient versus Time for P-TPM-217 Element ATT 195 Operating in the Nominal Temperature Interval of 700°/250°C in an Argon Atmosphere.

$\overline{S}$ = 276 ± 2.5 μv/°C, rel. to Pt (94 data points)

TABLE XII

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

ATT #	Operation	Mean & Standard Deviation of the Seebeck Coefficient (μv/°C rel. Pt)	% Standard Deviation of Seebeck Coefficient	Number of Data Points	Ingradient Composition (% excess Se)
192	20,700	285 ± 4.2	1.5	93	0.06 ± 0.01
195	20,700	276 ± 2.5	0.9	94	0.07 ± 0.01

TABLE

TABLE XIII

Summary of Test ATT 196 at 800°/300°C

ATT #	Hour of Operation	Mean & Standard Deviation of the Seebeck Coefficient (μv/°C rel. Pt)	% Standard Deviation of Seebeck Coefficient	Number of Data Points	Ingradient Composition (% excess Se)
196	20,600	289 ± 5	1.7	96	0.07 ± 0.01

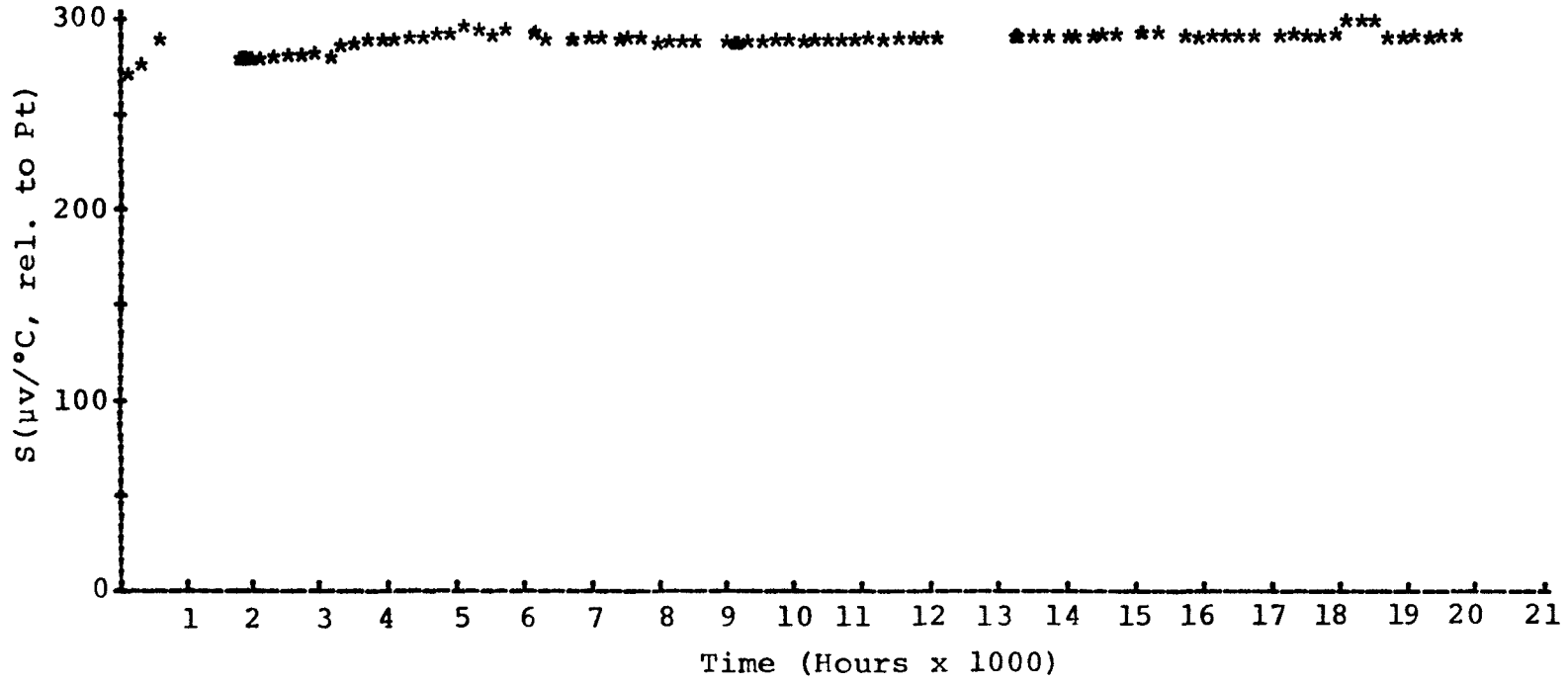


Figure 14. Average Seebeck Coefficient versus Time for P-TPM-217 Element ATT 196 Operating in the Nominal Temperature Interval of 800°/300°C in an Argon Atmosphere.

$\overline{S}$ = 289 ± 4.9 μv/°C, rel. to Pt (96 data points)

2.9.2 P-Type TPM-217 Elements at 565°/200°C

Three TPM-217 P-type elements with ball sockets bonded at the cold end and molybdenum hot junction electrodes have operated for 4500 hours. The predicted values for the tests have been updated to include the latest current dependence work and latest methods in calculation (Wang calculator, couple parameter program). The mean Seebeck coefficient and resistance of each element (ATT 287, 288, and 289) are tabulated in Table XIV.

The performance of these P-elements with the identical couple hardware and nearly identical test conditions are summarized in Table XIV. The mean Seebeck coefficients for the three tests are within 2% of the predicted values and the mean resistances of the three tests are 12% higher than the predicted values for the elements without hardware, thus the extraneous resistance is about 12%. These element tests are providing experimental guidance for couple and module design.

2.9.3 Air Vacuum Test (Exploratory Test)

The test initiated to explore the effects of operating a P-type TPM-217 element in an air atmosphere for short duration continues on test. To review the test history, the element operated in an air atmosphere in the temperature interval of 540°/150°C for 15 hours and then operated in vacuum at 565°/250°C for 1900 hours. The hardware used for this test is similar to the hardware used in the TPM-217 N-PbTe couple test (ATT 266).

Ingradient air operation for 15 hours caused the Seebeck coefficient and resistance to decrease from 259 to 94 μv/°C and from 17.7 to 1.4 mΩ, respectively. Visually, a chemical reaction was observed at the hot junction/element interface area, (Figure 15). The test was then continued without disturbing the element and has operated in a vacuum for 1900 hours at 565°/250°C. The Seebeck and resistance increased to 263 μv/°C and 17.6 mΩ, respectively, by operation in vacuum. The measured Seebeck coefficient

after 1900 hours is within 1% of the predicted value and the measured resistance is 14% higher than the predicted value for this temperature interval, (See Table XV).

The test indicated, as anticipated, that in air operation the TPM-217 material would be doped with oxygen (to higher carrier concentration), causing the Seebeck coefficient and resistance to decrease. When operated in vacuum the composition returned to about normal but, of course, an electrode reaction was observed. The test will be continued to determine if the initial operation in an air atmosphere will cause any long-term effects in the properties of the TPM-217 P-element.

2.9.4 Test Equipment Design and Construction

The mechanical assembly of the two six-station bell jars has been completed. Wiring of the fixtures will commence during the next quarter as soon as electrical feedthroughs, which are on order, are received. The integral load cell featured in each station has been checked out and found to be operating as designed. The cabinets containing the power supplies and controls for the heaters will be wired and the air lines and cooling ducts will be installed.

