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PROGRESS REPORT NO. 11
FOR A PROGRAM OF
THERMOELECTRIC GENERATOR TESTING
AND
RTG DEGRADATION MECHANISMS EVALUATION

Submitted to
The US Energy Research and Development Administration
Space Nuclear Systems Division
Washington, D. C.

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by
The Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

May 1975

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FOREWORD

This report is submitted to the Energy Research and Development Administration covering work conducted under Interagency Agreement No. AT(04-3)-959 by the Jet Propulsion Laboratory and documents all activities covering the period March and April 1975. This work is being performed under the technical direction of Mr. Patrick O'Riordan, Isotopes Technology Branch of the ERDA Space Nuclear Systems Division.

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Progress Report No. 11

March and April 1975

I. Silicon Germanium Technology

A. Experiments with Silicon Nitride Coated Hot Shoes

The weight loss measurement experiments of Si_3N_4 coated hot shoes are continuing. The experiments are being conducted in three different environments: vacuum ($p < 1 \times 10^{-7}$ torr), carbon monoxide ($p = 1 \times 10^{-4}$ torr) and carbon monoxide ($p = 1 \times 10^{-3}$ torr). The samples which are under test have two different coating thicknesses, as the original batch of hot shoes was coated with 6000 Å of Si_3N_4 which is only half the nominal thickness. The remaining samples all have coating thicknesses of 12000 Å. Throughout the text and graphs, reference to 6000 Å and 12000 Å coating is made wherever this difference is of significance. Table 1 gives an overall summary of the number of hours each sample has been under test. All testing at 1200°C has been completed and in the case of the carbon monoxide environment, the 1170°C temperature testing has also been concluded. Testing at the very lowest temperatures (1035°C and 1000°C) in a high vacuum environment is continuing, but as is indicated on the table, insufficient weight loss has occurred to allow this data to be properly analyzed.

1) Vacuum Operation. The weight loss measurements obtained from the Si_3N_4 coated hot shoes which have operated in a high vacuum are shown as a function of operating time in Figures 1-5. The weight loss of an uncoated SiMo hot shoe is also shown on all figures for reference. Examining these graphs, it becomes evident that the Si_3N_4 coating has been lost at the operating temperature of 1170°C for both thin and thick coated samples and at 1135°C for the thin (6000 Å) coated sample. On each of the graphs, a weight loss rate is shown for the coated sample (i.e. before an increase in weight loss is evident). Note that at 1100°C the thin coated sample appears to be partially losing its coating during the latter portion of the test. Although there are some differences in the rates at which the thick

Table 1. Si₃N₄ Coating Test Sample Matrix

Coating Thickness Temp (°C)	Vacuum		1 x 10 ⁻⁴ torr CO		1 x 10 ⁻³ torr CO	
	6000 Å	12,000 Å	6000 Å	12,000 Å	6000 Å	12,000 Å
1170	2500 h	2000 h	-	-	-	-
1135	2500 h	2000 h	-	S.T.	1380 h	470 h
1100	2500 h	2000 h	-	1322 h	-	470 h
1075	2500 h	2000 h	-	1322 h	-	-
1050	2500 h	2000 h	-	1322 h	-	470 h
1035	-	1000 h*	-	400 h	-	-
1000	-	1000 h*	-	750 h	-	1230 h
975	-	-	-	-	-	1020 h
950	-	-	-	-	1520 h	470 h

S.T. - short-term tests only

*not sufficient weight loss for analysis

Figure 1. Si_3N_4 Coated Hot Shoe Weight Loss in Vacuum Environment at 1170°C

Figure 2. Si_3N_4 Coated Hot Shoe Weight Loss in Vacuum Environment at 1135°C

Figure 3. Si_3N_4 Coated Hot Shoe Weight Loss in Vacuum Environment at 1100°C

Figure 4. Si_3N_4 Coated Hot Shoe Weight Loss in Vacuum Environment at 1075°C

Figure 5. Si_3N_4 Coated Hot Shoe Weight Loss in Vacuum Environment at 1050°C

and the thin coated samples lost weight, this difference may be simply data scatter and not connected to the coating thickness. The loss rate as a function of temperature is plotted in Figure 6. The graph shows some data scatter at the intermediate temperatures, but a reasonably straight line through all of the data can be obtained.

2) Carbon Monoxide 1×10^{-4} torr. The weight loss of the Si_3N_4 coated hot shoes which operated in an CO environment are shown in Figures 7-13, plotted as a function of operating time. Again for comparison, the uncoated hot shoe loss in a vacuum environment is also shown on all figures. From these figures, it can be seen that all of the thin coated samples have lost the coating as indicated by the increased weight losses. To date, thick coated samples have lost their coating only at the higher operating temperatures. The weight loss rate of the still coated hot shoe is again shown on each figure, based on the weight loss of the sample before the coating was lost.

An Arrhenus plot of the loss rate is shown in Figure 14. A best fit straight line loss rate is drawn on the figure through the data points. It should be noted that at 1035°C , only a relatively short test time has been recorded and that the eventual loss rate at this temperature is expected to be somewhat lower than is shown in the figure.

3) Carbon Monoxide 1×10^{-3} torr. The weight loss data for Si_3N_4 coated hot shoes operating at a pressure of 1×10^{-3} torr are shown in Figures 15-20. In this environment, some testing was performed using n-type uncoated SiMo hot shoe material. From this data, the loss rate of the uncoated material was established, and this is shown on all of the graphs in addition to the SiMo loss rate obtained in a vacuum environment.

B. Resistance and Thermal Conductivity of Multifoil Insulation

1) Shunt Resistance of Uncoated Couples. The behavior of the electrical

Figure 6. Weight Loss Rate of Si_3N_4 Coated Hot Shoes in Vacuum Environment

SEMI LOGARITHMIC 7 CYCLES X 60 DIVISIONS AD 2340-01

Figure 7. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-4} torr Carbon Monoxide Environment at 1170°C

Figure 8. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-4} torr Carbon Monoxide Environment at 1135°C

Figure 9. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-4} torr Carbon Monoxide Environment at 1100°C

Figure 10. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-4} torr Carbon Monoxide Environment at 1075°C

Figure 11. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-4} torr Carbon Monoxide Environment at 1050°C

Figure 12. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-4} torr Carbon Monoxide Environment at 1035°C

Figure 13. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-4} torr Carbon Monoxide Environment at 1000°C

Figure 14. Weight Loss Rate of Si_3N_4 Coated Hot Shoes in a 1×10^{-4} torr
 MODEL Environment of Carbon Monoxide DATE

Figure 15. Si_3N_4 Coated Ho Shoe Weight Loss in a 1×10^{-3} torr Carbon Monoxide Environment at 1135°C

Figure 16. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-3} torr Carbon Monoxide Environment at 1100°C

Figure 17. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-3} torr Carbon Monoxide Environment at 1050°C

Figure 18. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-3} torr Carbon Monoxide Environment at 1000°C

Figure 19. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-3} torr Carbon Monoxide Environment at 975°C

Figure 20. Si_3N_4 Coated Hot Shoe Weight Loss in a 1×10^{-3} torr Carbon Monoxide Environment at 900°C

conduction path between adjacent unicouples, which is the cause of additional output power shunting, has been analyzed in some detail. The data for this analysis is provided by the 18-couple modules and some 4-couple modules, all operating at RCA. Also included in the evaluation are the two ETGs (TBC-1 and TBC-4) which have sufficient operating time to show a significant decrease in the resistance between the circuit and the foil package.

