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**RADIOISOTOPE SPACE POWER GENERATOR
ANNUAL REPORT FOR THE PERIOD
OCTOBER 1978 THROUGH SEPTEMBER 1979**

**by
N. B. ELSNER, J. CHIN, H. G. STALEY, J. C. BASS,
C. C. MORRIS, C. H. SHEARER, and E. J. STEEGER**

**Prepared under
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Department of Energy**

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GENERAL ATOMIC COMPANY

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ABSTRACT

The emphasis of the Isotec Technology Program shifted from development of a Galileo generator to study of a segmented selenide element and couple technology. The goal of the FY 79 program was to determine the feasibility of fabricating segmented selenide P and N elements which exploit the high thermoelectric efficiency of $(\text{Cu,Ag})_2\text{Se}$ and Gd_2Se_3 materials. A preliminary evaluation of segmented element efficiencies, material compatibilities, and fabrication abilities was used to select $(\text{Cu,Ag})_2\text{Se}/\text{Fe}(\text{Bi,Sb})_2\text{Te}_3$ for the P element and $\text{Gd}_2\text{Se}_3/\text{PbTe}$ for the N element. The iron barrier between the $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$ prevented degradation of thermoelectric properties from copper contamination of the $(\text{Bi,Sb})_2\text{Te}_3$.

Fabrication processes for both elements were developed. Gd_2Se_3 was friable and difficult to fabricate crack-free. It also exhibited a phase transition from cubic to orthorhombic, which increased its susceptibility to microcracking and reduced its thermoelectric efficiency.

Life testing of an all-bonded couple with unsegmented $(\text{Cu,Ag})_2\text{Se}$ P-type and Gd_2Se_3 N-type elements was stopped after 3300 h in a nominal $830^\circ\text{C}/390^\circ\text{C}$ thermal gradient. The Gd_2Se_3 leg did not show any significant degradation during the test. Examination of the hot end of the P element showed the need for a less reactive hot cap material and an improved vapor suppression system.

Module testing of a 1-W $(\text{Bi,Sb})_2(\text{Se,Te})_3$ generator was performed for 5000 h with no degradation in power. High-temperature Thermid 600 adhesive curing cycles were examined, 75-mW module loading tests were performed, and diagnostic examination of RTG-2A and RTG-201 was completed.

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1. INTRODUCTION

General Atomic (GA) is conducting a two-part program for the Department of Energy (DOE) consisting of (1) a selenide thermoelectric materials development program to improve the performance and useful life of P-type $(\text{Cu,Ag})_2\text{Se}$ and N-type rare earth selenide thermoelectric materials and (2) a $(\text{Bi,Sb})_2(\text{Se,Te})_3$ thermoelectric materials improvement effort.

The general aim of the $(\text{Cu,Ag})_2\text{Se}$ and Gd_2Se_3 material studies is to make these materials in a high-temperature radioisotope thermoelectric generator (RTG) where efficiencies of $\geq 10\%$ can be achieved. These efficiencies could presumably be obtained with the GA design (radiation-coupled, many-parallel-circuit, 3.4-W/lb) or with designs pursued by other contractors. The studies with the P-type $(\text{Cu,Ag})_2\text{Se}$ material were directed toward further characterization and vapor suppression techniques, compatibility, and joining of hot and cold end caps.

The N-type alloy Gd_2Se_3 exhibits phase instability, undergoing a sluggish cubic-to-orthorhombic phase change near 1000°C . An objective of this year's effort is to gain a better understanding of this instability and to determine methods, if any, of avoiding it.

The use of $(\text{Bi,Sb})_2(\text{Se,Te})_3$ materials in small, rugged RTGs, where the mechanical properties of the thermoelectric materials are maximized, is being studied. In addition, techniques are being investigated for producing ultra-fine-grain and amorphous $(\text{Bi,Sb})_2(\text{Se,Te})_3$ materials, with the goal of reducing thermal conductivity. Various organic insulations and adhesives are being characterized for use in these low-temperature $(\text{Bi,Sb})_2(\text{Se,Te})_3$ generators, and promising candidate materials are being selected for long-term use.