It is anticipated that the six-station jars will not exhibit the difficulties experienced previously with air and water leaks in the system. All water cooling and threaded fittings have been eliminated from the jars to avoid difficulty.

The computerized data acquisition system will be programmed to calculate the actual load pressure on each element as a function of time.

Three high vacuum test stations for single element testing and one for couple testing were put into full operation.

TABLE XIV

Summary of P-TPM-217 Elements with Hot and Cold Junction Hardware Operating in the Nominal Temperature Interval 565°/200°C (1050°/392°F).. Data not Normalized.

ATT #	Test Time (hours)	Measured Average Seebeck Coefficient (μv/°C rel. to Pt)	Resistance mΩ
287	4500	247	15.6
288	4500	240	12.4
289	4500	246	14.6
Mean		244	14.2

Mean Seebeck Coefficient: 244 ± 4 μv/°C - within 2% of prediction for element without couple hardware.

Mean Resistance: 14.2 ± 1.6 mΩ - within 12% of prediction for element without couple hardware.

Predicted Values: Seebeck coefficient - 248 μv/°C rel. to Pt (no couple hardware)

Resistance (zero extraneous factor) - 12.7 mΩ

Data is not normalized to take into account the slightly different temperature intervals of operation for the individual tests.

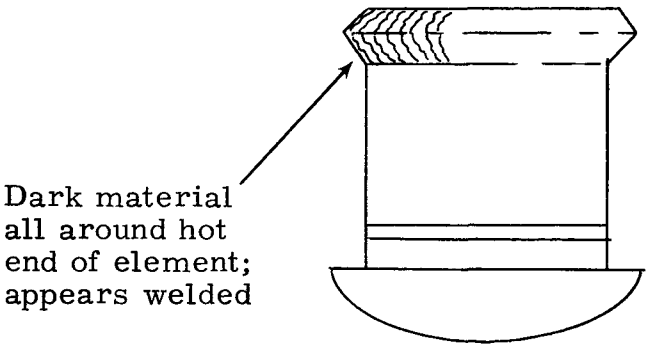


Figure 15. P-Type TPM-217 Element Operated at 540°/160°C in Air for 15 Hours

TABLE XV

History of a TPM-217 Element that Operated Fifteen Hours in Air and Subsequently in Vacuum

Time (Hrs)	T_h (°C)	T_c (°C)	Seebeck Coefficient (μv/°C)	Resistance (mΩ)	Atmosphere
0	556	205	260	17.6	Argon
5	537	159	108	1.9	Air
15	524	160	92	1.6	Air
16	588	285	147	5.9	Vacuum
250	531	229	249	16.7	Vacuum
400	561	245	257	18.0	Vacuum
500	569	246	260	18.2	Vacuum
1200	567	246	261	17.6	Vacuum
1900	564	245	263	17.6	Vacuum

Four high vacuum test stations are completed (three in use) for single element or couple testing.

2.9.5 Computerized Data Collection System

The hardware (disc, etc.) to upgrade the computerized data collection system has arrived. The disc system will be placed into operation, time permitting, when the remainder of the software arrives.

2.10 PERFORMANCE MAPPING

In order to determine the number and placement of partitions necessary to achieve small material loss for operating times in excess of 5 years, it is essential to know the steady state weight loss for a segment operating in a given temperature interval.

This information is available to some degree from the conventional free evaporation TGA and Knudsen cell measurements made earlier in the program. However, because of the unusually high diffusion rate of copper in the TPM-217 material, it is possible to determine the important relation between selenium sublimation rate and excess selenium concentration in a more precise manner using electrical techniques to measure the excess selenium concentration as a function of time. An experiment of this nature was initiated this month. Resistivity and Seebeck coefficient were measured as a function of time for an element held in the interval 800-700°C at 10^{-7} torr vacuum. The initial composition was 0.165% excess selenium; as the excess selenium decreased to its steady state value, the changes in Seebeck coefficient and resistivity were easily followed as functions of time. This data is currently being analyzed; it will be correlated with the vapor pressure data previously obtained by conventional techniques and will be used to calculate long-term performance of partitions.

2.11 PARTITION DEVELOPMENT

Five partitioned elements are currently on test with test times to 18,000 hours at 800°C. Table XVI is a summary of the status of the partitioned elements being tested during the quarter. There have been very few changes in any of the tests except as listed below. In most cases, the means and standard deviations are essentially the same as reported last quarter. Each of the partitioned tests will be reviewed in turn.

TABLE XVI

Status of Experimental Partition Leg Structures

ATT #	Fixture	Atmos.	T_h (°C)	T_c (°C)	Load Pressure (psi)	Total Test Time (Hrs)	Number of Segments
210	Performance	Argon	800	270	150	18,000	2
217	Performance	Argon	800	270	350	17,500	3
241	Performance	Argon	800	270	150	12,700	3*
278	Performance	Argon	800	270	150	7,300	4
269	Performance	Argon	800	270	150	10,000	2

*Bonded

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

The six-station vacuum bell jar in which test ATT 261 through 265 and ATT 223 were being tested has been shut down until it can be rebuilt with improved plumbing. All of the attempts to permanently stop leaks have been unsuccessful. The main sources of the leaks appear to be the Swagelok fittings used for the air and water cooling within the fixture. Apparently when the fittings get warm in normal operation they loosen enough to leak. Repeated tightening of the fittings has not solved the problem. This fixture will be rebuilt along with the construction of two six-station jars. It is anticipated that the design of the new bell jars will not include any compression fittings, but that all the internal fittings will be welded and leak checked before insertion into the fixture.

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°/270°C in an argon atmosphere for approximately 18,000 hours. This test, the original partitioned element, exhibited fluctuations in Seebeck coefficient and resistivity, but there is no apparent trend in the data to indicate any degradation. The average Seebeck coefficient has been approximately 280 μv/°C since about 4000 hours. This performance is similar to other long running partitioned tests such as ATT 241, 278, and 269. Partitioning appears to increase the stability of the legs. Table XVII summarizes the performance of this test.

TABLE XVII

Performance of Test ATT 210

Time (Hrs)	S(μv/°C rel. to Pt)	R (mΩ)	$\bar{\rho}$ (mΩ-cm)	$\bar{\rho}$ (mΩ-cm) (Predicted from $\bar{S}$)	Extraneous Resistance %
2,700	272	25.0	8.01	8.96	-11
3,300	277	29.2	9.36	9.62	- 3
3,900	280	32.2	10.32	10.04	3
4,800	281	29.8	9.55	10.18	- 6
5,600	278	36.2	11.7	9.76	19
6,300	278	37.4	12.0	9.76	23
7,090	279	37.4	12.0	9.9	21
7,850	281	31.7	10.17	10.19	0
8,500	284	35.6	11.42	10.63	7
9,260	282	43.2	13.85	10.33	34
10,000	282	41.4	13.18	10.33	28
10,720	285	39.7	12.73	10.77	18
11,500	281	42.4	13.60	10.18	34
12,200	281	41.6	13.34	10.18	31
12,900	282	42.3	13.56	10.33	31
13,450	286	39.0	12.50	10.93	14
14,380	280	43.7	14.0	10.04	40
14,700	279	43.4	13.9	9.90	40
15,750	280	45.3	14.5	10.02	45
16,430	279	43.5	13.9	9.9	40
17,300	282	45.3	14.5	10.3	42
18,000	283	44.8	14.3	10.4	38

Test 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°/270°C in an argon atmosphere for approximately 17,500 hours under a load pressure of 350 psi. The test originally had tungsten foil barriers pressure engaged to the sements, 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.