To compare all of this data on a common basis, the resistances of the different size modules are normalized to the equivalent resistance of a full up generator. Also the data is plotted as a function of the amount of weight being lost from a hot shoe, rather than as a function of operating time. The data from seven 18-couple modules, two 4-couple modules and two generators, all of which utilize uncoated hot shoes, are shown in Figure 21. Considerable spread in the data is apparent from the figure. The data does allow, however, conclusions to be drawn as to a "worst case" and a "best case" resistance which could be expected. This is shown in the figure. Also a "most probable" resistance, based on the majority of data points is also shown in the figure. The equivalent operating time at a constant hot shoe temperature of 1035°C is also shown. If one places the lower limit of tolerable resistance level at 10 ohms, then depending upon the rate of resistance decrease, this limit will be reached as early as one year of operation using the worst case curve. Using the most probable rate of resistance decrease, this lower limit will be reached between two and three years of operation.

2) Shunt Resistance of Si_3N_4 Coated Couples. The shunt resistance of 18-couple modules which use the Si_3N_4 coated unicouples can be compared to the uncoated uncouple module performance. Using the same normalizing technique as for the uncoated unicouples, the resistance of two 18-couple modules with coated hot shoes is plotted as a function of weight loss in Figure 22. The hot shoe weight loss for the two modules was obtained by using the Si_3N_4 coated hot shoe loss rates

Figure 21. Circuit to Foil Resistance as a Function of Hot Shoe Weight Loss, Normalized to Generator Equivalent Shunt Resistance

Figure 22. Circuit to Foil Resistance as a Function of Weight Loss Per Hot Shoe for Si_3N_4 Coated Unicouples

obtained for vacuum operation as part of the Si_3N_4 coating evaluation task. The figure shows that the shunt resistance of the two coated 18-couple modules decreases at a rate roughly equal to the worst case rate obtained from the coated modules. It should be noted that this data is plotted as a function of weight loss per hot shoe and when compared to operating times of 1035°C , the coated uncouple performance becomes considerably better than the uncoated condition. This can be seen from the time scale, given on the curve, which is based on the assumption that the Si_3N_4 coated rate at 1035°C is a factor of ten less than the uncoated loss rate at this same temperature. The lower rate again was obtained from the sublimation data of Si_3N_4 coated hot shoes under the Si_3N_4 coating evaluation task. The data shown in this figure might be somewhat misleading since it assumes that the Si_3N_4 coating life is infinite. In reality, of course, the coating has a finite lifetime, after which the rate of weight loss per hot shoe will increase to the rate of uncoated hot shoes. The DEGRA computer code, which is presently being updated, will be programmed to account for this finite coating lifetime and the subsequent increase in weight loss rate.

3) Thermal Conductance Change of Multifoil Insulation with Si_3N_4 Coated Uncouples. One of the output power degradation mechanisms of the MHW generator is the change in thermal conductance of the multifoil insulation. This change, which is brought about by the deposition of sublimation and reaction products, has been analyzed with the help of a computer program (Ref. 1) and is shown for the various 18-couple modules having uncoated couples in Figure 27 of the section of this report entitled "TBC-1 Generator Performance Analysis". The behavior of the thermal conductance of the insulation when Si_3N_4 coated uncouples are utilized is shown in Figure 23. It shows the average of the 18-couple module data with uncoated couples as a function of weight loss per hot shoe compared to the data obtained from modules 18-0 and SN-1, both of which utilize Si_3N_4 coated uncouples. Again, the rate for the weight loss of the coated uncouples was based on the

Figure 23. Change of Insulation Thermal Conductivity as a Function of Hot Shoe Weight Loss for Si_3N_4 Coated Unicouples

vacuum weight loss rate of Si_3N_4 coated hot shoes. The figure tends to indicate a worse performance than would be expected from the uncoated module data. However, if, as was the case for the resistance data, a "worst case" type curve were to be drawn for the uncoated module data, this curve would be very close to the data shown for the coated couples. Again, it should be noted that data plotted on this figure assumes that the coating remains completely intact. Based on the data from the coating evaluation task, the coating of the "N" portion of the hot shoes in these two modules has probably completely disappeared after a total test time of 2,500 hours. Thus, from that point onward, the data should be shifted further and further to the right since more and more of the hot shoe area is losing weight at the uncoated rate.

C. Material Compatibility Experiments

The initial test data on compatibility testing of a matrix of astroquartz, boron-nitride, silicon-nitride, alumina, graphite, silicon-germanium and silicon-molybdenum at 1050, 1100, 1150 and 1200°C was reported in the last test period. This testing has been continued with the results shown in Table 2.

The weight changes shown are based on an assumed area of 11.6 cm² for all samples. In the case of the vaporization loss samples, this area is fully exposed to the furnace on all faces. Other samples are sandwich structures with only one or none of the faces exposed. The BN, Si_3N_4 and graphite samples have one exposed face while the remaining materials (alumina, astroquartz, SiGe and SiMo) are sandwiched between BN, Si_3N_4 or graphite and have neither face exposed.

The furnace structures are alumina with tantalum heater wires and molybdenum heat shields. While the vacuum chamber is operating in the 10^{-7} torr range, the baffling provided by the individual furnace structures undoubtedly decreased effective pumping speed and the pressure in the furnaces and over the specimens is probably considerably higher.

Table 2. Compatibility Test Results

Weight Changes in gm/cm²/h for Temperatures and Test Durations Shown

Weight Change For:	In Contact With:	At 1050°C			At 1100°C			At 1150°C			At 1200°C		
		0-50h	0-100h	0-200h	0-50h	0-100h	0-200h	0-50h	0-100h	0-200h	0-50h	0-100h	0-200h
Astroquartz	Si ₃ N ₄	-1x10 ⁻⁶	-1x10 ⁻⁶	-1x10 ⁻⁶	-8x10 ⁻⁶	-8x10 ⁻⁶	-8x10 ⁻⁶	-6x10 ⁻⁶	-1x10 ⁻⁵	-1x10 ⁻⁵	-9x10 ⁻⁶	-3x10 ⁻⁵	-3x10 ⁻⁵
	BN	-1x10 ⁻⁵	-1x10 ⁻⁵	-8x10 ⁻⁶	-5x10 ⁻⁶	-5x10 ⁻⁶	-4x10 ⁻⁶	-6x10 ⁻⁶	-2x10 ⁻⁵	-2x10 ⁻⁵	-1x10 ⁻⁵	-1x10 ⁻⁵	-1x10 ⁻⁵
	Graphite	-9x10 ⁻⁶	-6x10 ⁻⁶	-3x10 ⁻⁶	-4x10 ⁻⁶	-8x10 ⁻⁶	-6x10 ⁻⁶	-7x10 ⁻⁶	-8x10 ⁻⁶	-7x10 ⁻⁶	-9x10 ⁻⁶	-2x10 ⁻⁵	-2x10 ⁻⁵
Al ₂ O ₃	Graphite	-1x10 ⁻⁶	-7x10 ⁻⁷	-3x10 ⁻⁷	-2x10 ⁻⁶	-0-	-1x10 ⁻⁷	-7x10 ⁻⁷	-2x10 ⁻⁶	-1x10 ⁻⁶	-5x10 ⁻⁶	-2x10 ⁻⁶	-2x10 ⁻⁶
SiGe	Si ₃ N ₄	-8x10 ⁻⁷	-2x10 ⁻⁶	-2x10 ⁻⁶	-7x10 ⁻⁶	-1x10 ⁻⁵	-8x10 ⁻⁶	+1x10 ⁻⁴	Bonded	Bonded	-2x10 ⁻⁵	Bonded	Bonded
	BN	-1x10 ⁻⁶	-8x10 ⁻⁶	-7x10 ⁻⁶	-7x10 ⁻⁶	-6x10 ⁻⁶	-5x10 ⁻⁶	-8x10 ⁻⁶	-6x10 ⁻⁵	-5x10 ⁻⁵	-1x10 ⁻⁴	-1x10 ⁻⁴	-1x10 ⁻⁴
SiMo	Si ₃ N ₄	-2x10 ⁻⁷	-5x10 ⁻⁷	-3x10 ⁻⁷	+2x10 ⁻⁶	-2x10 ⁻⁶	-2x10 ⁻⁶	+1x10 ⁻⁵	Bonded	Bonded	+1.5x10 ⁻⁵	-8x10 ⁻⁶	-7x10 ⁻⁶
	BN	+1x10 ⁻⁶	+4x10 ⁻⁶	+1x10 ⁻⁶	+2x10 ⁻⁵	+6x10 ⁻⁶	-0-	+2x10 ⁻⁵	-1x10 ⁻⁵	-1x10 ⁻⁵	+1x10 ⁻⁵	-2x10 ⁻⁶	-4x10 ⁻⁶