2. SELENIDE MATERIAL DEVELOPMENT

Cancellation of the Teledyne Energy Systems 3M Galileo program had the following effects on the FY 79 ISOTEC Technology Program:

1. The space-oriented technology is now directed toward fabrication of small, segmented elements in which many parallel circuits can be utilized. This fabrication effort is well under way, and various segmented designs are being analyzed.
2. Before January 1979, most of the effort was aimed at fabricating 3M size, vacuum-hot-pressed, N-type Gd_2Se_3 elements. This effort was reduced after January. Transit size, N-type materials currently being examined include Gd_2Se_3 or Nd_2Se_3 in series with N-type PbTe-2N .
3. Both triply and doubly segmented P-type elements were examined during FY 79. The high-temperature portion of each segment is $(\text{Cu,Pb})_2\text{Se}$. Materials used for other P-type element segments were PbSnMnTe-3P and $(\text{Bi,Sb})_2\text{Te}_3$.

2.1. DESIGN ANALYSIS OF SEGMENTED ELEMENTS

Segmenting is usually done to increase efficiency; however, with the $(\text{Cu,Ag})_2\text{Se}$ material, segmenting allows a greater latitude in system design. The segmenting studies were oriented toward better utilization of the $(\text{Cu,Ag})_2\text{Se}$ material so that its ΔT could be reduced to minimize the iL/A ratio; this would in turn minimize vaporization.

The performance of a thermocouple with segmented legs of various materials can be calculated by determining the effective material properties

for the segmented legs and then using these properties in the classical thermoelectric couple equations. The following equations show how effective properties and segment lengths can be determined for a triply segmented leg; these equations can also be used for a doubly segmented leg.

The hot and cold junction temperatures are known, and the temperatures at the segment interfaces are assigned. The thermoelectric properties for each segment of the corresponding temperature range are calculated from the material property curves or tables:

The heat through each segment is the same:

$$Q = \frac{\bar{k}_1 A_1 \Delta T_1}{L_1} = \frac{\bar{k}_2 A_2 \Delta T_2}{L_2} = \frac{\bar{k}_3 A_3 \Delta T_3}{L_3} \quad (2-1)$$

Since all segments have the same cross section, i.e.,

$$A_1 = A_2 = A_3 \quad , \quad (2-2)$$

from Eqs. 2-1 and 2-2,

$$L_1 = \frac{L_2 \bar{k}_1 \Delta T_1}{\bar{k}_2 \Delta T_2} \quad , \quad (2-3)$$

$$L_3 = \frac{L_2 \bar{k}_3 \Delta T_3}{k_2 \Delta T_2} \quad . \quad (2-4)$$

Assigning unit length to the leg, i.e.,

$$L_1 + L_2 + L_3 = 1 \quad , \quad (2-5)$$

then from Eqs. 2-3 through 2-5,

$$L_2 = \frac{1}{1 + \frac{\bar{k}_1 \Delta T_1}{k_2 \Delta T_2} + \frac{\bar{k}_3 \Delta T_3}{k_2 \Delta T_2}} \quad , \quad (2-6)$$

$$L_3 = \frac{k_3 \Delta T_3 / k_2 \Delta T_2}{1 + \frac{\bar{k}_1 \Delta T_1}{k_2 \Delta T_2} + \frac{\bar{k}_3 \Delta T_3}{k_2 \Delta T_2}} \quad , \quad (2-7)$$

The effective thermal conductivity (k_{EFF}) is then determined as follows:

$$Q = \frac{k_{EFF} A \Delta T}{L} \quad , \quad (2-8)$$

$$Q = \frac{\Delta T A}{\frac{L_1}{\bar{k}_1} + \frac{L_2}{\bar{k}_2} + \frac{L_3}{\bar{k}_3}} \quad . \quad (2-9)$$

Combining Eqs. 2-5, 2-8, and 2-9 yields

$$k_{EFF} = \frac{1}{\frac{L_1}{\bar{k}_1} + \frac{L_2}{\bar{k}_2} + \frac{L_3}{\bar{k}_3}} \quad . \quad (2-10)$$

The effective resistivity (ρ_{EFF}) is as follows:

$$R = \rho_{\text{EFF}} (L/A) \quad ,$$

$$R = R_1 + R_2 + R_3 \quad ,$$

$$\rho_{\text{EFF}} \frac{1}{A} = \bar{\rho}_1 (L_1/A) + \bar{\rho}_2 (L_2/A) + \bar{\rho}_3 (L_3/A) \quad , \quad (2-11)$$

$$P_{\text{EFF}} = \bar{\rho}_1 L_1 + \bar{\rho}_2 L_2 + \bar{\rho}_3 L_3 \quad . \quad (2-12)$$

