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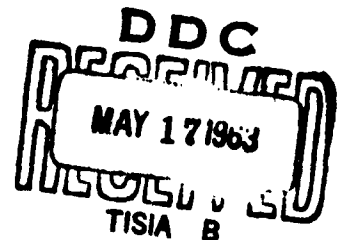
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I. SUMMARY

An experiment on the effect of changing the final sintering temperature of GaBiTe has shown that properties and consistency are improved by determining the solidus for each heat, and then setting the final sintering temperature at or slightly below that temperature. The efficiency of a multiple array of BiSbTe-PbTe couples has been measured and found to be 7 percent with a cold side temperature of 50°C and hot side temperature of 375°C-400°C. The mechanical and vaporization - oxidation properties of CoSbTeSe have been measured to 700°C. Additional results from investigation of "p" type Co-Sb base alloys are reported.

The work on Sn diffusion bonding, with and without protective recesses, has been completed, and processing details and life test results are reported. A gas pressure autoclave provides a means for subjecting materials and contacts to simultaneous pressure and temperature under controlled atmospheres. Results on properties and contacts are reported.

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**EFFECT OF SINTERING TEMPERATURE ON THE PROPERTIES AND
STRUCTURE OF GERMANIUM-BISMUTH-TELLURIDE**

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ABSTRACT

Some 160 pellets of three germanium-bismuth-telluride compositions were sintered at different temperatures. Results showed that there was a substantial change in the sintered density, thermoelectric and mechanical properties, and the microstructure of the material with a change in sintering temperature. These changes in properties are tentatively correlated to a possible liquid-solid transformation in the material.

INTRODUCTION

Germanium-bismuth-telluride ($\text{Ge}_{1-x}\text{Bi}_x\text{Te}$),⁽¹⁾ a Westinghouse developed "p" type thermoelectric compound, is widely used in thermoelectric devices because of its high thermoelectric efficiency in the 500-900°K temperature range.⁽²⁾ In the early stages of its development, two methods were used to produce this alloy, one being the Bridgman melting technique⁽¹⁾ which utilized the controlled solidification of the material in a temperature gradient to obtain the proper composition and crystallographic orientation, and the other, a hot pressing procedure which produced⁽³⁾ an extremely dense pellet. Although both of the techniques produced good thermoelectric material, both techniques had certain inherent disadvantages. For example, the Bridgman technique necessitated a cutting operation which was extremely difficult since the cast product was very brittle. Also, both methods produced material at such a very slow rate that they were not readily adaptable to production of pellets in large quantities. For that reason, batch type powder-metallurgy cold pressing and sintering techniques were developed for the processing of germanium-bismuth-telluride.⁽⁴⁾

Work on the powder metallurgy processing of $\text{Ge}_{1-x}\text{Bi}_x\text{Te}$ compounds was begun some three years ago. Since that time continuing effort has been applied to improve the properties and consistency. Primary effort has been on investigation of the various powder processing variables. One of the most frequent problems confronting the users of $\text{Ge}_{1-x}\text{Bi}_x\text{Te}$ has been the lack of consistency from one batch to another, and even within a given batch, from one sintering operation to the next. Although this problem still exists with germanium-bismuth-telluride, work during the last year has focused on one of

the main problems concerned with producing this material, namely sintering. This report describes an investigation of sintering of germanium-bismuth-telluride and the effects on structure and properties. The results, although at times somewhat conflicting, do indicate that with very close control of the sintering treatment better consistency of properties within each heat of material can be obtained.

Background

Before going into the detailed description of this investigation, some of the results of past work on the powder metallurgy of germanium-bismuth-telluride will be reviewed.

Historically, the two compositions that showed promise as possible device components were $\text{Ge}_{0.9}\text{Bi}_{0.1}\text{Te}$ and $\text{Ge}_{0.95}\text{Bi}_{0.1}\text{Te}_{1.1}$. Both of these compositions had good thermoelectric properties when made using the hot press or Bridgman methods. However, in early attempts to produce these compositions by cold pressing and sintering techniques, excessively high resistivity and Seebeck coefficients were obtained. Other compositions were then tried, among which were $\text{Ge}_{0.95}\text{Bi}_{0.05}\text{Te}$, $\text{Ge}_{0.935}\text{Bi}_{0.065}\text{Te}$ and $\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$. All of these compositions when cold pressed and sintered had good thermoelectric properties. ⁽⁴⁾ In addition to the three specific compositions listed above, a series of other alloys ($\text{Ge}_{1-x}\text{Bi}_x\text{Te}_y$) were made with tellurium levels varying from $y = 1.00$ to 0.85 with no apparent effect on the thermoelectric properties of the material. ⁽⁴⁾

In earlier work, germanium-bismuth-telluride was made in a rocking furnace in a sealed Vycor tube containing an argon atmosphere. Presently,

the alloy is melted in three kilogram quantities in a high frequency induction furnace with good results. The resultant material is then hand mortared and pestled to minus 60 mesh powder, which was found to be the best particle size. The best overall properties have been obtained by pressing at 35 TSI, followed by sintering for 1-1/2 hours at 600°C plus 1/2 hour at 685°C in a hydrogen atmosphere. The work presented in this report will show that the above sintering treatment was very close to the optimum one, but that greater consistency and slightly better properties can be obtained by raising the final sintering temperature.

Experimental Procedure

The processing procedure used in this investigation was the same as has been outlined above except that a series of final sintering temperatures were tried on four - 3000 gram heats of material. The procedure was as follows:

a) Compositions - $\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$ (2 heats)

$\text{Ge}_{0.935}\text{Bi}_{0.065}\text{Te}$ (1 heat)

$\text{Ge}_{0.95}\text{Bi}_{0.05}\text{Te}$ (1 heat)

b) Melting - The alloys were melted in a high frequency (3000 cps) induction furnace. Three thousand grams of high purity⁽⁴⁾ raw materials weighed out in the correct proportions were placed in a graphite crucible. Charge compositions are shown in Table I. The furnace was pumped down to less than 200 microns of Hg and backfilled with argon to 680 mm of Hg to provide an inert cover over the melt. A very fast heating rate was used (120 to 145°C/minute) so that the melt was ready for pouring in

7 to 8 minutes. The melt was poured at about 980°C into a copper-bottomed, graphite mold and allowed to solidify. Four 3000 gram heats were made having the following compositions:

Heat 3458 - $\text{Ge}_{0.95}\text{Bi}_{0.05}\text{Te}$

Heat 3471 - $\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$

Heat 3531 - $\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$

Heat 3532 - $\text{Ge}_{0.935}\text{Bi}_{0.065}\text{Te}$

- c) Grinding - The cast ingot was hand mortared and pestled to pass through a 60 mesh sieve.
- d) Pressing - The minus 60 mesh powder was pressed in a carbide-lined, tapered die at a pressing pressure of 35 TSI using double action pressing. In all, some 160 - 1/2" diameter by 1/2" long pellets were pressed for this investigation.
- e) Sintering - All of the 160 - 1/2" diameter x 1/2" long pellets were sintered for 1-1/2 hours at 600°C in a hydrogen atmosphere. Then pellets from each of the four heats of material were sintered for 1/2 hour at 670, 675, 680, 685, 690, 695, and 700°C in a hydrogen atmosphere. In addition pellets of Heat 3458 ($\text{Ge}_{0.95}\text{Bi}_{0.05}\text{Te}$) were sintered 1/2 hour at 705°C and 710°C, again in hydrogen. The other three heats melt at these temperatures. All sintering was done in a BTU-Belt furnace controlled to $\pm 2^\circ\text{C}$. After sintering the pellets were cooled in the hydrogen atmosphere. In all cases a recording thermocouple was attached to the graphite sintering boat for each 1/2 hour run, so that a

complete time-temperature record from heat up to cool down was available for each sintering treatment.

f) Testing - After sintering, the following tests were performed:

- 1) As sintered density measurements were made on all pellets (Table II).
- 2) Thermoelectric property measurements were made on selected pellets (Table III).
- 3) Room temperature tensile strengths of selected pellets were measured using a simple ceramic break test (Table IV).
- 4) A metallographic study of the various sintered pellets was made after the thermoelectric properties were measured.

g) Other Tests - To attempt to correlate the sintering characteristics to a possible phase transformation during sintering, a cooling curve was run for each heat of material. (Table V).

Results and Discussion

The sintered density is plotted as a function of final sintering temperature for each composition in Figures 1 through 4. The solidus temperature for each composition, as determined from the cooling curve, is shown on these graphs. The point of maximum density occurs very close to the solidus temperature. In two cases, $\text{Ge}_{0.95}\text{Bi}_{0.05}\text{Te}$ and $\text{Ge}_{0.935}\text{Bi}_{0.065}\text{Te}$, the maximum density appears to occur slightly above the solidus, while for $\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$ it occurs slightly below the solidus. The accuracy of the measurements is not great enough to precisely locate these points in relation to each other. However, it is apparent that maximum density can be achieved by determining the solidus

temperature and then controlling the final sintering temperature as close to that point as possible. Some small amount of liquid phase may be present and may enhance the sintering reaction. At higher sintering temperature, a greater amount of liquid phase would tend to cause swelling, and in cool down, would leave shrinkage voids and result in lower density.

The broad temperature range Seebeck, resistivity, and $\bar{S}^2/\bar{\rho}$ parameters of the four heats are plotted as a function of final sintering temperature in Figures 5 to 7.

The effect of increasing the final sintering temperature is generally to lower both the Seebeck and the resistivity in such relation as to increase the $\bar{S}^2/\bar{\rho}$ parameter. The best combination of thermoelectric properties appears to result from approximately the same final sintering temperature that gives maximum density.

The room temperature tensile strengths of the four heats following the various final sinter temperature treatments are listed in Table IV and plotted in Figure 8. Although there is considerable scatter in the results, probably due to the extreme brittleness of the material, there does appear to be some indication that the best strength and perhaps the greatest consistency would be obtained from a final sinter temperature very close to the solidus temperature. Compression tests made for two final sinter temperatures, 665°C and 685°C, have showed higher strength and greater consistency for the 685°C final sinter. ⁽⁵⁾

The effects of final sintering temperature on microstructure are shown in Figure 9. Although only one heat is shown, the structures are typical for all of the heats. At the lowest final sintering temperature (670°C) the

structure retains the as-pressed powder characteristics. There is a range of particle sizes, the particles are angular, and only point sintering has occurred between particles. At the next higher temperature (675°C) more sintering has occurred, and some growth appears to be commencing in the small particles. At 680°C, sintering is almost complete, and void annihilation by diffusion is starting. At 685°C, particles are no longer visible and pores are becoming rounded. At 690°C pores are even more rounded and a second phase (identified as germanium)⁽⁶⁾ is becoming more evident. The solidus for this heat was measured as 691°C with an estimated accuracy of $\pm 5^\circ\text{C}$. At 695°C and 700°C, the pores continue to grow and the second phase becomes more pronounced.

The results of this investigation on the sintering of germanium-bismuth-telluride show that the properties and microstructure of the final product are very much dependent on the final sintering temperature of a two-step treatment. There is also evidence that the sintering characteristics of the material are dependent on the solidus temperature of the particular composition. This work also shows that there is a definite variation from one heat to the next even with the same charge composition.

The results of the investigation suggest an additional process control to achieve good properties and greater consistency in germanium-bismuth-telluride. This is to measure solidus temperature of each heat of material and to set the final sinter temperature at or a few degrees below the solidus temperature.

Conclusions

- 1.) For each particular germanium-bismuth-telluride composition there is a particular sintering temperature that produces the maximum sintered density. The sintering temperature which produces this maximum is very near the solidus temperature for that composition.
- 2.) In most cases, the broad temperature range Seebeck coefficient decreases as the final sintering temperature increases.
- 3.) Broad temperature range electrical resistivity tends to decrease with increasing sintering temperature, reach a minimum, then in some instances, slightly increase.
- 4.) Use of the thermoelectric evaluation parameter, $\bar{S}^2/\bar{\rho}$ indicates that the higher sintering temperatures produce the best thermoelectric materials.
- 5.) The room temperature tensile property measurements show some change in tensile strength as a function of sintering temperature, and indicate that higher sintering temperature gives higher strength.
- 6.) Microstructure studies show a drastic change in the structure of the material as the sintering temperature is changed, from an angular partially sintered type of structure at the lower sintering temperature to a fully sintered structure containing round voids at the higher sintering temperatures. In addition, some cracking is noted on many of the samples.
- 7.) A change of only 5°C in the final sintering temperature of any of the germanium-bismuth-telluride alloys has a marked effect on the final properties and microstructure of the material.

Acknowledgements

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TABLE I

<u>Chemical Composition</u>	<u>w/o Ge</u>	<u>w/o Bi</u>	<u>w/o Te</u>
$\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$	32.19	6.97	60.84
$\text{Ge}_{0.935}\text{Bi}_{0.065}\text{Te}$	32.47	6.50	61.03
$\text{Ge}_{0.95}\text{Bi}_{0.05}\text{Te}$	33.31	5.05	61.64

Compositions of Three Standard Germanium-Bismuth-Telluride Alloys.

TABLE II

Samples Sintered 1-1/2 hours at 600°C plus 1/2 hour at 670°C
in a hydrogen atmosphere

Sample No.	Heat No.	Chemical Composition	Sintered Density (g/cc)	Sample No.	Heat No.	Chemical Composition	Sintered Density (g/cc)
8-1	3458	Ge _{0.95} Bi _{0.05} Te	5.56	1-1	3471	Ge _{0.93} Bi _{0.07} Te	5.81
-2	"	"	5.59	-2	"	"	5.82
-3	"	"	5.57	-3	"	"	5.79
-4	"	"	5.58	-4	"	"	5.81
Ave.	"	"	5.58	Ave.	"	"	5.81
2-1	3532	Ge _{0.935} Bi _{0.065} Te	5.59	31-1	3531	"	5.56
-2	"	"	5.61	-2	"	"	5.53
-3	"	"	5.62	-3	"	"	5.57
-4	"	"	5.63	-4	"	"	5.58
Ave.	"	"	5.61	Ave.	"	"	5.56

Samples Sintered 1-1/2 hours at 600°C plus 1/2 hour at 675°C
in a hydrogen atmosphere

Sample No.	Heat No.	Chemical Composition	Sintered Density (g/cc)	Sample No.	Heat No.	Chemical Composition	Sintered Density (g/cc)
8-5	3458	Ge _{0.95} Bi _{0.05} Te	5.60	1-5	3471	Ge _{0.93} Bi _{0.07} Te	5.81
-6	"	"	5.54	-6	"	"	5.81
-7	"	"	5.56	-7	"	"	5.80
-8	"	"	5.58	-8	"	"	5.80
Ave.	"	"	5.59	Ave.	"	"	5.81
2-5	3532	Ge _{0.935} Bi _{0.065} Te	5.62	31-5	3531	"	5.57
-6	"	"	5.63	-6	"	"	5.57
-7	"	"	5.60	-7	"	"	5.57
-8	"	"	5.61	-8	"	"	5.56
Ave.	"	"	5.62	Ave.	"	"	5.57

Sintered Densities of Various Germanium-Bismuth-Telluride
Composition with Varying Sintering Treatments.

TABLE II (cont)
Samples Sintered 1-1/2 hours at 600°C plus 1/2 hour at 680°C
in a hydrogen atmosphere

Sample No.	Heat No.	Chemical Composition	Sintered Density(g/cc)	Sample No.	Heat No.	Chemical Composition	Sintered Density(g/cc)
8-9	3458	Ge _{0.95} Bi _{0.05} Te	5.53	1-9	3471	Ge _{0.93} Bi _{0.07} Te	5.81
-10	"	"	5.54	-10	"	"	5.82
-11	"	"	5.59	-11	"	"	5.81
-12	"	"	5.61	-12	"	"	5.81
Ave.	"	"	5.57	Ave.	"	"	5.81
2-9	3532	Ge _{0.935} Bi _{0.065} Te	5.64	31-9	3531	"	5.71
-10	"	"	5.59	-10	"	"	5.73
-11	"	"	5.63	-11	"	"	5.73
-12	"	"	5.60	-12	"	"	5.71
Ave.	"	"	5.62	Ave.	"	"	5.72

Samples Sintered 1-1/2 hours at 600°C plus 1/2 hour at 685°C
in a hydrogen atmosphere

Sample No.	Heat No.	Chemical Composition	Sintered Density(g/cc)	Sample No.	Heat No.	Chemical Composition	Sintered Density(g/cc)
8-13	3458	Ge _{0.95} Bi _{0.05} Te	5.68	1-13	3471	Ge _{0.93} Bi _{0.07} Te	5.84
-14	"	"	5.63	-14	"	"	5.83
-15	"	"	5.62	-15	"	"	5.83
-16	"	"	5.62	-16	"	"	5.86
Ave.	"	"	5.64	Ave.	"	"	5.84
2-13	3532	Ge _{0.935} Bi _{0.065} Te	5.76	31-13	3531	"	5.83
-14	"	"	5.77	-14	"	"	5.83
-15	"	"	5.76	-15	"	"	5.84
-16	"	"	5.76	-16	"	"	5.85
Ave.	"	"	5.76	Ave.	"	"	5.84

TABLE II (cont)
Samples Sintered 1-1/2 hours at 600°C plus 1/2 hour at 690°C
in a hydrogen atmosphere

Sample No.	Heat No.	Chemical Composition	Sintered Density(g/cc)	Sample No.	Heat No.	Chemical Composition	Sintered Density(g/cc)
8-17	3456	Ge _{0.95} Bi _{0.05} Te	5.69	1-17	3471	Ge _{0.93} Bi _{0.07} Te	5.96
-18	"	"	5.65	-18	"	"	5.95
-19	"	"	5.63	-19	"	"	5.97
-20	"	"	5.66	-20	"	"	5.95
Ave.	"	"	5.66	Ave.	"	"	5.96
2-17	3532	Ge _{0.935} Bi _{0.065} Te	5.83	31-17	3531	"	5.83
-18	"	"	5.83	-18	"	"	5.83
-19	"	"	5.84	-19	"	"	5.84
-20	"	"	5.81	-20	"	"	5.81
Ave.	"	"	5.83	Ave.	"	"	5.83

Samples Sintered 1-1/2 hours at 600°C plus 1/2 hour at 695°C
in a hydrogen atmosphere

Sample No.	Heat No.	Chemical Composition	Sintered Density(g/cc)	Sample No.	Heat No.	Chemical Composition	Sintered Density(g/cc)
8-21	3458	Ge _{0.95} Bi _{0.05} Te	5.67	1-21	3471	Ge _{0.93} Bi _{0.07} Te	5.93
-22	"	"	5.62	-22	"	"	5.91
-23	"	"	5.68	-23	"	"	5.90
-24	"	"	5.67	-24	"	"	5.94
Ave.	"	"	5.66	Ave.	"	"	5.92
2-21	3532	Ge _{0.935} Bi _{0.065} Te	5.90	31-21	3531	"	5.90
-22	"	"	5.91	-22	"	"	5.88
-23	"	"	5.91	-23	"	"	5.85
-24	"	"	5.88	-24	"	"	5.86
Ave.	"	"	5.90	Ave.	"	"	5.87

TABLE II, (cont)

Samples Sintered 1-1/2 hours at 600°C plus 1/2 hour at 700°C
in a hydrogen atmosphere

Sample No.	Heat No.	Chemical Composition	Sintered Density(g/cc)	Sample No.	Heat No.	Chemical Composition	Sintered Density(g/cc)
8-25	3458	Ge _{0.95} Bi _{0.05} Te	5.84	1-25	3471	Ge _{0.93} Bi _{0.07} Te	5.83
-26	"	"	5.72	-26	"	"	5.84
-27	"	"	5.76	-27	"	"	5.84
-28	"	"	5.74	-28	"	"	5.80
Ave.	"	"	5.76	Ave.	"	"	5.83
2-25	3532	Ge _{0.935} Bi _{0.065} Te	5.88	31-25	3531	"	5.79
-26	"	"	5.85	-26	"	"	5.76
-27	"	"	5.84	-27	"	"	5.79
-28	"	"	5.88	-28	"	"	5.78
Ave.	"	"	5.86	Ave.	"	"	5.78

Samples Sintered 1-1/2 hours at 600°C plus 1/2 hour at 705°C
in a hydrogen atmosphere

Sample No.	Heat No.	Chemical Composition	Sintered Density (g/cc)
8-29	3458	Ge _{0.95} Bi _{0.05} Te	5.75
-30	"	"	5.68
-31	"	"	5.71
Ave.	"	"	5.71

Samples Sintered 1-1/2 hours at 600°C plus 1/2 hour at 710°C
in a hydrogen atmosphere

Sample No.	Heat No.	Chemical Composition	Sintered Density (g/cc)
8-33	3458	Ge _{0.95} Bi _{0.05} Te	5.64
-35	"	"	5.74
-36	"	"	5.67
Ave.	"	"	5.68

TABLE III
Typical Thermoelectric Properties of Germanium-Bismuth-Telluride

Heat No. (1)	Final Sinter Temperature (°C) (2)	Thermoelectric Properties				
		S RT ($\mu\text{V}/^\circ\text{C}$)	ρ RT ($\text{m}\Omega\text{-cm}$)	$\bar{S}$ 100-450°C ($\mu\text{V}/^\circ\text{C}$)	$\bar{\rho}$ 100-450°C ($\text{m}\Omega\text{-cm}$)	$\bar{S}^2/\bar{\rho}$ $\times 10^{-5}$
3458	670	+ 46	0.43	+ 143	1.08	1.90
"	675	39	0.42	139	0.95	2.04
"	680	45	0.41	143	1.00	2.05
"	685	46	0.37	144	1.12	1.85
"	690	47	0.36	148	0.92	2.38
"	695	45	0.36	142	0.86	2.19
"	700	45	0.35	141	0.67	2.96
"	705	43	0.35	131	0.78	2.20
"	710	38	0.38	122	0.71	2.10
3532	670	+ 60	0.62	+ 172	1.65	1.79
"	675	60	0.66	171	1.74	1.68
"	680	60	0.62	173	1.69	1.77
"	685	59	0.51	168	1.35	2.09
"	690	57	0.47	169	1.34	2.13
"	695	52	0.43	157	1.00	2.46
"	700	49	0.46	147	1.01	2.14
3471	670	+ 67	0.65	+ 132	0.88	1.98
"	675	64	0.71	133	1.13	1.57
"	680	64	0.71	135	0.99	1.85
"	685	66	0.68	134	0.97	1.86
"	690	66	0.61	135	0.86	2.12
"	695	61	0.58	138	0.95	2.01
"	700	54	0.56	137	0.93	2.02
3531	670	+ 72	0.84	+ 181	2.33	1.41
"	675	65	0.81	182	2.29	1.45
"	680	64	0.62	182	1.63	2.03
"	685	63	0.53	180	1.40	2.31
"	690	58	0.50	170	1.29	2.24
"	695	53	0.48	162	1.12	2.34
"	700	51	0.51	162	1.09	2.40

(1) Heat 3458 is $\text{Ge}_{0.95}\text{Bi}_{0.05}\text{Te}$, Heat 3532 is $\text{Ge}_{0.935}\text{Bi}_{0.065}\text{Te}$ and Heats 3471 and 3531 are $\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$.

(2) All samples were sintered for 1-1/2 hours at 600°C plus 1/2 hour at the temp. indicated, all in H_2 atmosphere.

TABLE IV

Heat No. (1)	Final Sintering Temperature (°C)	Room Temperature Ultimate Tensile Strength (PSI)	Heat No. (1)	Final Sintering Temperature (°C)	Room Temperature Ultimate Tensile Strength (PSI)
3458	670	1400	3471	670	1880
"	675	1340	"	675	1580
"	680	1290	"	680	1460
"	685	1270	"	685	1580
"	690	1200	"	690	1740
"	695	1240	"	695	1510
"	700	1520	"	700	1370
"	705	1410			
"	710	1220			
3532	670	1220	3531	670	1080
"	675	1110	"	675	1130
"	680	1270	"	680	1540
"	685	1350	"	685	1230
"	690	1760	"	690	1530
"	695	1680	"	695	1310
"	700	1460	"	700	1600

* Heat 3458 is $\text{Ge}_{0.95}\text{Bi}_{0.05}\text{Te}$, Heat 3532 is $\text{Ge}_{0.935}\text{Bi}_{0.065}\text{Te}$, and Heats 3471 and 3531 are $\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$.

Average Room Temperature Ultimate Tensile Strength Versus
Final Sintering Temperature

TABLE V

<u>Heat No.</u>	<u>Chemical Composition</u>	<u>Solidus Temperature (°C)</u>
3458	$\text{Ge}_{0.95}\text{Bi}_{0.05}\text{Te}$	697
3532	$\text{Ge}_{0.935}\text{Bi}_{0.065}\text{Te}$	693
3471	$\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$	691
3531	$\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$	691

Solidus Temperature of Various
Germanium-Bismuth-Telluride Alloys

CURVE 565796

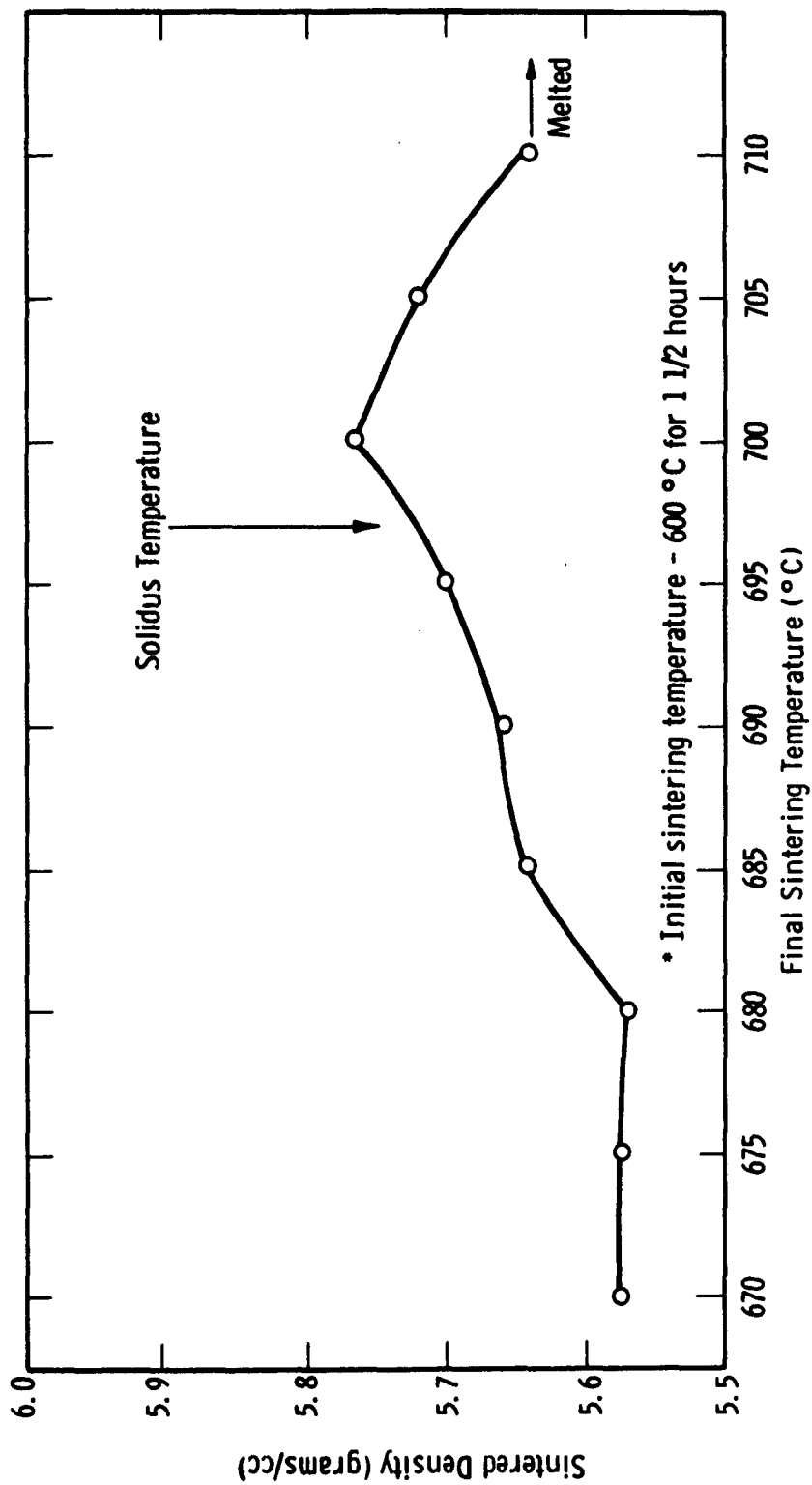


Fig. 1—Sintered density versus final sintering temperature*
Heat 3458 ($\text{Ge}_{0.95}\text{Bi}_{0.05}\text{Te}$)

CURVE 565797

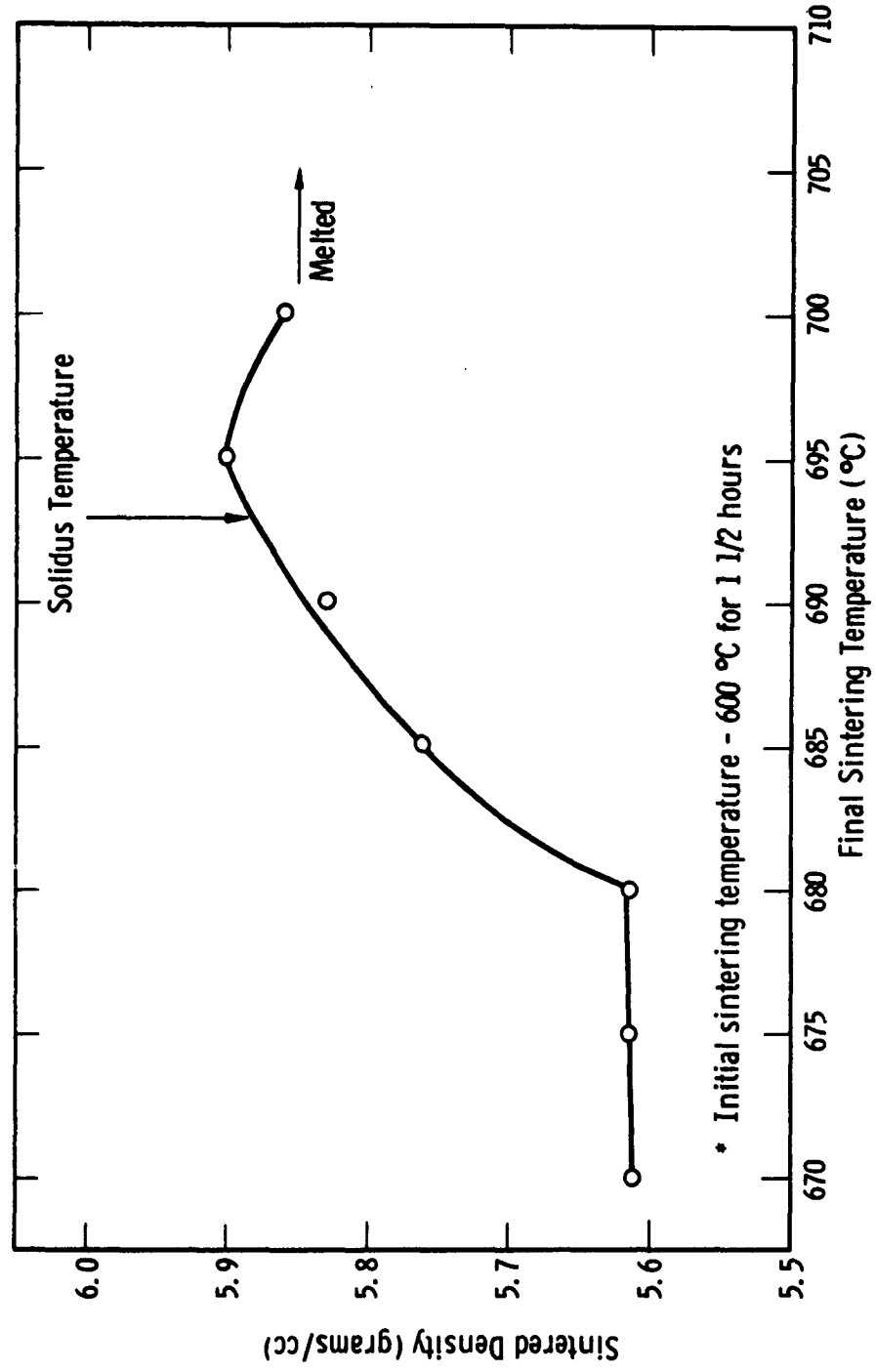


Fig. 2—Sintered density versus final sintering temperature*
Heat 3532 ($\text{Ge}_{0.935}\text{Bi}_{0.065}\text{Te}$)

CURVE 565798

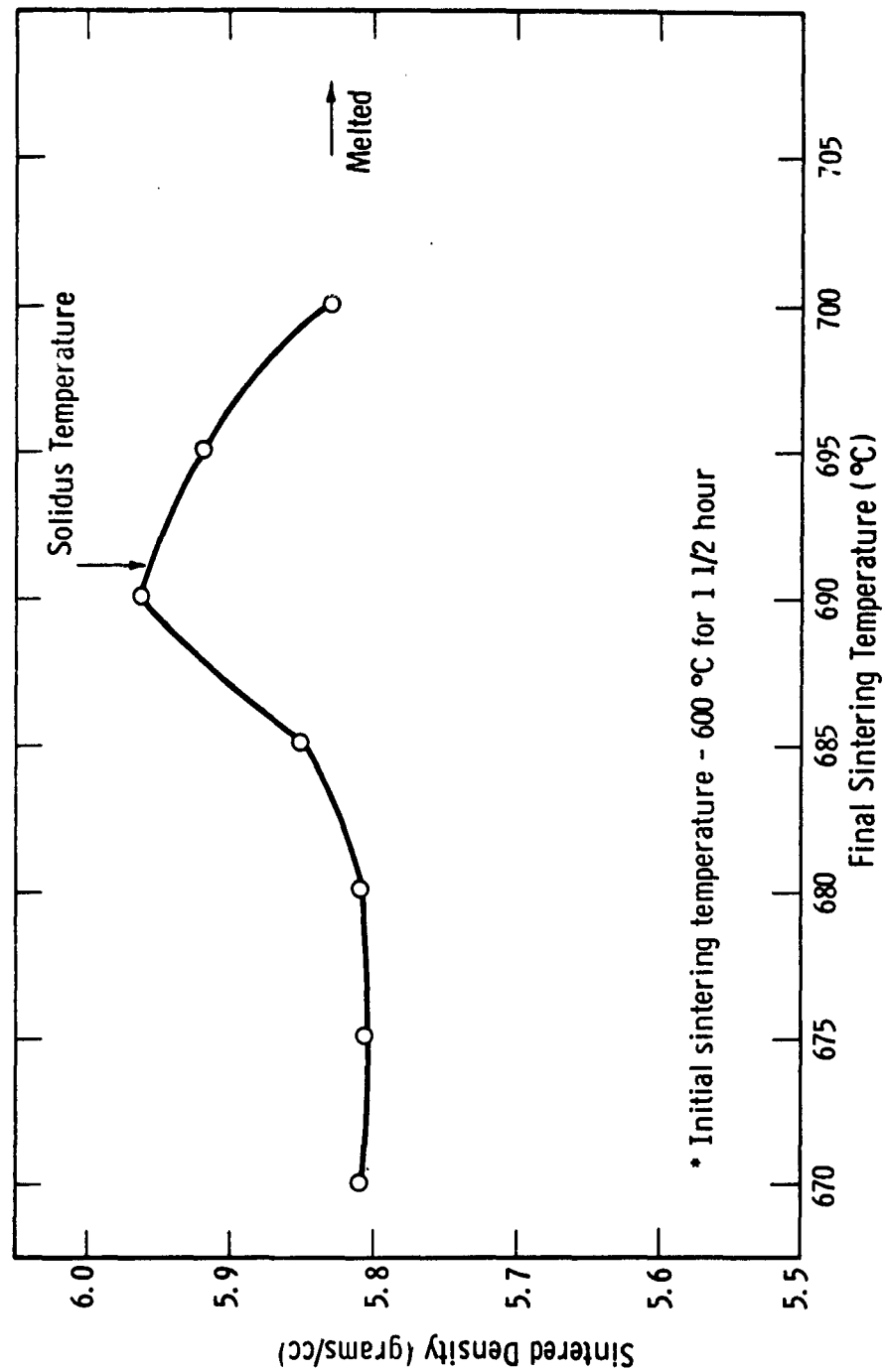


Fig. 3—Sintered density versus final sintering temperature*
Heat 3471 ($\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$)