Since the addition of platinum foils at the interfaces, this test has continued to display unusually low Seebeck coefficient and resistance values. However, during this quarter the Seebeck coefficient increased to approximately 290 μv/°C with a corresponding drop in extraneous resistance to near zero. Because there are fluctuations in the data, this is believed to be a fixture related problem but attempts to find the source have been unsuccessful. Table XVIII summarizes the performance of this test.

Test ATT 241:

Test ATT 241, initiated to determine the performance of a three-segment element with bonded tungsten-rhenium barriers and a eutectic cold end bond, has operated continuously in a TELPS performance fixture at 800°/270°C in an argon atmosphere for approximately 12,700 hours. This test continues to exhibit very stable electrical and mechanical operation as shown in Table XIX.

The tungsten-rhenium bonded barriers appear to be superior to the pressure engaged barriers previously used. The initial resistance was lower and the operation has been stable. The creep deformation of this leg is apparently much lower than that of unpartitioned legs.

TABLE XVIII

Performance of Test ATT 217

Time (Hrs)	$\overline{S}$ (μv/°C rel. to Pt)	R (mΩ)	$\overline{\rho}$ (mΩ-cm)	$\overline{\rho}$ (mΩ-cm) (Predicted from $\overline{S}$	Extraneous Resistance %
2,200	227	24.9	7.74	4.40	76
2,800	227	26.8	8.33	4.40	89
3,500	224	18.8	5.84	4.22	38
4,400	226	17.6	5.47	4.34	26
5,900	227	18.2	5.66	4.40	29
6,630	232	19.2	5.97	4.72	26
7,390	231	19.3	6.00	4.65	29
8,050	232	20.0	6.22	4.72	32
8,820	280	30.5	9.40	9.33	2
9,500	270	27.4	8.44	8.09	4
10,250	255	24.8	7.64	6.54	17
11,070	244	23.1	7.12	5.59	27
11,750	242	23.5	7.24	5.43	33
12,450	242	23.6	7.27	5.43	34
13,000	241	24.3	7.49	5.35	40
13,940	241	23.5	7.24	5.35	35
14,400	247	23.3	7.18	5.83	23
15,300	250	23.6	7.27	6.08	20
16,000	276	29.9	9.2	8.8	5
16,900	294	33.0	10.2	11.4	-11
17,500	294	36.8	11.4	11.4	0

TABLE XIX

Performance of Test ATT 241

Time (Hrs)	$\overline{S}$ (μv/°C rel. to Pt)	R (mΩ)	$\overline{\rho}$ (mΩ-cm)	$\overline{\rho}$ (mΩ-cm) (Predicted from $\overline{S}$	Extraneous Resistance %
300	302	59.4	17.95	13.70	31
1,000	290	41.3	12.48	11.56	- 8
1,750	289	41.7	12.6	11.4	11
2,509	289	40.9	12.35	11.4	8
3,150	289	39.7	11.99	11.4	5
3,950	290	41.6	12.56	11.56	9
4,600	289	38.3	11.56	11.40	1
5,360	290	42.9	12.95	11.56	12
6,180	289	38.3	11.56	11.40	1
6,860	290	45.7	13.79	11.56	19
7,558	291	43.3	13.07	11.7	11
8,100	291	44.0	13.28	11.7	14
9.020	291	48.0	14.49	11.3	24
9,500	295	35.3	10.7	12.0	-10
10,500	290	43.8	13.3	11.1	19
11,100	290	46.1	14.0	11.1	26
12,000	291	47.1	14.3	11.3	27
12,700	292	48.9	14.9	11.5	30

Test ATT 278:

Test ATT 278, an exploratory test to examine the use of barriers of tungsten electroplated with copper, has operated for 7300 hours in a TELPS performance fixture at 800°/270°C in an argon atmosphere. The element has displayed no apparent creep deformation and continues to look clean over most of its length, indicating low sublimation rates.

It can be assumed that copper was removed from the hot end of each section and driven out of the cold end. This forced the end section to the two-phase line immediately when operation began. The average Seebeck coefficient and resistance have decreased, indicating that the copper which was driven out of the leg may have partially shorted the leg.

The extraneous resistance of this leg is probably high because of the copper extrusion at the end of each section, and the contact surface created by the copper may be irregular. Table XX summarizes the performance of this test.

TABLE XX

Performance of Test ATT 278

Time (Hrs)	$\overline{S}$ (μv/°C rel. to Pt)	R (mΩ)	$\overline{\rho}$ (mΩ-cm)	$\overline{\rho}$ (mΩ-cm) (Predicted from $\overline{S}$	Extraneous Resistance %
1460	273	69.9	21.1	9.16	230
2160	272	71.1	21.5	9.02	138
2700	268	70.2	21.2	8.53	149
3640	272	72.2	21.8	9.03	141
4100	275	70.2	21.2	9.42	125
5000	276	70.0	21.1	9.56	121
5700	271	68.4	20.6	8.9	130
6600	259	66.3	19.9	7.5	165
7300	262	67.0	20.0	7.8	156

Test ATT 269:

Test ATT 269 has operated for approximately 10,000 hours in a TELPS performance fixture at 800°/270°C in an argon atmosphere. The purpose of this test is to evaluate the effect of polishing the ends of the sections and the use of tungsten foil barriers to improve the contact resistance. As seen in Table XXI, this test continues to display improvements in extraneous resistance. There are fluctuations in the data apparently caused by poor thermocuple (voltage probe) contact. If this condition persists, the test fixture will be shut down temporarily for repair.

TABLE XXI

Performance of Test ATT 269

Time (Hrs)	$\overline{S}$ (μv/°C rel. to Pt)	R (mΩ)	$\overline{\rho}$ (mΩ-cm)	$\overline{\rho}$ (mΩ-cm) (Predicted) from $\overline{S}$)	Extraneous Resistance %
6280	288	45.6	13.8	10.7	28
6670	289	44.0	13.3	10.9	22
7650	290	41.7	12.6	11.0	15
8300	289	39.7	12.0	10.8	
9250	***				
10,000	***				