Since the Seebeck voltage for the thermocouple leg is the sum of the individual Seebeck voltages, ρ_{EFF} is

$$\left. \begin{aligned} \alpha_{\text{EFF}}^T &= \bar{a}_1 \Delta T_1 + \bar{a}_2 \Delta T_2 + \bar{a}_3 \Delta T_3 \quad , \\ \alpha_{\text{EFF}} &= \frac{\bar{a}_1 \Delta T_1 + \bar{a}_2 \Delta T_2 + \bar{a}_3 \Delta T_3}{\Delta T} \quad . \end{aligned} \right\} \quad (2-13)$$

Figure 2-1 shows the theoretical efficiency for segmented couples using the segmented N leg $\text{Gd}_2\text{Se}_3/\text{Bi}_2\text{Te}_3$ -2N and the segmented P leg $(\text{Cu,Ag})_2\text{Se}/\text{BiTe}_3$ -3P.

2.1.1. iL/A

In the design of the thermoelectric couples for each leg, there is a unique current gradient [iL/A (amps/cm)] that is determined by the material properties of the couple and the hot and cold junction temperatures. This property is not changed by altering either area or length as long as the ratio of the cross sectional area of the N leg to the cross sectional area of the P leg (A_N/A_P) is kept constant. For an operating couple, there is a

Fig. 2-1. Theoretical efficiency of segmented couples: $T_H = 850^\circ C$, $T_C = 150^\circ C$, optimum A_N/A_P and M (sheet 1 of 2)

Fig. 2-1. Theoretical efficiency of segmented couples: $T_H = 850^\circ\text{C}$, $T_C = 150^\circ\text{C}$, optimum A_N/A_P and M (sheet 2 of 2)

voltage drop across the couple that is a function of the individual Seebeck voltages, the junction temperatures, and the resistance ratio (M):

$$E = \frac{\alpha_N(T_H - T_C) + \alpha_P(T_H - T_C)}{1 + \frac{1}{M}},$$

where $M = R_L/R_T$; i.e., (load resistance)/(couple resistance).

The voltage drop along a leg must conform to Ohms Law:

$$E = iR,$$

$$E = (iL/A)\rho,$$

where $R = \rho(L/A)$.

For any one material in a couple (unsegmented),

$$\frac{\alpha(T_H - T_C)}{\rho\left(1 + \frac{1}{M}\right)} = iL/A.$$

The equation above shows that iL/A is determined by the junction temperatures and the thermocouple material properties α and ρ . It is not a function of couple geometry. If iL/A is applied to just one material in a segmented couple, its value can change depending on the size and temperature of the material segment. Figure 2-2 shows the iL/A for P-type $(\text{Cu,Ag})_2\text{Se}$ in segmented and unsegmented couples.

The P material in the thermocouple combination $N = \text{Gd}_2\text{Se}_3$ and $P = (\text{Cu,Ag})_2\text{Se}$ is sensitive to vaporization at a high temperature and a high iL/A . The manner in which iL/A can be reduced for unsegmented couples is

Fig. 2-2. iL/A for P-type $(Cu, Ag)_2Se$ in segmented and unsegmented couples: optimum A_N/A_P and M , variation in $(Cu, Ag)_2Se$ -3P interface temperature

described below. This reduction is always accompanied by a reduction in thermoelectric efficiency.

For a couple operating at fixed hot and cold junction temperatures, where efficiency is maximized by using the optimum area ratio A_N/A_P and then optimum resistance ratio M , there is a unique value for iL/A . The current through a couple is

$$I = \frac{\bar{\partial}\Delta T}{r(M + 1)} \quad . \quad (2-14)$$

$$r = \left(\frac{\rho_N}{A_N} + \frac{\rho_P}{A_P} \right) \ell \quad . \quad (2-15)$$

The optimum area ratio is

$$\left(\frac{\rho_N}{k_N} \times \frac{k_P}{\rho_P} \right)^{1/2} = \frac{A_N}{A_P} \quad ,$$

$$r = \left(\frac{\rho_N}{A_N/A_P} + \rho_P \right) L/A_P \quad . \quad (2-16)$$

Substituting for r in Eq. 2-14 yields

$$I = \frac{\bar{\partial}\Delta T}{\left(\frac{\rho_N}{A_N/A_P} + \rho_P \right) L/A_P (M + 1)} \quad . \quad (2-17)$$

Multiplying both sides by L/A_P yields

$$iL/A_P = \frac{\bar{\partial}\Delta T}{\left(\frac{\rho_N}{A_N/A_P} + \rho_P \right) (M + 1)} \quad . \quad (2-18)$$

When a couple operates at fixed hot and cold junction temperatures under nonoptimum conditions because of a change of A_N/A_P or M , iL/A and couple efficiency change.