CURVE 565799

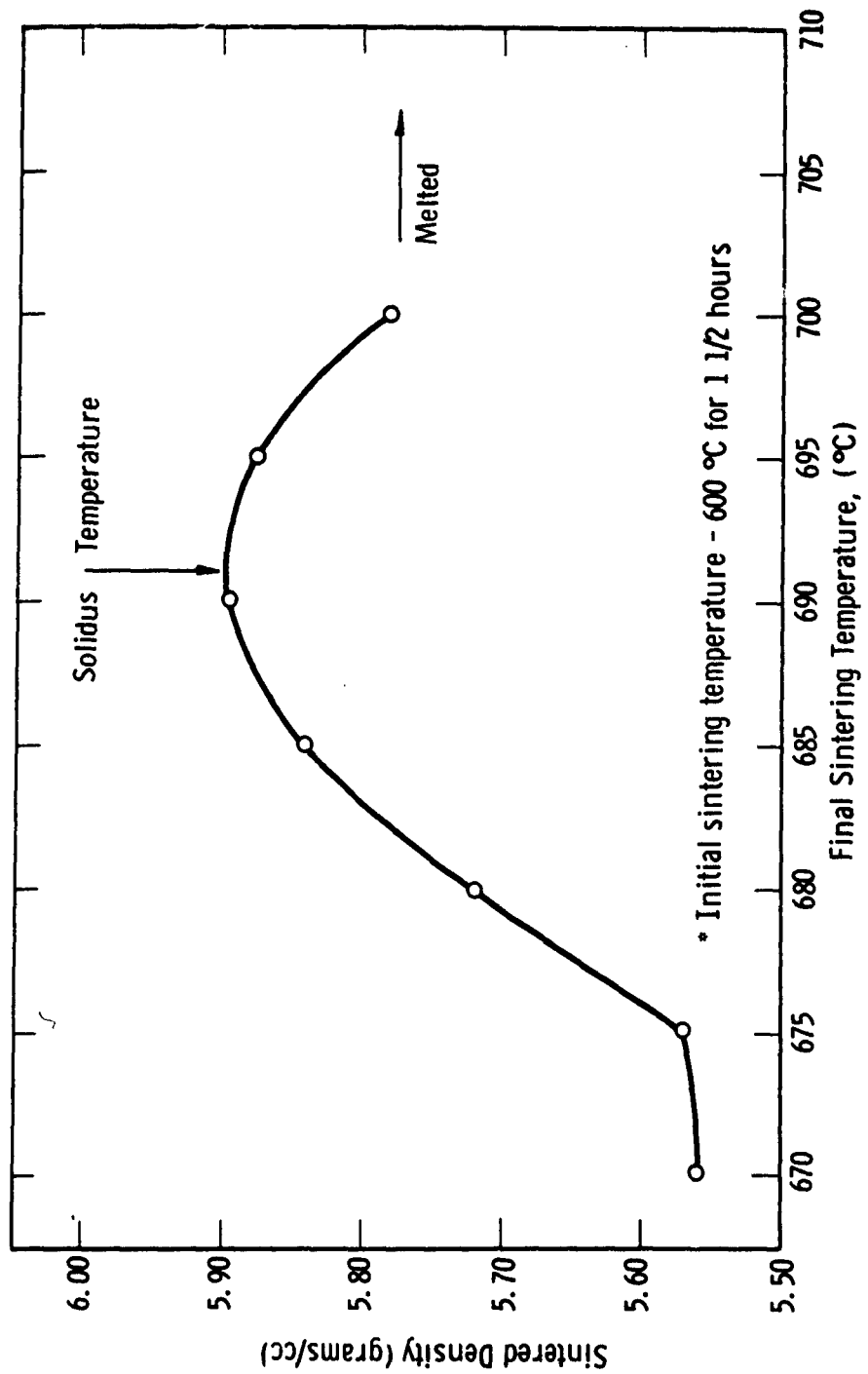


Fig. 4-Sintered density versus final sintering temperature*
Heat 3531 ($\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$)

CURVE 565800

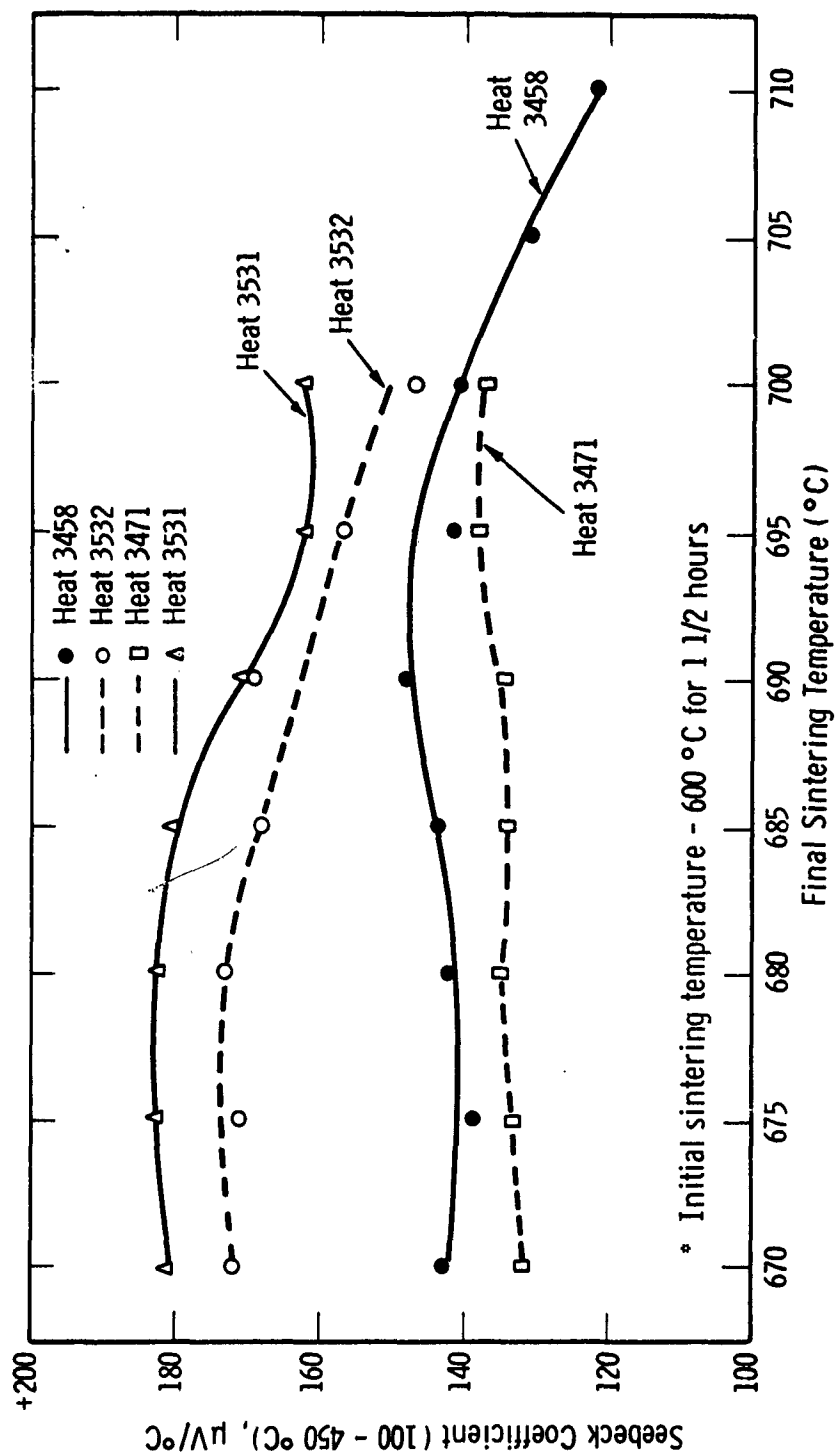


Fig. 5—Seebeck coefficient versus final sintering temperature*

CURVE 565801

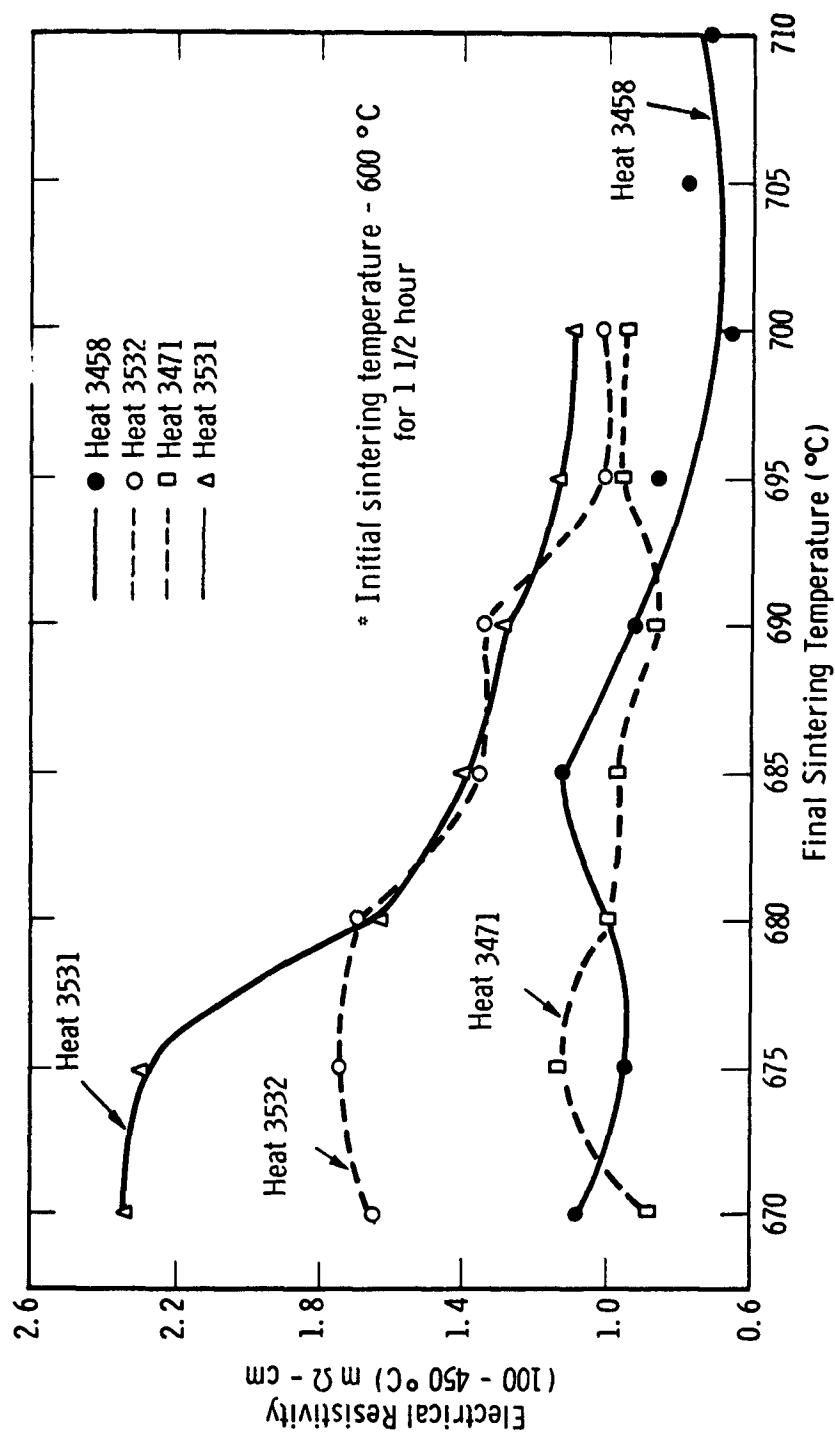


Fig. 6—Electrical resistivity versus final sintering temperature*

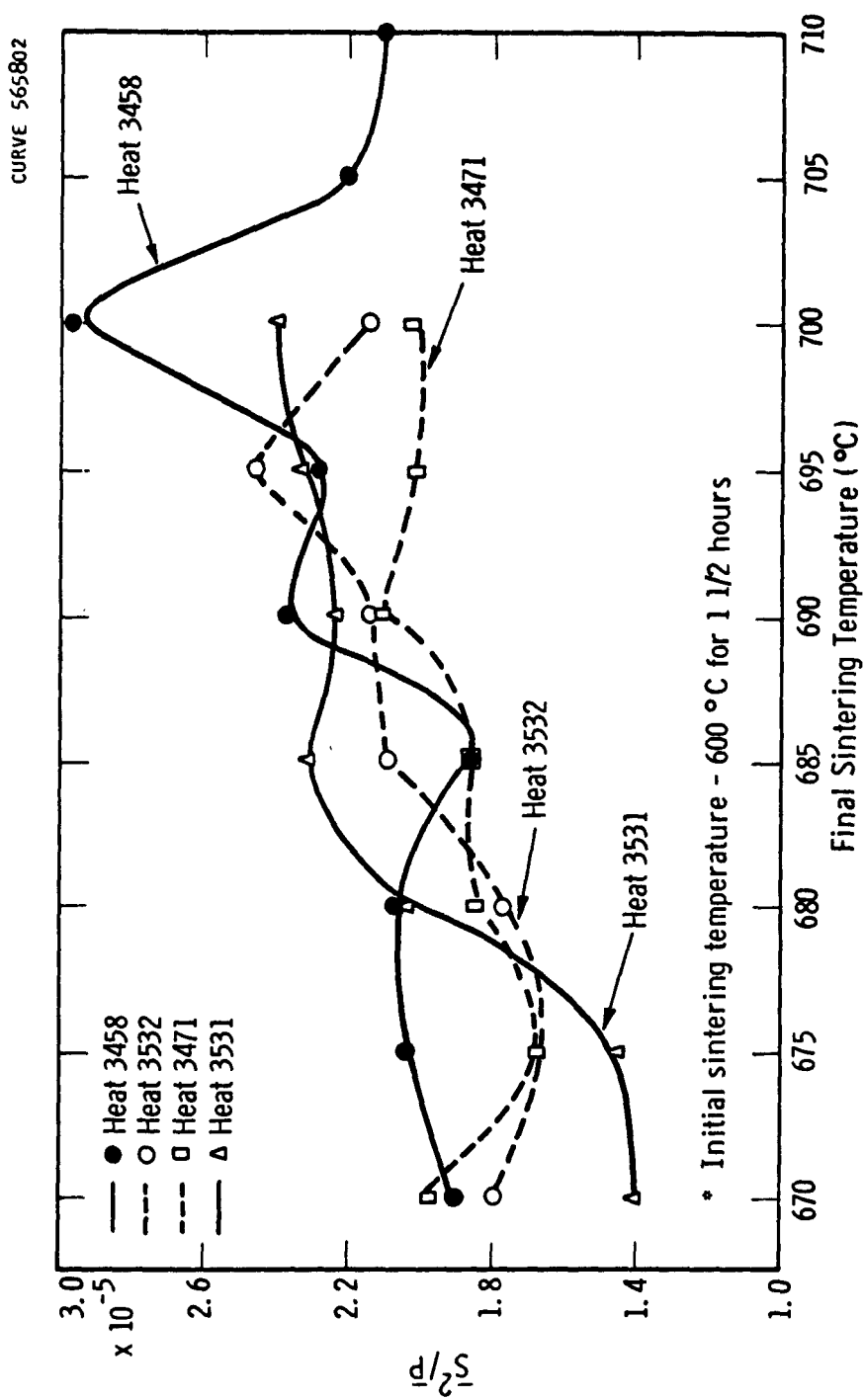


Fig. 7—Evaluation parameter versus final sintering temperature*

CURVE 565803

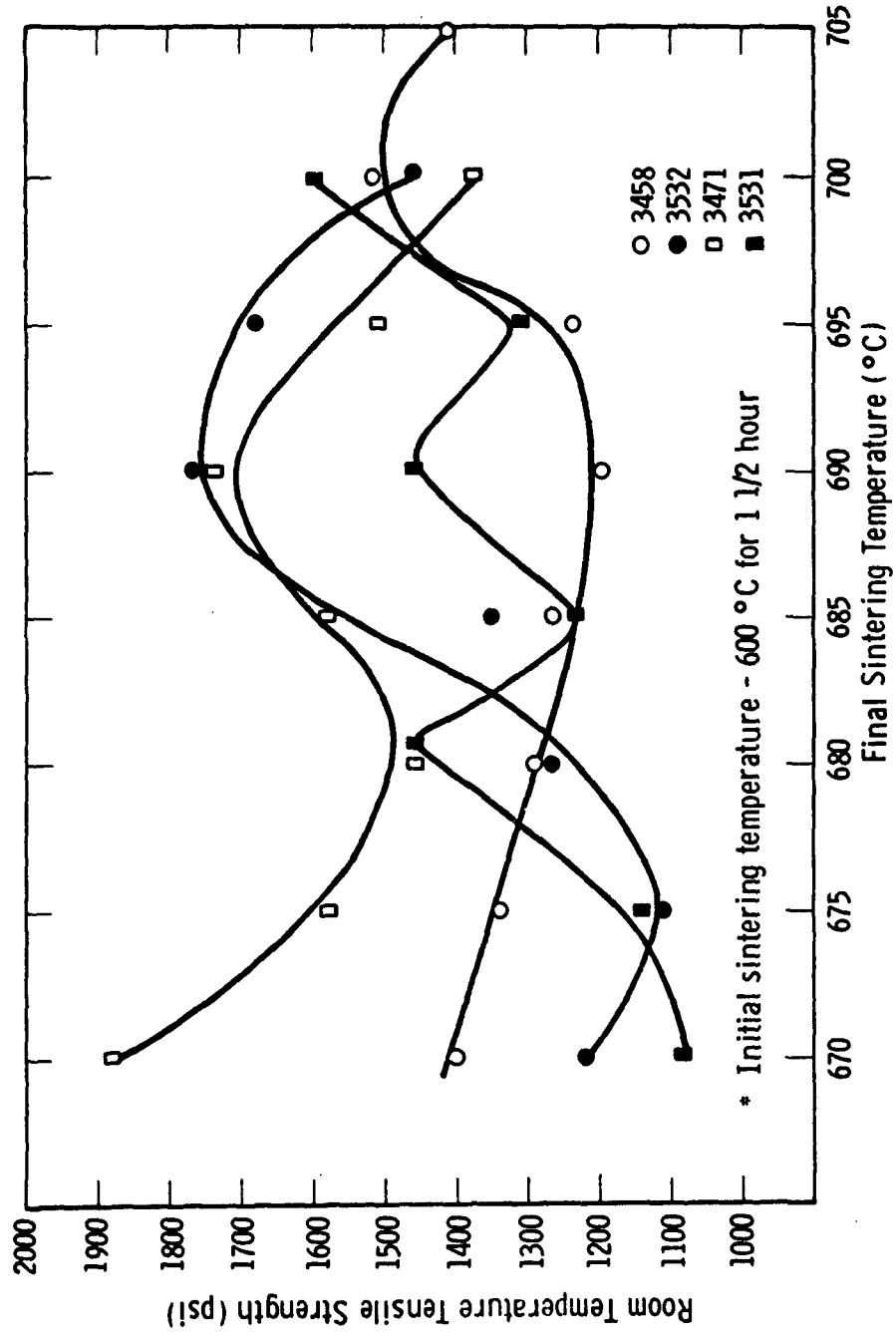
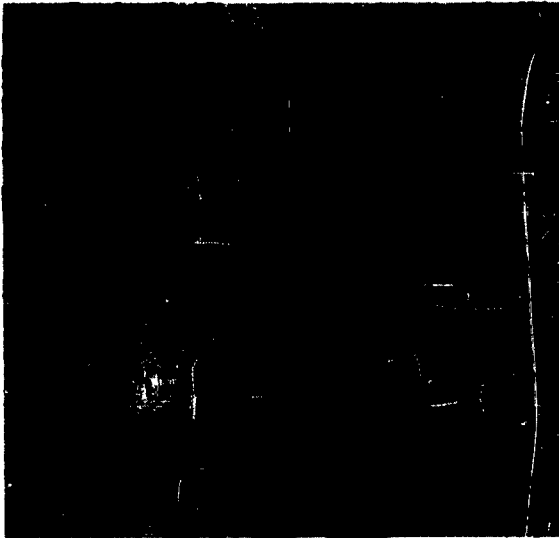
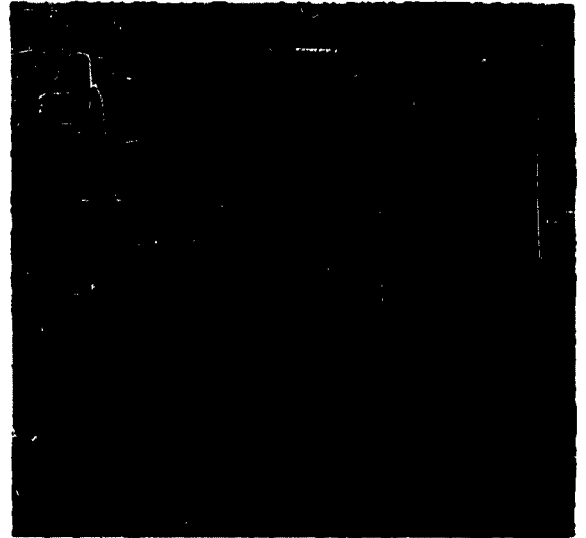


Fig. 8—Room temperature tensile strength versus final sintering temperature*

FIGURE 9



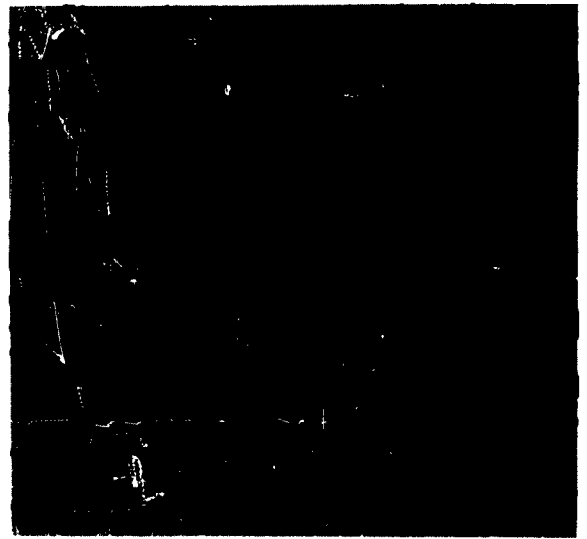
Neg. No. 62-281-8 As-Polished 100X
Final Sinter Temp. 670°C



Neg. No. 62-281-9 As-Polished 100X
Final Sinter Temp. 675°C



Neg. No. 62-281-10 As-Polished 100X
Final Sinter Temp. 680°C

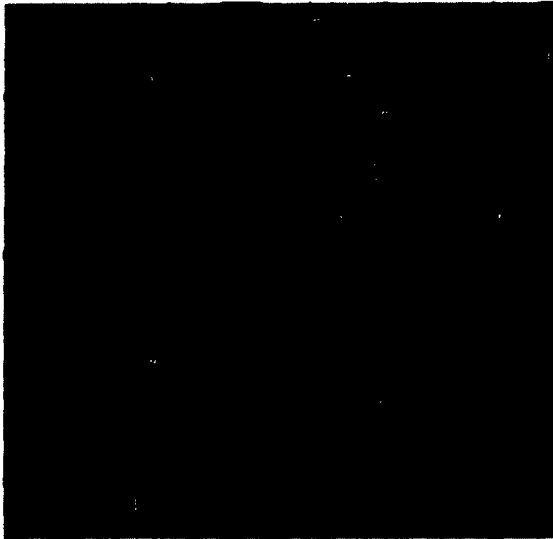


Neg. No. 62-281-11 As Polished 100X
Final Sinter Temp. 685°C

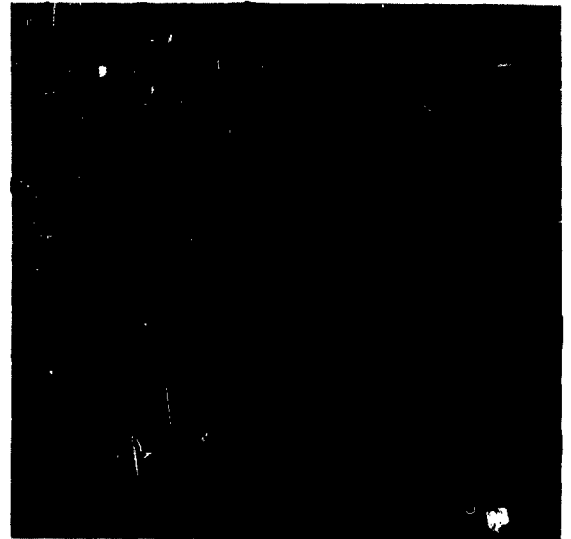
Typical Structure of Germanium-Bismuth-Telluride

Heat 3531 ($\text{Ge}_{0.93}\text{Bi}_{0.07}\text{Te}$)

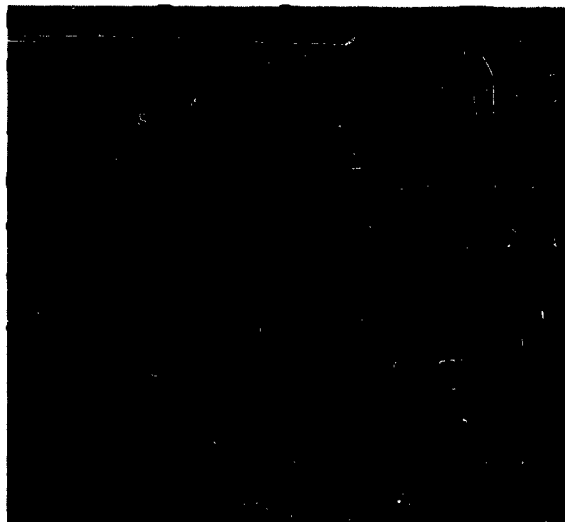
FIGURE 9 (cont)



Neg. No. 62-281-12 As-Polished 100X
Final Sinter Temp. 690°C



Neg. No. 52-281-13 As-Polished 100X
Final Sinter Temp. 695°C



Neg. No. 62-281-14 As-Polished 100X
Final Sinter Temp. 700°C

Sb-Bi-Te Power Generation Alloys

Life testing continues on couples and modules containing Sb-Bi-Te alloys as p-legs. Module X-12 (described in Quarterly Progress Report No. 2, August 1962) has now accumulated 6158 hours of operating time and 31 cycles, with a total degradation of 10% in power output.

An additional module of nine couples was constructed for an efficiency determination. The couples consisted of $1/4" \times 1/4" \times 1/4"$ pressed and annealed pellets of $\text{Sb}_{1.7}\text{Bi}_{0.3}\text{Te}$ and PbTe for the p and n-legs, respectively. Efficiencies, in terms of power out to heat in were determined for a variety of operating temperatures. The results are summarized in Figure 1. Each curve shows efficiency as a function of hot side temperature, measured at the hot straps, for a fixed cold side temperature, measured at the heat sink ends of the braids. The actual temperature gradient of the thermoelectric materials is somewhat less than that calculated from the measured hot and cold temperatures because of the thermal drop along the braids. An efficiency of nearly 7% is reached with cold side of 50°C and hot side of $375\text{-}400^{\circ}\text{C}$. The maximum power output for the nine couple module for the largest ΔT tested (50°C cold side, 425°C hot side) is 6.25 watts. This module has now been transferred from the efficiency checker to a standard life test station.

Life testing of Sb-Bi-Te alloys will be continued since preliminary analysis, based on efficiency, power output, and life indicated the possibility of designing both portable and remote power packs using this material.

CURVE 566052

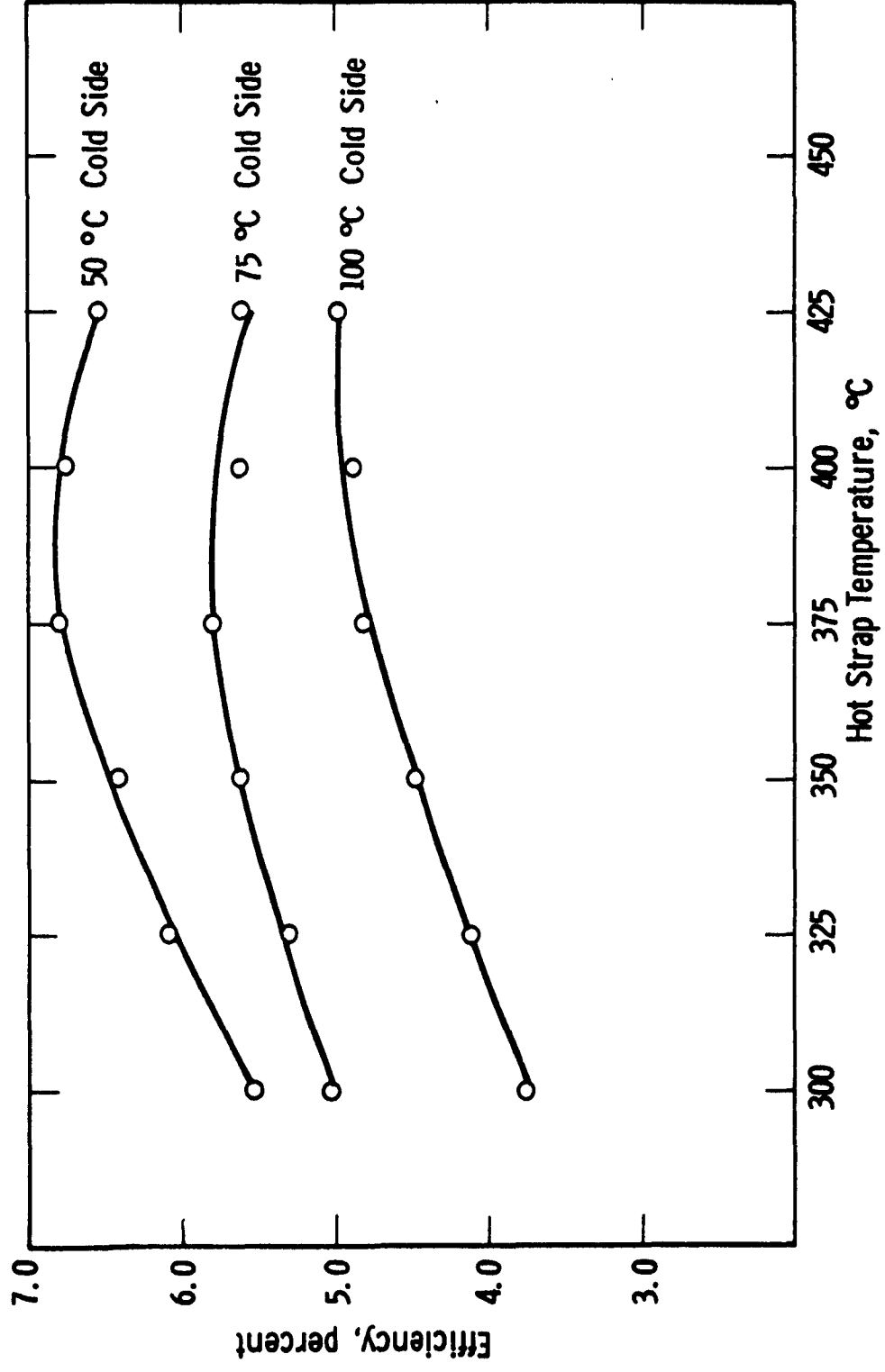


Fig. 1—Efficiency of 9 couple module of Sb-Bi-Te and PbTe couples

Cobalt-Antimony Alloys

Mechanical Properties

The mechanical properties were measured in tension and compression parallel to pressing. For the compression tests, most specimens were 1/2" diameter by 1/2" long, and two specimens were stacked for each elevated temperature test so that strains could be measured over a longer specimen. The compressive strain was measured over the 1" length with an SR-4 deflectometer so that the 0.2% yield could be computed. In some tests, two 1/2" diameter by 1" long specimens were stacked so that an SR-4 extensometer could be used to obtain a measure of the modulus of elasticity at the elevated temperatures. The extensometer measures the strain over a one-inch length, but a two-inch specimen is needed to accommodate the extensometer arms. At room temperature in those cases where the modulus of elasticity and Poisson's ratio were measured, SR-4 resistance gages were used. In these tests, only one 1/2" diameter by 1/2" long pellet was used for each test.

Two kinds of specimens were used for the tensile tests. At room temperature, 1/2" diameter by 1" long specimens were cemented to stainless steel adapters. At the elevated temperatures, the cements were not strong enough, so the specimen was redesigned as indicated in Figure 1. Split-nut adapters were designed to hold this specimen during testing. Attempts were made to use SR-4 resistance gages to measure the modulus of elasticity and Poisson's ratio at room temperature with the redesigned specimen. Because of the short gage length and small diameter, the gages could not be

fitted and bonded well enough to obtain accurate data. In the elevated temperature tests only the ultimate strength was measured. Because of the brittleness of the material, an extensometer could not be used for fear of breaking the specimens. The cemented specimens were large enough to mount strain gages on them so that the modulus of elasticity and Poisson's ratio were measured with them at room temperature.

All elevated temperature tests were conducted in a flooded argon gas atmosphere, and a resistance-type furnace was used to heat the specimens. The room temperature tests were conducted in air. In all tests, care was exercised to make certain that good axial alignment was obtained. The 50,000-lb Baldwin SR-4 FGT tensile machine and a 20,000-lb Wiedemann Mark B 20 tensile machine were used to apply the loads. The ultimate strength, 0.2% yield strength, the modulus of elasticity, and Poisson's ratio were measured.

The tension and compression data are presented in tabular form in Tables 1 and 2, and are plotted in Figures 2 and 3. The dimensions of tensile specimen are given in Figure 1.

The results show that the ultimate strength of CoSbTe in compression is about ten times as great as in tension. The spread in the tension and compression data is greater at room temperature than at the higher testing temperatures, being a minimum at the maximum testing temperature, 700°C. In tension and compression, the ultimate strength decreases much more rapidly from 250°C to 700°C than it does from room temperature to 250°C.