*** Data fluctuations apparently due to poor connections.

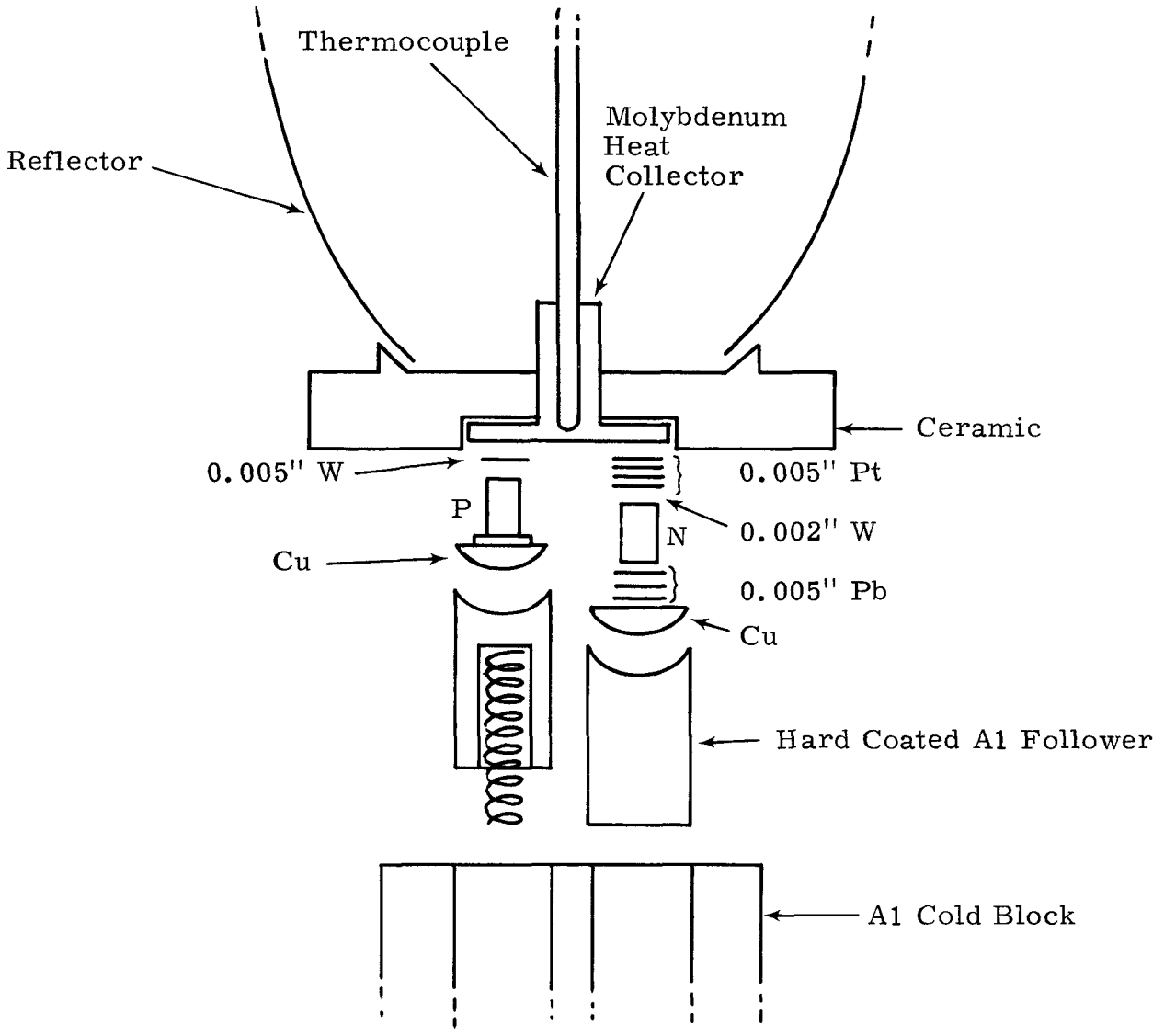
TASK 3.0 - COUPLE DEVELOPMENT

3.3 PRELIMINARY DESIGN AND DEVELOPMENT OF TPM-217/N-RARE EARTH CHALCOGENIDE COUPLE

Exploratory experiments continue to be done to examine the feasibility of the all TPM-217 thermoelectric couple. To accomplish this objective, one of the new high temperature vacuum fixtures has been modified to accept a couple. Followers were inserted into an aluminum block machined to fit into a standard TELPS cold end. To achieve the relatively high spring forces (30 pounds) needed to contact the N-type element, the N-leg follower was mounted rigidly in the block to allow the standard TELPS cold end springs to pressure load it. The P-leg was loaded with a SNAP-27 type spring located in its follower. The hot end was enlarged to heat the total couple area and a single hot end thermocouple was centrally located in the collector.

Couple Test ATT 291:

A third couple test (ATT 291), initiated last quarter and described in Technical Task Report No. 42, has operated for 3300 hours in the temperature interval of 800°/220°C and in a vacuum of 2×10^{-6} torr. The dimensions and design characteristics are shown in Figure 16. The primary objective of this test was to improve the mechanical assembly of the individual elements so that an even distribution of load pressure would be applied to the element to prevent cracking of the leg in operation. The couple is essentially identical to the previous couple tests except that the N-leg was pressed and sintered (N-2263-SIA) and the heat collector was modified to prevent misalignment with the N-leg. The N-leg has not exhibited cracking as did the N-leg in test ATT 290, a previous exploratory test described in Technical Task Report No. 42.



P-Leg	L = 0.383"	D - 0.170"
N-Leg	L - 0.350"	D - 0.174"

Test Condtions:

- T_h 800°C T_c 220°C
- Matched Load Current
- Vacuum of 5 microns
- P Load Pressure = 150 psi
- N Load Pressure = 1100 psi

Figure 16. All TPM-217 Couple - Test ATT 291

Some misalignment occurred with the P-leg during assembly and, at 930 hours, the test was temporarily shut down to incorporate a partitioned P-type TPM-217 leg structure into the couple configuration.

The barrier was inserted in the P-element 0.050 inch from the hot end. The test was restarted and the reseating of the pressure engaged contact on the N-leg after the thermal cycle is being carefully monitored. The power output of the couple is essentially the same as it was at the initiation of the test (Figure 17). Further improvement should be expected since the resistance of the N-leg is high due to incomplete seating in following the thermal cycle at 930 hours to room temperature.

Reviewing the normalized power versus time curve for the couple shown in Figure 17 reveals that the initial increase in power between 0 and 200 hours was caused by the seat-in of the N-leg (30% total improvement in 930 hours). The slight downward trend following 300 hours was due to an increasing P-leg resistance caused by the leg being tilted. This tilting condition increased with time because of the instability of a leg with such a high geometry. The short-term fluctuations (10%) were due to changes in P-leg electrical properties with time as the leg tilted. To remedy this problem, and yet continue the positive features of the test, a P-leg was partitioned and placed in the test with careful alignment at 930 hours.

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

3.4.1 Ball-Socket Hardware

The three P-TPM-217/3N-PbTe couples, ATT 266, ATT 275, and ATT 273, continue to operate with no change in power output. Tests ATT 266 and 275 utilize the ball-socket cold end and pivoting hot end and have operated for 8650 and 7900 hours, respectively, at 565°/200°C (1050°/392°F). The third test, ATT 273, utilizing the pivoting hot end and an all-bonded cold end (on the TPM-217 leg only) has operated for 9000 hours at 540°/140°C (1000°/285°F). The unnormalized power out versus time for these three tests is shown in Figures 18-20.