Table 2. (cont.)

Weight Change For:	In Contact With:	At 1050°C			At 1100°C			At 1150°C			At 1200°C		
		0-50h	0-100h	0-200h	0-50h	0-100h	0-200h	0-50h	0-100h	0-200h	0-50h	0-100h	0-200h
Si ₃ N ₄	Astroquartz	-2x10 ⁻⁷	-3x10 ⁻⁷	-3x10 ⁻⁷	-8x10 ⁻⁷	-1x10 ⁻⁶	-1x10 ⁻⁶	+2x10 ⁻⁶	-4x10 ⁻⁶	-3x10 ⁻⁶	-3x10 ⁻⁶	-6x10 ⁻⁶	-1x10 ⁻⁵
	Graphite	-1x10 ⁻⁶	-8x10 ⁻⁷	-5x10 ⁻⁷	+1x10 ⁻⁶	+2x10 ⁻⁶	+8x10 ⁻⁷	+3x10 ⁻⁶	-0-	-0-	-2x10 ⁻⁶	-3x10 ⁻⁶	-2x10 ⁻⁶
	SiGe	+2x10 ⁻⁷	-4x10 ⁻⁷	-4x10 ⁻⁷	-5x10 ⁻⁷	-1x10 ⁻⁶	-1x10 ⁻⁶	+2x10 ⁻⁶	Bonded	Bonded	-1x10 ⁻⁶	Bonded	Bonded
	SiMo	-2x10 ⁻⁷	-6x10 ⁻⁷	-4x10 ⁻⁷	-1x10 ⁻⁶	-1x10 ⁻⁶	-1x10 ⁻⁶	+2x10 ⁻⁶	Bonded	Bonded	-4x10 ⁻⁶	-8x10 ⁻⁶	-7x10 ⁻⁶
	Vaporiza- tion Loss	-4x10 ⁻⁷	-7x10 ⁻⁷	-4x10 ⁻⁷	-7x10 ⁻⁷	-1x10 ⁻⁶	-1x10 ⁻⁶	+2x10 ⁻⁶	-4x10 ⁻⁶	-2x10 ⁻⁶	-3x10 ⁻⁶	-6x10 ⁻⁶	-6x10 ⁻⁶
BN	Astroquartz	-1x10 ⁻⁶	-4x10 ⁻⁷	-2x10 ⁻⁷	-1x10 ⁻⁶	-1x10 ⁻⁶	-8x10 ⁻⁷	-2x10 ⁻⁶	-8x10 ⁻⁷	-1x10 ⁻⁶	-2x10 ⁻⁶	-2x10 ⁻⁶	-1x10 ⁻⁶
	Graphite	-1.5x10 ⁻⁶	-6x10 ⁻⁷	-4x10 ⁻⁷	+4x10 ⁻⁷	+3x10 ⁻⁷	-1x10 ⁻⁷	-5x10 ⁻⁷	-2x10 ⁻⁷	-2x10 ⁻⁷	-2x10 ⁻⁶	-8x10 ⁻⁷	-4x10 ⁻⁷
	SiGe	-5x10 ⁻⁷	+2x10 ⁻⁷	-2x10 ⁻⁷	-1x10 ⁻⁶	-1x10 ⁻⁶	-8x10 ⁻⁷	-1x10 ⁻⁶	-2x10 ⁻⁶	-1x10 ⁻⁶	-2x10 ⁻⁶	-1x10 ⁻⁶	-1x10 ⁻⁶
	SiMo	-8x10 ⁻⁷	-5x10 ⁻⁷	-4x10 ⁻⁷	-1.5x10 ⁻⁶	-1x10 ⁻⁶	-7x10 ⁻⁷	-1x10 ⁻⁶	-1x10 ⁻⁶	-1x10 ⁻⁶	-4x10 ⁻⁶	-2x10 ⁻⁶	-1x10 ⁻⁶
	Vaporiza- tion Loss	-1.5x10 ⁻⁶	-3x10 ⁻⁷	-6x10 ⁻⁷	-3x10 ⁻⁶	-2x10 ⁻⁶	-1x10 ⁻⁶	-1.5x10 ⁻⁶	-3x10 ⁻⁶	-2x10 ⁻⁶	-5x10 ⁻⁶	-3x10 ⁻⁶	-2x10 ⁻⁶
Graphite	Astroquartz	-1.5x10 ⁻⁶	-6x10 ⁻⁷	-4.5x10 ⁻⁷	+2x10 ⁻⁶	+4x10 ⁻⁶	+2x10 ⁻⁶	+5x10 ⁻⁶	+7x10 ⁻⁷	-1x10 ⁻⁷	-2x10 ⁻⁶	-2x10 ⁻⁶	-2x10 ⁻⁶
	Al ₂ O ₃	-1.5x10 ⁻⁶	-6x10 ⁻⁷	-4x10 ⁻⁷	+3x10 ⁻⁶	+2x10 ⁻⁶	+7x10 ⁻⁷	-1x10 ⁻⁶	-1x10 ⁻⁶	-1x10 ⁻⁶	-3x10 ⁻⁶	-2x10 ⁻⁶	-2x10 ⁻⁶
	BN	-1.5x10 ⁻⁶	-6x10 ⁻⁷	-4x10 ⁻⁷	+3x10 ⁻⁶	+3x10 ⁻⁶	+1x10 ⁻⁶	-2x10 ⁻⁶	-1x10 ⁻⁶	-8x10 ⁻⁷	-2x10 ⁻⁶	-2x10 ⁻⁶	-2x10 ⁻⁶
	Si ₃ N ₄	-1.5x10 ⁻⁶	-6.5x10 ⁻⁷	-4x10 ⁻⁷	+4x10 ⁻⁶	+4x10 ⁻⁶	+1x10 ⁻⁶	+3x10 ⁻⁶	-0-	-3x10 ⁻⁷	-2.5x10 ⁻⁶	-2x10 ⁻⁶	-8x10 ⁻⁷
	Vaporiza- tion Loss	-2x10 ⁻⁶	-1x10 ⁻⁶	-5x10 ⁻⁷	+5x10 ⁻⁶	+5x10 ⁻⁶	+3x10 ⁻⁶	+6x10 ⁻⁶	+2x10 ⁻⁷	+2x10 ⁻⁷	-1x10 ⁻⁶	-1x10 ⁻⁶	-1x10 ⁻⁶

Because of the tremendous amount of data being generated from the test matrix, it is more effectively presented as numbers rather than curves to more readily allow comparisons.