TABLE 1

**MECHANICAL PROPERTIES OF CoSbTe, HEATS #3435 AND 3262T
FROM ROOM TEMPERATURE TO 700°C IN COMPRESSION**

<u>Mark</u>	<u>Diameter</u>	<u>Test Temp. °C</u>	<u>Compression Strength</u>		<u>Modulus of Elasticity 10⁶ Psi</u>	<u>Poisson's Ratio</u>
			<u>Lbs.</u>	<u>Psi</u>		
3435-1	.505	250	8600	42950	*	*
-2	.504	"	5800	29050	*	*
-3	.504	"	7300	36600	*	*
-4	.505	500	2260	11300	*	*
-5	.507	"	2665	13200	*	*
-6	.505	"	2635	13150	*	*
-7	.504	700	380	1900	*	*
-8	.505	"	424	2100	*	*
-9	.505	"	281	1400	*	*
-10	.505	R.T.	6800	33950	+	+
-11	.505	"	2200	11000	+	+
-12	.505	"	5180	25850		
-13	.505	R.T.	7140	36650	2.5	.34
-14	.505	R.T.	9400	46950	2.0	.28
-15	.505	R.T.	5380	26850	2.7	+
-16	.505	R.T.	11000	54900	4.4	+
3262T-1	.505	200	1320	6600	7.6	*
-2	.505	400	2350	11750	7.5	*
-3	.505	600	2750	13750	4.1	*
-4	.505	R.T.	9880	49300	*	*
-5	.500	R.T.	8670	44150	+	+
-6	.500	R.T.	3200	16300	+	+

* This property was not measured.

+ The results obtained for this property are not accurate and are not reported.

- NOTE:
- 1) CoSbTe does not exhibit 0.2% yield in compression. The specimen always fails before 0.2% yield is reached.
 - 2) The modulus of elasticity for specimens 3262T-1, -2, & -3 were measured with SR-4 strain gages.
 - 3) An SR-4 extensometer was used to measure the modulus of elasticity of specimens 3262T-1, -2, & -3.
 - 4) Specimens of Heat 3435 were two pellets 1/2" diameter by 1/2" long stacked.
 - 5) Specimens of Heat 3263T were two pellets 1/2" diameter by 1" long stacked.

TABLE 2

**MECHANICAL PROPERTIES OF CoSbTe, HEAT #3435
FROM ROOM TEMPERATURE TO 700°C IN TENSION**

Mark	Diameter	Test Temp. °C	Ultimate Strength		Modulus of Elasticity	Poisson's Ratio
			Lbs.	Psi		
3435-1	.250	250	149	3050	*	*
-2	.250	"	126	2550	*	*
-3	.250	"	169	3450	*	*
-4	.250	500	57	1150	*	*
-5	.250	"	130	2650	*	*
-6	.250	"	98	2000	*	*
-7	.250	700	10	200	*	*
-8	.250	"	9	200	*	*
-9	.250	"	14	300	*	*
-10	.250	R.T.	138	2800	+	+
-11	.250	"	174	3550	+	+
-12	.250	"	126	2550	+	+
-13	.500	"	309	1550	10.3 x 10 ⁶	0.29
-14	.500	"	225	1150		0.29

* This property was not measured.

+ The results obtained for this property are not accurate and are not reported.

- NOTE: 1) CoSbTe does not exhibit 0.2% yield in tension. The specimen always failed before 0.2% yield was reached.
- 2) The modulus of elasticity and Poisson's ratio for specimens #13 and #14 were measured with SR-4 gages.
- 3) Specimens 1 to 12 are the redesigned type shown in Figure 1.
- 4) Specimens 13 and 14 were 1/2" diameter by 1" long cemented to stainless steel adapters.

DWG. 625A936

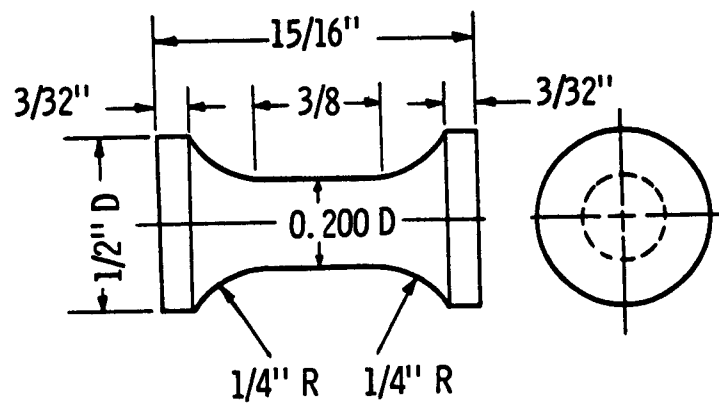


Fig. 1—CoSbTe tensile specimen

CURVE 566053

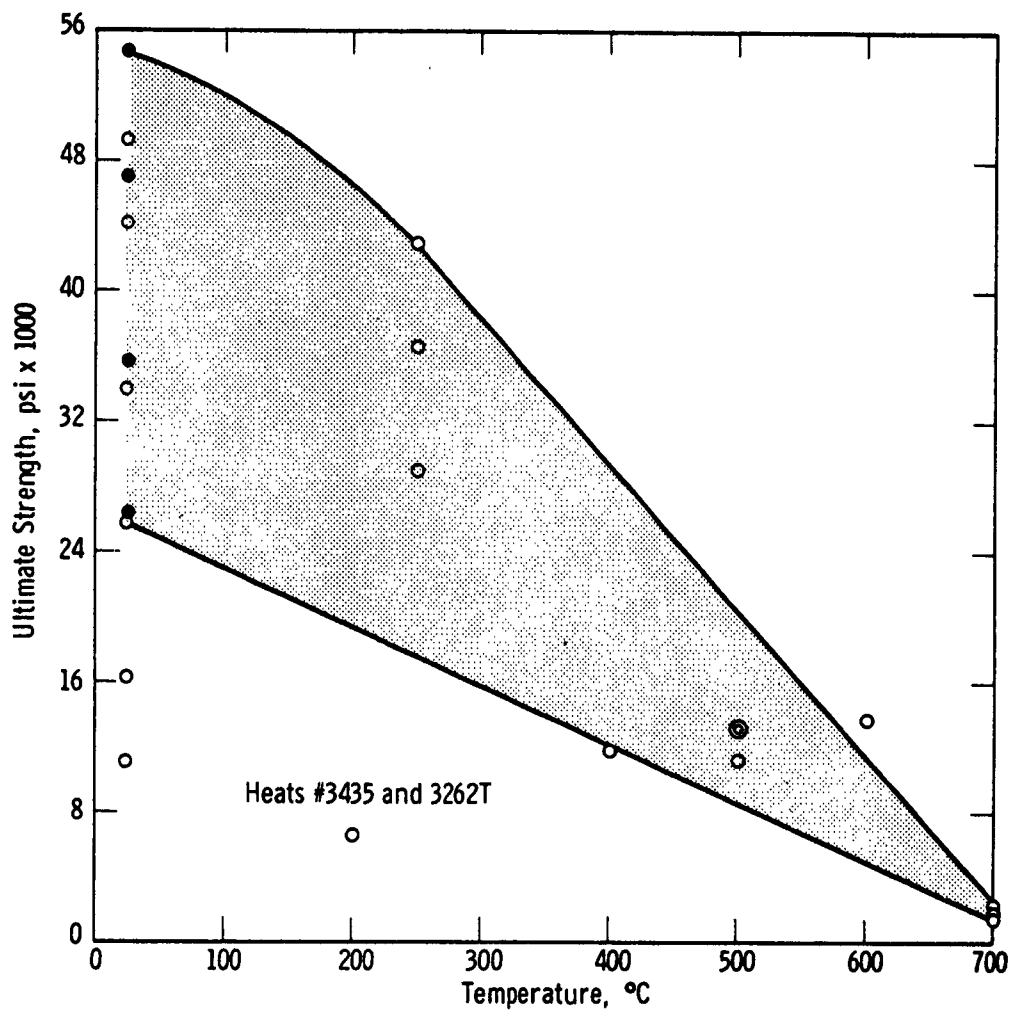


Fig. 2—Ultimate strength of CoSbTe from R. T. to 700 °C in compression

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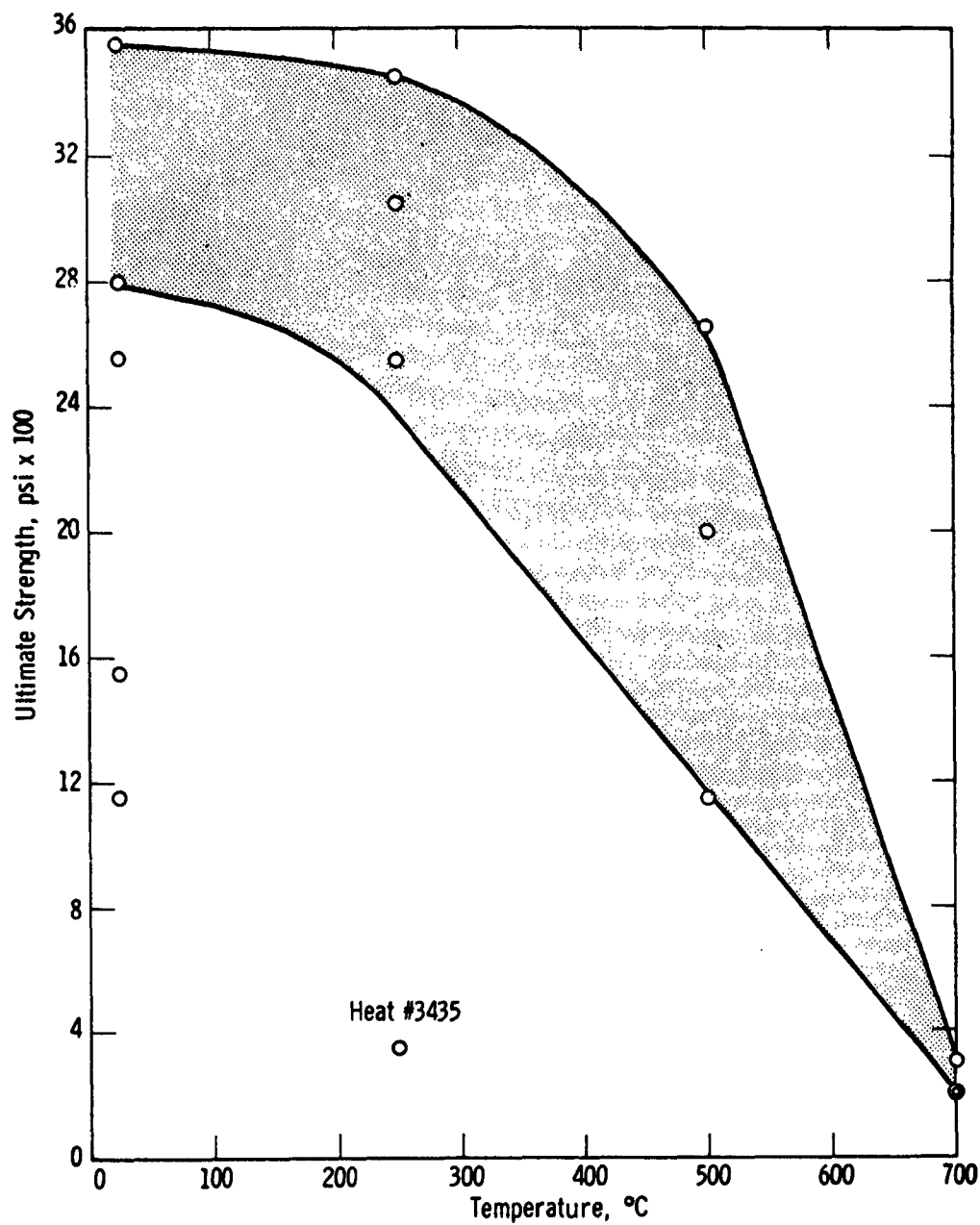


Fig. 3—Ultimate strength of CoSbTe from R. T. to 700 °C in tension

Exposure Tests

To evaluate the stability of the Co-Sb alloys, exposure tests are being run at 550°C and 700°C in various environments. Some data has been obtained for short time tests (100 hour) and the 1000 hour tests are in progress. The following graphs show the results on two properties: Seebeck and resistivity, and weight change. At 500°C, the thermoelectric properties are relatively constant for the short time tests, but show erratic behavior at 700°C in air and vacuum. As would be expected, there is a weight increase for samples exposed in air as a result of oxidation, whereas samples heated in vacuum or argon show a weight loss resulting from vaporization. The weight losses are very small relative to the weight gains. At 550°C, oxidation appears to follow parabolic law, possibly indicating the formation of a protective oxide layer. However, the probability of using the material in air at 550°C for extended times is low because a non-oxidizing contact would have to be found.

"p" Type Alloy Development

The $\text{CoSb}_{3-x}\text{Sn}_x$ and $\text{Co}_{1-x}\text{Fe}_x\text{Sb}_3$ systems are currently under investigation. It is known from previous work that Sn and Fe are "p" type dopants if oxygen is excluded during processing. Data is presented in Table 1 on a series of doped CoSb_3 alloys prepared by melting the elements together in evacuated Vycor tubes at approximately 1200°C. The melting stock had been deoxidized prior to use by a hydrogen reduction and vacuum degassing treatment. After melting the ingots were aged for 22 hours at

700°C, then sectioned for testing.

As can be seen from the data in Table 1, the thermal and electrical properties have not yet been optimized. Since the CoSb_3 compound has been produced by the Battelle Laboratories with a room temperature Seebeck coefficient of $+400 \mu\text{V}/^\circ\text{C}$, our alloys have the appearance of being over-doped. Spectrographic analysis of the melting stock revealed that certain impurities in the Sb, such as Fe, could be responsible for this condition. The concentration of Fe as an impurity ranged from 100 to 1000 ppm, whereas the concentration of Fe used as a dopant in the $\text{Co}_{.9975}\text{Fe}_{.0025}\text{Sb}_3$ composition is only 340 ppm. A different grade of Sb in which the concentration of the major impurity is 3 ppm has been obtained and will be used in all future experiments.

TABLE 1

Alloy No.	Formula	Room Temperature			$\Delta T: 550-150^{\circ}\text{C}$	
		$\alpha (\mu\text{V}/^{\circ}\text{C})$	$\rho \times 10^3 (\Omega\text{-cm})$	$\frac{\text{Watts}}{\text{K cm}^{\circ}\text{C}}$	$\bar{\alpha} (\mu\text{V}/^{\circ}\text{C})$	$\bar{\rho} \times 10^3 (\Omega\text{-cm})$
400-1	CoSb ₃	+98	4.65	0.0436	+143	7.69
419-1	CoSb _{2.9975} Sn _{.0025}	+22	0.76	0.0599	+67	2.17
419-3	CoSb _{2.9925} Sn _{.0075}	+21	0.67		+80	2.18
419-6	CoSb _{2.96} Sn _{.04}	+7	0.79	0.0345	+69	2.06
419-7	CoSb _{2.8} Sn _{.2}	+4	0.82			
419-8	Co _{.9975} Fe _{.0025} Sb ₃	+11	0.67	0.0528	+86	2.13
419-11	Co _{.96} Fe _{.04} Sb ₃	+30	0.95		+107	1.91
419-12	Co _{.93} Fe _{.07} Sb ₃	+29	1.29	0.0440	+110	2.19
419-13	Co _{.9} Fe _{.1} Sb ₃	+25	1.44	0.0410	+101	2.32

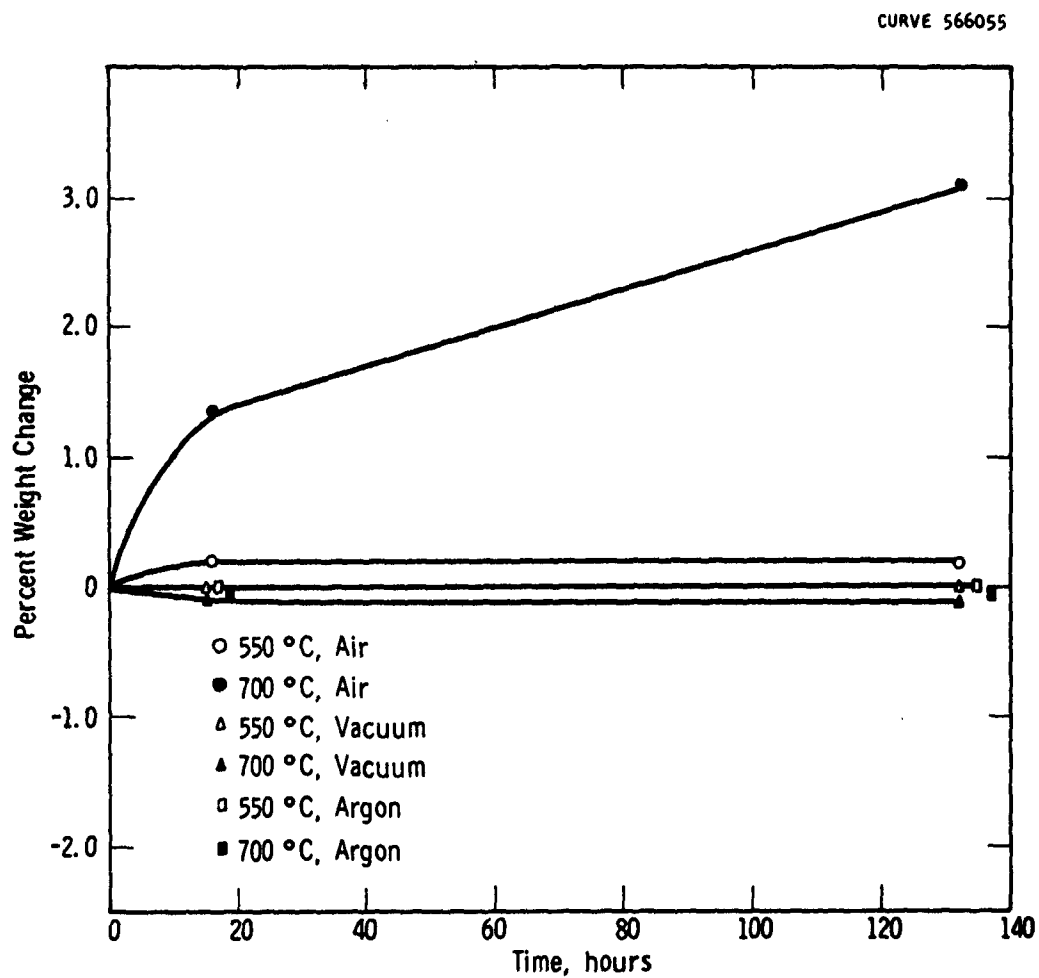


Fig. 4—Weight change of $\text{CoSb}_{2.6}\text{Te}_{.1}\text{Se}_{.3}$ in various environments

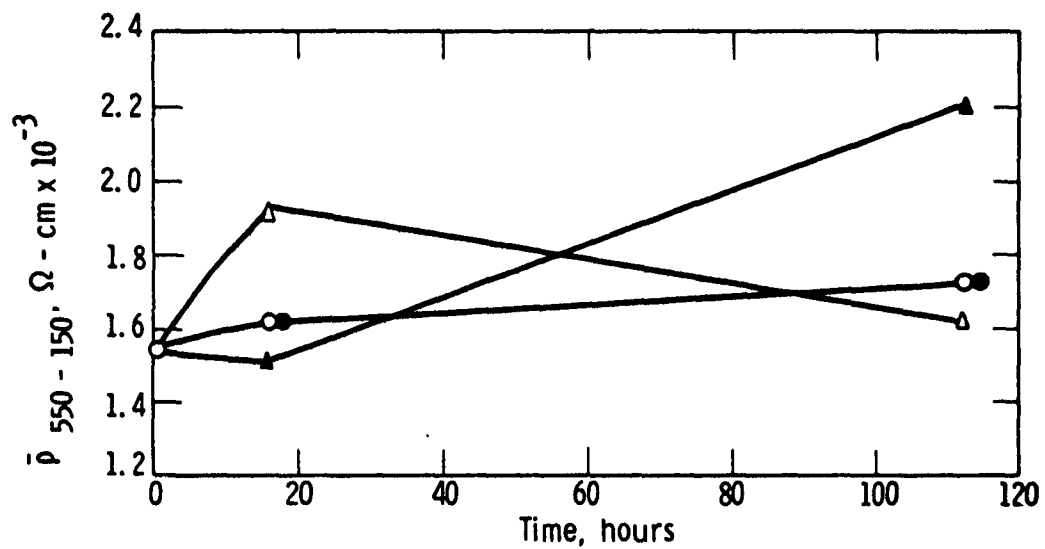
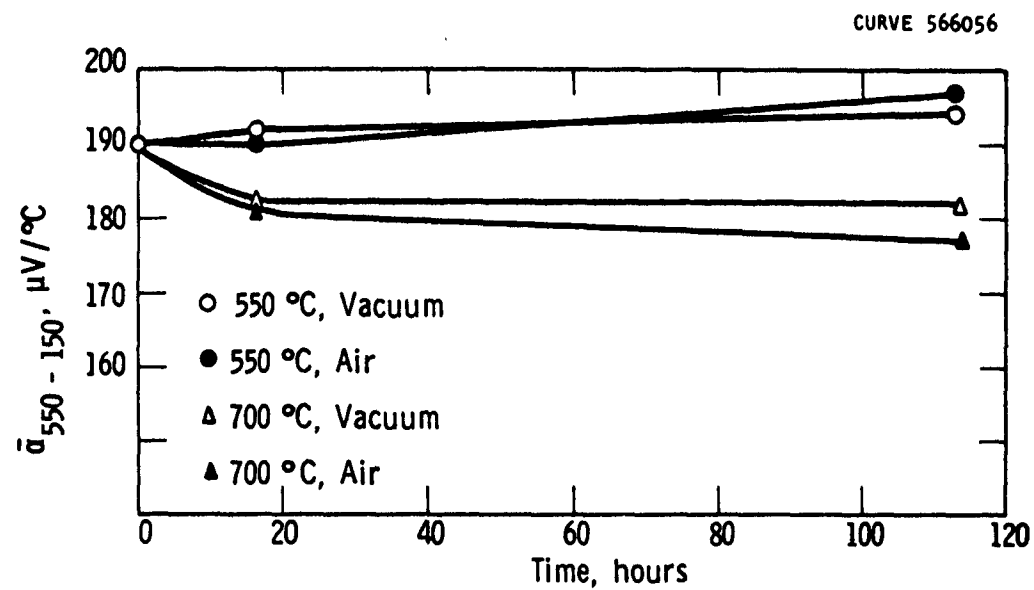


Fig. 5—Change in properties of $\text{CoSb}_{2.6}\text{Te}_{.1}\text{Se}_{.3}$ with time at temperature

Gas Pressure Sintering and Bonding

Introduction

A basic limitation to successful thermoelectric generator application has been the insufficient life obtained when designing to the required application specifications with the thermoelectric properties and temperature limitations of presently available materials. This is true with both basic types of terrestrial generators: the high-power density, highly cycled portable generators which have a life requirement in excess of 1000 hours, and the stationary generators of a relatively higher efficiency and much lower cycling rate which have a life requirement in excess of 10,000 hours. In the high power density generator the major problems result from mechanical failure of the thermoelements caused by the necessarily high mechanical and thermal stresses this type of design incurs. In the other type of generator the problem is basically one of thermal and chemical stability of the thermoelements and their contacts. Suffice it to say, then, that if stronger, more homogeneous thermoelectric material could be processed, and lower stresses obtained by better thermal match and reduction of physical constraints, a solution to the one generator problem would be nearly obtained. Similarly the determination of more compatible contact materials and better encapsulation would bring the problems of the other generator much closer to solution. Partial results from one approach, that of gas pressure sintering and bonding, are described in the sections that follow.

Stresses

The stresses involved may be somewhat arbitrarily divided into three basic areas:

1. Shear Stress

Cause - Induced by mismatch between thermal expansion of pellet materials and straps. This stress may be further increased by the presence of brazing alloy or diffusion barrier layers.

Methods of Reducing Stress - Use of more closely matched strap alloys, joint forming at lower temperature to reduce magnitude of mismatch, use of pressure, liquid or sliding contacts, or reduction of barrier layer thickness.

2. Doming Stress

Cause - Temperature gradient across pellet causes diameter of one end of the pellet to expand more than the other with consequent flexure of pellet.

Methods of Reducing Stress - Use of pressure, liquid, or sliding contacts, use of thin flexible straps, multiplicity of thermal elements with higher length to diameter ratios.

3. Externally Induced Stress

Cause - Pressure loading of pellets to obtain necessary heat transfer and/or low electrical contact resistance.

Solution - Use of liquid, or better pressure contacts and refined mechanical designs to reduce moments on pellets.

Another factor which would reduce the stress problem would be an improvement in the mechanical strength and homogeneity of the pellets.

Several possibilities suggest themselves in this respect:

- a) determination of optimum particle size and distribution
- b) improved sintering schedules and atmospheres
- c) improved pressing techniques including hot pressing and isostatic forming
- d) inclusion of reinforcing fibers and crack stoppers
- e) alloy strengthening

Some or all of the resulting improvements in mechanical properties obtained using the above techniques may reduce the figure of merit of the thermoelectric materials. However, degradation of 10 to 20 percent would be tolerable if sufficiently greater strengths or improved homogeneity could be obtained.

Reduction of Shear Stresses

In the past, joining alloys, powder layers, and strap materials used in contacting the thermoelements were picked on the basis of chemical compatibility and joinability. As a consequence, with some combinations, severe shear stresses were introduced into the contact region.

Attempts to obtain compatible joining materials with better matched thermal expansion coefficients have not been successful to date. Attempts

at reducing the thickness of the barrier layers by plating or plasma spraying have not been successful because of poor adherence or porosity which permits penetration by liquid brazing alloys. Hot working of such layers has shown promise and this technique is presently being investigated.

Two techniques are being employed. One involves the use of thin layers of metallic powders which are chemically compatible with the thermoelements and which have characteristics that permit their sintering under the pressures (up to 10,000 psi) and temperatures (up to 700°C) used to hot work the thermoelectric materials. However, this approach does not eliminate possible porosity or thermal mismatch problems completely even though very dense and thin layers have been obtained and the use of pressure, spongy metal, or liquid contacts in conjunction with these layers appears feasible.

The other basic technique is the use of plasma coated foils. In this approach a thin, rough layer of compatible metal is sprayed onto a thin (.003" to .005") foil which matches the thermoelement in expansion. The plasma coated foil is then hot worked onto the end of the thermoelement to obtain an intimate mechanical bond. Porosity of the plasma layer still presents a problem since the foil materials in general are not compatible with the thermoelectric materials. However, thin plated layers of compatible materials may be used between the plasma and foil to obtain a barrier layer without appreciably affecting the expansion match of the foil. Good bond adherence and low contact resistance can be obtained with this technique.

Presently plasma-foil combinations are being made and evaluated by

metallography, resistance measurements, and thermal cycling tests, and efforts are being made to improve plasma-spraying techniques and also to obtain better diffusion barriers on the foils.

Doming Stress

The doming stresses are determined by the length to diameter ratio, thermal gradient, thermal expansion coefficient of the thermoelectric material, and the extent to which the pellet is constrained from assuming its natural shape.

The major reduction in this stress for a given geometry may be obtained by the use of thin wafer or foil contacts which are sufficiently flexible to follow the domed contour of the pellet. Use of liquid or pressure contacts with the thin foils or powder wafers permits such deflections without inducing high stress. Noble metal pressure contacts and liquid contacts are consequently being investigated and are proving to be quite acceptable in terms of contact resistance.

Mechanical Strength

It is obvious that improved mechanical strength of thermoelectric pellets would simplify the stress problems. Since examination of failures has shown that pellets have often cracked at locations other than the highest stress point, and since a reasonably high percentage of units from a particular run perform without cracking, it is felt that greater homogeneity and uniformity might provide a partial solution to the problem. As a consequence, a review and investigation of powder processing from the ingot

material through the sintering operation is being carried out.

Among the variables being considered are crushing technique (and thus particle shape) and particle size and distribution. Although somewhat higher strengths have been obtained by some of these variations than with the previous standard, some lack of uniformity remains. This non-uniformity stems partially from die friction and the consequent density variations. In an attempt to reduce this factor and improve homogeneity, isostatic pressing, and hot working are both being investigated. The latter is being carried out in conjunction with the foil contact work described previously. At present, hot working of this type has shown definite improvement in ultimate mechanical strength but improvement is still needed in homogeneity.

The use of fiber reinforcing is also being investigated. As in the case of the foil contact, a problem exists in that the metals which match the coefficient of expansion of the thermoelectric materials are reactive with them. In addition these metals (Cu, Ag, Al, etc.) have lower moduli than desired. Consequently, the majority of this work is being done with materials having a lower expansion coefficient than desired. However, this may not be as serious a problem as it first appears, since successful work has been done with ceramics and metal fibers in which the thermal expansion mis-match was in this direction. If proper fiber mixing techniques can be developed and some further promise is shown on tested samples, this work will be extended to include coated wire fibers having a compatible material jacket and matched thermal expansion.

Metallic encapsulation, in which the pellet is contained in a thin metallic sheath is also being investigated. Early work indicated that,

from the encapsulation point of view, this was a very promising approach, but very little mechanical improvement was obtained. Assembly and cost of material were prohibitively high in the early designs. A new technique is presently being tried in conjunction with the hot working which, if successful, should circumvent these objections.

In the sections that follow, three gas pressure cycles are described. These experiments were designed to investigate the variables that have been discussed.

Cycle 'A'

Cycle 'A' was the initial experiment on the gas pressure forming thermoelectric pellets inside a hermetically sealed container. In this cycle one pressure and two temperatures were investigated: 10,000 psi at 600°C and 650°C. In addition, two clean-up procedures were tested. The experiment involved 12 tube assemblies each containing 10 pellets, 1/2 inch diameter by 1/2 inch in length.

I - Tube Preparation

Six of the tube assemblies were evacuated at room temperature to approximately 17 microns of mercury pressure and then heated in a furnace. During heating, the tubes were alternately evacuated and purged with an argon-hydrogen mixture (95% argon - 5% hydrogen) until a temperature of 400°C was reached. The tubes were then purged with the inert gas mixture for approximately 24 hours at 400°C. At this point, the tubes were allowed to cool to room temperature, while continuing the purge. After cooling, the tubes were evacuated to approximately 1 micron of mercury pressure and sealed off under vacuum. Throughout the entire purge cycle, the dew point of the exhaust gas was checked to determine the amount of water vapor being removed from the samples and assembly.

As a comparison check of clean-up procedure, the six remaining tubes were not evacuated. These tubes were flushed with the argon-hydrogen mixture and heated to approximately 450°C. Each tube was provided with an exhaust port so that the flow could be regulated. The tubes were allowed

to cool to room temperature still under flushing conditions and were then sealed off with a positive pressure of argon-hydrogen gas. The dew point was also checked in this clean-up procedure.

The samples to be tested were arranged in the 12 tubes so as to have duplication in the two different test environments. An additional parameter was introduced in this test, that of sleeve material. Three tubes incorporated boron nitride sleeves, four tubes had low density, low compressive strength graphite sleeves, and five tubes had average density and strength graphite sleeves. Again, these fillers or sleeve materials were so placed as to have duplication and cross checks on their effect on the various thermoelectric materials in both the vacuum and inert gas environments as well as the two temperature conditions.

II. Temperature - Pressure Cycle in Autoclave

Due to the fact that this test was the first attempt to sinter and contact the thermoelectric material in one operation, no previous knowledge was available on the correct or most advisable temperature-pressure combination in the autoclave furnace. Based on limited material strength and chemical compatibility data at various temperatures, and on past work in hot pressing plain pellets, it was decided to try two temperatures at one pressure. The tubes containing GeBiTe were run at 600°C and 10,000 psi external pressure. The PbTe tubes were run at 650°C and 10,000 psi. With the various pressure drops across the stainless steel clad and filler sleeves, this resulted in approximately 7500 psi radial pressure on the thermoelectric material.

It was also decided that the pressure and temperature would be increased simultaneously so that maximum temperature would be reached at the same time as maximum pressure. The samples were held at temperature and pressure for two hours after which the pressure and temperature were reduced, again simultaneously. The samples were then pressure checked for any leaks that might have occurred during the pressure sintering process.

III. Contact Material Investigated

1. GeBiTe

Based on previous compatibility tests and on desired combinations determined from stress considerations, both plasma sprayed foils (thin-metal discs) and pre-formed powder wafers were included as contact possibilities. The contacts investigated on GeBiTe were:

- (a) Tungsten foil
- (b) Armco iron foil and powder wafer
- (c) Tungsten plasma spray on 302 stainless steel foil
- (d) Nickle-phosphorous plasma spray on 302 stainless steel foil
- (e) Nickle-phosphorous pressed caps
- (f) Cobalt pressed caps
- (g) Type 430 stainless steel cups and sleeves

2. The contacts investigated for PbTe were:

- (a) Type 302 stainless steel foil
- (b) Armco iron foil
- (c) Iron powder wafer
- (d) Nickle-phosphorous wafer

- (e) Iron plasma spray on 302 stainless steel foil
- (f) Nickle-phosphorous spray on 302 stainless steel foil
- (g) Type 304 stainless steel cups and sleeves

IV. Results

In general, radial distortion of both the stainless steel cladding and thermoelectric pellets was excessive in all the tubes containing graphite sleeves. The low density graphite sleeves experienced the most distortion. The tubes containing boron-nitride sleeves showed the least distortion. Examination of the tubes also indicated that the greatest distortion occurred where GeBiTe was located in conjunction with graphite sleeves, although some radial distortion in boron-nitride was evident (concave at center).

The distortion occurred as a local collapsing (buckling) of the stainless steel clad with resultant distortion of the thermoelectric sample ranging in form from oval-shaped pellets to tear-drop shaped in the more excessive cases.

The PbTe samples showed less distortion in the graphite sleeves and relatively no distortion in the boron-nitride sleeves. In all cases, this distortion had a concave (hour-glass) shape, located very nearly at the center of the pellet.

Examination of metallographic samples of various pellets indicated that many of the plasma sprayed foils did not bond, although in some cases the plasma did not adhere to the base foil but did bond to the thermoelectric material. The pressed iron cap on PbTe looked very good as did

the nickel-phosphorous contact on GeBiTe. The plain foils did not adhere where no reaction was present. It should be noted that the lack of contact bonding may have been influenced by the great distortion of the pellet.

Cracking of the thermoelectric pellets was evident in many cases where distortion was great and where obvious expansion differences (contact to thermoelectric material) were involved. However, there were cases of cracking which could not be explained as readily. For example, some highly distorted pellets showed no cracking where pellets with relatively no distortion had many cracks.

In general, thermoelectric property tests showed that the Seebeck coefficient was increased and resistivity was decreased in gas pressure sintering. Also room temperature tensile strength was nearly doubled. These tests were made on samples that were not greatly distorted.

V. Conclusions

The results of Cycle 'A' were generally very encouraging, with the primary question of feasibility being answered. Mechanical properties as well as thermoelectric properties were improved by gas pressure sintering. Evaluation of the results of both macroscopic and microscopic examinations pointed out many areas of further study and development to be investigated in future test cycles. An attempt to improve the integrity of plasma sprayed layers on contact foils was definitely indicated as a major work area. Better expansion matching of contact material to thermoelectric material was also an important factor to be considered.