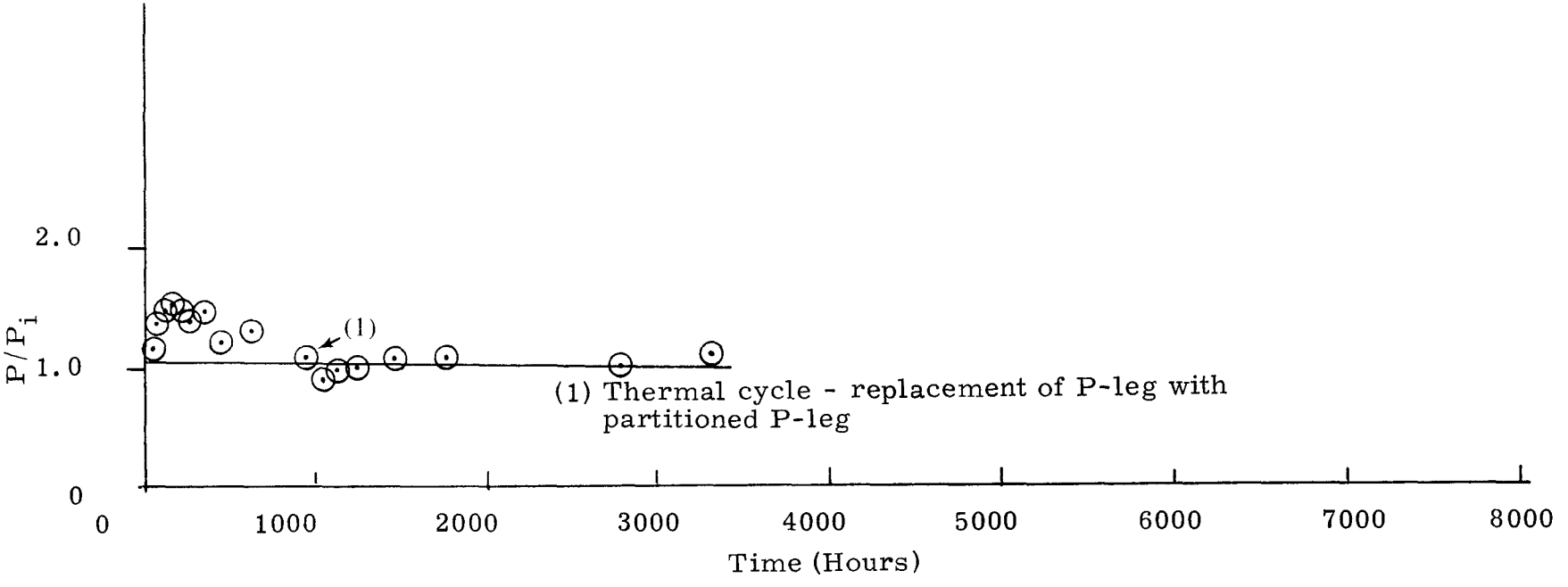


Figure 17. Power Output of All TPM-217 Couple ATT 291 Normalized to the Initial Output - 800°/200°C

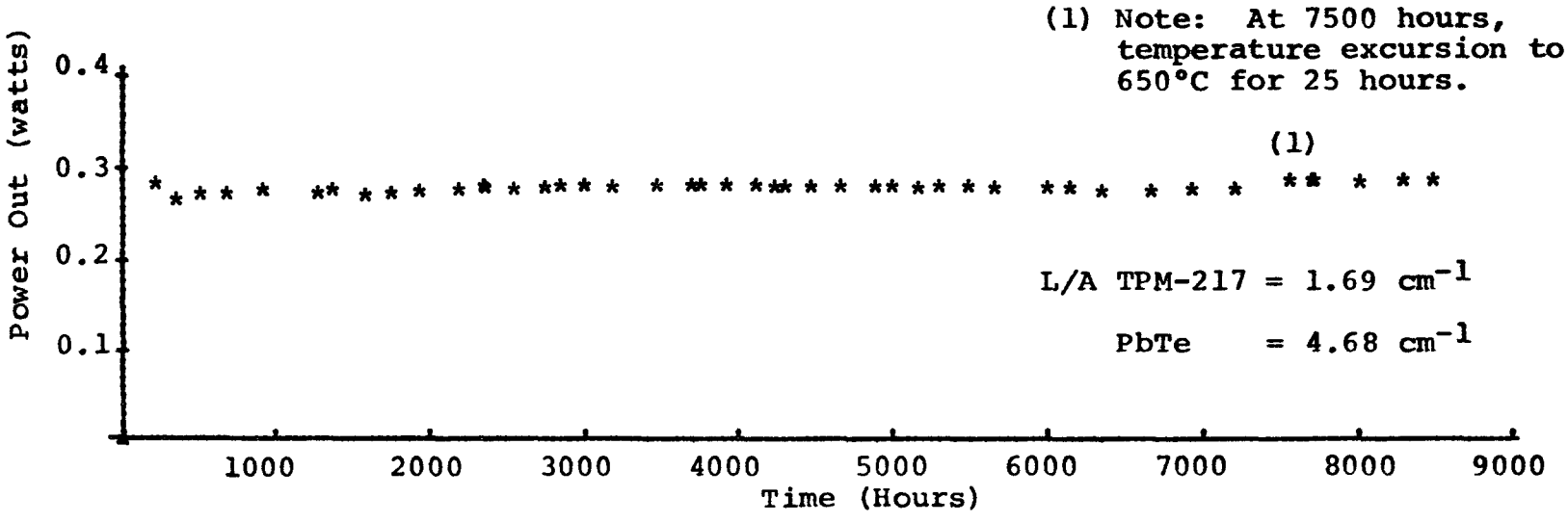


Figure 18. Power Out of TPM-217/3N-PbTe Couple (ATT 266) with Ball-Socket Hardware Operating in a Temperature Interval 565°/200°C (1050°/392°F) in Argon Atmosphere (data not normalized).

Mean - 0.277 ± 0.004 (45 data points)

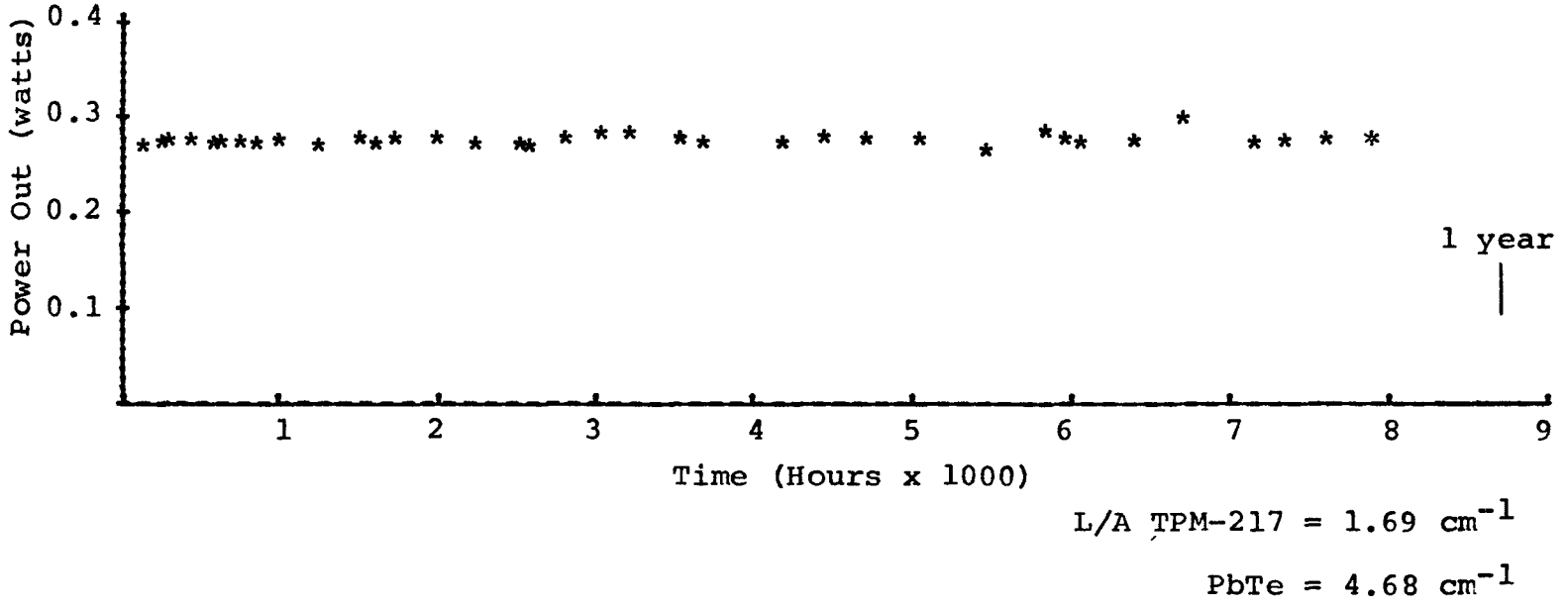


Figure 19. Power Out of TPM-217/3N-PbTe Couple (ATT 275) with Ball-Socket Hardware Operating in a Temperature Interval 565°/200°C (1050°/392°F) in Argon Atmosphere