The following is a preliminary analysis of the data.

- 1) Astroquartz - This material is disintegrating as a result of handling during weighing. As a result, the numbers represent handling losses rather than chemical reaction losses.
- 2) SiGe - There is indication of melting of this material at the higher temperatures in contact with Si_3N_4 .

The accuracy of weighing of the samples is approximately ± 0.0002 gm which results in a rate accuracy of $\pm 1 \times 10^{-7}$ gm/cm²/h at 200 h.

Most of the data presented at the 0-200 h test increment appears to be reaching the equilibrium rate of weight change with the possible exception of some of the graphite samples which are still displaying weight gains. The testing is being continued and the next test increments should provide the desired equilibrium data.

D. TBC-1 Generator Performance Analysis

The TBC-1 generator has been operated at JPL for a total test period of almost three years. During this time, the recorded performance data has been periodically reported in our bimonthly progress reports. The following analysis compares the measured generator performance with the performance that is calculated based on known generator degradation modes. Four basic degradation mechanisms will change the available generator output power:

- 1) fuel decay
- 2) dopant precipitation within the thermoelectric legs
- 3) insulation degradation (thermal)
- 4) insulation degradation (electrical)

In this analysis, the effect of each of these four mechanisms on the available

generator output power has been examined and calculated. All of the changes have been referenced to the available generator output power at 3000 hrs. This particular time base was used, as it corresponds to the beginning of the generator testing at JPL and thus the beginning of consistent performance data.

1) Fuel Decay. During the early portion of the generator testing at JPL (3000h to 6000h), the input power to TBC-1 was maintained constant at 2361 watts. However, after 6000 hours of total generator operating time, the decision was made to simulate the anticipated isotope decay by continuously decreasing the input power to the generator. Thus, from 6000 hours of operation onward, the input power to the generator was decreased at weekly intervals. The effect of these small changes in generator input power on the available output power can be ascertained from data which was obtained during the initial heat up of the generator. Figure 24 shows the output of the TBC-1 generator as a function of input power at a constant output voltage of 28.2 volts. Over the limited range of input power (2175 to 2375 watts), the output power changes linearly and has a sensitivity to a change in input of 10%, i.e. a 10 watt change of input power corresponds to a 1 watt change of output power.

The effect which this decrease of input power has on the performance of TBC-1 is shown in Figure 25. The figure shows the output power normalized to the 6000 hour point of operation of TBC-1 assuming the output power change alone affects the output power.

2) Dopant Precipitation. The changes in thermoelectric properties caused by the dopant precipitation mechanism proceed throughout the operating time of the generator. The two primary parameters which are affected by this mechanism are the Seebeck coefficient (α) and the resistivity (ρ) of the thermoelectric material. Although it has been found that the thermal conductivity (k) of the material changes, insufficient data has been collected on this parameter to date to allow its incorporation into this analysis. The effect of the property changes on the power output

Figure 24.

OUTPUT POWER SENSITIVITY TO INPUT POWER

(TBC-1)

Figure 25.

of a typical MHW generator has been previously documented (Ref. 2). From this reference, the change in output power of the TBC-1 generator was established and is shown in Figure 26 as a function of time. The curve shows the decrease in output power which is expected to occur due to the dopant precipitation process, normalized to the 3000 hour point of operation.

3) Insulation Degradation (Thermal). The thermal insulation of the MHW RTG system is of a multi-foil construction. It has been established that the thermal conductance of this insulation system will be adversely affected by the deposition of sublimation and reaction products within the foil system. The extent of this change in thermal conductance was established by the various 18-couple modules which have been operated at different temperatures at RCA. The performance of these modules was analyzed by JPL with the aid of a computer program (Ref. 1), and the results show the change in thermal insulation as a function of sublimed silicon per hot shoe. Figure 27 shows the change of thermal conductivity as a function of silicon per hot shoe for several different 18-couple modules. Also shown in the figure is an average change which is used for the purpose of this analysis. Since the amount of change in the thermal insulation is based upon the silicon loss per couple, this parameter has to be determined for the TBC-1 generator. The hot shoe temperature instrumentation of the generator originally consisted of several thermocouples which established the thermal profile of the generator. By the time the generator was set up for life testing at JPL, only two hot shoe thermocouples were still operative. Both of these, however, were located at one extreme end of the generator, and thus the average temperature of the generator is felt to be considerably higher than the recorded temperature. Data from the earlier experiments, during which all of the instrumentation was operative, indicated that there was a 20°C ΔT between the extreme thermocouple readings and the average temperature of the thermocouple. Through the life test,

Figure 26.

CHANGE OF OUTPUT POWER DUE TO DOPANT PRECIPITATION NORMALIZED TO 3000h

Figure 27.

the recorded hot shoe temperature has varied between 1020°C and 1030°C . For this analysis, the average hot shoe temperature for the purpose of silicon sublimation was assumed to be constant at 1045°C . Using the silicon loss rates given in Reference 2, the rate at which the insulation thermal conductivity changes as a function of operating time can be obtained and is shown in Figure 28. The value obtained for the thermal conductance of the insulation was used in the thermal balance of the generator. The amount of heat flowing through the thermal insulation system (at BOL) was considered to be 10% of the total input power in the case of TBC-1. With the use of the curve of sensitivity of input power to output power, established for the fuel decay, the decrease in output power due to the insulation thermal conductance change was established. This is shown in Figure 29, normalized to the available output power at 3000 hours.

4) Insulation Degradation (Electrical). The same deposition of sublimation and reaction products which causes the thermal conductivity of the foil system to change also affects the electrical conductivity of the system. The deposited material (primarily SiO) disassociates into Si and SiO_2 . The Si is an electrical conductor and thus decreases the resistance between the foil package and the uni-couples. This resistance was measured throughout the testing of TBC-1 and is shown in Figure 30. A portion of the data shown in the figure (17,000 hours to 19,000 hours) is represented by a dashed line. It was determined that during this time, the recorded resistance was considerably lower (about 2 ohms) and that this extremely low resistance was caused by a single point "short" somewhere within the generator. Since such a short would not result in any additional shunt power loss, the generator resistance during this portion of the test was assumed to continue its decrease as indicated by the dashed curve. Also shown in the figure is a sudden decrease in shunt resistance at about 13,000 hours. The resistance decreased from 11.5 ohms to 4.6 ohms. The actual recorded data showed that the resistance decreased to about 7 ohms for one data point only, then up to 9 ohms, again only for one data

Figure 28.

Figure 29.