Since distortion of both the stainless steel clad and the thermoelectric pellets was a very important problem in this cycle, it was concluded that both filler sleeve density and pellet density were very important factors in deciding whether or not distortion would be excessive. Measurements indicated that the density of both the GeBiTe and PbTe were increased to very nearly 100 percent. This change in dimension must be taken up in the outer clad and filler sleeves. For this reason, higher compressive strength, higher density graphite sleeves were planned for Cycle 'B'. The boron-nitride sleeve material was eliminated since it had little or no strength at forming temperature and could be replaced by a high strength graphite material. In addition to sleeve material changes, it was concluded that the temperature-pressure cycle in the autoclave furnace would be changed to allow the tubes to reach working temperature before they were subjected to pressure. This was based on the theory that the material would be more plastic and therefore might pressure form more uniformly without cracking.

CYCLE 'B'

A second cycle of the series of gas pressure bonding tests was planned using the information obtained in Cycle 'A'. Both green and pre-sintered samples of "n" PbTe and "p" PbTe as well as green and pre-sintered samples of GeBiTe were included in this cycle. It was felt that the sintered samples being more dense would reduce the amount of distortion due to densification. In addition to changes in sample preparation, three grades of graphite sleeves were tested. These grades ranged from low density, low compressive strength material to high density, high strength graphite

similar to die material. The samples were arranged to compare and cross-check the effects of pre-sintering and sleeve density and strength. Twelve tubes, each containing 10 sample pellets, were included in this cycle.

I. Tube Preparation:

Six of the twelve tubes were evacuated to approximately eight microns of mercury pressure at 120°C, then heated to 600°C while under vacuum and allowed to heat soak for approximately 40 hours. The tubes were then allowed to cool and were sealed off under a vacuum of 3 microns.

The remaining six tubes were evacuated to less than one micron of Hg pressure at 150°C. In contrast to the previous samples, these tubes were heated to slightly less than 450°C under vacuum and heat soaked for 40 hours at three microns of mercury pressure. The tubes were then cooled and sealed.

II. Temperature-Pressure Cycle in Autoclave

The plan for the cycle was as follows: The tube assemblies would be heated to 650°C at 300 psi pressure. After heating the pressure would be increased to 10,000 psi. The samples would then be held at 650°C and 10,000 psi for two hours. At this point, the pressure would be released but the temperature maintained at the 650°C level. When the pressure had been reduced to 1000 psi, the samples would be allowed to cool to room temperature. The cooling time would be twelve hours. Overall, the samples would be held at 650°C for six and one-half hours and under full pressure for two hours of this time.

It was felt that many of the cracks occurring in Cycle 'A' were due

to brittle fracture since the pressure was applied while the samples were in a brittle state. At 650°C, experimental test data has shown that the thermoelectric material is plastic and, therefore, should flow without cracking. Also, the stainless steel clad would have a lower yield point and tend to flow more uniformly. It was realized that chemical reaction might be more of a problem in this cycle since the samples and contacts were at a high temperature for a longer period of time.

III. Contact Material Investigated

1. GeBiTe

Efforts in improving plasma sprayed contact material on a variety of foils was still under intensive investigation at the time of this cycle and, therefore, the contacts were mostly limited to powder wafers. Only two plasma contacts, both on 430 stainless steel clad copper, were tested. These contacts were:

- (a) Nickel-phosphorous wafer
- (b) Nickel-phosphorous pre-pressed caps
- (c) Nickel-phosphorous plasma spray on 430 stainless clad copper foil
- (d) Tungsten plasma on 430 stainless clad copper foil
- (e) Ultrasonic tin contact

2. The following contact materials were tested for "p" and "n" type PbTe:

- (a) Nickel-phosphorous pressed cap
- (b) Nickel-phosphorous wafer

- (c) Iron wafer
- (d) Nickel foil
- (e) Cobalt pressed caps
- (f) Nickel-phosphorous plasma spray on 304 stainless steel foil
- (g) Tungsten plasma spray on 304 stainless steel foil

IV. Results

Contrary to original thinking, distortion was extreme, particularly in the case of GeBiTe. The PbTe samples again exhibited the least distortion with the pre-sintered pellets showing less than the green samples.

The tube assemblies that combined low density, low strength graphite with GeBiTe samples were so badly distorted that acceptable samples for metallographic studies and property tests were difficult to find. However, samples of all materials and sleeve combinations were obtained. The distortion referred to in this cycle can best be described as a tear-drop shape caused by local collapse of the stainless steel clad and graphite sleeves.

Metallographic examination indicated that the nickel-phosphorous and cobalt contacts were compatible and bonded very well with both the "p" and "n" type PbTe. The nickel-phosphorous plasma spray on 304 stainless clad copper also appeared compatible and metallurgically sound. Although many of the PbTe samples were badly distorted, no excessive cracking was observed. Some obvious expansion mis-match cracks were observed but these could be explained from thermal stress considerations.

Nickel-phosphorous and cobalt contacts were also favorable with GeBiTe although to a lesser degree. Definite reaction did take place with the nickel-phosphorous but the reaction did not appear detrimental to either thermoelectric properties or pellet resistance. Cobalt, on the other hand, reacted to a much greater degree, but the bond was primarily mechanical.

It was observed that violent reaction took place between the GeBiTe and the nickel-phosphorous plasma sprayed 430 stainless clad copper. Further examination indicated that this reaction was mainly with the copper itself and not the stainless.

V. Conclusions

The main conclusion drawn from this cycle was that pre-heating the tube assembly before application of pressure does not eliminate radial distortion but in fact increases the chance of clad buckling. Since the thermoelectric materials have little or no strength at the high temperature, the clad loses all of its back up support. In addition, initial machining stresses and eccentricities magnify the problem. The result was collapse of the stainless steel clad with the resultant distortion of the thermoelectric pellets.

This leads to the conclusion that pre-pressurizing at room temperature will allow the clad to yield and absorb all of the assembly clearances but still be backed up by the thermoelectric pellets. Considering the pressure drops across the clad and graphite sleeves, the pressure on the pellets would still be less than the compressive strength of the weakest material and, therefore, no initial cracking of the pellets should occur. There is a chance, however, due to local conditions that the thermoelectric pellet

may be fractured by an uneven pressure distribution. For this reason, a preliminary test of six tubes containing all three thermoelectric materials and three different sleeve materials was planned. The "cold forming" experiment will be discussed in Cycle 'C'.

Another important conclusion drawn from this test is that the thermoelectric materials, both GeBiTe and PbTe, can be hot worked and that they both exhibit limited plastic flow. This conclusion is based on metallographic examination of samples that were extremely distorted and obviously extruded and formed but were not cracked or fractured as might be expected under such conditions.

Cycle 'C'

Six tube assemblies were prepared to determine the effect of "cold forming" the clad-sleeve assembly. The pressure was set at 20,000 psi to exaggerate the effect of pressure on the thermoelectric pellet samples. Five of the six samples incorporated a relatively high density, high strength graphite sleeve (National Carbon Type AUC). The remaining tube contained a very high strength, high density graphite. (Speer Carbon Co. 580 graphite).

I. Tube Preparation

The six tubes were alternately evacuated and inert gas purged at 450°C for approximately 96 hours and were then purged while being cooled to room temperature. Finally, the assemblies were evacuated to less than 1 micron of mercury pressure at which point they were sealed.

This preliminary test was made in an isostatic pressure vessel at room

temperature. At 20,000 psi external pressure, the thermoelectric pellets would experience approximately 15,000 psi pressure. Although this pressure is above the compressive strength of either the GeBiTe or PbTe pellets, it is below the cold pressing pressure of 60,000 psi commonly used for compacting pellets. It was thought here that the sleeve-clad environment would approach the constraint of the die once the clad and sleeve were cold formed against the pellet.

A variety of contact wafers and foils were included in the cold forming test to simulate actual cycle conditions.

II. Results

As expected, the clad and sleeve did "cold form" evenly and without distortion. On the average, there was a decrease in diameter of .025 inches for both the GeBiTe and PbTe tubes having AUC graphite as the sleeve material, and the tube containing 580 graphite experienced a dimetrical decrease of .014 inches. Since the total assembly clearances were .010 inches maximum, an apparent densification did take place.

Upon examination of the tubes and samples, it was found that the GeBiTe or PbTe pellets had not densified to any measurable extent. The graphite on the other hand did densify 7-10% which was very much contrary to available data on graphite. Also, neither GeBiTe or PbTe (n) showed any excessive cracking or distortion when examined microscopically. PbTe (p) did show an excessive amount of cracking regardless of sleeve material.

Based on this test, six additional tubes were assembled, all tubes having AUC graphite as sleeve material. Two contact materials were investi-

gated, namely cobalt and nickel-phosphorous wafers and pre-pressed powder caps.

In addition to the six sample tubes, four tubes of the previous high pressure test were included to check the effect of overpressurizing and to determine if any cracks might re-bond during the gas pressure sintering cycle.

A further extension of gas pressure sintering thermoelectric pellets in a sealed tube was also investigated in Cycle 'C'. This consisted of pressure forming in a larger container (cylinder) using graphite disks machined with concentric holes to accept the pellet samples. The ultimate goal of gas pressure sintering was to use this type of geometry which could be produced cheaply and in large quantities. The graphite disks would act as a die, in effect, and the pellet would essentially be hot pressed from the ends. This initial test was designed to determine the compressibility of various graphite materials and to test the mechanical stability of the assembly. The container was simply a thin walled stainless steel cylinder welded to two thick end plates which were provided with evacuation tubulation. This assembly is referred to as a "Stack" in subsequent discussion.

Ia. Tube Preparation

The six additional tubes and the stack assembly were evacuated at room temperature to approximately 5 microns of mercury pressure. They were then placed in a furnace preheated to 150°C and allowed to reach steady state temperature. A constant vacuum was maintained for three hours. The temper-

ature was then increased to 450°C and the tube assemblies alternately purged with argon and evacuated for 10 hours. After cool down, the tubes were evacuated to less than 1 micron of mercury pressure at room temperature and sealed.

IIa. Temperature-Pressure Cycle in Autoclave

In accordance with the previous cold forming test, the sample tubes and the stack were pre-pressurized to 10,000 psi at room temperature. The temperature was then increased to 650°C with the pressure being maintained at 10,000 psi. The samples were held at temperature for 2 hours and then allowed to cool with the pressure maintained. During cool down, the pressure dropped to 7,000 psi due to the change in volume of the gas in the autoclave furnace.

IIIa. Results

The results were very encouraging. Distortion was at a minimum and all tubes showed uniform and symmetrical pressure forming. Metallographic examination of samples of GeBiTe and PbTe (n) and (p) did, however, indicate some cracking of the pellets. In general both the cobalt and nickel-phosphorous contacts were very satisfactory on both "p" and "n" type PbTe from a mechanical bond standpoint. The cobalt appeared to be more compatible with the "p" type PbTe than did the nickel-phosphorous. The cracks present in "n" type PbTe were axial fractures propagating from the contact interface at the center of the pellet. These cracks indicate expansion mis-match with the contact material having the lower expansion.

The "p" type PbTe showed many cracks and fractures and in general looked very poor. Many of the cracks that were caused in the pre-pressurizing test did not re-bond and appear as large cracks after being pressure sintered.

The GeBiTe samples with the nickel-phosphorous wafer contacts looked good. The contact appeared very dense and homogeneous, and the bond was very strong. Some axial and radial cracks were noticed under microscopic investigation. These failures seemed to appear at random and without cause.

The stack assembly was highly deformed but nevertheless intact. Each layer of different density graphite fillers could be seen in the wall of the container as indentations and steps. Mechanically the concept was feasible, however, graphite deformation and thermoelectric pellet forming resulted in extreme difficulty in removal of the samples. This indicated higher strength, higher density graphite would be required.

Conclusions

In general, cold forming will reduce distortion at the expense of brittle fracture. Due to assembly tolerances and clearances, cold forming (pre-pressurizing) is absolutely necessary if a useable sample is to be obtained. This is the inherent weakness of this method of pressure sintering in concentric cylinders, (tube assembly).

All axial loading on the pellet sample and forming in the tubes is due primarily to radial loading and deformation which can and does cause cracks as well as necking down of the pellet samples. Although many varied

contacts can be bonded in this way, cracking remains the biggest problem.

Ideally, isostatic loading of the pellet would result in uniform bonding and densification. The tubular cylinder method approaches this ideal case in one dimension only and relies on plastic flow to obtain three dimensional loading. Plastic flow, although present at the cycle temperatures and pressures, is not uniform and predictable in the thermoelectric materials investigated to date.

Pure axial loading (hot pressing) may result in acceptable contact bonds but at the expense of cracking due to non-uniform densification and sintering.

At this point of material development, considerable interest was given to the idea of isostatic pressure forming at temperatures which would permit contact bonding. The stack concept using an isostatic media was conceived.

Chemical and Metallurgical Compatibility

I. Scope of Experiment

An investigation of the compatibility of various ferrous and non-ferrous contact materials with three thermoelectric materials was undertaken. This investigation was primarily an experiment in which all materials that seemed at all feasible as a thermoelement contact were tested.

Three results were expected: (1) no perceptible chemical reaction, (2) a favorable reaction characterized by a low electrical resistance alloying or diffusion joint, and (3) a failure or high electrical resistance reaction layer or alloy.

II. Description of Experimental Setup

All samples were tested in a hermetically sealed stainless steel tube (Type 304). Two inert filler materials were used: high purity graphite (National Carbon, Type ACU) and an aluminum oxide powder, - 240 mesh size. The majority of the tests were run with the aluminum oxide powder.

All thermoelectric samples were 1/2 inch diameter, 1/4 inch long. The materials were GeBiTe and "p" and "n" type PbTe, with the greatest emphasis being place on contact compatibility with GeBiTe, due to its greater chemical reaction with most materials. Tests with "p" and "n" type PbTe were limited to a small number of contacts that were known or suspected to be compatible with these materials.

(A) Assembly of Tubes

Graphite was initially considered as the ideal filler material, being

inert, having low strength, and having the ability to act as a getter. Later, interest was given to the aluminum oxide as a filler.

Where graphite was used, a cylindrical tube or sleeve of graphite was machined to accept the 1/2 inch diameter pellet sample. The contact material was placed directly against the pellet in the form of a preformed disc or as a wafer in the case of powders. A more detailed discussion of the powder wafers will be given in a subsequent section. A contact was placed against each end of the pellet. These samples assemblies (i.e. contact, pellet, contact) were isolated from each other by mica separator discs.

The use of aluminum oxide as a filler material presented one major problem. Since most of the contact materials were not pre-joined or pre-pressed but were simply placed against the pellet sample, a method to insure that the aluminum oxide would not get between the contact and the thermoelectric pellet had to be found. Past work on material compatibility had indicated that aluminum was non-reactive with GeBiTe and only slightly reactive with PbTe up to about 450°C. Therefore, each sample assembly was wrapped in aluminum foil as a protection measure. For the PbTe samples, the aluminum foil was sprayed with graphite to reduce contamination. A mica disc separated the contact material from the aluminum at the ends.

To assemble the experimental tubes, the pellets were centrally placed in stainless steel tube and the aluminum oxide sand was poured and vibrated around the pellet samples.

(B) Tube Cleanup and Sealing

Four different cleanup procedures were investigated to determine the

effect of both atmosphere and temperature on chemical compatibility. These procedures were as follows:

- (1). Evacuate from room temperature to 450°C, cool and seal under vacuum. (approximately 5 microns of mercury pressure)
- (2). Room temperature evacuation only and sealed in vacuum.
- (3). Inert gas purge (95% argon - 5% hydrogen) at 450°C, cooled while purging, and seal in an inert atmosphere.
- (4). Room temperature evacuation to remove moisture, expose to air, and seal in air.
- (5). Each assembly had an evacuation tube which was sealed by both crimping and welding.

(C) Heat Soak

After sealing, a thermocouple was attached to each tube, which was then placed in a furnace preheated to 600°C. The tube was held at temperature for 2 hours. Transient time was approximately 1-1/2 hours. After soaking, the tube was removed from the furnace and allowed to air cool. The cooling cycle took approximately 1 hour.

III. Contact Materials Investigated

The contact materials investigated in this experiment covered a very wide range of thermal expansion values and chemical reactivity. These materials were in the forms of pre-punched metal foils and pre-formed powder wafers. All metals that seemed remotely feasible were tested.

(A) Metal Foils

The term "foil" is used to emphasize the fact that the contact layers

or caps were very thin, (in most cases .010 inch or less). The foil samples were punched from either commercially available sheet or heavier stock that had been cold rolled to the desired thickness. In addition to pure metals and alloys, plasma spray coatings on the base metals were investigated. The plasma spray technique allowed a known compatible material of low expansion coefficient to be applied to a reactive material that had an expansion match with the various thermoelectric materials.

(B) Powder Wafer

The powder wafer samples included metals that were not readily available as thin sheets or foils and materials that are most commonly used as brazing alloys.

In all cases, these powders were made into pre-formed wafers approximately .020 inch thick. The wafers were made by punching discs from a sheet of the powder that had been impregnated with a #500 Microbrazing cement. This binder is primarily a nitro-cellulose compound that will decompose under heat (300°C) and will leave no contaminating residue. This technique allowed a great variety of materials to be tested that would otherwise be unavailable.

In addition to pure metal wafers, a combination of powders were mixed to form a wafer in the same manner as described. This was done in an attempt to match expansion without unfavorable chemical reaction. As an example of this test, aluminum and nickel powders were mixed in the ratio of 80 atomic percent aluminum to 20 atomic percent nickel. In this mixture it is known that the aluminum is highly compatible with GeBiTe but difficult or impossible to join. Nickel on the otherhand will bond to BiBiTe but with a high

electrical resistance joint. It was hoped that the combination would exhibit the good characteristics of both materials.

Finally, the powder wafers and metal foils were combined in an attempt to obtain a favorable match. In this instance, the wafer usually acts as a barrier layer for the metal foil. An example of this would be aluminum powder-gold foil combination.

IV. Results and Conclusions

Based on visual observations and limited electrical resistance checks only preliminary conclusions can be drawn. The experiment was primarily a process of elimination where the obviously poor combinations were eliminated. Further and more intensive work is necessary to evaluate the reaction where it occurred to determine whether it is favorable or unfavorable from a standpoint of metallurgical integrity and electrical resistance.

The following table summarizes the results:

Contact Material	Atmosphere in Test Tube	Visual Observations			Pellet Resistance If Measured		
		GeBiTe	PbTe(N)	PbTe(P)	GeBiTe	PbTe N	PbTe P
Microbrazo 10	Vacuum	Dark Powder Reaction Layer	No Apparent Reaction	Not Tested	-	-	-
	Argon-Hydrogen	Dark Powder Reaction Layer	No Apparent Reaction	Not Tested	1.9	.45	-
	Air	Slight Reaction Layer Evident	Not Tested	Not Tested	-	-	-
	Vacuum	Black Reaction Layer	No Apparent Reaction	No Apparent Reaction	-	-	-
CoBalt	Argon-Hydrogen	Black Reaction Layer	No Apparent Reaction	No Reaction	2.1	.41	.44
	Air	Black Powder Reaction Layer	No Apparent Reaction	No Reaction	-	-	-
	Vacuum	No Reaction	Slight Reaction	Slight Spot Reaction	-	-	-
Aluminum	Argon-Hydrogen	No Reaction	Not Tested	Not Tested	-	-	-
	Air	No Reaction	Slight Reaction	Not Tested	-	-	-
	Vacuum	No Reaction	Slight Reaction	Slight Spot Reaction	-	-	-

Contact Material	Atmosphere in Test Tube	Visual Observations			Pellet Resistance if Measured		
		GeTe	PbTe(N)	PbTe(P)	GeTe	PbTe N	PbTe P
Type 302 S.St.	Argon-Hydrogen	302 S. St. Badly Oxidized	Not Tested	Not Tested	1.4	-	-
	Air	302 S. St. Slightly Oxidized	Not Tested	Not Tested	-	-	-
Type 430 S.St.	Air	430 S. St. Very Badly Oxidized	Not Tested	Not Tested	-	-	-
Microbrazed 10 Plasma on 302 S.St.	Vacuum	Moderate Reaction with NiP	Not Tested	Not Tested	-	-	-
	Air	Slight Reaction Noticeable	Not Tested	Not Tested	-	-	-
Microbrazed 10 Plasma on 304 S.St. Clad Cu	Vacuum	Pellet and Foil Badly Oxidized	Not Tested	Not Tested	-	-	-
	Air	Violent Reaction with Copper	Not Tested	Not Tested	-	-	-
304 S.St. Clad Cu	Argon-Hydrogen	304 S.St. Very Badly Oxidized	Not Tested	Not Tested	-	-	-
Kanigen Coated Cu	Vacuum	Violent Reaction and Alloying	Not Tested	Not Tested	-	-	-
	Air	Violent Reaction and Alloying	Not Tested	Not Tested	-	-	-
Nickel	Air	Diffusion Layer Evident	Not Tested	Not Tested	-	-	-

Contact Material	Atmosphere in Test Tube	Visual Observations				Pellet Resistance If Measured			
		GeBiTe Reaction Layer Formed	PbTe(N)	PbTe(P)		GeBiTe	PbTe N	PbTe P	
Tin	Air		Not Tested	Not Tested		-	-	-	
Silver	Air	Diffusion and Alloy- ing Evident	Not Tested	Not Tested		-	-	-	
Gold	Air	Complete Diffusion of Gold	Not Tested	Not Tested		-	-	-	
Platinum	Air	Very Slight Reaction	Not Tested	Not Tested		-	-	-	

Contact Material	Atmosphere in Test Tube	Visual Observations			Pellet Resistance If Measured Ω
		GeSiTe	PbTe(M)	PbTe(P)	
Columbium	Air	Heavy Reaction Layer	Not Tested	Not Tested	0.34
Nichrome	Air	Some React. of Contact & Pellet Surfaces	"	"	
Manganese	Air	Wafer Badly Oxidized Interface looked clean	"	"	
Phosphor-Bronze	Air	Diffusion and Alloying Evident	"	"	2 samples 1.15 and 1.02
Beryllium-Copper	Air	Badly Reacted	"	"	
GeSiTe - NiP 50-50% by Wt.	Air	Slight Reaction Layer	"	"	
PbTe (n)	Air	Slight Reaction at Interface	"	"	
NiP Plasma on Silver	Air	Reaction Layer Evident	"	"	
Aluminum-Gold Mix. 10% at. wt. Au	Air	Slight reaction on Pellet Surface	"	"	
Aluminum-Silver mix. 20% at. wt. Ag	Air	Reaction with Silver	"	"	

Contact Material	Atmosphere in Test Tube	Visual Observations			Pellet Resistance If Measured mΩ
		GeBiTe	PbTe(N)	PbTe(P)	
Aluminum-Micro- Braz 20% At. wt. NiP	Air	Reaction same as with Pure NiP.	Not Tested	Not Tested	0.36
Aluminum-Nickel 20% at. wt. Ni	Air	Reaction with Ni Evident	"	"	0.37
Aluminum-Titan- ium Hydride 20% at. wt. Ti	Air	Reaction next to Pellet	"	"	
Gold-Nickel mixture 80% at. wt. Ni	Air	Reaction next to Pellet	"	"	0.39
Aluminum-Cobalt Mix. 20% at. wt. Co	Air	Reaction zone next to Pellet	"	"	0.43
Gold-Titanium 80% at. wt. Ti	Air	No Apparent React- ion	"	"	
Gold Plated Nickel	Air	Very Little React- ion some Alloying	"	"	0.32
Gold Plated 304 S.St. Clad Copper	Air	Very Little Reaction	"	"	.31
Titanium-Hydride	Air	Some Powder Oxida- tion. Pellet clean	"	"	.31
#81 Solder Sheet	Air	Slight Reaction no Diffusion	"	"	

Contact Material	Atmosphere in Test Tube	Visual Observations		Pellet Resistance If Measured mΩ
		GeBiTe	PbTe(N) PbTe(P)	
#12 Brazing Sheet	Air	Slight Reaction Layer Evident	Not Tested	Not Tested
95% Zinc 5% Aluminum	Air	Severe Reaction	"	"
Ge-Ni Eutectic	Air	No Apparent Reaction	"	"
NiP-GeBiTe Mixture 50-50% by wt.	Air	No Apparent Reaction	"	"
Advance Metal	Air	Diffusion and Alloying Evident	"	1.45
#3 Silver Solder	Air	Reaction Evident on Pellet Surface	"	"
Tungsten	Air	No Apparent Reaction	"	"
Brass	Air	Diffusion and Alloying Evident	"	4.22
Emerson Cummings ECCO 58-C	Air	Black Reaction Layer	"	"
H & H 431	Air	Same as ECCO 58-C	"	"
H & H 545	Air	Similar to ECCO but appearance Better	"	"

Contact Material	Atmosphere in Test Tube	Visual Observations			Pellet Resistance If Measured mΩ
		GaBiTe	PbTe(N)	PbTe(P)	
Pre-tinned Ni Plasma 304 S.St. Clad Copper	Air	Pellet clean, sur- face of disc some- what reacted	Not Tested	Not Tested	
Titanium	Air	No apparent reaction	"	"	
Pre-tinned Nickel	Air	Very good bond. Pellet Clean	"	"	0.59 1 cont. & pellet
Pre-tinned 302 S.St.	Air	Pellet clean, but no bond.	"	"	0.85 1 cont. & pellet
Pre-tinned Aluminum	Air	Pellet & disc clean but no bond	"	"	
Pre-tinned #81 Solder Sheet	Air	No reaction No bond	"	"	
Pre-tinned Phosphor-Bronze	Air	Reaction with foil	"	"	1.02 2 cont. & Pellet
Pre-tinned Brass	Air	No Bond - Pellet & disc faces reacted	"	"	
Pre-tinned Platinum	Air	clean, and some bonding	"	"	
Pre-tinned Gold Plated 304 S.St. Clad Copper	Air	Very good bond at both ends.	"	"	0.46 1 cont. & Pellet

Contact Material	Atmosphere in Test Tube	Visual Observations			Pellet Resistance If Measured mΩ
		GeBiTe	PbTe(M)	PbTe(P)	
Tin-NiP Wafer	Air	Wafer and pellet quite reacted	Not Tested	Not Tested	
Pre-tinned Silver	Air	Very good bond fused shim	"	"	2.00 2 cont. & Pellet
Tin-NiP Mixture 80% wt. NiP	Air	Pellet blackened but wafer clean.	"	"	
Aluminum-tin mix. 85% wt. Al.	Air	No apparent reaction	"	"	
Ge-Ni Eutectic Tin Mix. 75% wt. GeNi	Air	No apparent reaction	"	"	

Research Report 63-929-242-R1

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**THERMOELECTRIC POWER-GENERATING COUPLES
UTILIZING DIFFUSION BONDED TIN CONTACTS**

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ABSTRACT

Long-lived power-generating thermoelectric couples have been developed by this project. They are highly resistant to the combined effects of thermal aging and thermal cycling as proven in continuing life-tests now ranging to beyond 6000 hours and 250 thermal cycles. Germanium-bismuth-telluride and n-type lead-telluride are operated at 500°C hot junction temperature with large ΔT 's. The measured operating efficiency closely approaches the value which can be calculated by using the thermoelectric properties of the materials used.

Construction of these couples features diffused tin contacts and a method for control of vaporization of germanium-bismuth-telluride. Assembly details, which are given herein, are entirely adequate for pilot production purposes.

INTRODUCTION

The primary objective of this program is the development of power-generating couples suitable for use in the construction of portable thermoelectric generators. In order that a couple qualify as acceptable for this application, the following minimum requirements have been adopted: 1) must be operable to hot junction temperatures of at least 500°C , 2) power degradation must not exceed 25% as caused by the combined conditions of 250 thermal cycles and 5000 hours under operating conditions, 3) couple thermal efficiency must closely approach the maximum value allowed by the thermoelectric material parameters, 4) couple fabrication methods which provide a high degree of manufacturing reproducibility, and 5) power density per couple must be equivalent to material area/length ratios of greater than 1.0 cm with one-half inch leg diameter.

A secondary objective of this program is the development of couples suitable for a modified duty cycle: not greater than 25% power degradation as caused by the combined conditions of 100 thermal cycles and 10,000 hours under operating conditions. In addition, the power density requirement is relaxed to allow A/l values as small as 1.0 cm.

LIFE PERFORMANCE OBTAINED WITH VARIOUS TYPES OF EXPERIMENTAL CONTACTS AND COUPLES

Figures 1 through 11 illustrate life performance that has been obtained with couples prepared by a variety of selected methods, which were developed in this program. Each figure is accompanied by two related figures which show the performance of the individual P and N legs of each couple. Thus each thermocouple test is a complete test of each leg as well as a test of the couple.

The couple test curve shows "relative power capability, %" plotted against the number of thermal cycles and the number of hours under loaded operating conditions. The expression "relative power capability, %" as used here requires some explanation. It is a plot of what the power degradation would have been if the following conditions had been maintained throughout the test: 1) constant ΔT per leg, and

2) load closely matched for maximum power transfer. Also, the power degradation is shown in relative rather than actual values with the initial power value shown as 100%. For reference, the actual initial power output value is shown for each couple. The actual power values for couples should be used for rough comparison only since different leg A/l ratios and material lots were used and since cold junction temperatures and, accordingly, applied ΔT 's were only approximately equal.

Single leg test data also shows relative power capability for each leg considered as if it were operating independently of the other leg. Also, the resistance value and Seebeck coefficient for each leg is plotted versus thermal cycles and hours. Single leg information is essential for the ultimate design of couples for it enables one to select the optimum contact method and to compute the most favorable geometry for each leg.

In order to enhance comparison of contacting methods all curves in this report are plotted with identical scales on both axes. Also, the hot junctions were universally maintained at 500°C although cold junctions were maintained at only roughly 150°C. All tests shown were performed in an atmosphere of welding grade argon.

The thinwall recess type of hot junction construction is illustrated in Figure 12 and life test results are shown in Figures 1 through 4, 1P through 4P and 1N through 4N. This mode of construction is designed to combine in a single contact a provision for partial encapsulation and a means for accomodating the "dome effect." The encapsulation is achieved by virtue of the fact that in operation a ΔT develops along the vertical dimension of the thinwall recess. Thus the hottest portion of the thermoelectric pellet is encased in the thinwall cavity and vaporization is prevented. A diffused tin bonding technique is employed to join the pellet leg and the thinwall recess to provide a contact and a vapor seal. The "dome effect" which has been described by C. K. Strobel, Research Memo 929-8900-M8, is the property of a pellet to effect a hot end convex curvature when a ΔT is applied along its axis. Since this condition is reversible it contributes strongly

to the degradation attributed to thermal cycling. Such degradation has been shown to be greatly reduced by the use of a recessed type contact which joins not only to the hot end of the thermoelectric pellet but also to the pellet sidewall near the hot end. It should be noted that Figures 1 through 4 concern couples with a variety of leg and thinwall dimensions, and, as such, are not strictly comparable. This contacting method is suitable for use with both P- and N-type materials.

Figure 13 illustrates the heavywall type of recess contact design and life performance is shown in Figures 5, 5P, 5N, 8P and 9P. The joining is again accomplished by a diffused tin bonding technique as in Figure 12. When this design is used at 500°C the hottest portion of the P-leg not confined in the recess must be protected against harmful vaporization. It has been found that a thin coating of tin will very effectively serve this purpose. Comparison of Figures 8, 8P and 8N with 9, 9P and 9N illustrates the mechanical loading ("pressure") dependence of this contact. The method is suitable for both P- and N-type material.

Figure 14 illustrates a modified version of "pressure" contact and Figures 6N, 7N, 10N and 11N indicate life test results. This contact, suggested by C. K. Strobel, differs from conventional "pressure" contacts in that the hot end of the pellet leg is prepared with a curvature which is concave at room temperature. The result of this feature is that the pellet end becomes planar coincident with the application of the intended ΔT of operation. Comparison of 10N and 11N illustrates the mechanical loading ("pressure") dependence of this contact. This method has been found useful only for PbTe.

Another contact arrangement is given in Figure 15; life test results are shown in Figures 6P, 7P, 10P and 11P. This method employs the diffused tin joining technique as with Figures 12 and 13. The hottest portion of the material leg would otherwise be subject to harmful vaporization but is effectively protected by a thin tin layer. The mechanical loading ("pressure") dependence of this method can be seen by comparison of Figures 10P and 11P.

Figures 1 through 11 in each instance indicate life performance of complete couples. With the exception of the couples of Figures 9 and 11 all of the couples are of designs and operating conditions which provide long life. Couples shown in Figures 1 through 5 employ identical contact methods for both P and N legs. The remaining couples have different contact methods for the two legs. Generally, it is possible to combine in a single couple any of the N-type and P-type contacts which may be desired for obtaining optimum results. It is important therefore that each thermoelectric material contact method be considered on its own merits alone.

Cold junctions used in these couples are in all instances prepared by a diffusion bonded tin method. The necessary techniques for preparing this contact will be described later in this report.

SELECTION OF CONTACT METHOD FOR MOST FAVORABLE LIFE

Couples prepared by the method of Figure 12 easily meet the primary objective of this program as described in the Introduction. It is not yet apparent, since not enough hours have passed, whether some of the other contact methods will prove to be superior to the method of Figure 12. The life tests reported are continuing and the relative merits of the various methods will in time become apparent.

There appears to be a very strong likelihood that the secondary objective given in the Introduction will also be met with some margin to spare. At this time there is, unfortunately, only one couple, Figure 4, under life test which is being operated at the required duty cycle.

EFFICIENCY OF COUPLES

The measurement of thermal efficiency of couples made by methods reported here have been performed by C. K. Strobel and reported in the following Research Memos:

62-929-243-M1

62-929-243-M2

62-929-243-M3

62-929-242-M1

62-929-242-M2

Couples prepared according to Figure 10 have efficiency as follows:

<u>ΔT</u>	<u>Overall Efficiency</u>	<u>Thermoelectric Efficiency</u>
500°C to 156°C	~ 6.3%	~ 14.1%
450°C to 48°C	~ 7.1%	~ 12.8%
500°C to 47°C	~ 7.8%	~ 13.4%

These values are very similar to the values which can be obtained by calculation of the expected efficiency based on the material parameters. Initial contact and strap resistances are negligible. Similarly, the heavywall contact method provides efficiency closely approaching the value allowed by the materials properties. Some loss of efficiency is experienced with the thinwall contact method, roughly 0.5% depending upon the dimensions used. Also, upward of 0.5% efficiency can be lost with the use of stainless steel as a strap material, again depending upon dimensions used.

TIN AS A JOINING MATERIAL

All cold junction contacts and, with one exception, all hot junction contacts described here utilize tin as a joining material. Tin is a very fortunate choice in that it alone has been found to satisfy each of the following requirements: 1) high degree of compatibility with both germanium bismuth telluride and N-type lead telluride to at least 500°C, 2) low melting point, and 3) low vapor pressure. Another very desirable feature, but not necessarily a requirement, is the great ease with which it is used in these contacting methods. The exact techniques required for tin contacts are given in the following section.

COUPLE ASSEMBLY TECHNIQUES

The methods for couple fabrication, Figures 12 through 15, which have been developed by this project are simple to perform and provide a very high degree of reproducibility. All tin-bonded contacts are prepared in a similar manner; initially all areas to be joined are ultrasonically wetted with tin. These areas are, specifically, the appropriate portions of the thermoelectric pellets and the hot and cold junction contacts as shown in the aforementioned Figures. The tin is then diffusion bonded to GeBiTe and PbTe by heat treating the wetted pellets for 10 minutes at 550°C in argon. Similarly, diffusion bonding of tin to stainless steel is accomplished by a heat treatment of 10 minutes at 800°C in argon. The couple parts are then assembled in the intended position and heated to above the melting point of tin during which time a mechanical load of approximately 45 pounds is applied axially to each leg. When the melting point of tin is reached the mechanical load will force out all excess tin from both the hot- and cold-junction contacts. Excess tin, while molten, is easily removed with a cotton swab. The couple is then completed by cooling to below the melting point of tin while the mechanical loading is maintained.