Mean = 0.276 ± 0.005

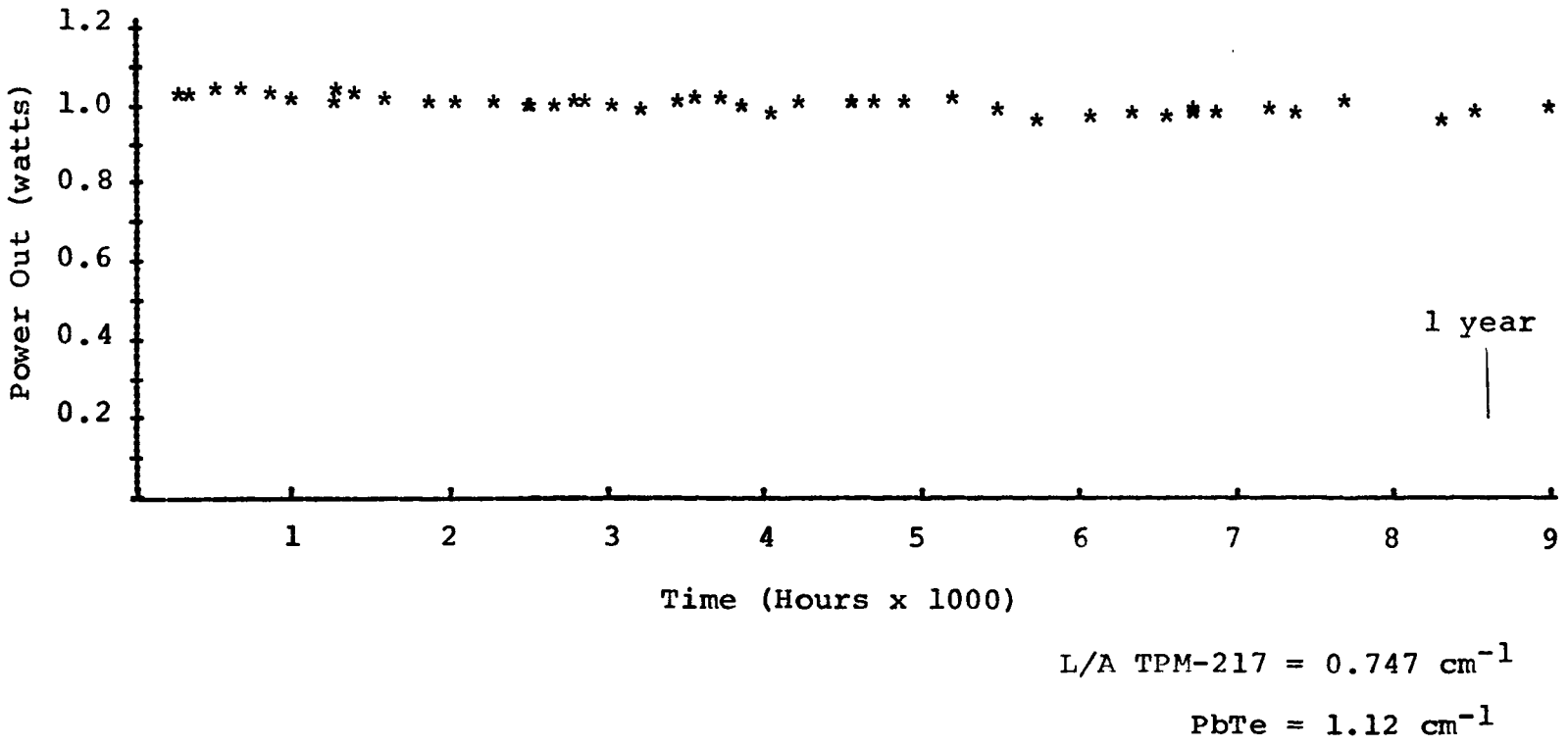


Figure 20. Power Out of TPM-217/3N-4N PbTe Couple (ATT 273) with Rigid Hardware Operating in a Temperature Interval of 540°/140°C (1000°/285°F)

Mean - 1.00 ± 0.02

Test ATT 266:

Test ATT 266, which employs the ball-socket cold end (US 3,075,030) and the pivoting hot end (US 3,496,028) hardware that was similar to or residual from the SNAP-27 thermoelectric generator program, has operated for 8650 hours with stable electrical performance. 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. A configuration drawing of this one-couple test with the unique hot and cold end hardware features was presented in Technical Task Report No. 39, page 64.

At about 7500 hours the hot junction temperature of this test, normally operating at 565°/200°C (1050°/392°F), increased to about 650°C (1200°F) for 25 hours. This temperature excursion caused the 3N-PbTe element to vaporize and coat the bell jar and enabled the pressure engaged TPM-217 leg to reseat itself at the hot end. The contact resistance of the TPM-217 leg had increased when the test was interrupted at about 500 hours to replace the hot end heaters. The temperature excursion and vaporization did not affect the electrical properties of the 3N-PbTe leg and the reseating of the pressure contact enabled the resistance of the TPM-217 leg to return to its original value. This can be seen in Figure 18 where the power output of the couple increased to its original value. This couple has now operated one year (8650 hours) at zero degradation and no extraneous resistance.

Test ATT 275:

A P-TPM-217/3N-PbTe couple (ATT 275) utilizing the ball-socket cold end, pivoting hot end, and other couple hardware identical to test ATT 266 except that Min-K 2020 thermal insulation surrounds the elements, was placed on test in a TELPS soak fixture. The test has operated in the nominal temperature interval 565°/200°C (1050°/392°F) and in an argon atmosphere for 7900 hours with stable electrical properties. Because of the fixture hardware used, the N-PbTe leg is operating at 210°-215°C cold junction, a

temperature above the expected device operating cold junction temperature. The couple is producing 0.280 watt of power compared with a theoretical power output of 0.276 watt, indicating the couple has a -2% extraneous resistance factor. Figure 19 displays the power as a function of time for this test.

3.4.2 Semi-Rigid Hardware Configurations

A P-TPM-217/N-PbTe couple (ATT 273) with low L/A geometry elements and modified rigid hardware (refer to Technical Task Report No. 39, Figure 24) continues on test. The couple has operated for 9000 hours in a temperature interval of 540°/140°C (1000°/285°F) in an argon atmosphere in a bell jar. The power out is stable at approximately 0.97 watt per couple; the predicted power out for this couple is 1.14 watt. This couple is operating with an extraneous resistance factor of 15% which is the same as that obtained for the last rigid hardware couple that was on test. This test replaced the couple with rigid hardware that was terminated due to air leakage into the bell jar. Figure 20 displays the power out as a function of time for this test.

Table XXII summarizes the three P-TPM-217/N-PbTe couple tests currently in operation.