CHANGE OF OUTPUT POWER DUE TO INSULATION CONDUCTIVITY CHANGE NORMALIZED TO 3000K

Figure 30.

point, before it decreased to 4.6 ohms for the next several thousand hours. In this case there was a corresponding decrease in output power. It is possible that this shift is due to a number of point shorts behaving much like a continuously distributed short. Why the sudden occurrence of point shorts is not clear, but it appears that after 19,000 hours, all (or most) of the point shorts disappeared. The amount of power which is lost due to a distributed shunt resistance is given in Reference 3.

$$P_{\text{shunt}} \text{ (watts)} = \frac{P_{\text{meas}}}{f} - P_{\text{meas}}$$

$$\text{where } f = 2 - \frac{1}{2}\sqrt{\beta} \coth\left(\frac{1}{2}\sqrt{\beta}\right)$$

$$\text{and } \beta = \frac{R_{\text{internal}}}{R_{\text{shunt}}}$$

Using the above equation and the data as recorded for internal generator resistance and R_{shunt} (see Figure 30), the decrease in generator output power due to the shunting effect was calculated and is shown in Figure 31 when normalized to the power available at 3000 hours of operation. Note that in calculating the power loss in the 13,000 hour time period where there was a sudden drop in shunt resistance, it was assumed that the power loss behaved as though the short was evenly distributed. This assumption gives a good match between measured results and predicted results. It may well be that a number of point shorts will act like a distributed short.

5) Comparison of Measured and Calculated Performance. The total reduction in the available output power due to the four degradation mechanisms which are discussed above can now be calculated. Using the results for each of the mechanisms (summarized in Figure 32), the resultant total output power is calculated and shown in Figure 33. Also shown in this figure is the actual measured generator output power. The same information is plotted in Figure 34 where the output powers are normalized to the 3000 hour point. The data shown in the figures indicate a very

Figure 31.

CHANGE OF OUTPUT POWER DUE TO SHUNT RESISTANCE NORMALIZED TO 3000h

Figure 32.

Figure 33. COMPARISON OF MEASURED & CALCULATED TBC-1 GENERATOR PERFORMANCE

Figure 34. COMPARISON OF MEASURED & CALCULATED TBC-1 PERFORMANCE
NORMALIZED TO PERFORMANCE AT 3000 HRS

close agreement between the measured and the calculated generator performance. The largest deviation between the two sets of data occurs at 19,000 hours at which point the measured output power is 3 watts less than the calculated value. Overall, however, the calculated and the measured values are within $\pm 1\%$ and, what is equally important, the apparent discrepancy is random, thus not indicating a trend of diverging agreement which would be indicative of an additional degradation mechanism.

E. Thermoelectric Property Characteristics

The characterization of the time and temperature behavior of the n- and p- type silicon-germanium alloy used in the Multi-Hundred Watt Radioisotope Thermoelectric Generator (MHW-RTG) is primarily concerned with the 78 a/o Si - 22 a/o Ge alloy, although some work is also being performed on the 80 a/o Si - 20 a/o Ge alloy. The former of these two alloys is currently in use in the MHW-RTG; during the initial phase of the program, it was the latter alloy that was being used.

The isothermal testing task of the contract pertains to the determination of the long-term behavior of the electrical properties, the Seebeck coefficient and electrical resistivity, of the two alloys as determined from data obtained from the isothermal testing of samples of this material. Of the two electrical properties, it is the electrical resistivity that is determined experimentally; the Seebeck coefficient is determined from a previously established relationship that relates the electrical resistivity and Seebeck coefficient of n- and p- type silicon-germanium alloys at different temperatures. The isothermal testing task consists of two parts. The first part of the task concerns itself with the continued isothermal testing of 22 n- type and 12 p- type samples of 80 a/o Si - 20 a/o Ge alloy started on a previous contract. The samples undergoing this test are being isothermally annealed in the range of temperatures of 300 to 950°C. As of 30 April 1975, this isothermal test had accumulated a total of 27,889 hours of test time. As of that date, the test samples of this, the original isothermal test, had been reinstrumented three times because with time some of the samples lose one or more of their instrumentation lead wires as a result of reaction between the wires and the test samples. Therefore, it is required that the samples be periodically reinstrumented. A set of thermoelectric properties has been generated for both type alloys after each reinstrumentation. The most recent reinstrumentation and the associated thermoelectric property projections were performed in the April to June time period of 1974. The test is continuing at present. It is still planned to interrupt it in the

May to June time period of this year for the next test sample reinstrumentation. At that time, new thermoelectric property projections will be made for the alloy. The special testing of two n-type and one p-type 80 a/o Si-20 a/o Ge alloy test samples on the original isothermal test is continuing. It will be recalled that the annealing temperature of each of these samples was shifted in order to determine the effect of sudden temperature shifts on the performance characteristics of the Multi-Hundred Watt RTG. The two n-type samples were shifted from their original annealing temperature of 500°C to a new annealing temperature of 650°C. The p-type sample was shifted from an annealing temperature of 700°C to a new temperature of 880°C. Although each of these samples had been annealed in excess of 20,000 hours at their original annealing temperatures, it was found that the sudden shift to a higher operating temperature resulted in a reversion of the properties of all samples to an earlier effective annealing time. Subsequent annealing at the new temperatures caused the properties of the samples to start changing in a manner quite similar to that experienced by unannealed samples, although it is becoming apparent that the rate of property change is somewhat faster for the previously annealed samples than it is for unannealed material. As of the end of the present reporting period, the three samples had undergone some 2500 hours of annealing at the new test temperatures. Testing is continuing.

The isothermal annealing tests were interrupted for two days during the present reporting period because of an interruption in the electrical power by the local utilities company. Prior to the power interruption, all test samples were cycled relatively rapidly to room temperature. When the tests were re-started, after the power interruption, all samples were returned to their original test temperatures. Temperature cycles such as this must be performed fairly rapidly in order that the test samples not be affected by their being at other than their original test temperatures, and yet slowly enough to minimize the loss of instrumentation lead wires as a result of thermal shock.

The second part of the isothermal testing task involves the isothermal testing of 51 n- type and 39 p- type 78 a/o Si - 22 a/o Ge alloy test samples of material currently in use on the MHW-RTG. The range of test temperatures used for the second, or expanded isothermal test, spans the temperatures of 300 to 950°C. As of 30 April 1975, the expanded isothermal test had accumulated a total test time of 9096 hours. At that time, 12 of the total of 90 samples on test had lost one or more of their instrumentation lead wires. The test is presently continuing and it is unclear at present whether it will be interrupted for reinstrumentation at the same time as the original isothermal test. The reason for this is that the bulk of all test samples are still providing adequate test data and a reinstrumentation would require not only the reinstrumentation of the 12 samples with defective instrumentation, but possibly, the reinstrumentation of all test samples because upon thermal cycling it is commonly found that the integrity of lead wire to sample contact is compromised. Thermal cycling to room temperature, of course, is necessary prior to the removal of test samples from the test fixture. The decision on the reinstrumentation of the expanded isothermal test will be reserved until the time just prior to the reinstrumentation of the original isothermal test. Irregardless of whether the test is re-instrumented or not, the data obtained from it will be subjected to analysis around mid-year and long-term thermoelectric properties will be projected for the n- and p- type 78 a/o Si - 22 a/o Ge alloy on the basis of the test results up to that time.