For thermoelectric legs utilizing either thinwall, Figure 12, or heavywall, Figure 13, recess designs a pellet to recess diametral clearance of 0.004 inches has been found to be satisfactory. The required tin wetting of pellet sidewalls, as required for Figures 12, 13 and 15, can be accomplished accurately by use of an ultrasonic soldering iron and positioning arrangement. The thermoelectric pellet material will not be readily wetted except on the exact areas which are touched with the tin wetted ultra-sonic iron.

The modified "pressure" contact is novel in that the pellet hot end is concave as previously described. Lapped faces for both the hot junction strap and the pellet end are desirable; the concave pellet end shape can be obtained as a part of the lapping operation. For large volume

purposes, pellets can be pressed with a built-in concave end. For thermoelectric legs using "pressure" hot junction contacts, the cold junctions are prepared by the tin method described earlier.

THERMOELECTRIC MATERIALS

N-type lead telluride used with these couples was bismuth doped pressed and sintered material prepared by either the Semiconductor Department at Youngwood or by the Materials Laboratories. Germanium bismuth telluride used was of the composition $\text{Ge}_{0.965}\text{Bi}_{0.035}\text{Te}$ and was prepared by the Semiconductor Department at Youngwood. All material used was of one-half inch diameter; lengths were one-quarter, three eighths, and one half inch.

APPARATUS FOR TESTING

Life test apparatus built specially for this program consists of two model types as shown schematically in Figures 16 and 17. An essential feature of these testers is the arrangement by which each leg is measured independently. This feature is essential because thermocouple development and design can be properly conducted only with independent initial and life-span measurements for each leg. Measurements for the complete couple are also readily obtainable from this apparatus.

Full utilization of these testers requires that couples intended for test be provided with appropriate hot and cold junction measurement thermocouple wells and voltage pick-off holes. The details of this apparatus and its use will be the subject of a forthcoming Research Memo by W. R. Miller.

CONCLUSION AND RECOMMENDATIONS

The life test results given for thinwall recess couples, Figures 1 through 3, clearly show that this design will more than satisfy the

primary objective (see Introduction) of this program. Some of the other designs give strong indications that they too will exceed the minimum requirements although life tests to this date have not yet accumulated the required hours and thermal cycles. Assuming that some or all of the more recent designs will satisfy the primary program objective, a choice of couple design types will be available to the user. The more recent couples, Figures 7, 8 and 10, have two advantages over thinwall recess couples: 1) efficiency is higher by 0.5% to 1.0% because the losses attributed to the thinwall feature and the losses attributed to the high resistance stainless steel strap are eliminated, and 2) cost will be lower because the thinwall feature is not required.

Although the secondary objective of this program has not yet been fully achieved it can be reasonably predicted that the couple of Figure 4 will prove to be satisfactory. This is presently the only test being operated on a duty cycle appropriate to the secondary objective although additional tests are planned.

The effect of axially applied mechanical loading ("pressure") is vividly demonstrated by the comparison of Figure 8 with Figure 9 and Figure 10 with Figure 11. The minimum loading recommended is 150 pounds per square inch. An increase to 250 psi appears to provide no further improvement. A loading of 50 psi is entirely inadequate.

For each of the couple types proposed, the required fabrication techniques are simple and can be performed with a very high degree of reproducibility.