P-Type TPM-217 Elements at 565°/200°C:

Three TPM-217 P-type elements with ball socket cold ends and molybdenum hot junction electrodes have operated for 4500 hours. The hardware and test conditions are identical to the ball-socket couple development tests. The operating conditions are: junction temperatures of 565°/200°C, matched load current of 3.25 amps, L/A of 1.69 cm^{-1}, and a 3 psi argon ambient atmosphere. The two elements in tests ATT 287 and 288 are bonded to the copper ball by the eutectic isothermal process whereas the element in test ATT 289 is bonded to the copper ball by the eutectic ingradient process.

TABLE XXII

Summary of P-TPM-217/N-PbTe Couple Tests in Operation

ATT No.	Hours of Operation	Power Out (watts)		Operating Temperature °C		Current (amps)	L/A cm^{-1}	
		Measured	Predicted	T_h	T_c		P	N
266	8,650	0.282	0.282	565	200	3.25	1.69	4.68
275	7,970	0.280	0.276	565	200	3.32	1.69	4.68
273	9,020	0.97	1.14	540	140	13.0	0.75	1.12

The average Seebeck coefficients of the elements and the resistances measured (includes the molybdenum hot junction electrode cap and the copper ball cold junction electrode) are detailed in Table XXIII along with the percentage differences from the expected values calculated for the given temperature interval. The predicted values for the tests were updated to include the latest current dependence work and latest methods in calculations (Wang calculator, couple parameter program). The average Seebeck coefficient of the three elements is within 0-3% of the predicted values and the resistances are within 0-23% for the three tests.

3.5 INGRADIENT COMPATIBILITY

The N-PbTe/TPM-217 ingradient compatibility samples have been on test for 14,300-16,300 hours and appear to be operating satisfactorily. These tests are operating in the temperature interval of 520°/220°C and under an argon atmosphere in the TELPS soak fixtures. The test conditions were described in Top Summary Report No. 50, page 21.

3.6 ADVANCED CONVERTER CONCEPTS

Thermoelectric couple design considerations for the "Economic Radioisotope Thermoelectric Generator" study have begun utilizing the TPM-217 thermoelectric technology. Preliminary converter design parameters to size the thermoelectric couple consistent with the system design requirements have been made. The data are derived from computer calculations incorporating the unique ingradient operating parameters of a TPM-217 couple, including the effect of current on the average resistivity and Seebeck coefficient of the P leg. The calculation of the heat flux into the leg includes the usual contributions from thermal conductivity, Peltier, Thomson, and Joule heating effects. Calculations have been made to examine the effects of extraneous resistance and heat flux on converter design and performance.

TABLE XXIII

Average Seebeck Coefficient and Resistance of Three TPM-217 P-Elements Operating Between 565°/200°C

ATT #	Time	Average Seebeck Coefficient (μV/°C)		Average Resistance (mΩ)		Comments
		Measured	% Difference from Predicted*	Measured	% Difference from Predicted*	
287	170	236	-5	12.2	-4	Isothermal
	1100	242	-2	14.1	11	eutectic cold
	2400	245	-1	14.6	15	end bond
	3100	246	-1	15.0	18	
	3800	248	0	15.5	22	
	4560	247	0	15.6	23	
288	160	245	-1	12.9	2	Isothermal
	1100	237	-4	12.0	-6	eutectic cold
	2400	245	-1	13.6	7	end bond
	3100	234	-6	11.5	-10	
	3800	239	-4	12.1	-5	
	4560	240	-3	12.4	-2	
289**	1500	244	-2	14.5	14	Ingradient
24	2400	241	-3	14.0	10	eutectic cold
	3100	244	-2	14.3	13	end bond
	3800	245	-1	14.6	13	
	4560	246	-1	14.6	15	

$$\% \text{ Difference} = \left(\frac{\text{Measured - Predicted}}{\text{Predicted}} \right) \times 100$$

* Test interrupted at 1500 hours to repair measurement error.

The following are some of the effects of extraneous resistance that were considered:

- Couple design characteristics V, Q L/A, P L/A, efficiency, i L/A versus extraneous resistance from 0-50% for the temperature interval 800°/200°C for current standard N-type material at i L/A of maximum efficiency.

- Couple design characteristics V, Q L/A, P L/A, efficiency versus i L/A calculated for the temperature interval 800°/200°C for current standard N-type material and an extraneous resistance factor of 10%.

- The dependence of current, number of couples, geometry of couples, and hot frame area on % extraneous resistance when the diameter of the couple is increased to maintain constant power out. For 400 watts output at temperature interval 800°/200°C, current standard N-type material, and i L/A maximum efficiency.

- The dependence of current, voltage, number of couples, heat source area, and diameter of the P-leg on extraneous resistance when the number of couples is increased to maintain constant power out, assuming (1) i L/A set at maximum efficiency, and (2) i L/A adjusted to produce constant voltage. For 400-watt output at temperature interval 800°/200°C, current standard N-type material, and fixed N geometry.

The following are the conditions of heat flux that were considered:

- Dependence of couple voltage, power, efficency, and junction temperatures on current for a fixed heat input. Calculated for current standard N-type material and an extraneous resistance factor of zero.

- Dependence of input heat, power, and efficiency on current for a fixed temperature interval (800°/200°C). Calculated for current standard N-type material and an extraneous resistance factor of zero.

- Dependence of heat input, power out, efficiency, cold junction temperature, and couple voltage on current for fixed hot junction temperature (800°C) and radiation controlled cold junction temperature. Calculated for current standard N-type material and an extraneous resistance factor of zero.

- Effect of isotope decay on couple performance when the current is continuously adjusted to the maximum efficiency value. Case (1): hot junction temperature initially 800°C; and case (2): hot junction temperature 850°C. Cold junction temperature assumed constant at 200°C. Couple voltage efficiency, power, hot junction temperature, and current shown as functions of time.

One element of this study involved sizing the couple to the ERTG mission requirements. The combination of the specified ERTG mission requirements with our experience in fabrication of the TPM-217 materials provides strong constraints on couple geometry. For example, insertion of the proper partitioning for 5-year operation at 800°C necessitates that the P-element be a minimum of 0.3 inch long. In combination with voltage and power requirements, this essentially determines a unique couple geometry. It should be stressed that the TPM-217 couple design presented represents an optimum utilization of our knowledge of the materials.

A standard set of TPM-217 couple design parameters as a function of current density (i L/A) are presented in Tables XXIV through XXVII. These data, representative of some typical temperature intervals of operation where the TPM-217 couple may be applied, include the following.

- TPM-217 couple employing standard N-material

Hot Junction	Cold Junction Temperature
850°C	225°, 200°, 175°C
800°C	225°, 200°, 175°C
775°C	225°, 200°, 175°C

- TPM-217 couple employing potential future N-material

Hot Junction	Cold Junction Temperature
1000°C	200°C
900°C	200°C
850°C	225°, 200°, 175°C
800°C	225°, 200°, 175°C

TABLE XXIV

TPM-217 Couple Design Characteristics:

V, Q L/A, P L/A, Efficiency Versus i L/A Calculated for the Temperature Interval 800°/200°C for Current Standard N-Type Material and an Extraneous Resistance Factor of Zero.