It is common to plot the electrical resistivity of isothermal test samples in terms of electrical resistivity as a function of the logarithm of time because in this form the plots reflect the characteristic shape associated with diffusion limited processes. Dopant precipitation in silicon-germanium alloys is thought to be such a process; when electrical resistivity is plotted as a function of the logarithm of time it is found that the plots have the characteristic elongated S shape. On a linear time plot, however, the electrical resistivity appears to have a near exponential time dependence. This is best illustrated by actual

data. Figure 35 shows plots of electrical resistivity as a function of time for one n-type and one p-type sample of 78 a/o Si-22 a/o Ge alloy; the data are shown plotted as functions of linear time as well as functions of the logarithm of time. Although it is very obvious from the logarithmic plots that the electrical resistivity values are still significantly changing after some 9,000 hours of testing, this is not nearly as apparent in the linear plots. This fact in itself, illustrates the usefulness of the logarithmic plots. The plots shown in Figure 35 pertain to an n-type sample annealed at 400°C and a p-type sample annealed at 800°C. These temperatures represent the respective temperatures of greatest electrical resistivity change for the two type alloys and thus help to best illustrate the foregoing discussion.

The in-gradient test also consists of two parts just as does the isothermal test. The first part pertains to the continuation of the in-gradient testing of two n-type and two p-type 80 a/o Si-20 a/o Ge alloy test samples started on a previous contract. The second part of the test pertains to the duplication of the first part of the test with samples of 78 a/o Si-22 a/o Ge alloy material currently in use on the MHW-RTG program. Even though the two tests were started at separate times, they are presently being conducted in the same test facility, although in separate test fixtures, with both fixtures being identical. Both test fixtures are designed such that the samples contained in them are being tested between the approximate hot and cold side temperatures of 120 and 960°C. Each of the four test samples contained in each fixture consist of two cylinders of 0.5 inch diameter and 0.75 inch height placed in an end-to-end configuration. Each half of each test sample is instrumented with two niobium-tungsten thermocouples that are welded close to the ends of each half of each test sample. This enables the obtainment of two completely independent sets of electrical property measurements on each sample. One set of measurements yields data at the high temperature end of each

Figure 35.

sample; the other set of measurements yields corresponding data on the cold temperature end of each sample. Continuous measurements of Seebeck coefficient and electrical resistivity are obtained for each half of each test sample. These properties represent temperature-averaged values over the range of temperatures spanned between instrumentation thermocouples. As of 30 April 1975, the original in-gradient test had accumulated a total of 16,195 hours of test time. The expanded in-gradient test had undergone some 5,568 hours of test time at that time. Both tests are presently continuing.

No analyses of the data obtained from the in-gradient test were performed during the present reporting period, although preparations were started for such analyses to be performed during the next few reporting periods. The preparations involve an analytical study of the heat flow in the in-gradient test set-up in an attempt to derive a fairly accurate temperature gradient for each sample when under test. The reason for the importance of knowing the temperature gradient of each in-gradient test sample is that this enables the standard property data for the 78 at/o Si - 22 at/o Ge and 80 at/o Si - 20 at/o Ge alloys to be integrated over identical temperature gradients for purposes of meaningful data comparison. Although such an analysis was previously performed, it is now felt that an even more rigorous analysis is necessary in order to completely eliminate the effects of test procedure from a data comparison.

The in-gradient test samples are heated at one end and water cooled at the other end. Each test sample is completely surrounded by a cylindrical sleeve of silicon-dioxide thermal insulation. Because the silicon-dioxide thermal insulation and the silicon-germanium alloys possess different values as well as different temperature dependencies of thermal conductivity, and because heat is lost by radiation from the surface of the silicon-dioxide thermal insulation sleeve, it may be expected that appreciable radial temperature gradients exist in the experimental test set-up. This causes a continuous, but varying heat interchange between the test samples and the thermal insulation. The result of such a heat interchange is that the temperature gradient of each test sample is modified from what it would be without the interchange. The temperature gradients of the test samples would be non-linear even without a

heat interchange between the test samples and the thermal insulation because of the temperature dependence of the thermal conductivity of silicon-germanium alloys.

An analytical model for determining the test sample temperature gradient values must therefore in detail account for the continuous heat interchange between the thermal insulation and the test samples. This is accomplished by subdividing each test sample and thermal insulation cylinder into small axial segments and treating each axial segment in terms of two-dimensional geometry, with heat flow taking place radially in each such segment. The various axial segments are interconnected at their boundaries by means of boundary conditions derived from one-dimensional heat flow in the axial direction. The three dimensional heat flow problem is thereby reduced to two separate, but interconnected problems involving one- and two-dimensional heat flow. The two-dimensional radial heat flow problem is further reduced to an one-dimensional problem because of radial symmetry. The whole problem is therefore handled by means of two one-dimensional heat flow relationships, with the relationships interconnected by means of boundary conditions.

The thermal conductivity testing task originally consisted of two parts, just as do the isothermal and in-gradient testing tasks. As discussed in the last several reports, the two parts of the thermal conductivity testing task are, however, being combined into a single overall test sequence. Work on combining the two parts of the task has been conducted over the last several reporting periods and, in fact, as of the end of the present reporting period, has been essentially completed. The combined thermal conductivity task consists of a total of 48 n- and p- type samples of 80 at/o Si - 20 at/o Ge and 78 at/o Si - 22 at/o Ge alloy. Of these, 16 test samples belonged to the original thermal conductivity test, with the remaining 32 as a part of the expanded thermal conductivity test. The former samples represent material with the higher silicon content. The latter samples are those with a 78 atomic percent silicon content and represent the material currently in use on the MHW-RTG program. In the modified thermal conductivity testing task, all samples annealed at temperatures of 900°C and below are being annealed in vacuum furnaces. All samples being annealed at temperatures of 950°C and above are being annealed in argon annealing furnaces.

The reason for the annealing of the high temperature samples under an argon atmosphere is the desire to minimize the loss of sample material as a result of sublimation. The total range of annealing temperatures cover the values of 300 to 1100°C. As previously discussed, periodic thermal conductivity measurements are performed on each of the test specimens annealed at 750°C or below at the temperature at which each sample is being annealed. All samples annealed at higher temperatures are measured at about 200°C because accurate comparative thermal conductivity measurements are not possible at high temperatures. Whenever measurements of thermal conductivity of each of the test specimens are made, the values of the electrical properties, electrical resistivity and Seebeck coefficient, are also determined. The measurement of all three thermoelectric properties is performed in a comparative thermal conductivity apparatus and the measurements are performed concurrently. It should be added, however, that the electrical resistivity data measured on the samples do not appear to be especially consistent. Electrical resistivity determinations are made by introducing an electrical current into the test samples by means of wires spot-welded to small tabs extending from the tantalum metal foil disks placed between the hot and cold side calorimeters and the test sample. Voltage measurements are made between the common legs of the three thermocouples located on the test sample and also between the common legs of the thermocouples located on the tantalum disks. The inconsistency of the electrical resistivity values obtained from measurements between the sample thermocouples may be ascribed to the fact that these thermocouples are placed into small holes drilled radially into the sample and the contact between the sample and the thermocouples is not electrically good; the thermal contact is excellent because each hole acts like a black body. Electrical resistivity determinations made between the thermocouples spot-welded to the tantalum disks are not consistent because of the bunching of current flow lines at the ends of the sample as a result of imperfect contact between the tantalum disks and the sample. Attempts to correct this situation have not been successful and it now appears that the only way to obtain good electrical resistivity data is to spot-weld the

voltage probes/thermocouples to the sample. Because this procedure is not consistent with the obtainment of good thermal conductivity measurements, it has been decided to sacrifice the electrical resistivity data in favor of thermal conductivity measurements. It should be noted that the Seebeck coefficient data appear excellent when measurements are made between the thermocouples spot-welded to the tantalum disks at the ends of the test samples.