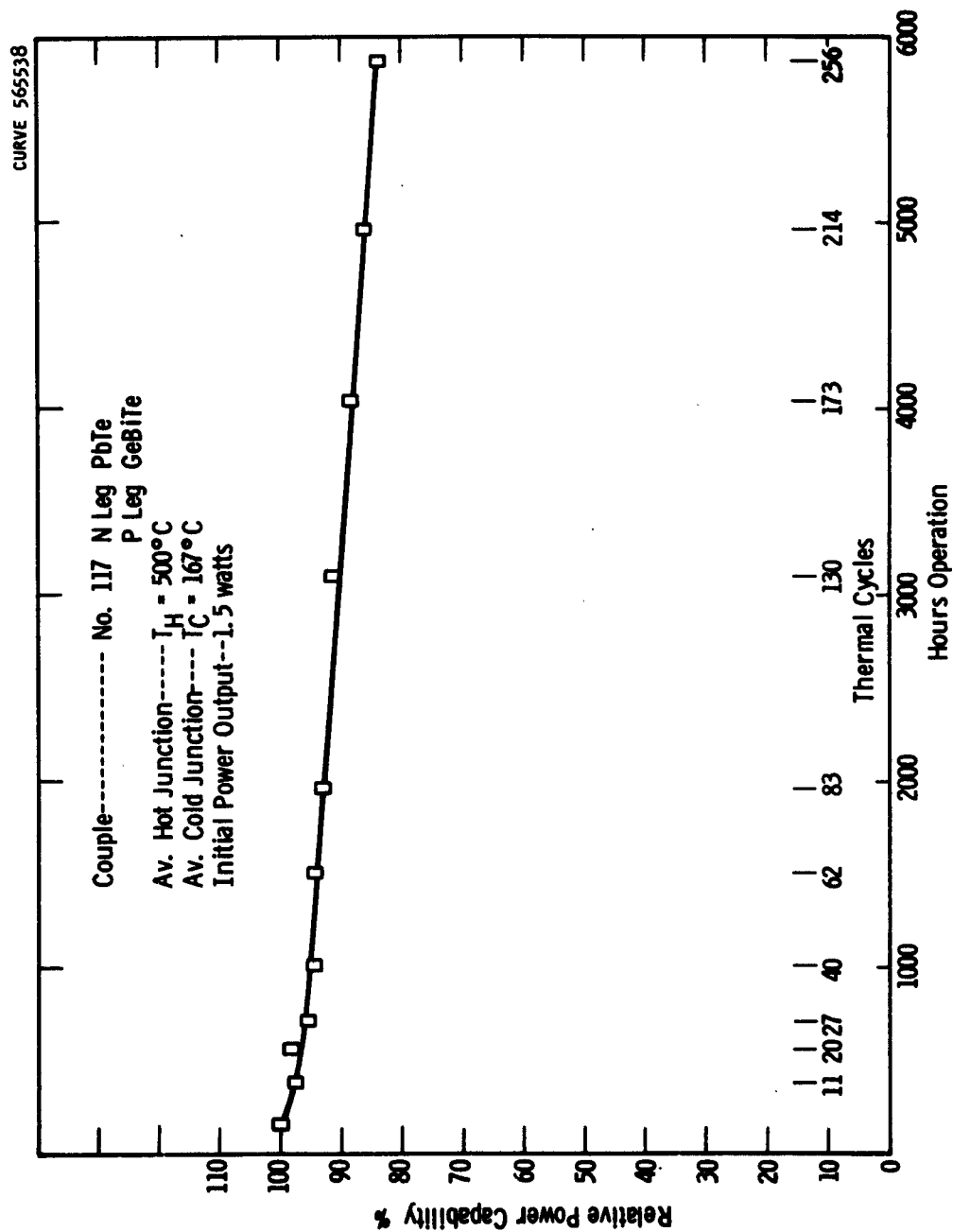


Fig. 1

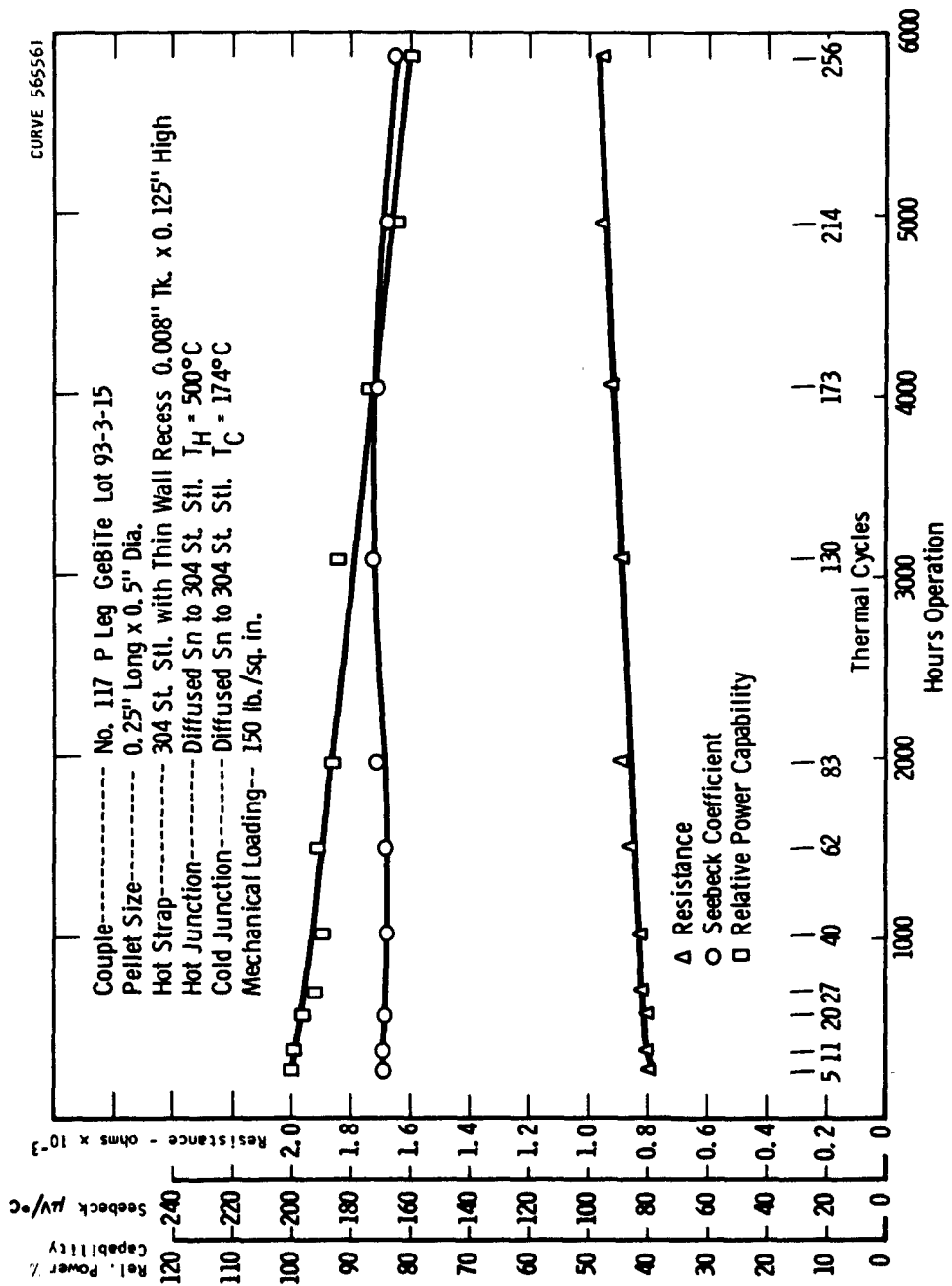


Fig. 1P

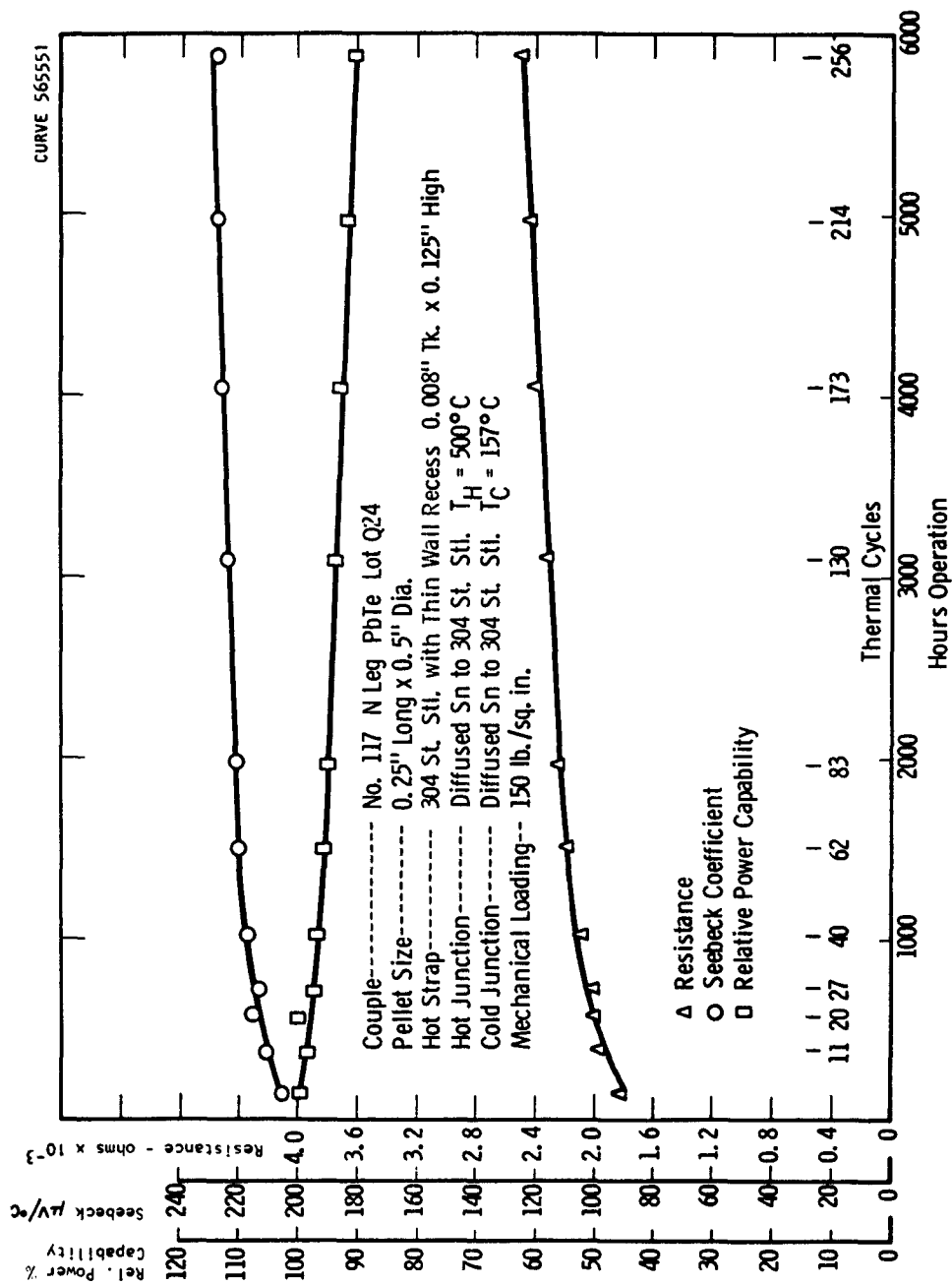


Fig. 1N

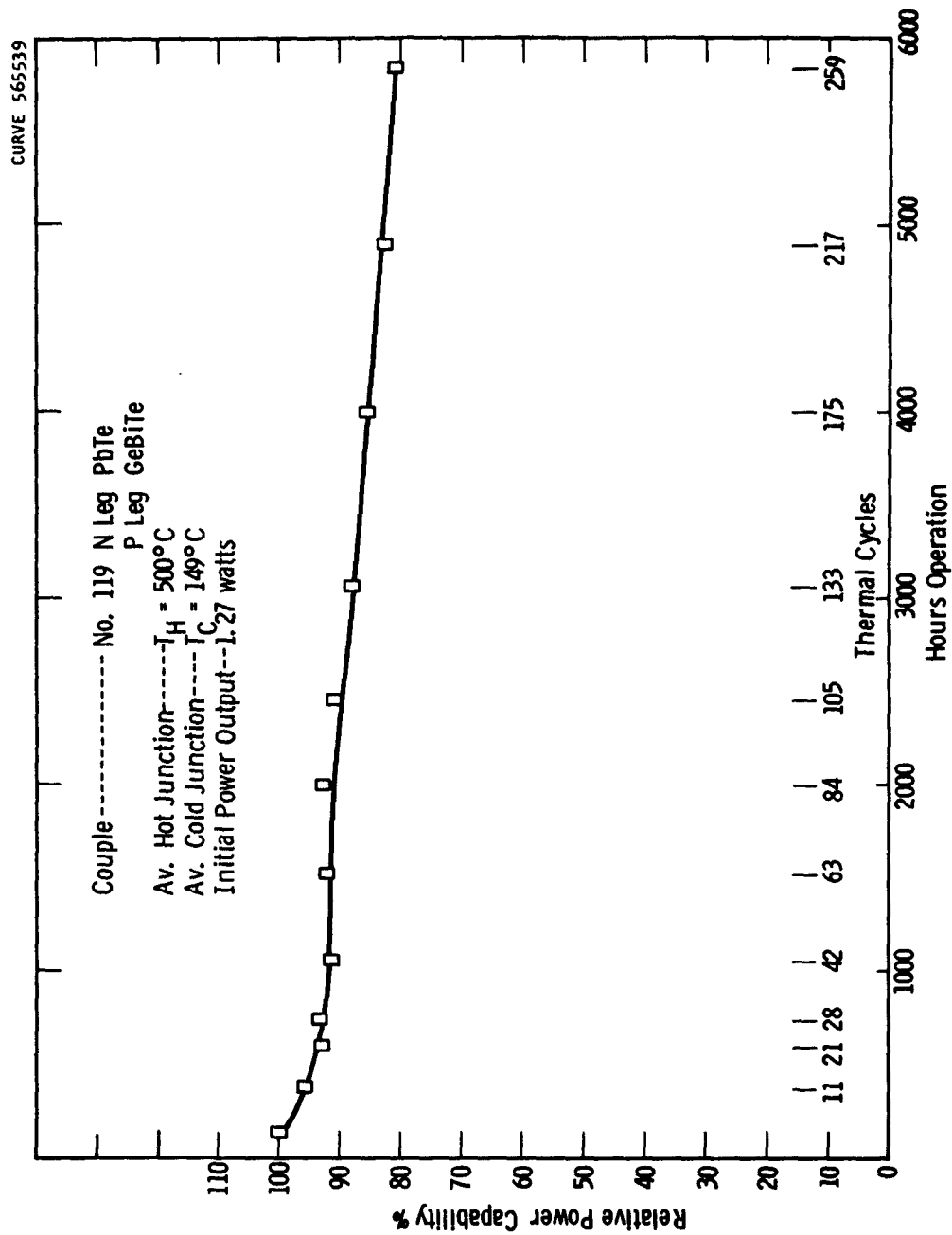


Fig. 2

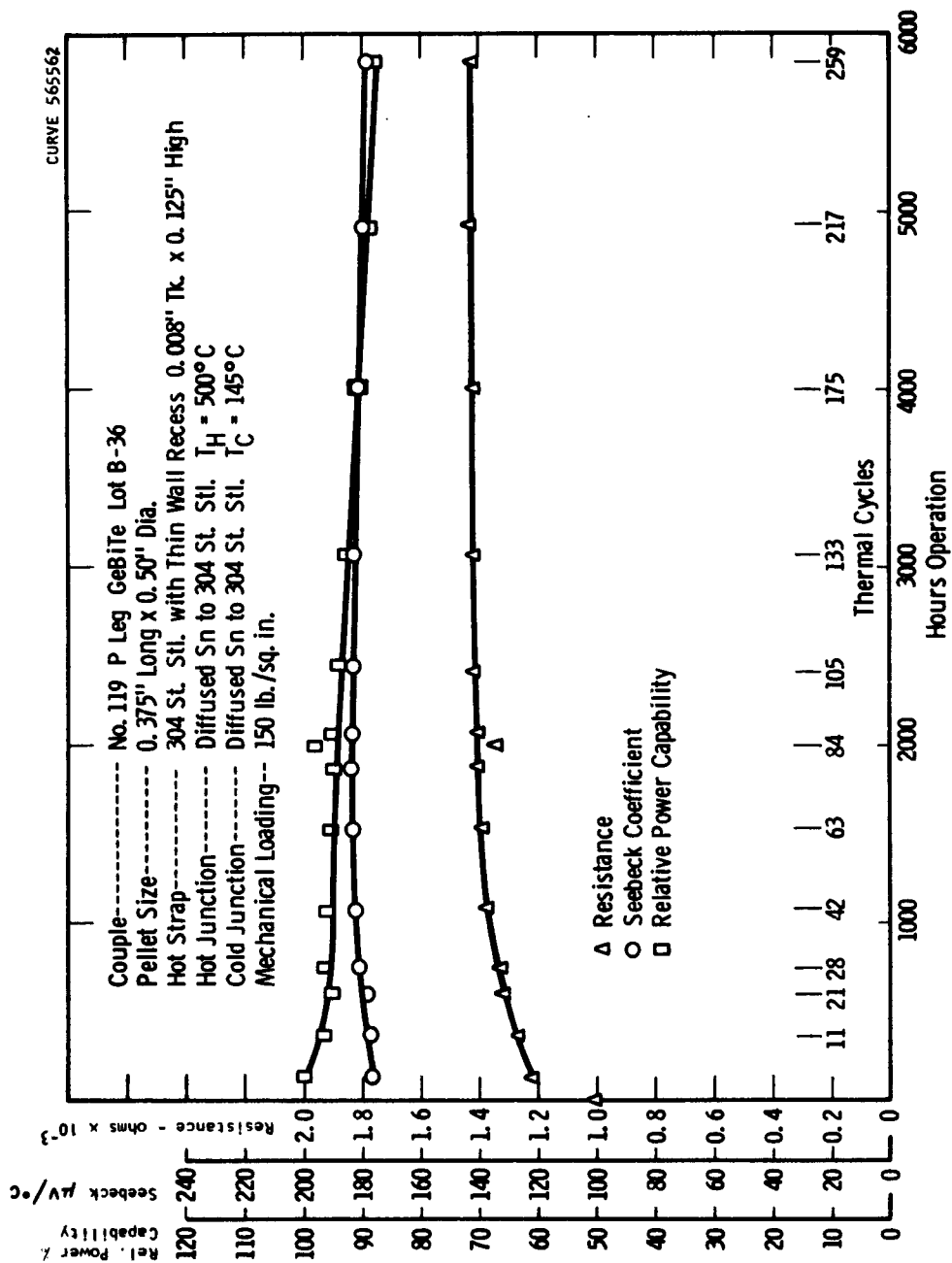


Fig. 2P

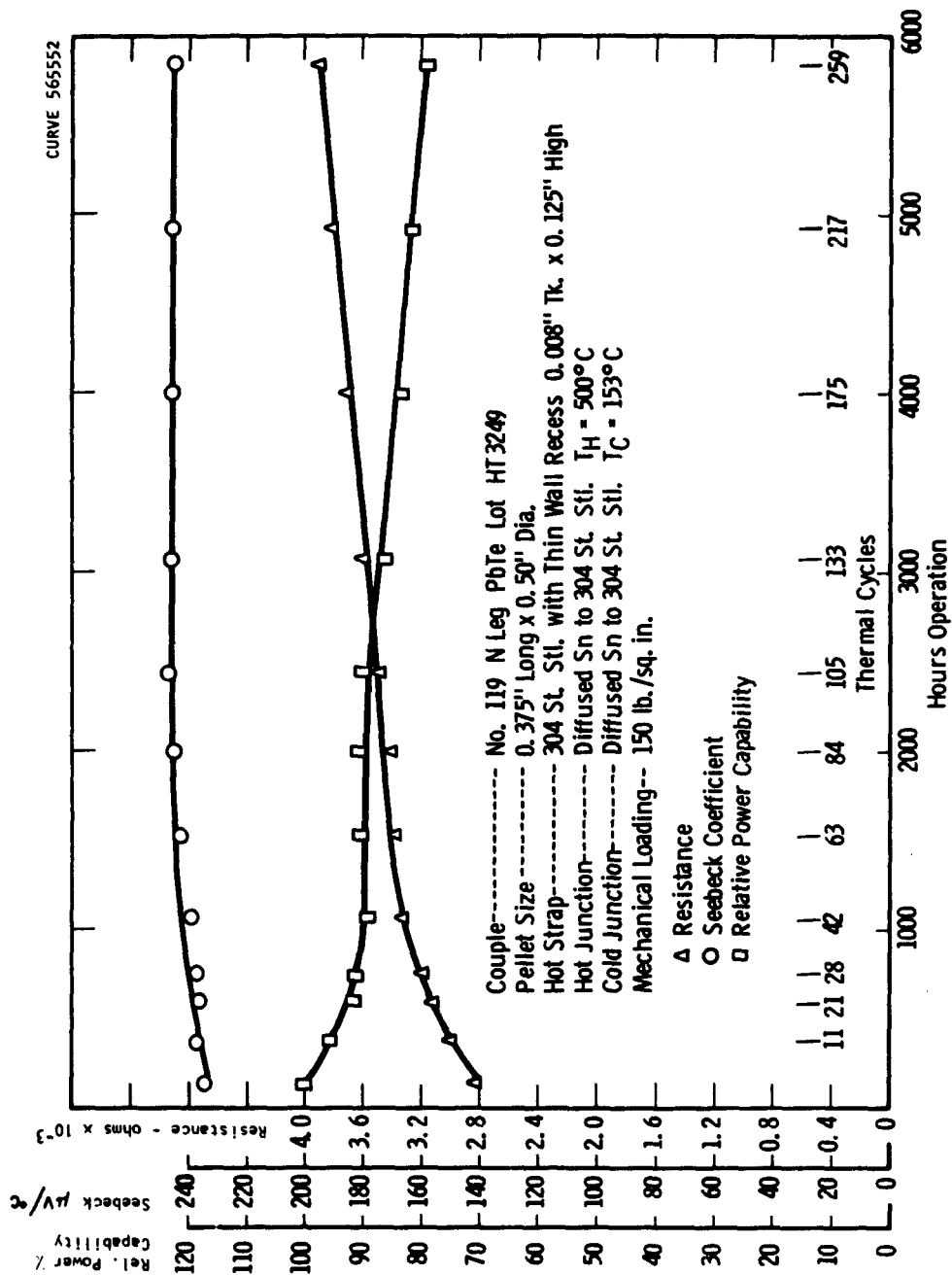


Fig. 2N

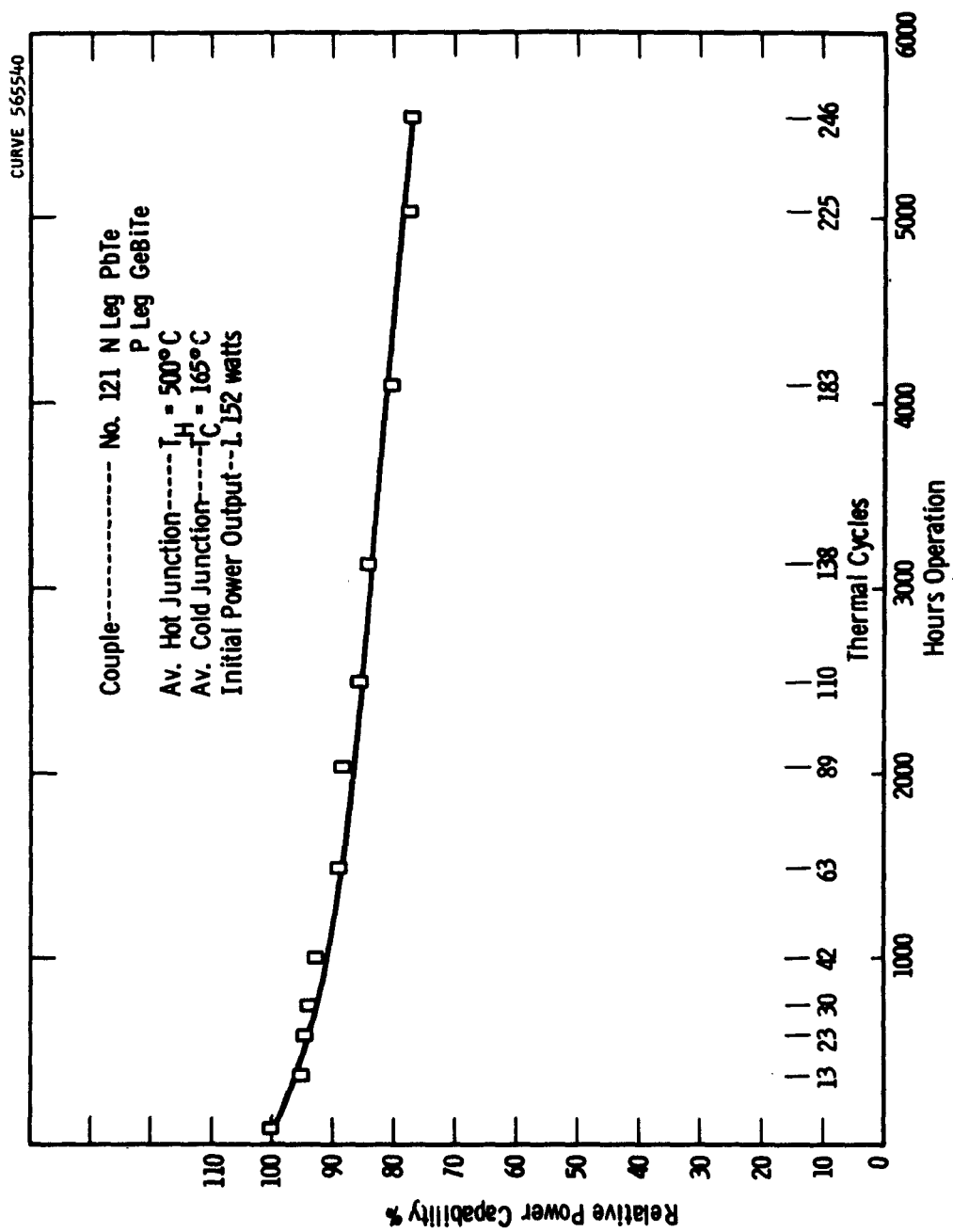


Fig. 3

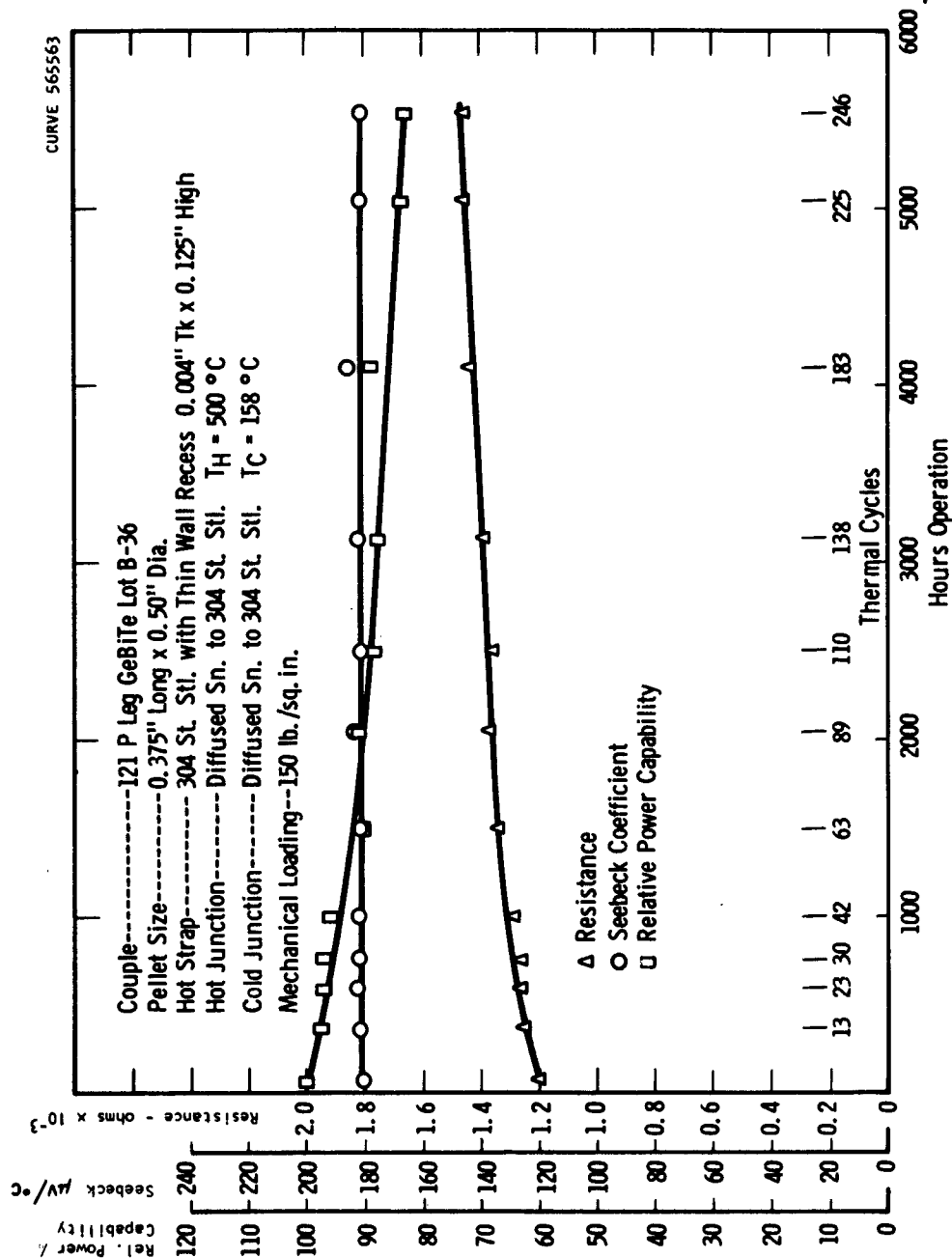


Fig. 3P

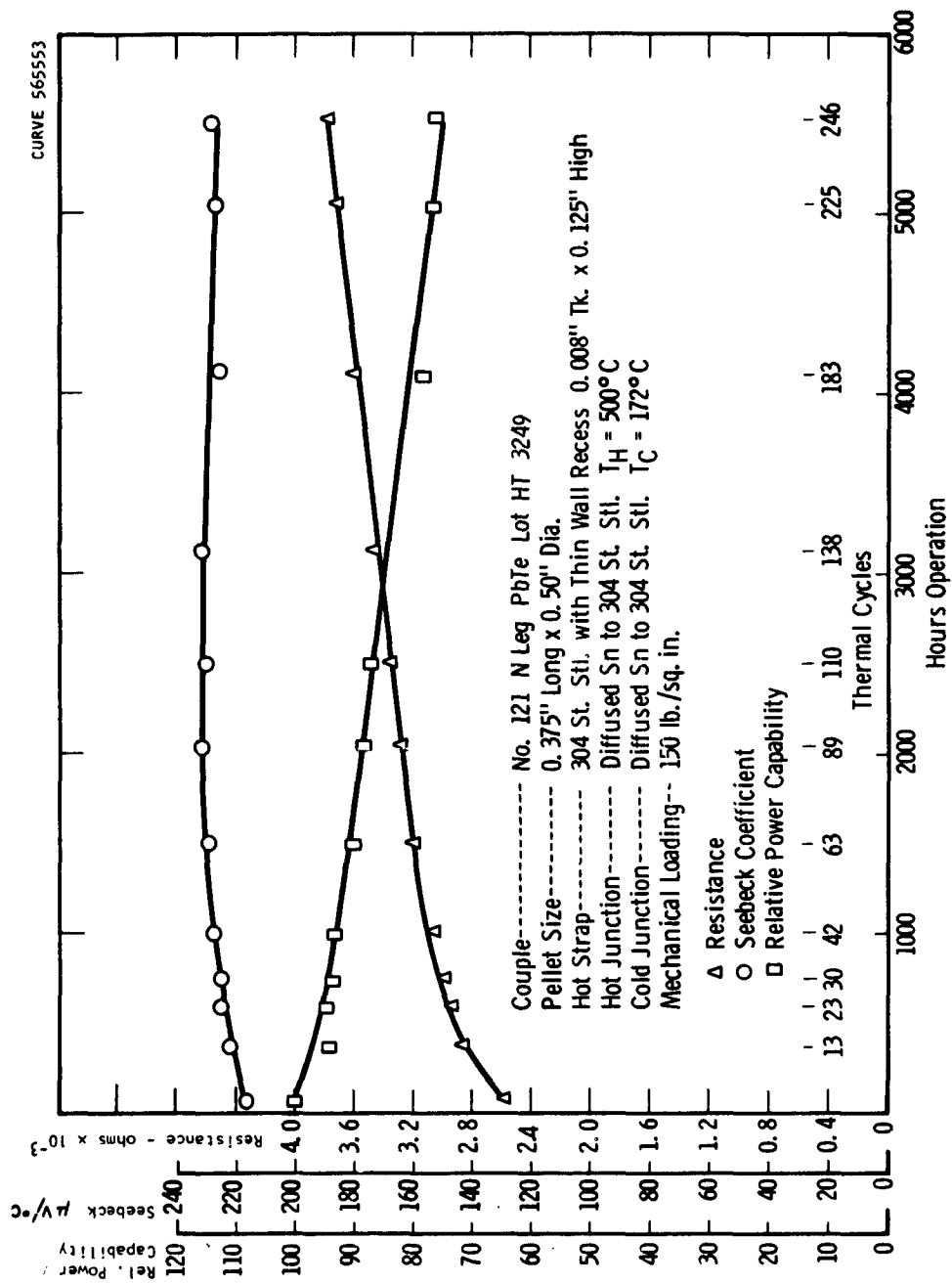


Fig. 3N

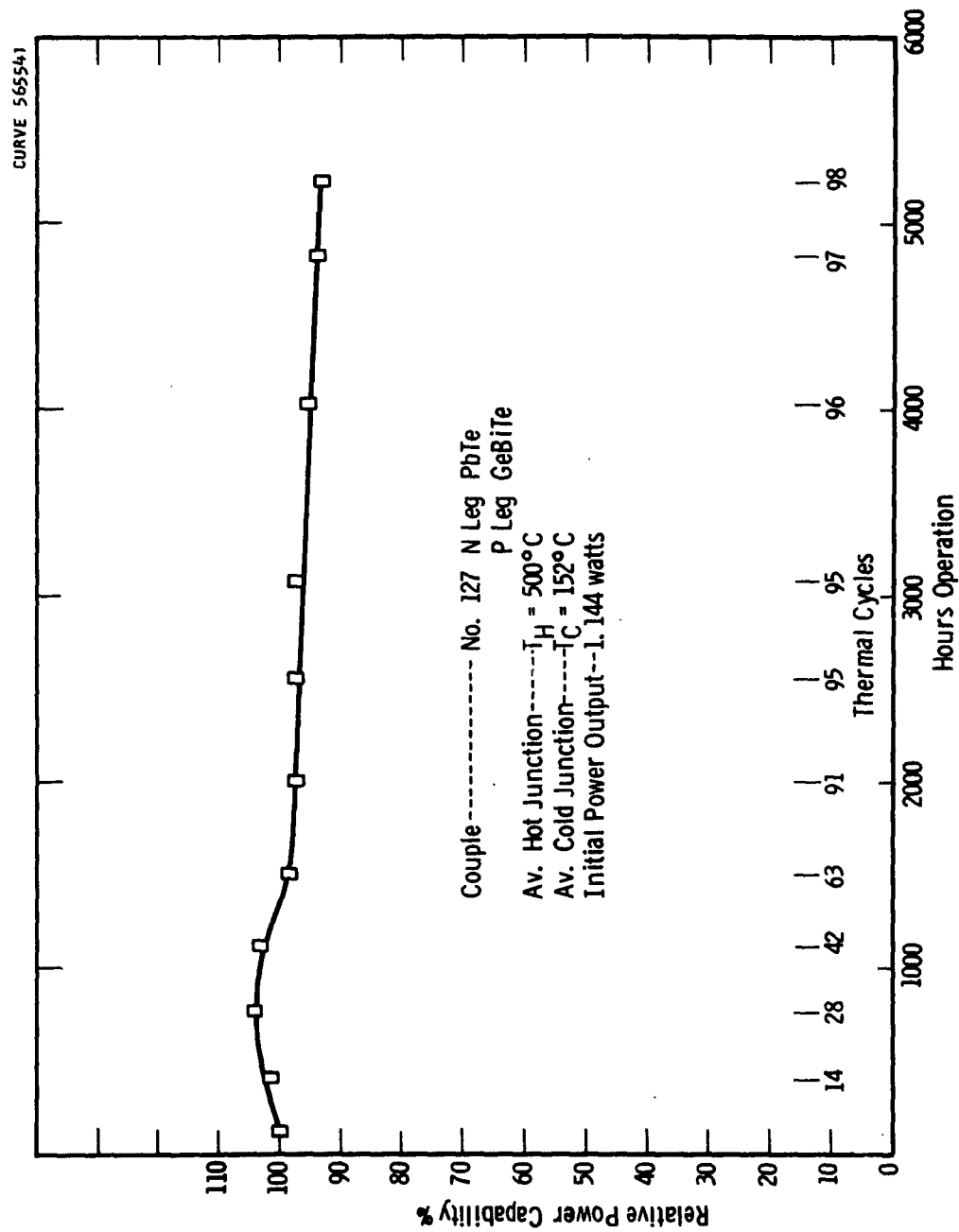


Fig. 4

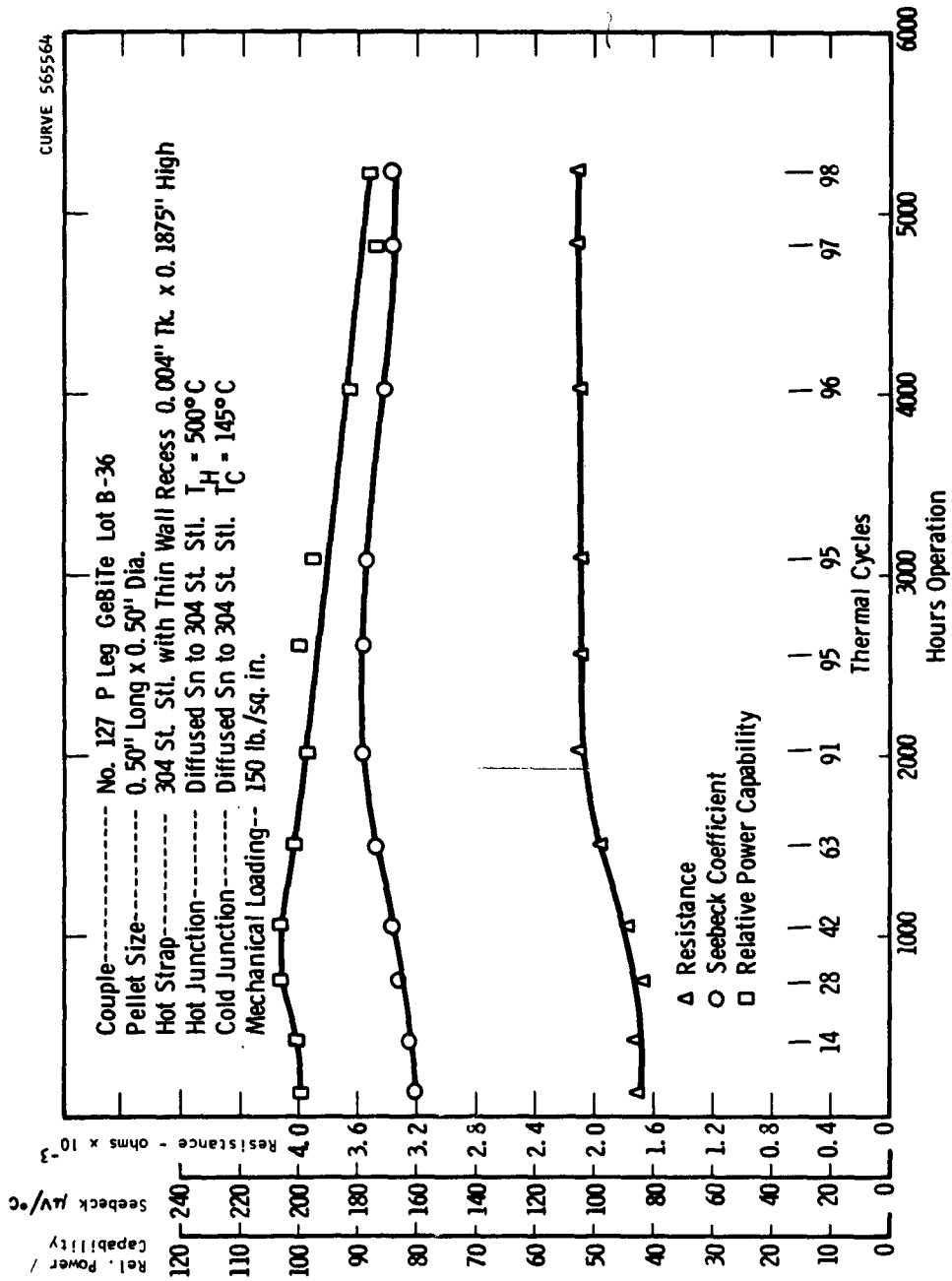


Fig. 4P

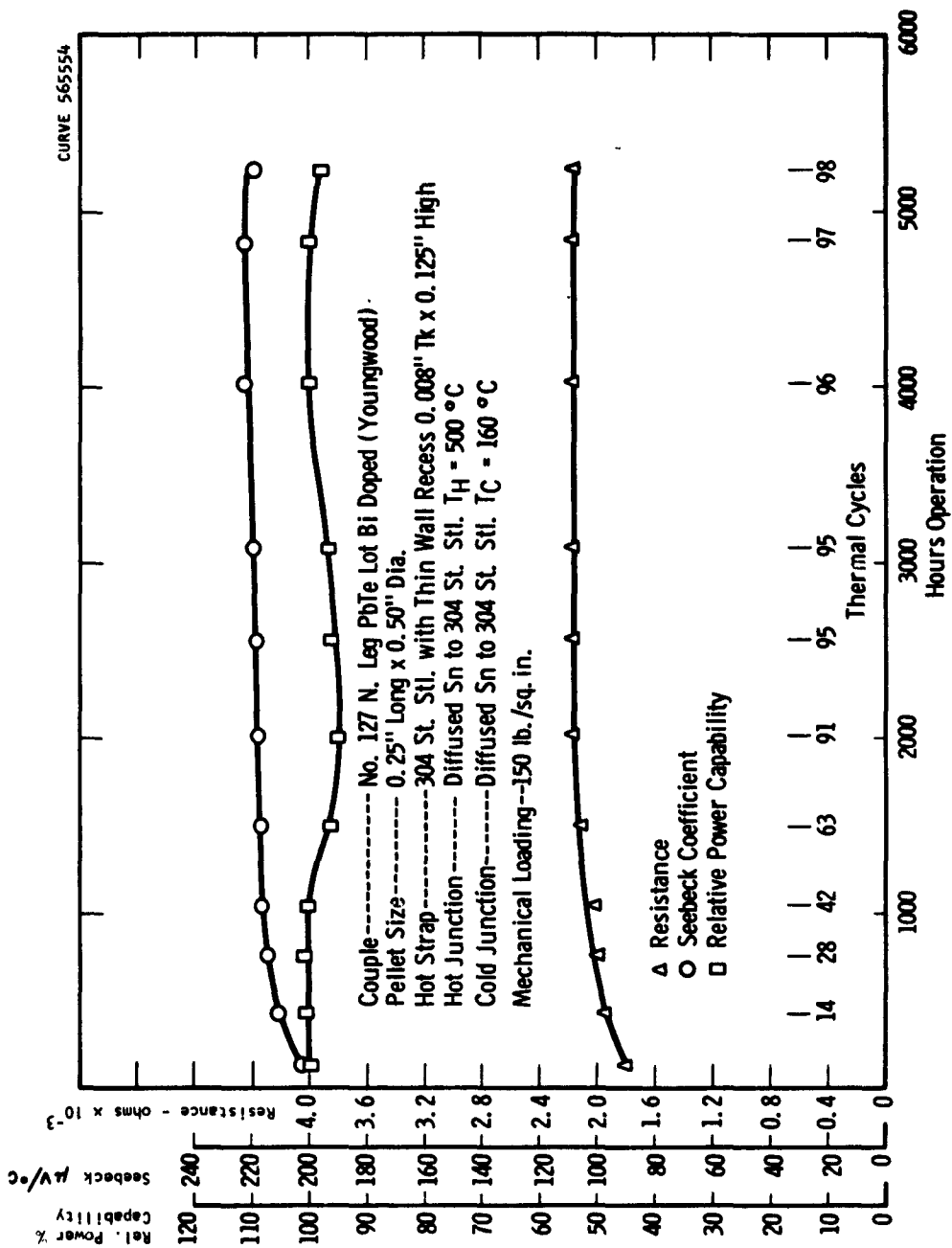


Fig. 4N

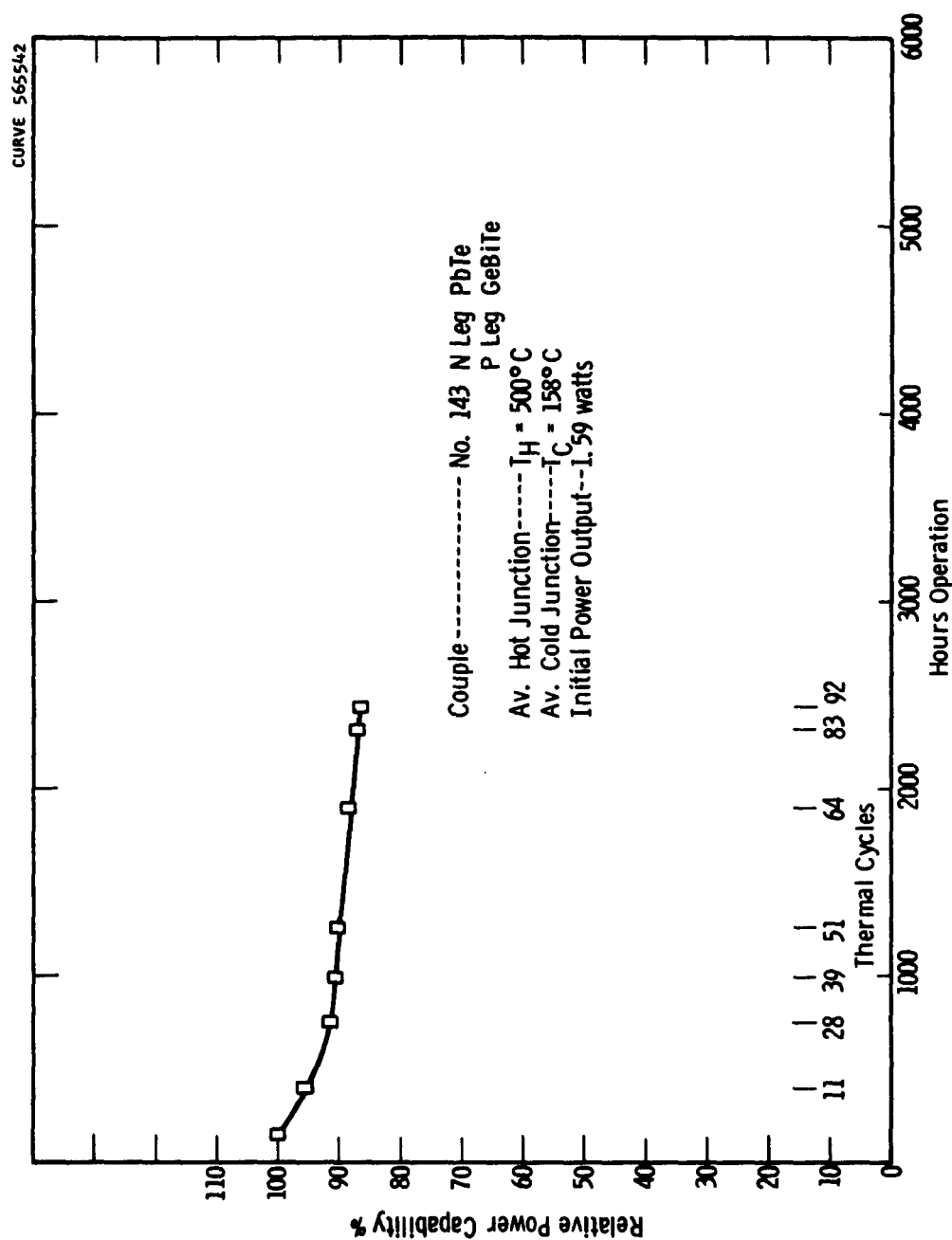


Fig. 5

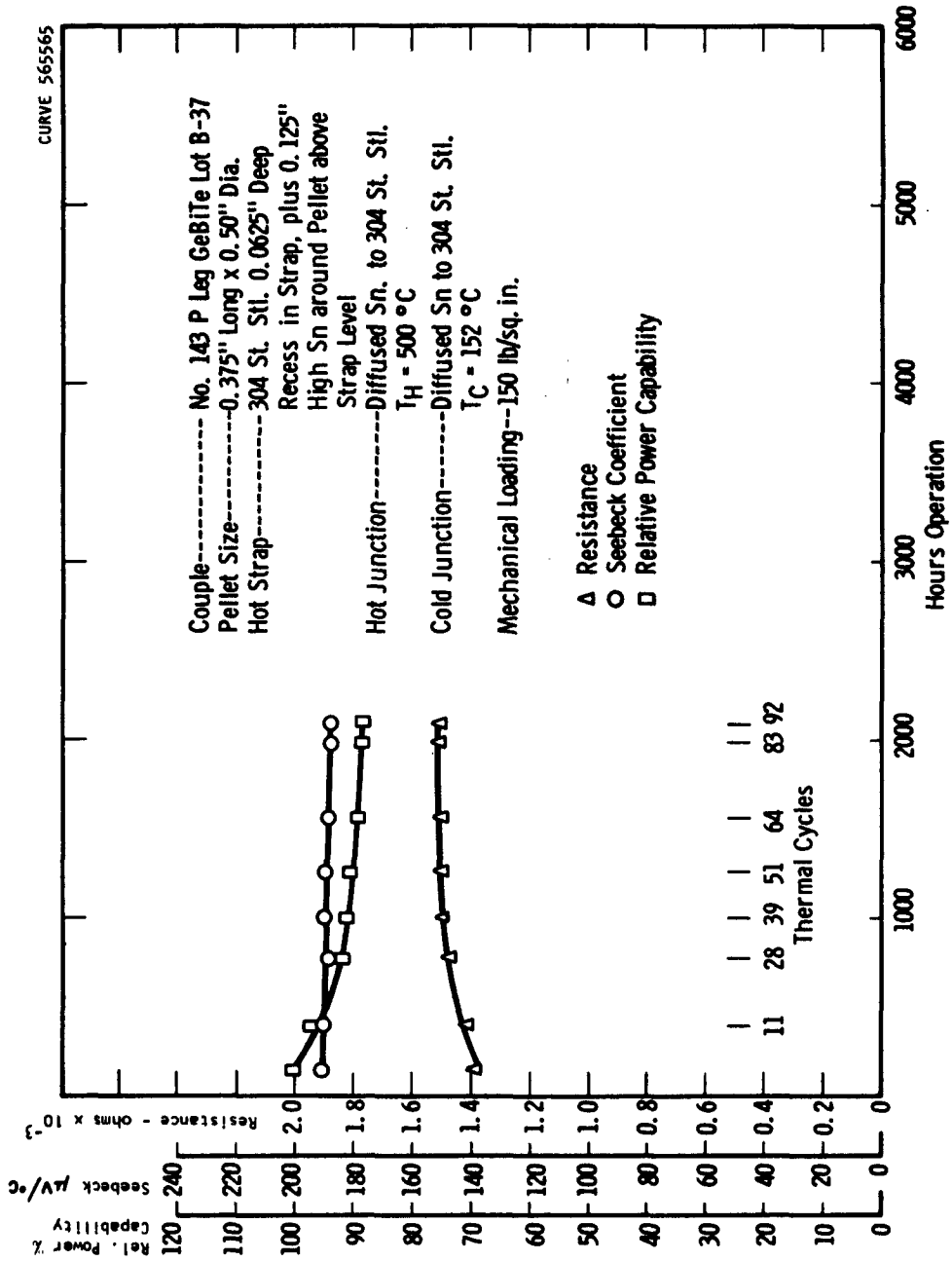


Fig. 5P

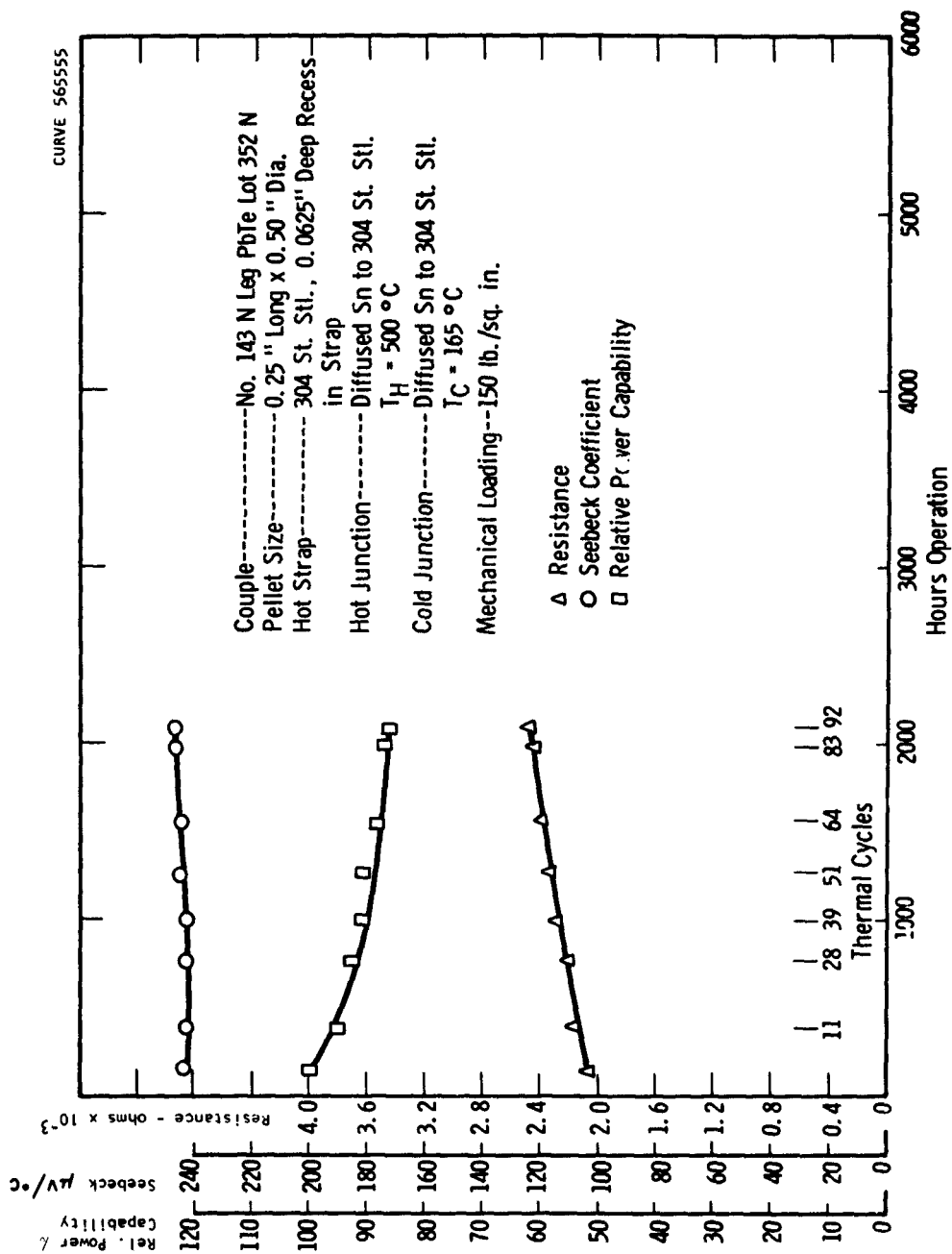


Fig. 5N

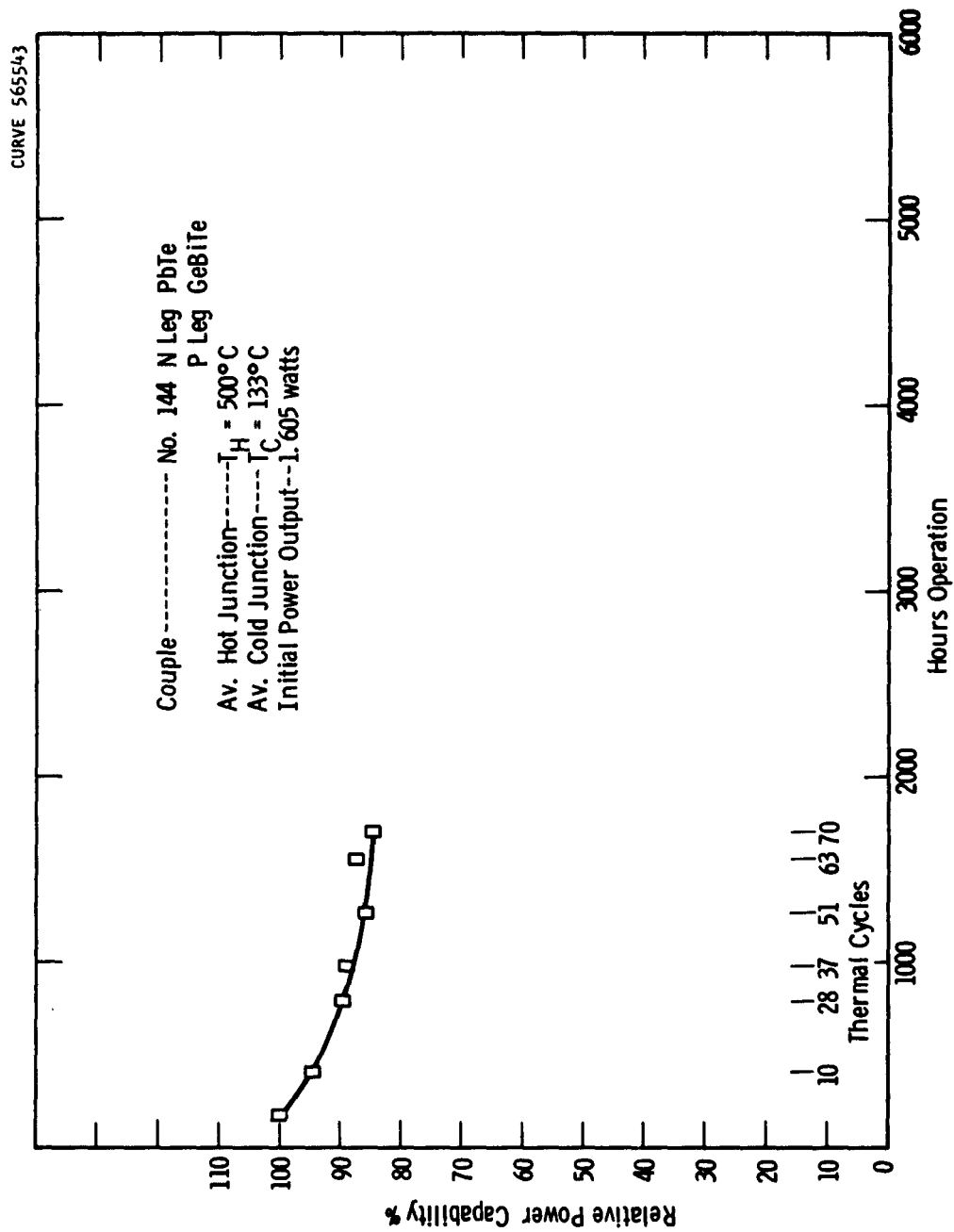


Fig. 6

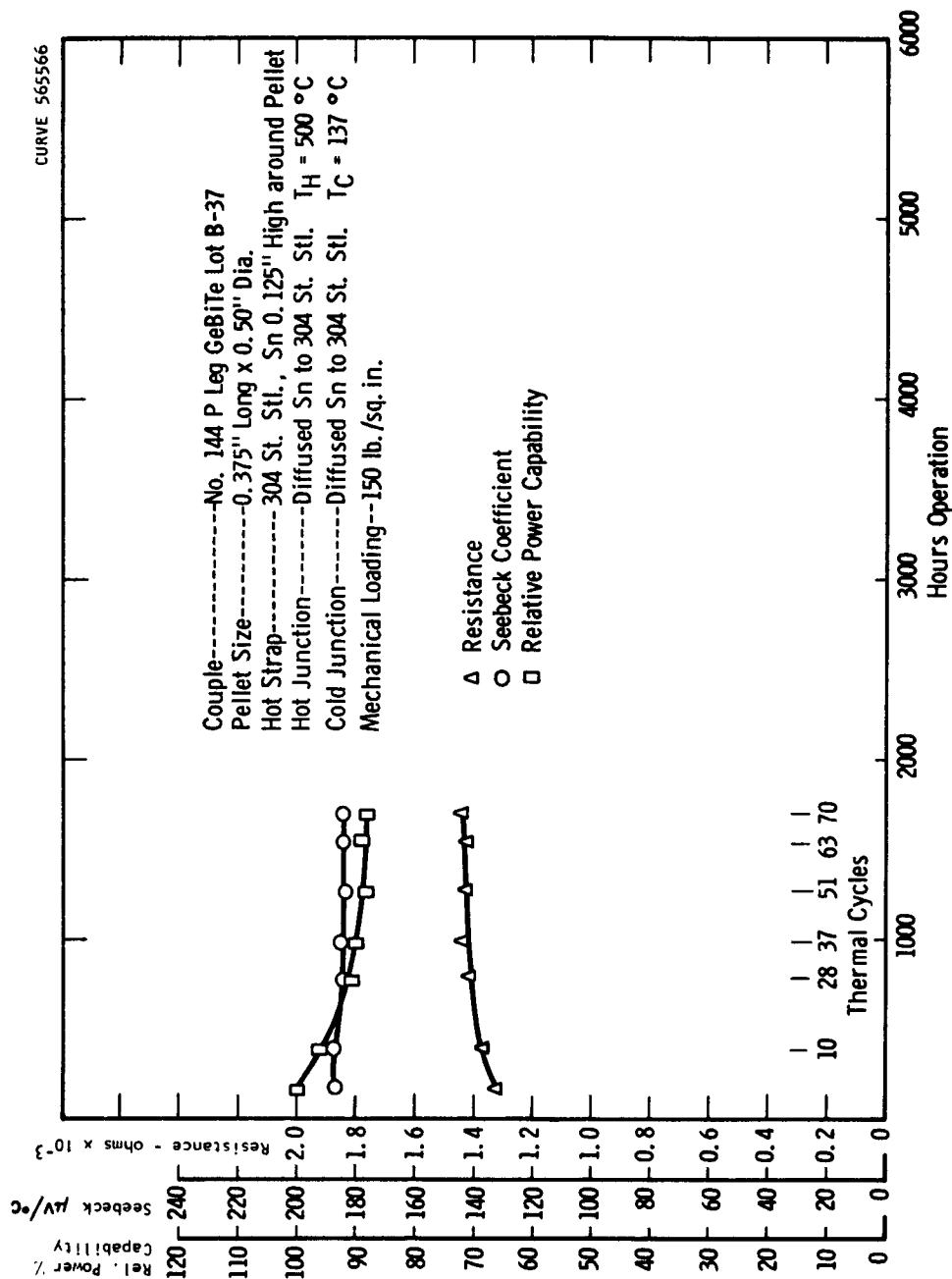


Fig. 6P

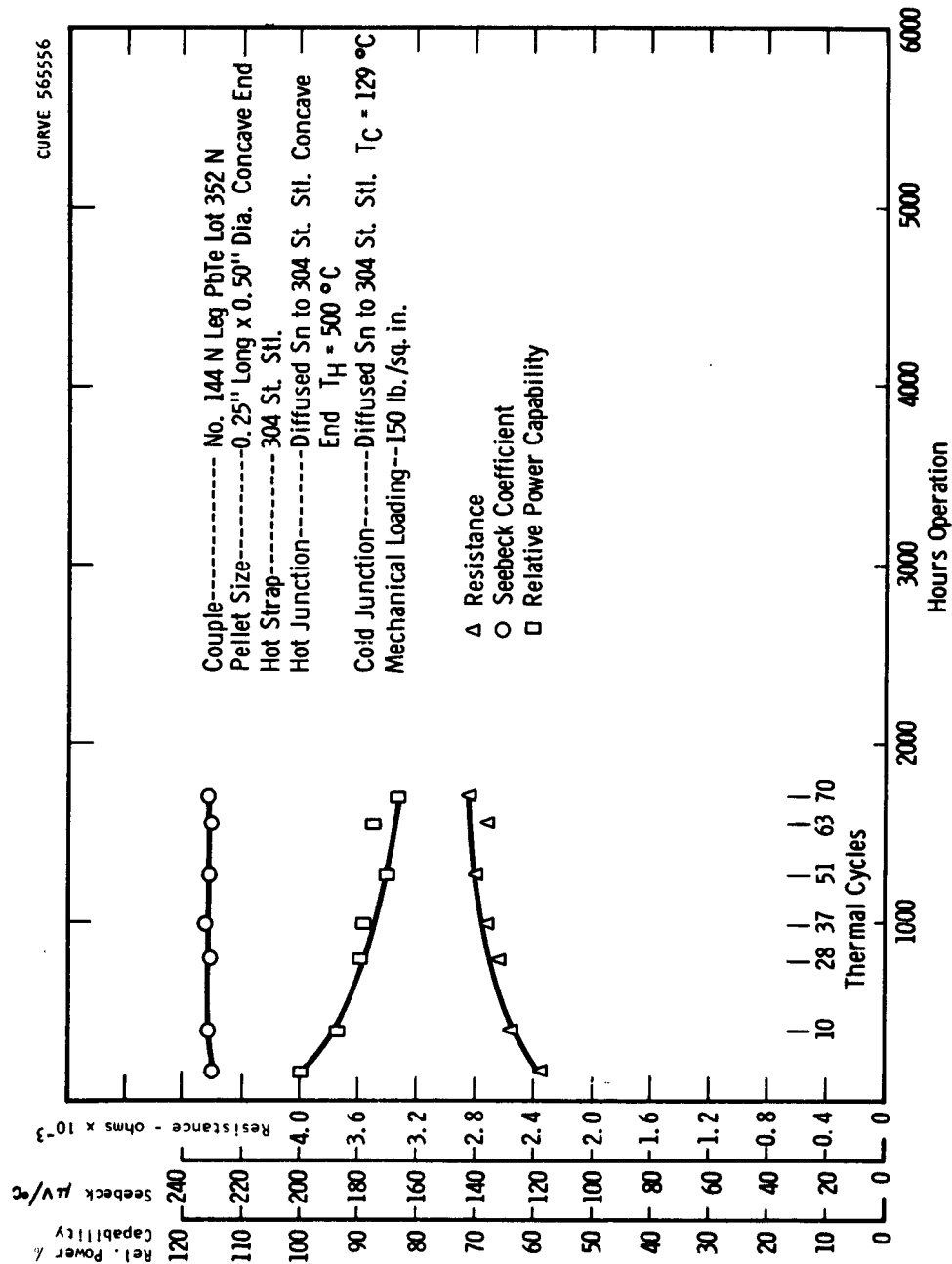


Fig. 6N

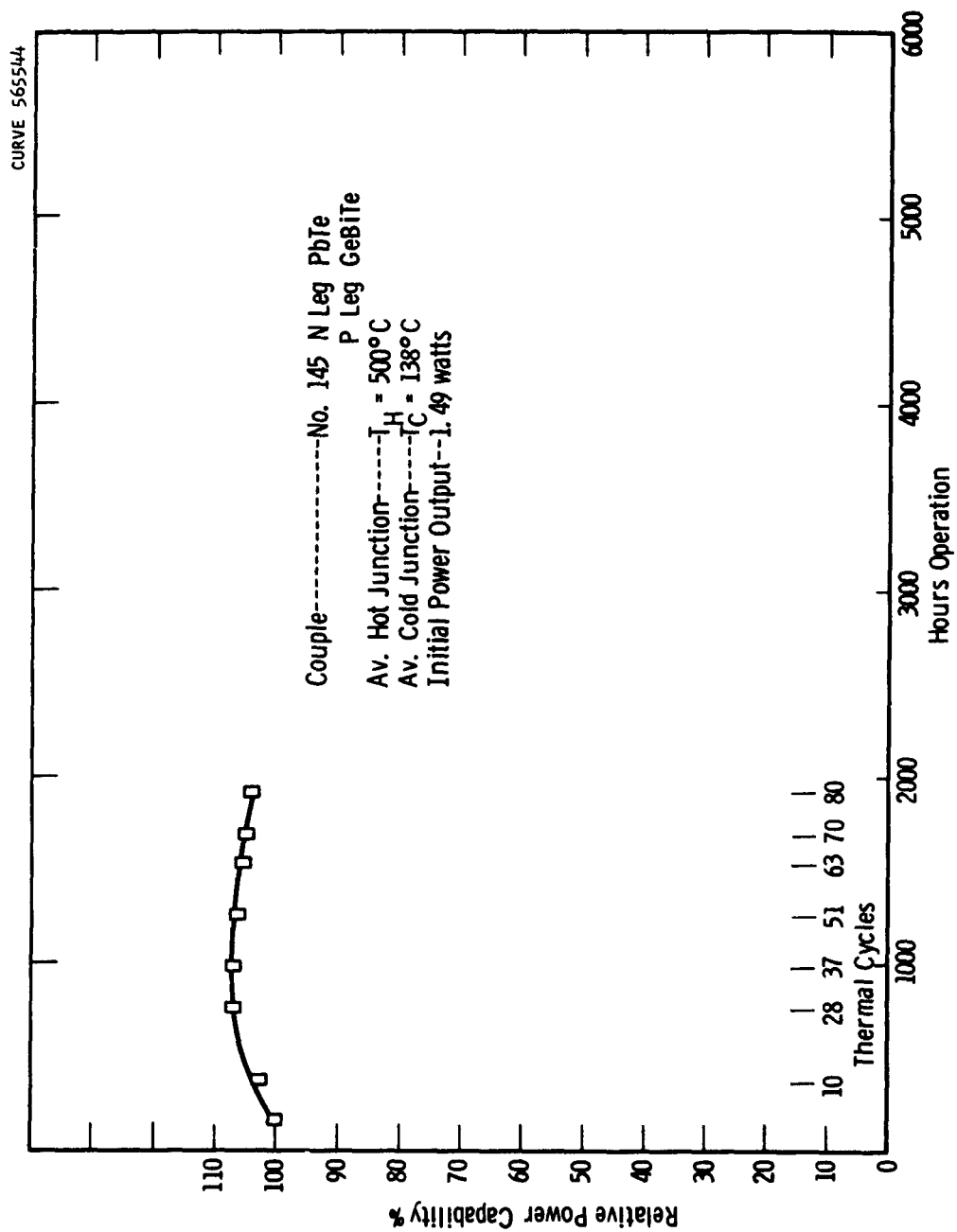


Fig. 7

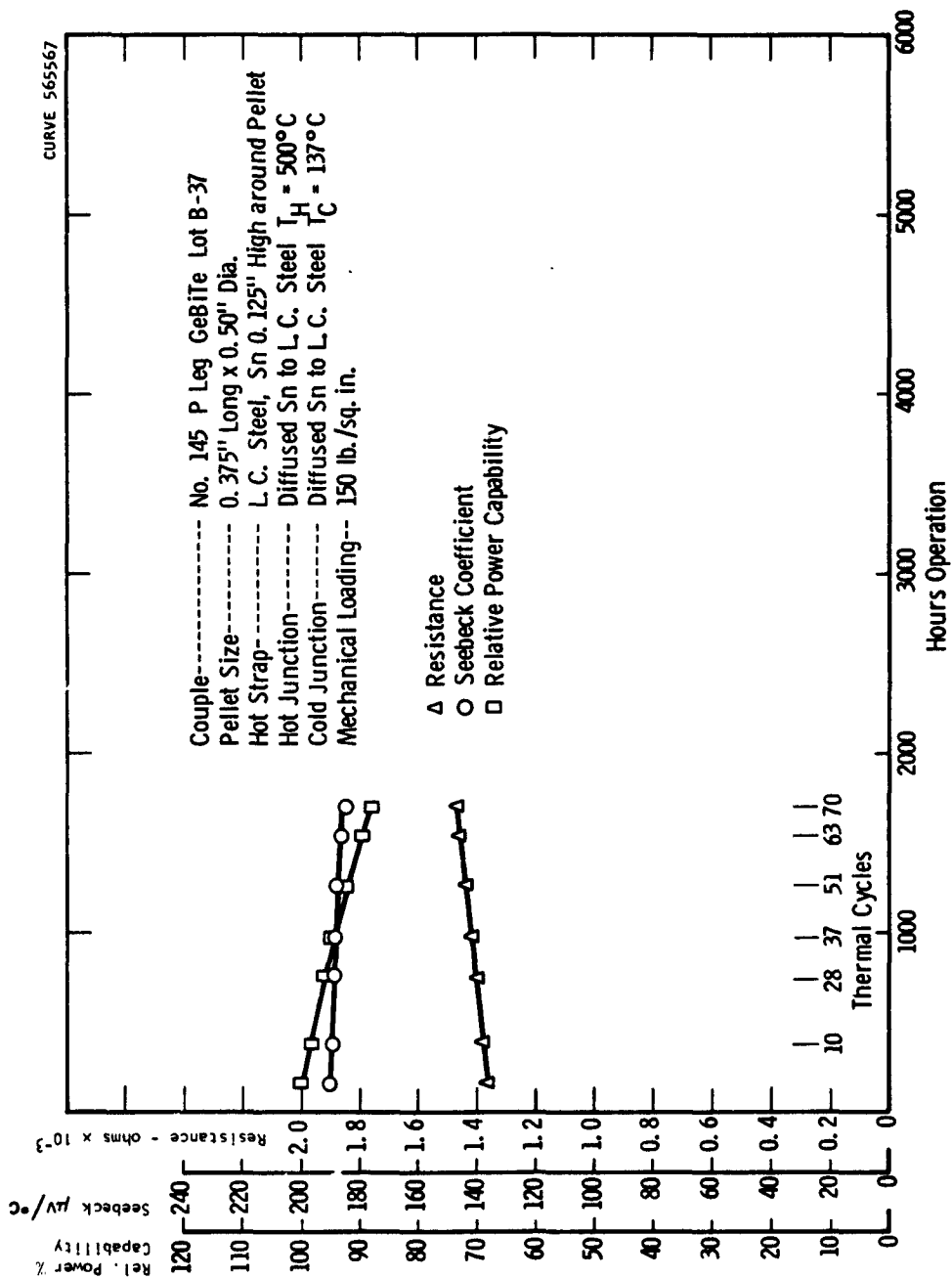


Fig. 7P

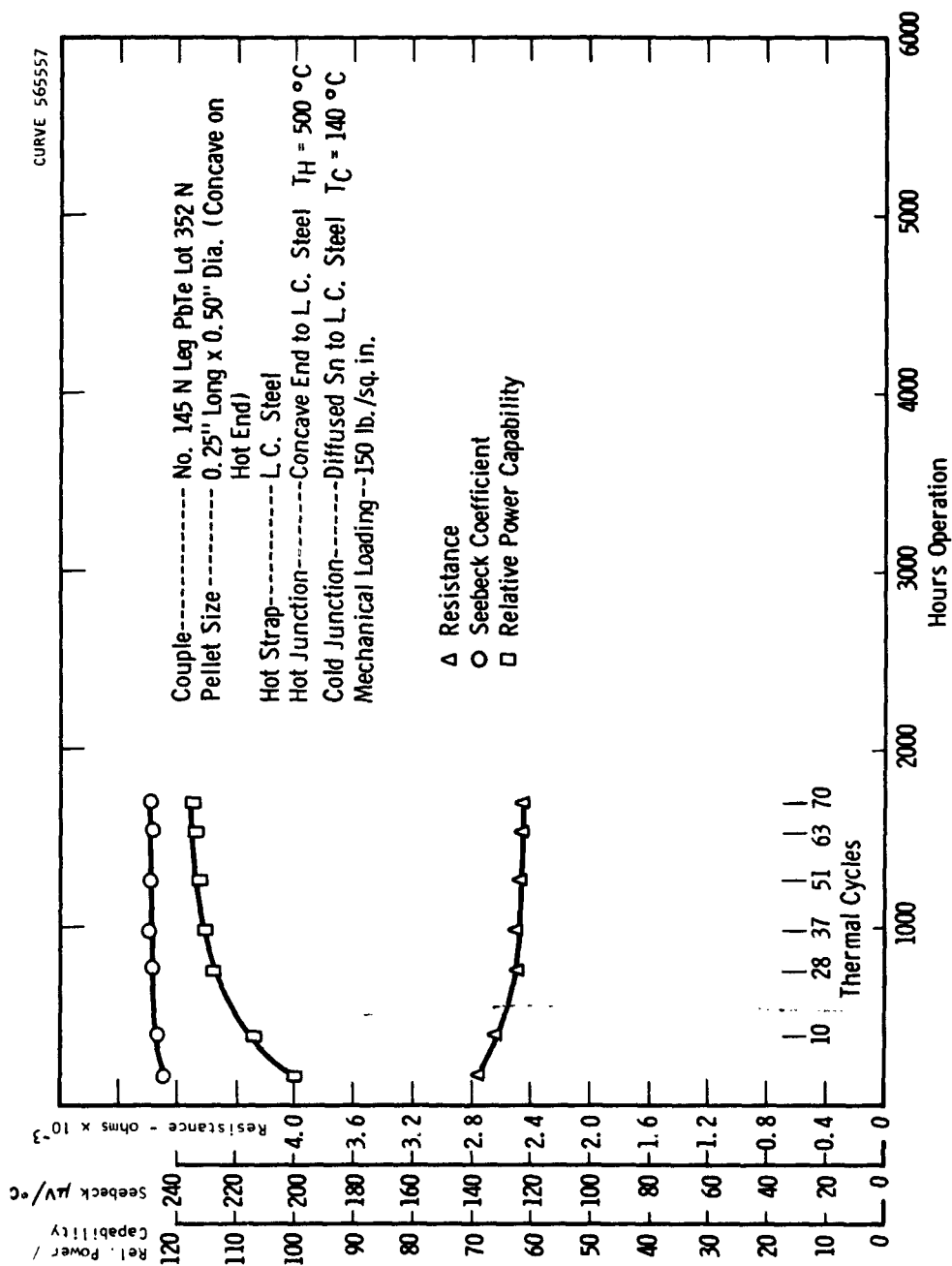


Fig. 7N

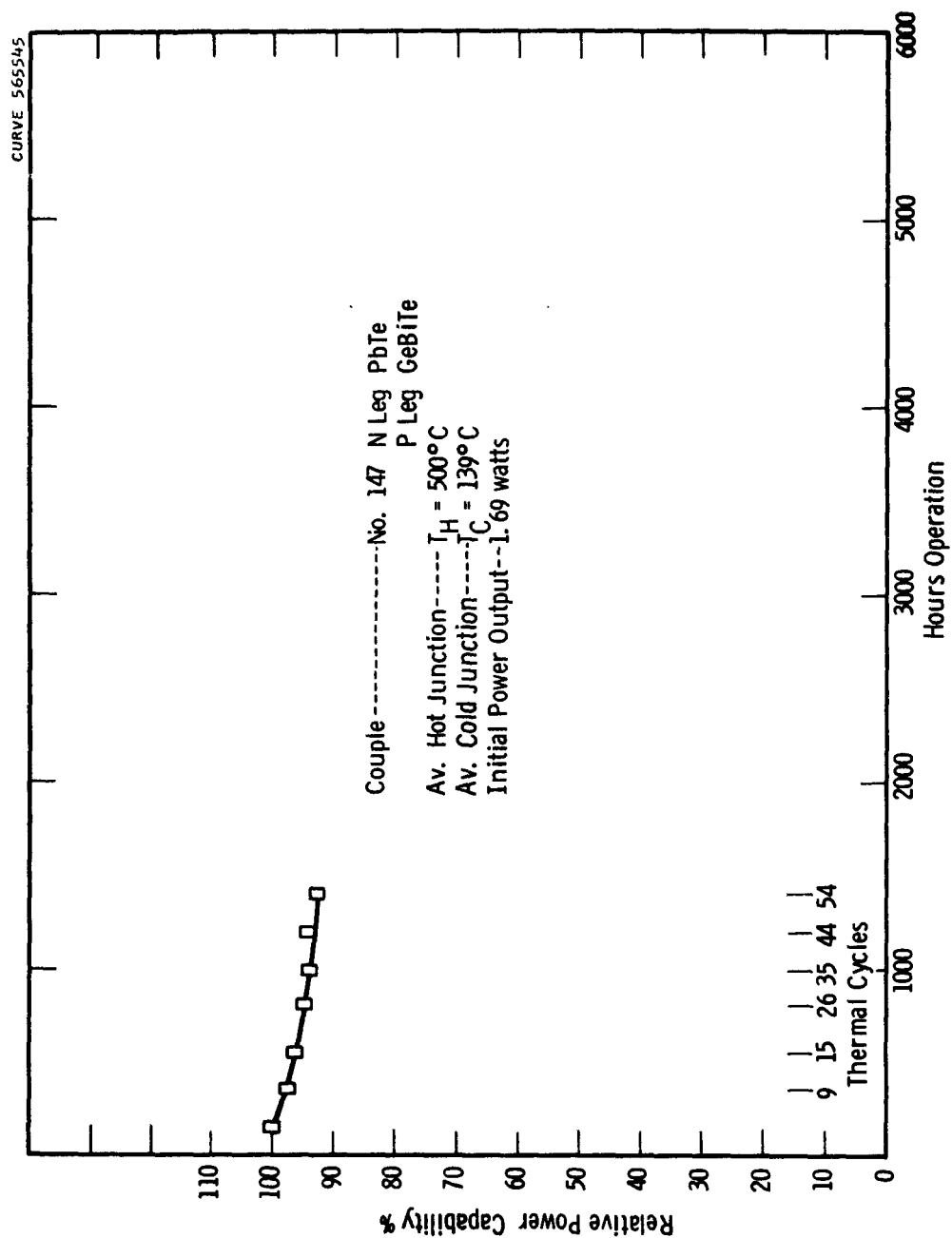


Fig. 8

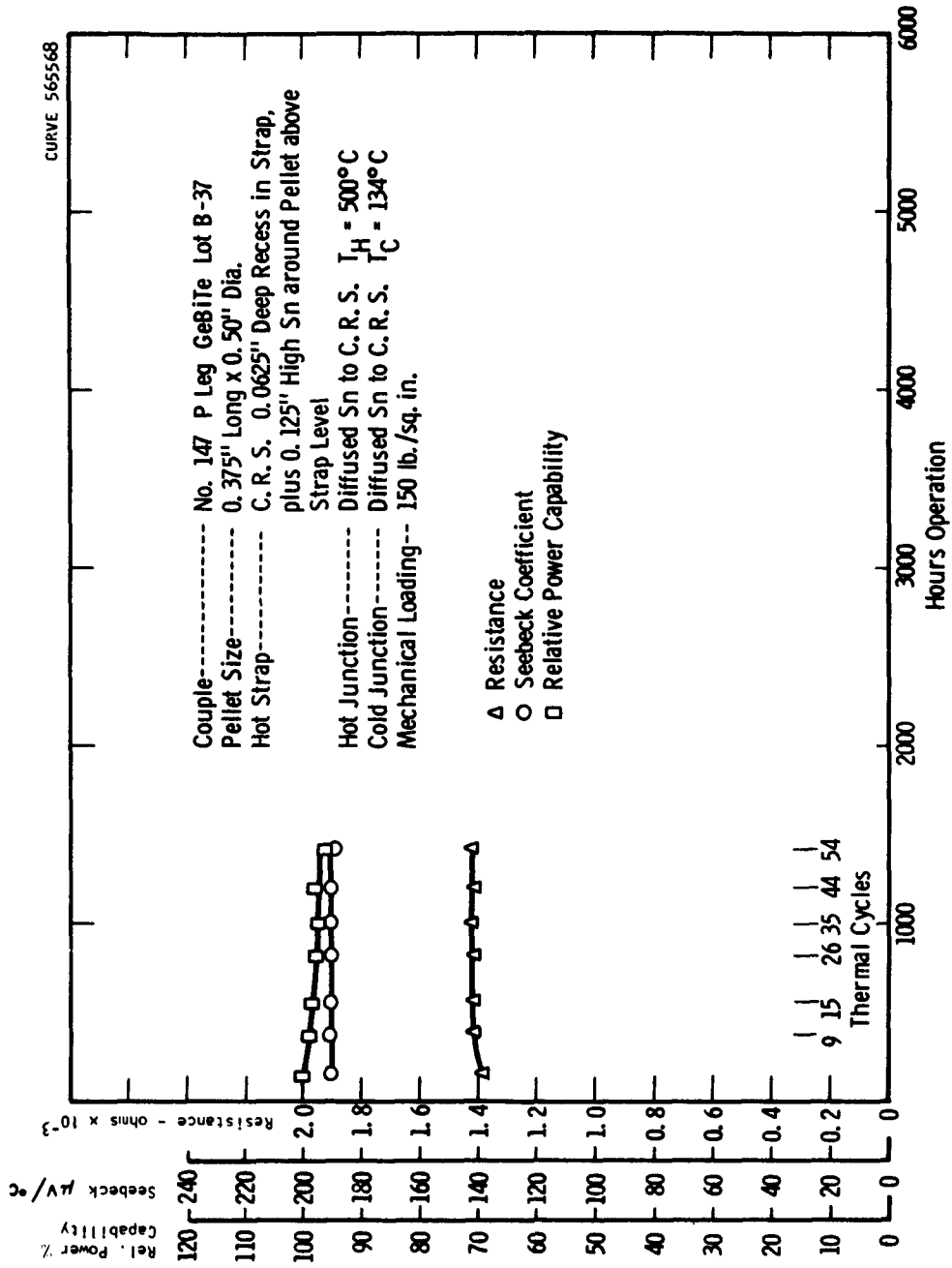


Fig. 8P

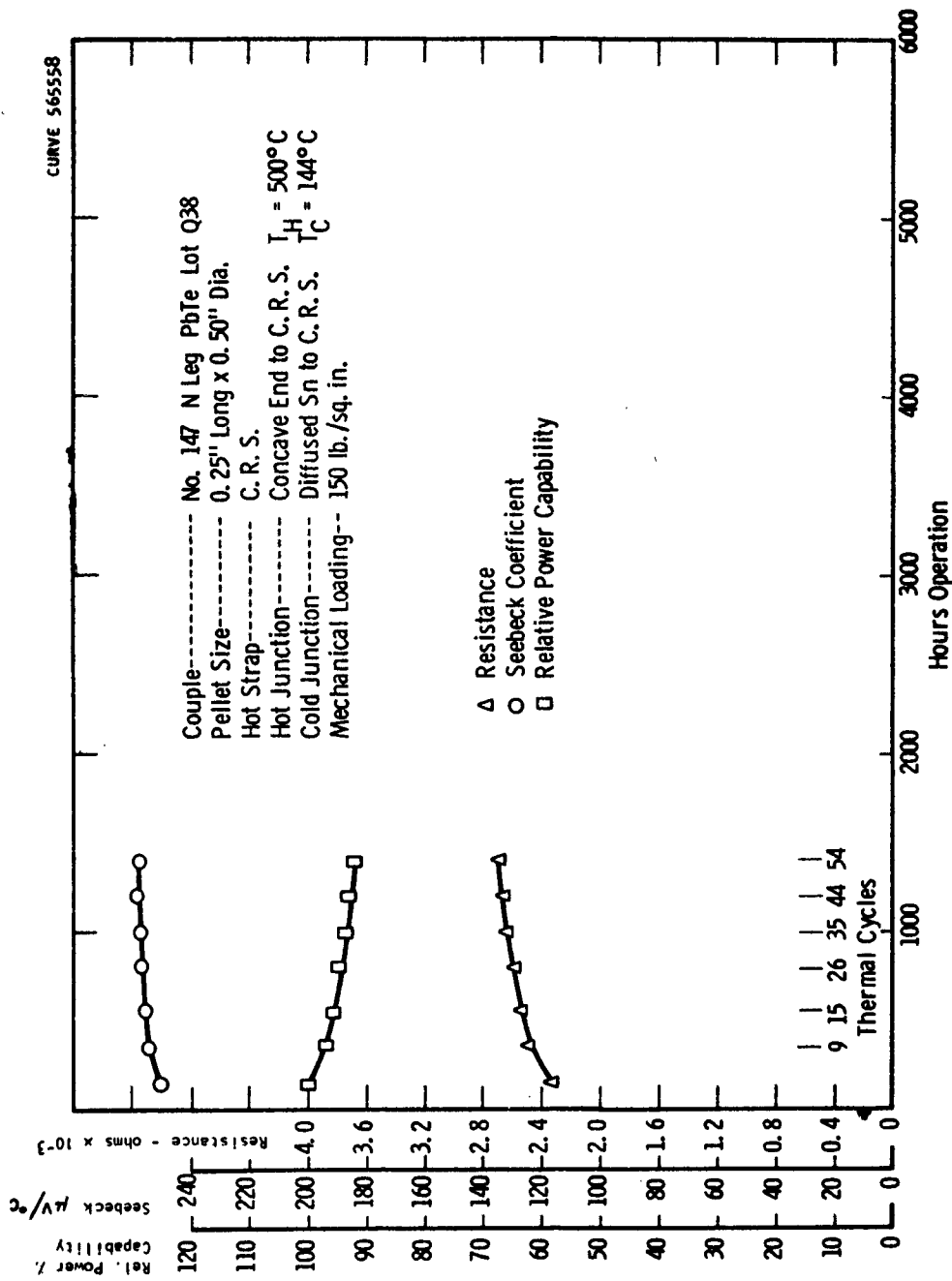


Fig. 8N

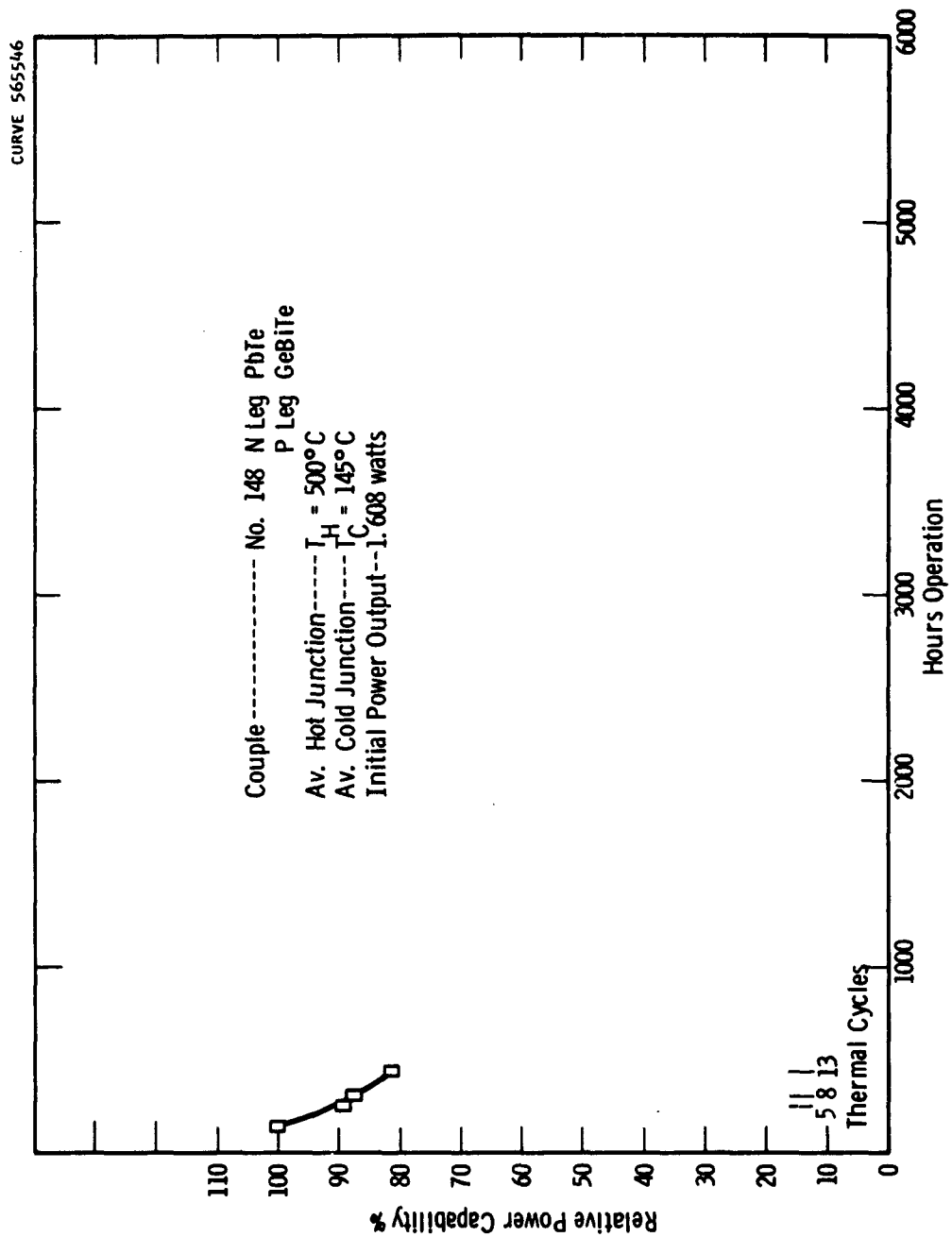


Fig. 9

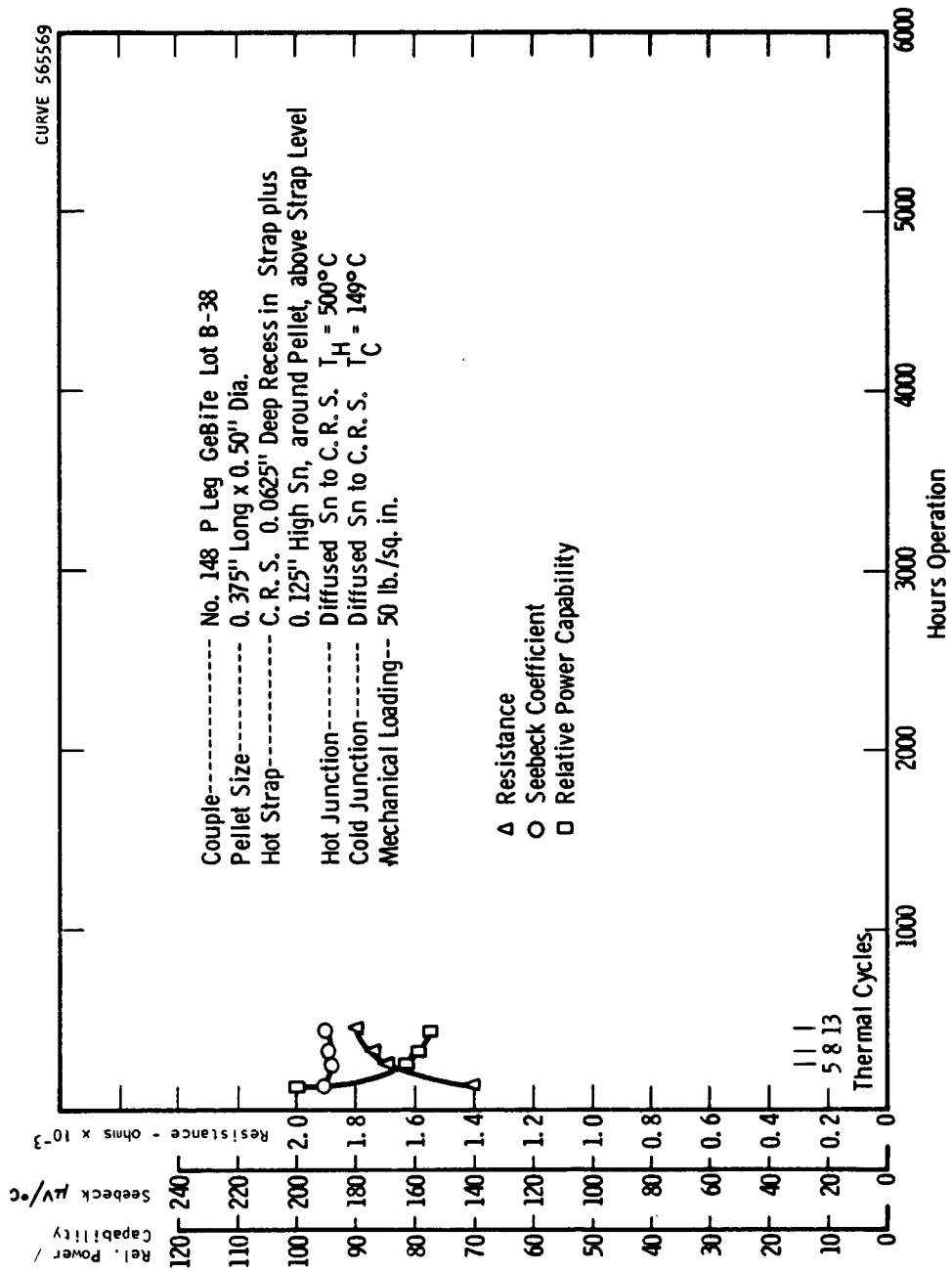


Fig. 9P

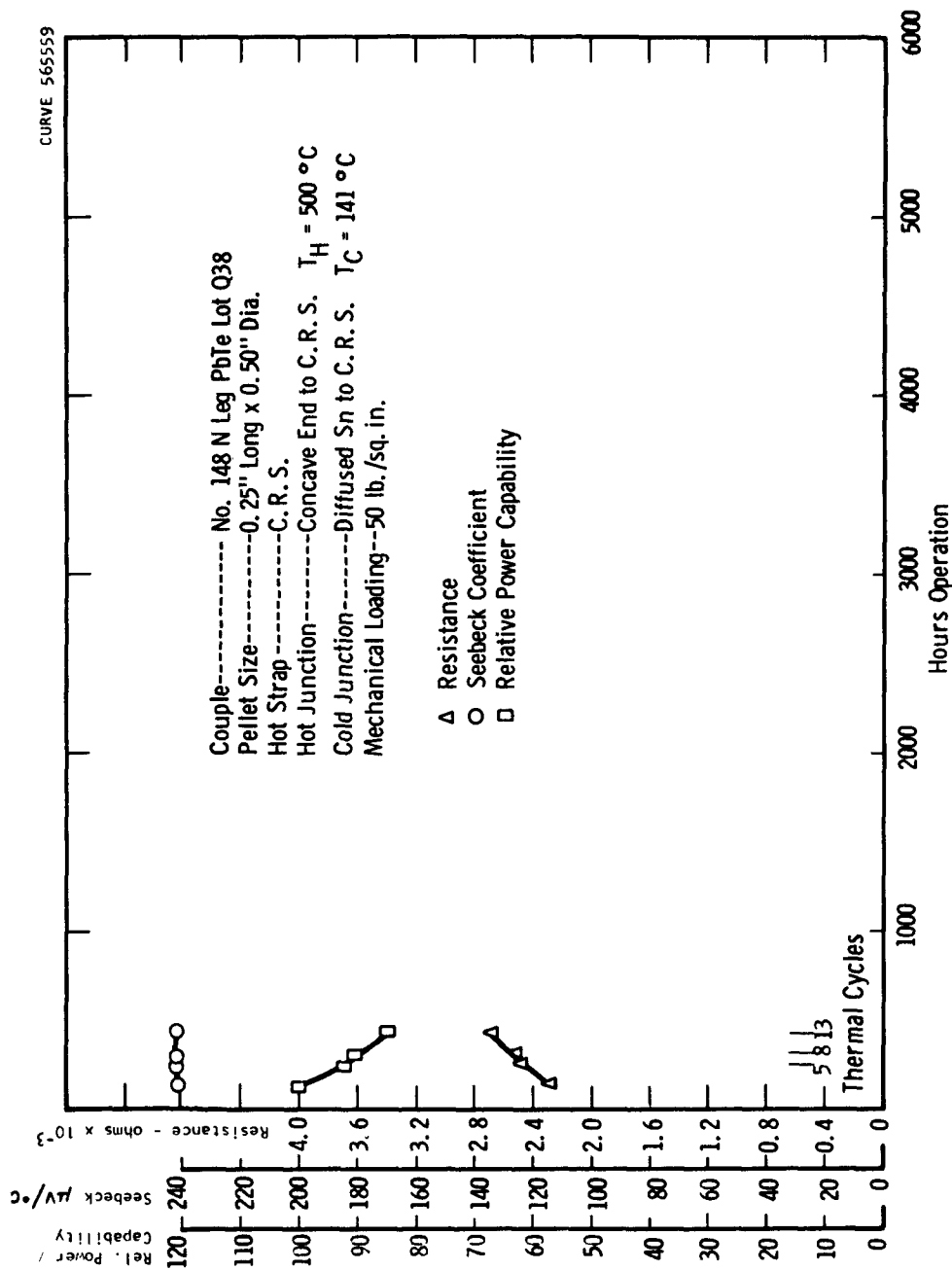


Fig. 9N

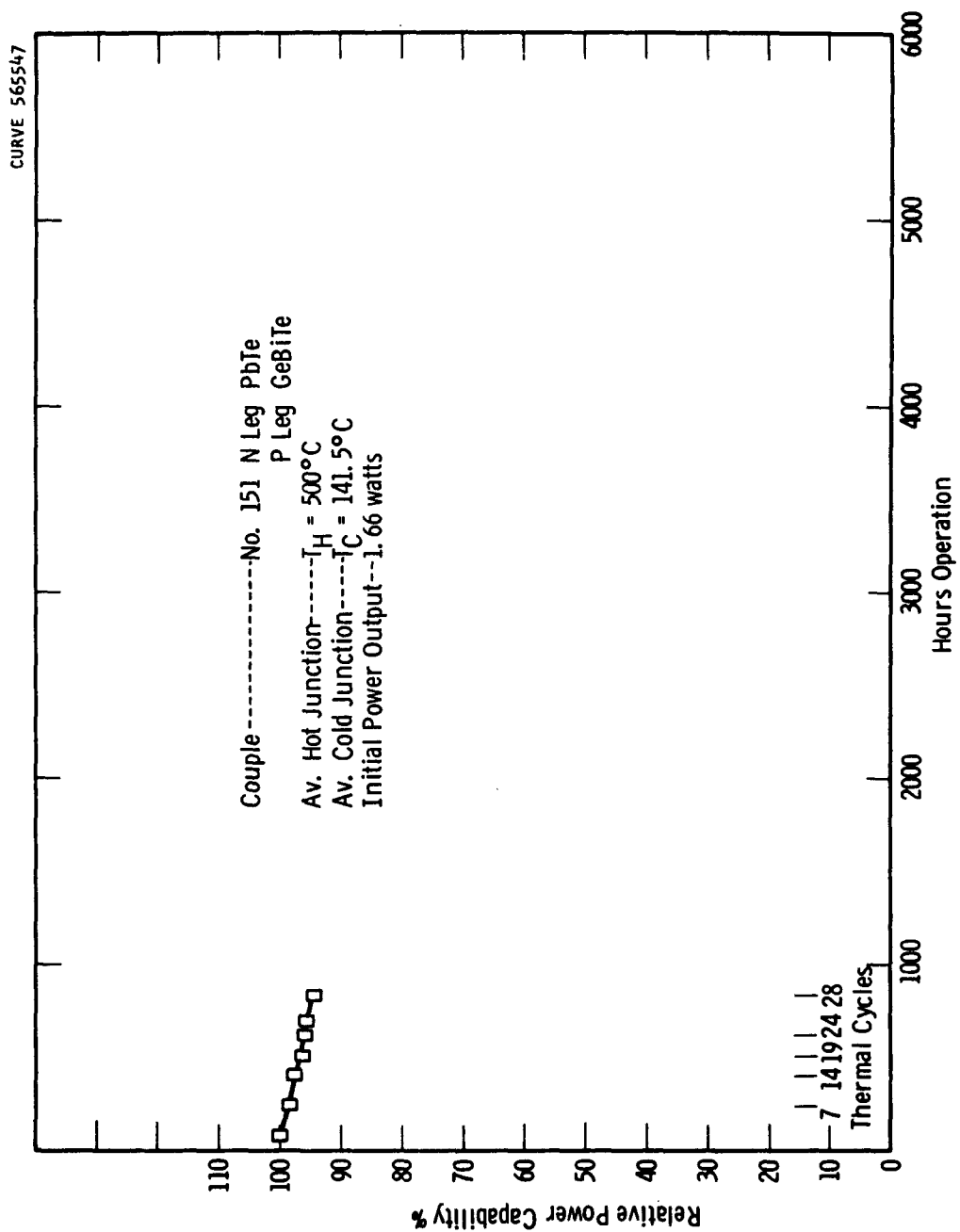


Fig. 10

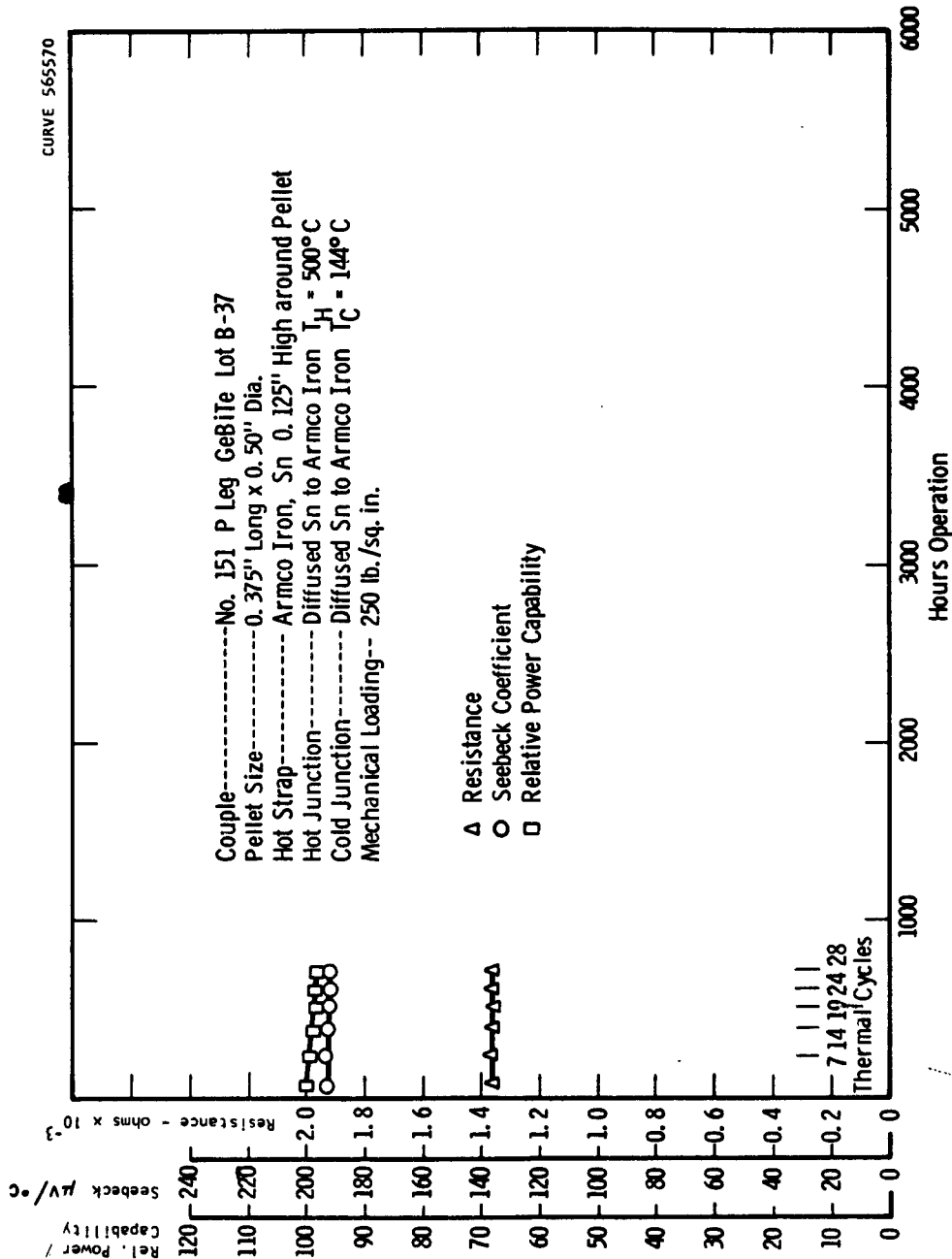


Fig. 10P

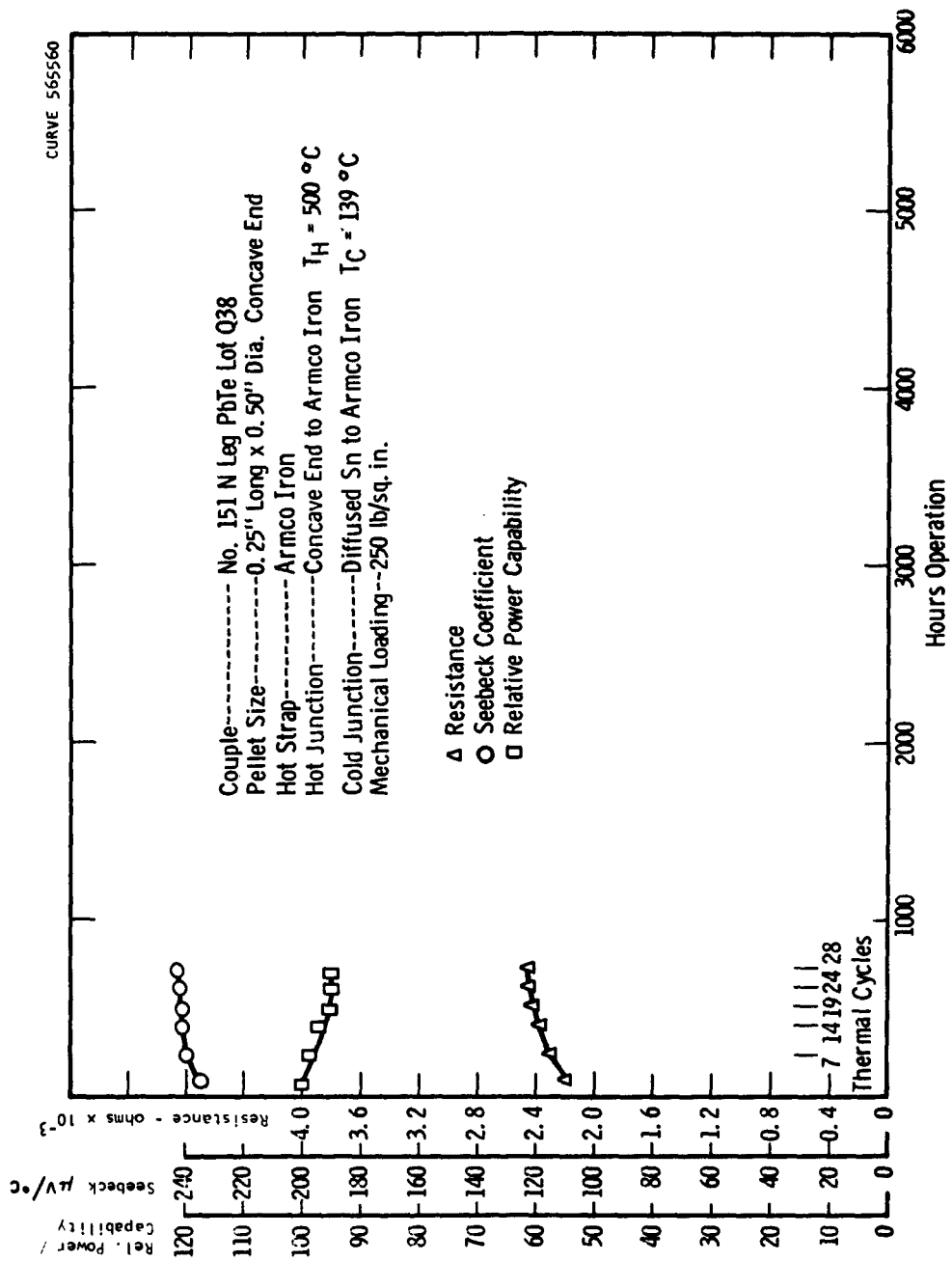


Fig. 10N

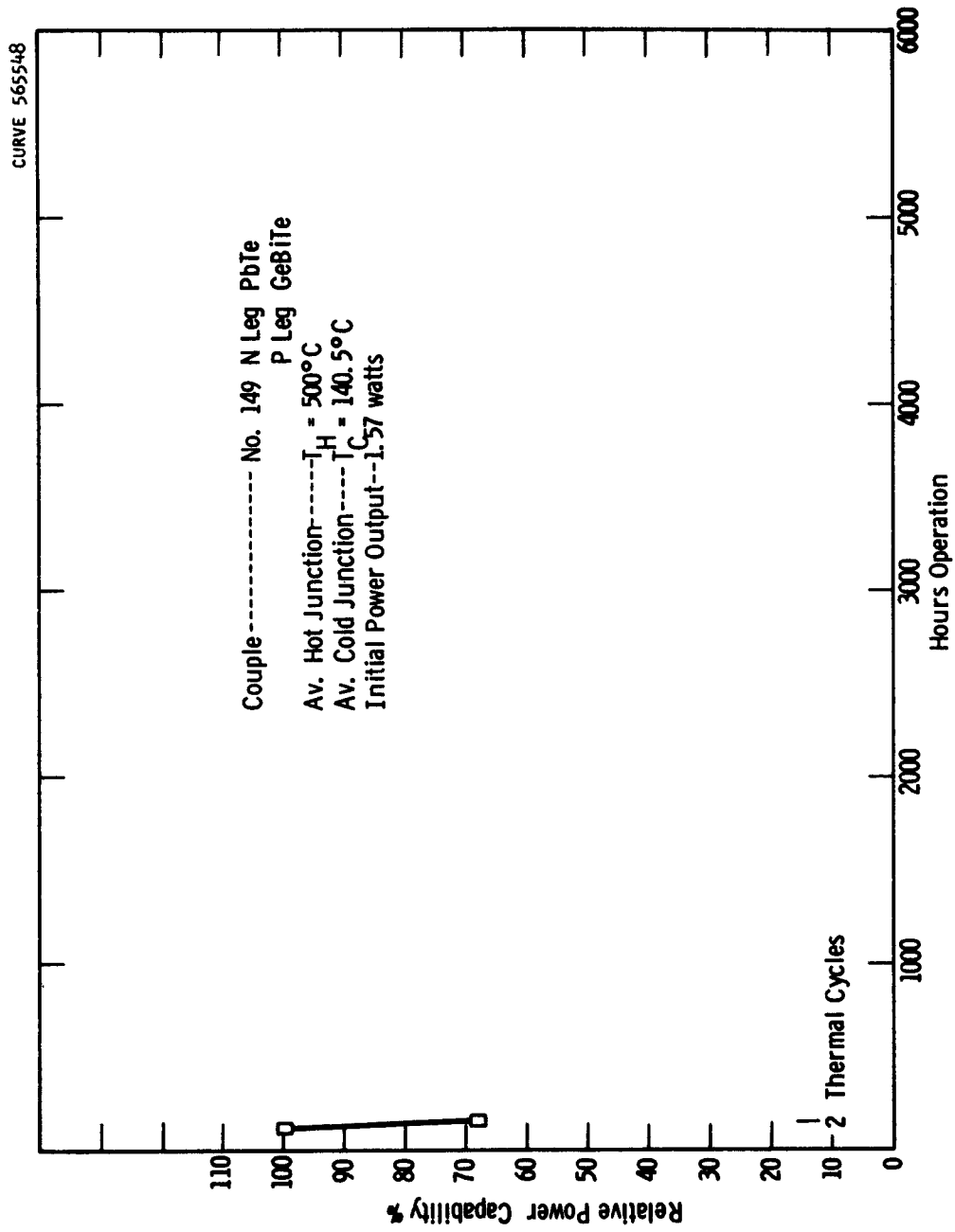


Fig. 11

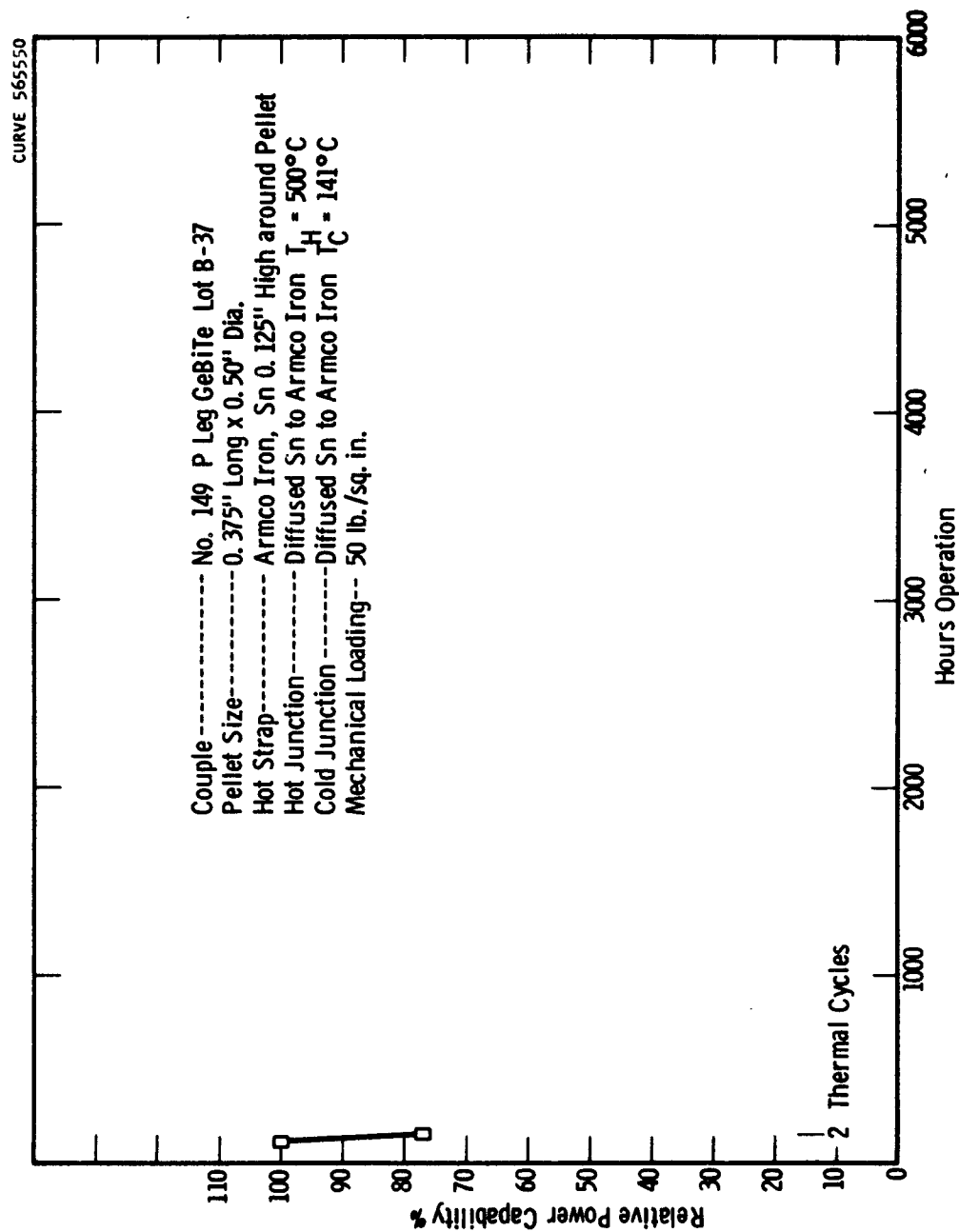


Fig. 11P

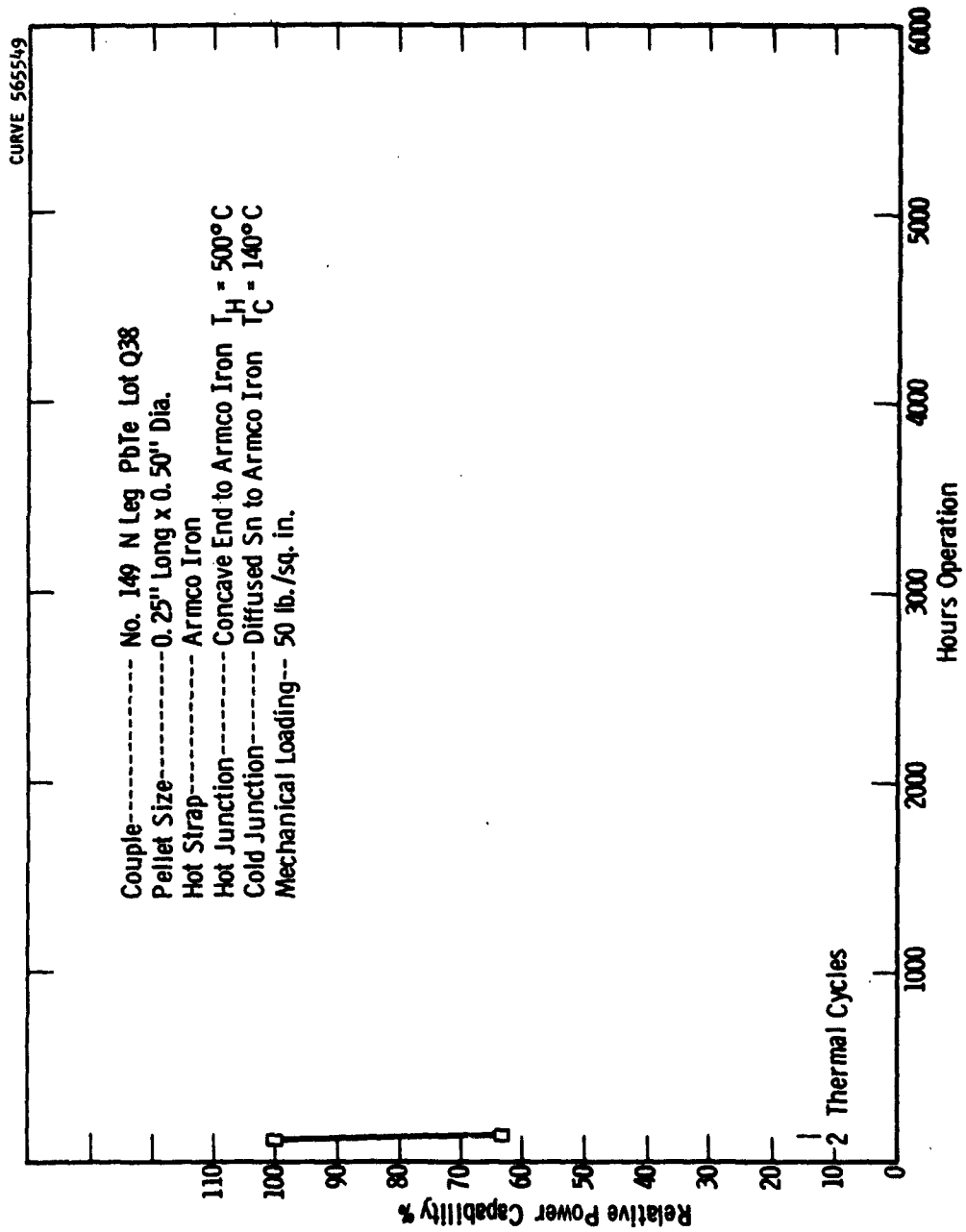
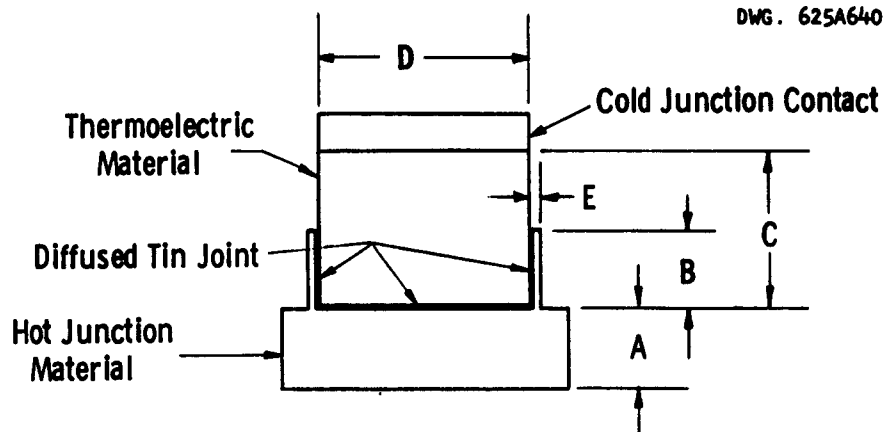


Fig. 11N