Percent Off Matched Load	i L/A (amps cm^{-1})	Volts (volts)	Q L/A (watts cm^{-1})	P L/A (watts cm^{-1})	Efficiency %
0	15.5	0.137	21.7	2.11	9.74
-10	13.9	0.150	21.1	2.08	9.85
-20	12.4	0.163	20.5	2.01	9.81
-30	10.8	0.176	19.9	1.91	9.60
-50	7.7	0.206	18.6	1.59	8.56
+10	17.0	0.125	22.3	2.12	9.51
+20	18.6	0.113	20.8	2.09	9.16
+30	20.1	0.101	23.5	2.04	8.70
+50	23.2	0.079	24.5	1.84	7.51

$L/A \equiv \left(L_N/A_N + L_P/A_P\right)$

TABLE XXV

TPM-217 Couple Design Characteristics:

V, Q L/A, P L/A, Efficiency Versus i L/A Calculated for the Temperature Interval 800°/200°C for Potential Future N-Type Material and an Extraneous Resistance Factor of Zero.

Percent Off Matched Load	i L/A ($amps\ cm^{-1}$)	Volts (volts)	Q L/A ($watts\ cm^{-1}$)	P L/A ($watts\ cm^{-1}$)	Efficiency %
0	19.7	0.151	23.7	2.97	12.58
-10	17.7	0.164	22.9	2.92	12.74
-20	15.8	0.179	22.7	2.81	12.71
-30	13.8	0.193	21.4	2.67	12.48
-50	9.9	0.226	19.8	2.22	11.25
+10	21.7	0.138	24.4	2.99	12.27
+20	23.6	0.126	25.1	2.96	11.82
+30	25.6	0.113	25.8	2.90	11.25
+50	29.6	0.090	27.1	2.65	9.79

$$L/A \equiv \left(L_N/A_N + L_P/A_P\right)$$

TABLE XXVI

Effect of Variation of Hot and Cold Junction Temperature on Couple Design Characteristics:

V, Q L/A, P L/A, Efficiency, i L/A Versus Hot and Cold Junction Temperature for Current Standard N-Type Material and an Extraneous Resistance Factor of Zero.

Hot Junction Temperature (°C)	Cold Junction Temperature (°C)	i L/A (amps cm^{-1})	Efficiency %	Volts (volts)	Power In Q L/A (watts cm^{-1})	Power Out P L/A (watts cm^{-1})
850	225	13.6	10.03	0.162	22.0	2.21
	200	15.0	10.52	0.163	23.3	2.45
	175	16.5	10.98	0.165	24.7	2.71
800	225	12.6	9.36	0.148	19.9	1.86
	200	13.9	9.85	0.149	21.1	2.08
	175	15.4	10.31	0.150	22.4	2.31
750	225	11.6	8.66	0.134	17.9	1.54
	200	12.9	9.15	0.135	19.0	1.74
	175	14.3	9.62	0.137	20.3	1.95

$L/A \equiv \left(L_P/A_P + L_N/A_N\right)$

TABLE XXVII

Effect of Variation of Hot and Cold Junction Temperature
On Couple Design Characteristics:

V, Q L/A, P L/A, Efficiency, i L/A Versus Hot and Cold Junction Temperature
for Potential Future N-Type Material and an Extraneous Resistance Factor of Zero.

Hot Junction Temperature (°C)	Cold Junction Temperature (°C)	i L/A (amps cm^{-1})	Efficiency %	Volts (volts)	Power In Q L/A (watts cm^{-1})	Power Out P L/A (watts cm^{-1})
850	225	17.5	12.90	0.177	23.98	3.09
	200	19.2	13.58	0.179	25.38	3.44
	175	21.1	14.21	0.181	26.87	3.82
800	225	16.0	12.06	0.162	21.59	2.60
	200	17.7	12.74	0.165	22.92	2.92
	175	19.6	13.38	0.167	24.34	3.25
750	225	14.6	11.17	0.147	19.29	2.15
	200	16.3	11.85	0.150	20.56	2.43
	175	18.0	12.49	0.152	21.91	2.73

$$L/A \equiv \left(L_N/A_N + L_P/A_P\right)$$

Tables XXIV and XXV show the design characteristics versus current density (V, Q L/A, P L/A, efficiency versus i L/A) of a TPM-217 couple employing the standard N-type (Table XXIV) and the "future potential" N-material, operating in the temperature interval 800°/200°C.

Tables XXVI and XXVII show the design characteristics of a TPM-217 couple at maximum efficiency current loading for the standard N-type (Table XXVI) and future potential N-type for hot junction temperatures of 750°, 800°, and 850°C and for cold junction temperatures of 175°, 200°, and 225°C.

Tables XXVIII and XXIX show the design characteristics versus current density of a TPM-217 couple employing the "future potential" N-material operating in the temperature intervals 900°/200°C and 1000°/200°C.

The data presented were derived from computer calculations incorporating the unique ingradient operating parameters of a TPM-217 couple, including the effect of current on the average resistivity and Seebeck coefficient of the P-leg. The effect of partitioning the P-leg on $\overline{S}$, $\overline{\rho}$, and $\overline{K}$ has not been included in this preliminary design data; this effect is dependent on the details of the geometry and barrier spacing and will be included at a later stage. The calculation of the heat flux into the leg includes the usual contributions from thermal conductivity, Peltier, Thomson, and Joule heating effects. Two sets of temperature dependent thermoelectric parameters have been used for the N-TPM-217 leg--the "current standard" material and a future potential" N-type material that hopefully, with further material development, can be produced on more than a random basis. This "future potential" N-material data is included to indicate the possible growth of the system.

The final report, covering the first phase of this design study, is being prepared along with the development plan.

TABLE XXVIII

TPM-217 Couple Design Characteristics:

V, Q L/A, P L/A, Efficiency Versus i L/A Calculated for the Temperature Interval 900°/200°C for the Potential Future N-Type Material and an Extraneous Resistance Factor of Zero.

Percent Off Matched Load	i L/A (amps cm^{-1})	Volts (volts)	Q L/A (watts cm^{-1})	P L/A (watts cm^{-1})	Efficiency (%)
0	23.0	0.178	28.9	4.10	14.20
-10	20.7	0.194	27.9	4.01	14.37
-20	18.4	0.210	27.0	3.87	14.34
-30	16.1	0.227	26.0	3.66	14.09
-50	11.5	0.265	24.0	3.05	12.23
+10	25.3	0.163	29.8	4.13	13.87
+30	29.9	0.134	31.5	4.02	12.77
+50	34.6	0.107	33.2	3.71	11.18

$$L/A \equiv \left(L_N/A_N + L_P/A_P \right)$$

TABLE XXIX

TPM-217 Couple Design Characteristics:

V, Q L/A, P L/A, Efficiency Versus i L/A Calculated for the Temperature Interval 1000°/200°C for Potential Future N-Type Material and an Extraneous Resistance Factor of Zero.

Percent Off Matched Load	i L/A (amps cm^{-1})	Volts (volts)	Q L/A (watts cm^{-1})	P L/A (watts cm^{-1})	Efficiency %
0	26.6	0.203	34.4	5.39	15.77
-10	23.9	0.221	33.3	5.27	15.83
-20	21.2	0.239	32.2	5.07	15.77
-30	18.6	0.259	31.0	4.80	15.48
-50	13.3	0.301	28.6	4.00	13.99
+10	29.2	0.186	35.5	5.43	15.33
+30	34.5	0.154	37.5	5.32	14.19
+50	39.8	0.124	39.4	4.94	12.53

$$L/A \equiv \left(L_N/A_N + L_P/A_P \right)$$

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:

Top Summary Report No. 65, dated August 8, 1973
Top Summary Report No. 66, dated September 7, 1973
Top Summary Report No. 67, dated October 8, 1973
Technical Program Plan, Rev. 3, dated September 19, 1973

Milestone No. 24 was met on schedule during September 1973.