The test samples involved in the thermal conductivity testing task are tabularized in Table 3 in terms of the measured values of properties of each sample prior to the start of sample annealing. It is noted that as of the end of the present reporting period, initial measurements had been obtained on 40 of the total number of 48 samples involved in the task. Although not shown in Table 3, the properties of a number of samples have also been measured after various periods of annealing and some of the results found to date are given below. It should be noted that all samples being annealed at temperatures of 800°C and higher are subjected to property measurements at about 200°C because accurate thermal conductivity measurements are not possible at very high temperatures. Additionally, most samples being annealed at temperatures below 800°C are now subjected to property measurements at their annealing temperature as well as at 200°C in order that the thermal conductivity values determined at 200°C can be experimentally related to values at higher temperatures. The results of this procedure are shown in Figure 36 in terms of plots of the ratio of thermal conductivity at any temperature to that at 200°C as a function of temperature for n-type and p-type 78 a/o Si - 22 a/o Ge alloys. The solid curves in Figure 36 represent the so-called "standard" thermal conductivity values of the 80 a/o Si - 20 a/o Ge alloy. Although the test samples represented in Figure 36 differ slightly in composition from the material represented by the "standard" thermal conductivity curves, it is felt that the difference is not significant. In fact, it is noted that good agreement exists between the data and the curve for the n-type material. The agreement for the p-type alloy is not as good and at present the reason for this is not known.

The initially measured values of thermal conductivity given for all of the samples in Table 3 are plotted as a function of temperature in Figure 37.

TABLE 3
INITIAL VALUES OF THERMAL CONDUCTIVITY

Sample Number	Material	Annealing Temp. -°C	Measurement Temp. -°C	Electrical Res. - Ω -cm	Seebeck Coeff. - μ v/°C	Thermal Cond. -mw/°C-cm
A2-15	80a/oSi(N)	300	305	1.39	196	44.5
A3-22	78a/oSi(N)	300	302	1.43	193	44.3
A2-02	80a/oSi(N)	350	362	2.40	233	49.8
A3-33	78a/oSi(N)	350	355	-	229	49.0
A2-14	80a/oSi(N)	400	408	2.29	235	41.5
A3-34	78a/oSi(N)	400				
A2-01	80a/oSi(N)	450	440	1.90	256	48.4
A3-35	78a/oSi(N)	450				
A2-13	80a/oSi(N)	500	493	2.06	256	40.9
A3-23	78a/oSi(N)	500	500	-	265	41.4
A3-17	78a/oSi(N)	550	559	-	275	39.3
A3-36	78a/oSi(N)	550				
A3-21	78a/oSi(N)	600	592	-	271	43.4
A3-37	78a/oSi(N)	600				
A2-04	80a/oSi(P)	650	660	2.25	223	42.4
A3-30	78a/oSi(P)	650	647	-	233	43.5
A3-16	78a/oSi(N)	700	704	-	264	40.9
A3-24	78a/oSi(N)	700	701	-	273	41.0
A2-11	80a/oSi(P)	700	695	2.14	240	43.6
A3-31	78a/oSi(P)	700	705	-	-	48.5
A2-03	80a/oSi(P)	750	752	2.71	244	46.1
A3-32	78a/oSi(P)	750	741	-	245	43.4
A3-18	78a/oSi(N)	800	203	-	180	46.5
A3-25	78a/oSi(N)	800	203	-	176	46.9
A2-10	80a/oSi(P)	800	196	0.97	169	53.0
A3-26	78a/oSi(P)	800	197	1.22	165	54.1
A3-19	78a/oSi(P)	850	202	-	160	52.6
A3-27	78a/oSi(P)	850	198	0	167	53.1
A2-12	80a/oSi(N)	900	202	1.16	146	45.4
A3-28	78a/oSi(N)	900	200	-	153	46.2
A2-09	80a/oSi(P)	900	194	0.96	160	53.3
A3-29	78a/oSi(P)	900	201	-	164	53.6
A3-20	78a/oSi(N)	950	203	-	180	46.0
A3-38	78a/oSi(N)	950	202	-	172	46.2
A3-39	78a/oSi(P)	950				
A3-40	78a/oSi(P)	950				
A2-06	80a/oSi(N)	1000	202	0.94	156	48.5
A3-41	78a/oSi(N)	1000	195	-	172	46.1
A2-05	80a/oSi(P)	1000	211	1.49	157	53.0
A3-42	78a/oSi(P)	1000	197	-	165	53.1
A3-43	78a/oSi(N)	1050	200	-	169	46.2
A3-48	78a/oSi(N)	1050				
A3-44	78a/oSi(P)	1050	200	-	164	53.3
A3-45	78a/oSi(P)	1050				
A2-08	80a/oSi(N)	1100	195	1.04	158	46.5
A3-46	78a/oSi(N)	1100	198	-	170	46.2
A2-07	80a/oSi(P)	1100	190	1.20	155	51.3
A3-47	78a/oSi(P)	1100	202	-	165	53.5

Figure 36.

Figure 37.

The data points shown in Figure 37 pertain to actual data, while the solid curves pertain to the so-called "standard" thermal conductivity of the 80 a/o Si - 20 a/o Ge alloy. The actual data for the two different alloy compositions are distinguished by the two different symbols: the crosses pertain to 80 a/o Si - 20 a/o Ge alloy and the circles pertain to 78 a/o Si - 22 a/o Ge alloy. For the n-type alloy it is noted that the actual thermal conductivity is fairly consistent with the "standard" values, except for a few samples. It is of interest to also note that with the exception of the samples measured at 200°C, those representing the samples annealed at 800°C and above, all samples that have a thermal conductivity fairly close to the "standard" curve essentially retain their initial thermal conductivity as a function of time - the thermal conductivity of such samples does not appear to vary much with time. The thermal conductivity of the samples that initially are appreciably higher than the "standard" curve decreases as a function of time and appears to approach the "standard" curve. The time dependence of n-type samples being annealed at 350, 400, 450 and 500°C is shown in Figure 38 in terms of plots of thermal conductivity as a function of time. The thermal conductivity values of the p-type samples shown in Figure 37, with the exception of the high temperature samples measured at 200°C, generally fall below the "standard" curve. Most of the p-type samples annealed and measured in the 650 to 750°C range appear to be relatively constant with time.

The high temperature samples measured at 200°C have initial values of thermal conductivity very close to those of the "standard" curves, as seen in Figure 37. They all, however, exhibit a decreasing thermal conductivity with time, as seen in Figure 39. In fact, the amount of decrease of thermal conductivity is quite significant and may have serious implications for the performance of high temperature silicon-germanium alloy devices. It is not yet known, however, whether the results of the measurements performed at 200°C can be directly translated to the higher temperatures. In other words, it is not known whether the changes observed at 200°C also occur to the same extent at the higher temperatures. Prior to the formulation of definitive conclusions, however, it is necessary to unambiguously relate low temperature thermal conductivity data to

Figure 38.

Figure 39.

those at the high temperatures. Present efforts in this area are being concentrated on analytical methods. It is planned to also consider possible experimental methods, although such methods are of necessity either very elaborate or subject to considerable uncertainty because of the difficulties inherent to the performance of accurate high temperature thermal conductivity measurements.