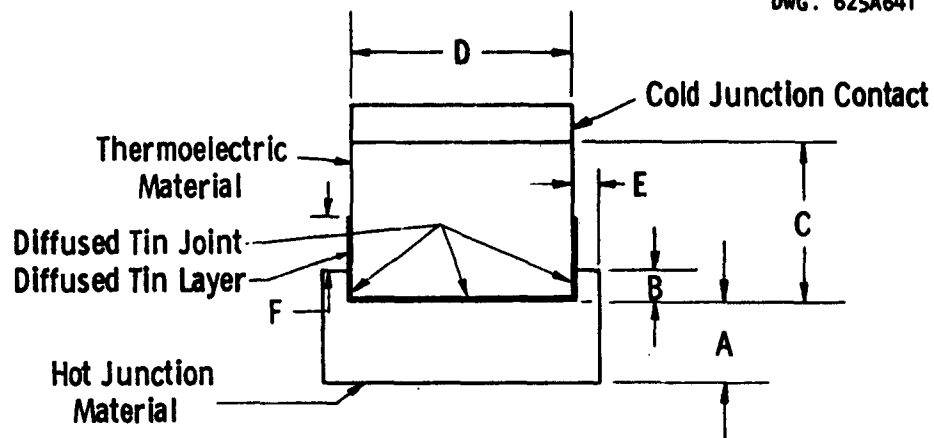
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Couple Number	Thermo-electric Material	Hot Junction Material	A inches	B inches	C inches	D inches	E inches
117	GeBiTe	304 S. Stl.	0.125	0.125	0.250	0.500	0.008
117	PbTe	304 S. Stl.	0.125	0.125	0.250	0.500	0.008
119	GeBiTe	304 S. Stl.	0.125	0.125	0.375	0.500	0.008
119	PbTe	304 S. Stl.	0.125	0.125	0.375	0.500	0.008
121	GeBiTe	304 S. Stl.	0.125	0.125	0.375	0.500	0.008
121	PbTe	304 S. Stl.	0.125	0.125	0.375	0.500	0.008
127	GeBiTe	304 S. Stl.	0.125	0.1875	0.50	0.500	0.004
127	PbTe	304 S. Stl.	0.125	0.125	0.25	0.500	0.008

Fig. 12—Thinwall Recess Contact

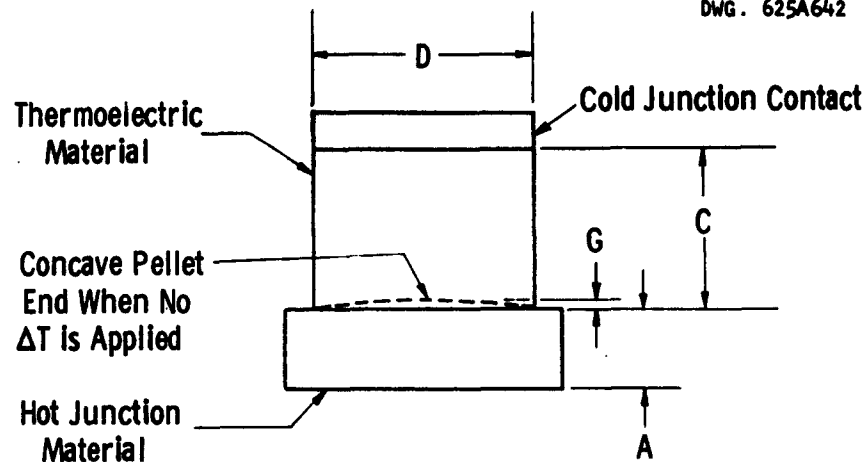
DWG. 625A641



Couple Number	Thermo-electric Material	Hot Junction Material	A inches	B inches	C inches	D inches	E inches	F inches
143	GeBiTe	304 S. Stl.	0. 1875	0. 0625	0. 375	0. 500	>0. 060	0. 125
143	PbTe	304 S. Stl.	0. 1875	0. 0625	0. 250	0. 500	>0. 060	0
147	GeBiTe	Cold Rolled Steel	0. 1875	0. 0625	0. 375	0. 500	>0. 060	0. 125
148	GeBiTe	Cold Rolled Steel	0. 1875	0. 0625	0. 375	0. 500	>0. 060	0

Fig. 13—Heavywall Recess Contact

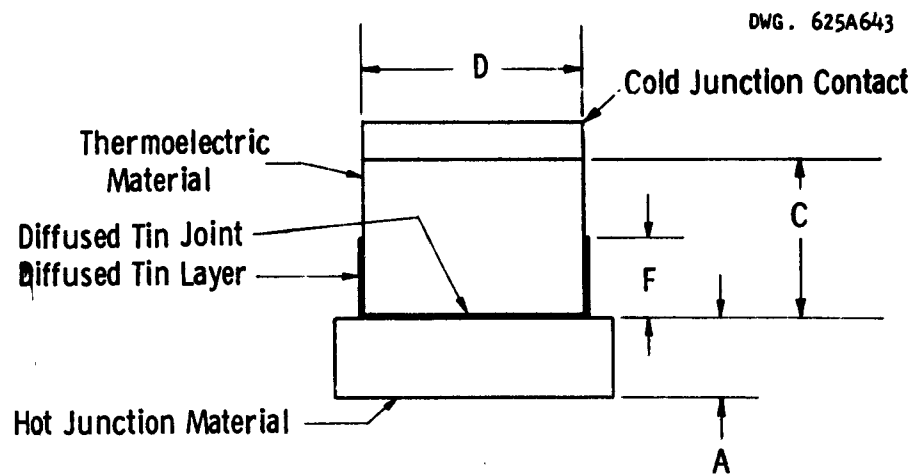
DWG. 625A642



Couple Number	Thermo-electric Material	Hot Junction Material	A inches	C inches	D inches	G inches
144	PbTe	304 St. Stl.	0.125	0.25	0.50	0.0008
145	PbTe	Low Carbon Steel	0.25	0.25	0.50	0.0008
147	PbTe	Cold Rolled Steel	0.25	0.25	0.50	0.0008
148	PbTe	Cold Rolled Steel	0.25	0.25	0.50	0.0008
149	PbTe	Armco Fe	0.1875	0.25	0.50	0.0008
151	PbTe	Armco Fe	0.1875	0.25	0.50	0.0008

* Contact surface of hot junction material treated with diffused Sn

Fig. 14—Modified Pressure Contact



Couple Number	Thermo-electric Material	Hot Junction Material	A inches	C inches	D inches	F inches
144	GeBiTe	304 St. Stl.	0.125	0.25	0.50	0.125