Figure 2-3 shows the efficiency and iL/A values for couples operating under optimized conditions with a cold junction temperature of 150°C and a hot junction temperature which varies from 650° to 850°C . Figures 2-4 and 2-5 show the relationship between iL/A and efficiency at given temperatures as A_N/A_P is varied from optimum. Calculations were also made holding A_N/A_P constant and varying the resistance ratio M off optimum. For this case, the relationship between efficiency and iL/A is the same as that which occurs when M is held constant and A_N/A_P is varied (Fig. 2-6).

One method of reducing both the hot junction temperature and the P $(\text{Cu,Ag})_2\text{Se}$ current gradient (iL/A) and increasing the efficiency is to segment the N and P legs. Segmenting the P leg reduces the length of $(\text{Cu,Ag})_2\text{Se}$, decreasing the value of iL/A . Figure 2-7 shows the iL/A values for the P leg and the efficiencies for the combination $N = \text{Gd}_2\text{Se}_3$ and $P = (\text{Cu,Ag})_2\text{Se}$. The calculations were done for $T_H = 700^\circ$ and 725°C and $T_C = 130^\circ$ and 150°C . Figure 2-8 shows the same variables over the same temperature ranges, but with both legs segmented. Efficiency increases and iL/A for $(\text{Cu,Ag})_2\text{Se}$ decreases. This decrease is primarily due to the reduction in the length of $(\text{Cu,Ag})_2\text{Se}$.

2.1.2. Segment Interface Analysis

The amount of Fe powder that can be used at an interface between segments was analyzed as shown in Table 2-1. The ΔT across a typical 5-mil gap is only a couple of degrees. The electrical resistance across the gap is also probably low if the correct barrier is selected. Measurements to confirm the low joint resistance will be done on segmented elements.

Fig. 2-3. Thermocouple efficiency and P leg iL/A for the system $N = \text{Gd}_2\text{Se}_3$, $P = (\text{Cu}, \text{Ag})_2\text{Se}$ at varying hot junction temperatures: cold junction = 150°C , A_N/A_P and M are optimum

Fig. 2-4. Change in efficiency and iL/A for P leg $(\text{Cu,Ag})_2\text{Se}$ as couple area ratio varies from optimum: N leg = Gd_2Se_3 , $T_C = 150^\circ\text{C}$

Fig. 2-5. Change in efficiency and iL/A for P leg $(\text{Cu,Ag})_2\text{Se}$ as couple area ratio varies from off-optimum: N leg = Gd_2Se_3 , $T_C = 150^\circ\text{C}$

Fig. 2-6. Thermocouple efficiency and P leg iL/A for the couple $N = \text{Gd}_2\text{Se}_3$, $P = (\text{Cu}, \text{Ag})_2\text{Se}$

Fig. 2-7. Efficiency of unsegmented couples

Fig. 2-8. Efficiency of segmented couples

TABLE 2-1
PENALTY FOR USING Fe AS INTERFACE MATERIAL
IN (Cu,Ag)₂Se/PbTe SEGMENTED ELEMENT

Let (Cu,Ag)₂Se = Material 1,

Fe = Material 2.

Then,

$$(Q/A)_1 = (Q/A)_2 = \frac{K\Delta T}{\Delta X} \quad ,$$

$$\frac{K_1 \Delta T_1}{\Delta X_1} = \frac{K_2 \Delta T_2}{\Delta X_2} \quad ,$$

$$\Delta T_2 = \left(\frac{K_1}{K_2} \right) \left(\frac{\Delta X_2}{\Delta X_1} \right) \Delta T_1 \quad ,$$

where

$$K_1 = 0.45 \text{ Btu/hr-ft-}^\circ\text{F},$$

$$K_2 = 36.6 \text{ Btu/hr-ft-}^\circ\text{F},$$

$$\Delta X_1 = 0.1 \text{ in.},$$

$$\Delta X_2 = 0.001 \text{ in.},$$

$$\Delta T_1 = 750^\circ - 400^\circ = 350^\circ\text{C},$$

$$\Delta T_2 = \left(\frac{0.45}{36.6} \right) \left(\frac{0.001}{0.1} \right) (350),$$

$$= 0.043^\circ\text{C/mil of Fe},$$

$$\Delta T = 0.645^\circ\text{C},$$

for 15 mils, $\Delta T = 0.645^\circ\text{C}.$

2.2. FABRICATION OF P AND N SEGMENTED ELEMENTS

Figure 2-9 shows the design initially adopted because of the high efficiency that might be obtained at relatively low temperatures ($\geq 725^{\circ}\text{C}$); $\geq 725^{\circ}\text{C}$ is an easier operating maximum temperature for $(\text{Cu,Ag})_2\text{Se}$. Figure 2-10 gives the design ratio suggested for the first elements.