II. Thermoelectric Generator Test and Evaluation

Thermoelectric generators representing silicon germanium and lead telluride advanced technology are on test at JPL. The generators are the MHW-TBC-1 and the 25 W(e) Reference Generator, both representative of the SiGe technology, and the HPG, the Transit and the Ring Converter, representing the PbTe and TAG-85 technology.

A. High Performance Generator, HPG SN-2

This generator has operated for a total accrued time of 12,536 hours. Over the last 1,372 hours of operation, which covers the present test period, the power output from the generator decreased by 1.80 watts to its present value of 157.5 watts. This represents a degradation rate of 0.49%/1000 hours when calculated over the last 5000 hours of operation.

During this period, there has been a gradual increase of 13°F in the hot junction and an increase of 17°F in the cold junction and the fin root temperatures, with practically no change in the open circuit voltage but with a slight increase in the internal resistance. In all probability, more of the heat pipes, used to distribute the rejected heat along the fins, are becoming inoperative. As a result of being overloaded, the remaining pipes are likely to become inoperative as well. A new evaluation of the heat pipe operation will be made during the month of May.

A parametric evaluation of the electrical and thermal characteristics of the generator, made at 12,381 hours, is presented in Figure 40. Comparison of the data presented in this figure with those observed after 340 hours of operation shows a decrease in power output and an increase in the other parameters (T_h , R_{in} and E_{oc}). The Peltier cooling reduction resulting from a 1.0 amp decrease in current output should result in an increase of 12.5°F in the average value of the hot junction temperature at 15 volts output. Experimentally, we have measured a 42°F increase in temperature over the generator lifetime (12,381 hours). The remaining 29.5°F

Figure 40.

PARAMETRIC TEST OF HP6 S/N-02

QIN 2430 WATTS

4-17-75

12,394 HRS AE

increase can be explained by a measured increase of 30.8°F in the average value of the cold junction temperature. The difference in the values of the measured average fin root temperature between the data observed at 340 hours and at 12,381 hours was calculated to be 22°F . The 8°F unaccounted for are probably due to slight changes in the heat transfer in the cold end hardware resulting from the distorted heat reject paths in half of the generator (fins 1, 5 and 6). The test history of the generator is illustrated in Figure 41. Test of the generator continues.

B. Transit Generator QM-III

This generator has operated for a total accrued time of 13,331 hours. In the last 1,201 hours of operation, representing the present test period, the total power output from the generator has decreased by 0.62 watts to its present value of 22.33 watts. The overall hot junction temperature of this generator has increased by $10\text{-}15^{\circ}\text{C}$ over the last 4000 hours.

The following conditions exist at present.

1) G₁ Subgenerator (Flight Type Panels). The output from this subgenerator increased slightly by 0.15 watts to its present value of 6.90 watts. The hot junction temperature increased by 2°C during this period.

2) G₂ Subgenerator (New Elements of Cold Pressed Vacuum Technology). The output power of this subgenerator decreased by 0.17 watts to its present value of 5.29 watts. The hot junction temperature is still increasing.

3) G₃ Subgenerator (Cold Pressed Vacuum Element Technology Previously Used in Other Tests). The power output from this subgenerator decreased by 0.60 watts to its present value of 10.14 watts. The average hot junction and cold junction temperatures remained constant at their respective values of 415°C and 154°C . The behavior of the three generators and that of the assembly is illustrated in Table 4.

Figure 41.

HISTORY OF HPG S/N-2 QW 2430 W E. 151

Table 4.

Module	Power Out (W) (13,331 h)	Power Decay (W) (this period)	Rate of Power Decay (last 5000 h)
G ₁	6.90	+0.15	0.116%/1000 h
G ₂	5.29	-0.17	1.75%/1000 h
G ₃	10.14	-0.60	3.10%/1000 h
G Total	22.33	-0.62	1.89%/1000 h

The increase in power of generator G₁ is probably due to the fact that the other two generators have degraded more significantly causing a loss in Peltier cooling and an increase in temperature for all submodules. This is an artifact of the test setup.

A parametric evaluation of the three subgenerators at a common value of input power of 765.1 watts was performed during this test period. The measurements were made at an average time of 13,338 hours. The results of these measurements are graphically illustrated in Figures 42, 43 and 44. The test histories of the subgenerators are presented in Figures 45, 46 and 47. Test of the generators continues.

C. Ring Converter

This generator has operated for a total accrued time of 9,564 hours. During the last 1,347 hours of operation, which covers this reporting period, the power output from the generator decreased by 0.03 watts to its present value of 13.46 watts. The average hot junction temperature decreased by 4°C to its present value of 449°C while the average cold junction temperature remained unchanged at 176°C. Calculation of the rate of degradation in output power over the last 5,000 hours of operation indicates a value of 0.28%/1000 hours. A parametric evaluation of the electrical characteristics of the generator was performed at 9,605 hours of operation. The results are presented in Figure 48. Comparison of this data with that observed on 4/19/74, approximately 1 year ago, shows that at the operating output

Figure 42.

PARAMETRIC TEST OF TRANSISTOR GENERATOR No. 1

4-17-75

Q IN 765 W

Figure 43.

PARAMETRIC TEST OF TRANSISTOR C/M III
GEN. NO. 2 4-17-75
GRIN 765W

Figure 44.

PARAMETRIC TEST OF TRANSIT Q/M III
GEN. NO. 3 4-18-75
Q IN 765 W

Figure 45.

Figure 46.

Figure 47.

Figure 48.

PARAMETRIC TEST OF RING CONVERTER
Q IN 388 W 4-24-75 9.605 HRS

voltage of 2.40 V, the power output decreased by 0.3 watts, corresponding to a decrease in output current of 0.125 amps. It also can be observed that the ΔT did not change, but that the open circuit voltage and the internal resistance decreased which would indicate changes in the material properties. The history of the generator is presented in Figure 49. Test of the generator continues.

D. MHW-TBC-1

The TBC-1 generator has operated for a total accrued time of 22,779 hours. During the last 1,346 hours of operation, no changes in output power were observed; the power has remained at 119 watts. The average hot and cold junction temperatures also remained unchanged at $1027 \pm 1^\circ\text{C}$ and $300 \pm 1^\circ\text{C}$ respectively. This resulted in an unchanged value of E_{oc} of 48.9 volts. The internal resistance also remained unchanged at a value of 4.9 ohms. The value of the resistance of the thermopile to case remained constant at 5.38 ± 0.05 ohms. Calculation of the rate of power output degradation over the last 5000 hours of operation show a value of 0.52%/1000 hours. The test history of the generator is presented in Figures 50 and 51. Test of the generator continues.

E. RCA Reference Generator

This generator has operated at JPL for a total accrued time of 38,976 hours. In the last 1,467 hours of operation, corresponding to the present reporting period, the power output from the generator remained unchanged at a value of 23.65 watts. Calculation of the rate of degradation in output power over the last 5,000 hours of operation indicates a value of 0.17%/1000 hours. The test history of the generator is presented in Figure 52. Testing of the generator continues.

Figure 49.

Figure 50.

Figure 51.

Figure 52.

III. References

1. JPL Report 342-282 (900-690), "GE18MD: A Computer Program Designed for the Reduction of Eighteen-Couple Module Test Results", E. L. Noon, December 1974.
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3. Schock, A. "Effect of Shunt Resistance on Power Output Comparison of Approximate and Exact Analyses", Fairchild Space and Electronics Company, FSEC-NSG-217-74/36, June 1974.