145	GeBiTe	Low Carbon Steel	0.250	0.25	0.50	0.125
149	GeBiTe	Armco Fe	0.1875	0.25	0.50	0.125
151	GeBiTe	Armco Fe	0.1875	0.25	0.50	0.125

Fig. 15—Modified Tin (Sn) Contact

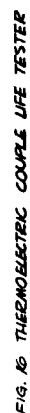


FIG. 16. THERMOELECTRIC COUPLE LIFE TESTER

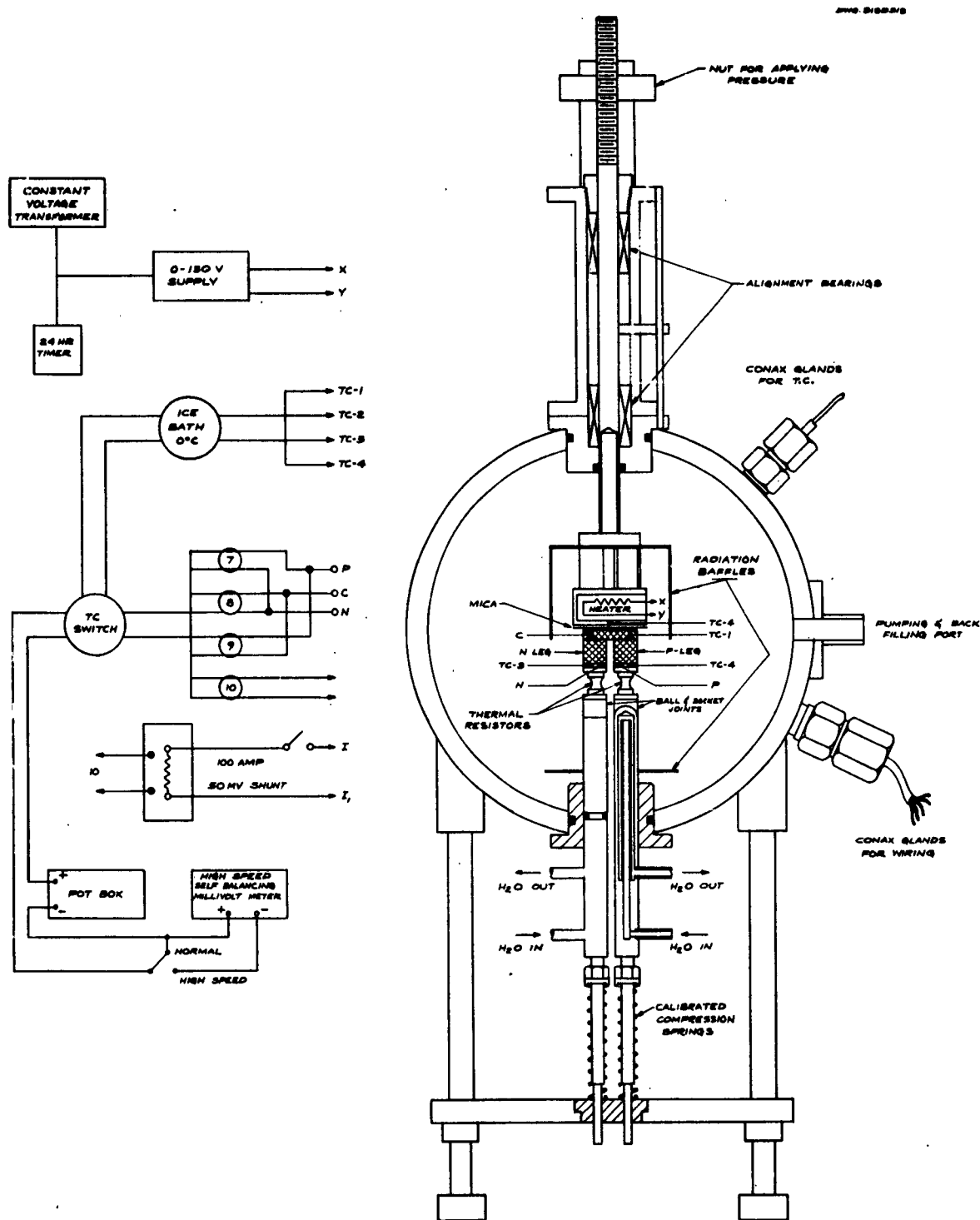


FIG. 17 - DUPLEX THERMOELECTRIC COUPLE LIFE TESTER

U. S. Navy, Bureau of Ships, Washington 25, D. C. THERMOELECTRICITY, Quarterly Prog. Rpt. No. 4, December, 1962 Unclassified Report Improved properties for GeBiTe result from setting final sinter temperature at or near solidus temperature. Efficiency of BiSbTe-PbTe measured at 7% for 375°C-50°C ΔT. Mechanical and vaporization properties of CoSbTeSe were measured to 700°C. Further results on "p" CoSb are given. Processing detail and test results for Sn diffusion and recess joints are given. Experiments in (over)	1. Thermoelectric Materials, Power Generation I. Contract NObs 86595 II. Westinghouse Electric Corp. Central Res. Laboratories Pgh. 35, Pa. Horigan, W.L. Ed.	U. S. Navy, Bureau of Ships, Washington 25, D. C. THERMOELECTRICITY, Quarterly Prog. Rpt. No. 4, December, 1962 Unclassified Report Improved properties for GeBiTe result from setting final sinter temperature at or near solidus temperature. Efficiency of BiSbTe-PbTe measured at 7% for 375°C-50°C ΔT. Mechanical and vaporization properties of CoSbTeSe were measured to 700°C. Further results on "p" CoSb are given. Processing detail and test results for Sn diffusion and recess joints are given. Experiments in (over)	1. Thermoelectric Materials, Power Generation I. Contract NObs 86595 II. Westinghouse Electric Corp. Central Res. Laboratories Pgh. 35, Pa. Horigan, W.L. Ed.
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