Fabrication studies were performed with the Transit size, i.e., 0.325-cm diameter x 0.675-cm length, Se elements. Emphasis has been placed upon utilizing the Transit couple design techniques and existing tooling for fabrication of the next Se couple. Thus far, most of the old tooling has been used without any significant modifications.

2.2.1. Triply Segmented P Elements

One reason for selecting $\text{PbSnMnTe}/(\text{Bi}_2\text{Sb})_3\text{Te}_3$ for the lower portion of the segmented P element was the known stability of this combination. Early General Atomic (GA) work on developing thermoelectric materials demonstrated the thermal and chemical compatibility of these materials in (1) 28,000-h life tests and (2) 8-yr of use of PbTe and PbSeMnTe in the Transit RTG space power system. A second reason for selecting this combination was to optimize the T_C value of the $(\text{Cu,Ag})_2\text{Se}$ segment and hence to minimize enhanced vaporization of $(\text{Cu,Ag})_2\text{Se}$ when operating with current flow in a thermal gradient.

The triply segmented P legs were fabricated using $(\text{Cu,Ag})\text{Se}$ for the upper segment, which was joined to a PbSnMnTe middle segment, which was then joined to a BiSbTe lower segment. A thin layer of Fe powder acted as a reaction barrier at the interface of the $(\text{Cu,Ag})_2\text{Se}/\text{PbSnMnTe}$. No barrier or interface component was used at the interface of the $\text{PbSnMnTe}/\text{BiSbTe}$, since this joint has been proven in past work. Fe powder was also put at the outer end of the $(\text{BiSb})_2\text{Te}_3$ to form the P leg cold shoe; this is another proven concept. The entire assembly was set up in a die and hot-pressed as a unit at 450°C . All three matrix materials have been successfully

PbTe TO Ni COLD CAP USES CONVENTIONAL TRANSIT BOND

PbTe JOINED TO Gd_2Se_3 VIA DIFFUSION BONDING

Gd_2Se_3 JOINED TO Ni HOT CAP VIA DIFFUSION BONDING

Fe COLD CAP TO Fe SHOE IS SAME AS THAT USED IN RING CONVERTER

ALL LEG COMPONENTS, INCLUDING MESH, ARE HOT-PRESSED AS A SINGLE UNIT

MOLYMESS IS JOINED TO HOT CAP VIA SPOT WELDING

Fig. 2-9. N and P leg fabrication plan for Se couples

Fig. 2-10. Optimum material ratios for best efficiency and iL/A

fabricated with the same pressing parameters. Figure 2-11 presents the fabrication sequence for these triply segmented elements. All die sticking problems experienced during early fabrication were remedied.

There were two problems with the final product: (1) the optimum hot-pressing temperatures of the three materials were different, and (2) it was difficult to get segments of uniform length in multiple powder pressings. Mechanical failures of the P element occurred after handling and during gradient testing, and the Fe barrier was nonuniform. Failure occurred as a fracture through the PbSnMnTe segment of the element. No failures were seen in $(\text{Cu,Ag})_2\text{Se}$ or $(\text{BiSb})_2\text{Te}_3$, or at any of the interfacial joints. Micro-cracks were found in PbSnMnTe, the inherently weaker segment. Material and process modifications were made in several experimental pressing runs to minimize cracking. Fewer cracks were noted in some of the modified hot-pressed samples, and cracks that did occur were parallel to the direction of the applied pressure. Hot-pressing at higher temperatures, higher pressures, and longer times was examined. When the temperature was raised to 475°C or higher, excessive $(\text{BiSb})_2\text{Te}_3$ extrusion occurred, causing serious die sticking problems and difficulty in removing the elements. Increasing the time and the pressure resulted in higher densities. Lightly cold-pressing the powder in the die just prior to hot-pressing improved the element fabrication process.

Cold-pressing was developed during early fabrication of the ring converter elements and helps overcome the nonuniform Fe barrier. Cold-pressing tends to cause the segment interfacial zones to become flatter and more uniform. Prior to using this technique, these zones were more ragged and, in some cases, varied in thickness. This nonuniformity might have been a contributing cause of cracks. Separate cold-pressing of each component powder as it was loaded into the die was examined (i.e., after the Se powder was loaded it was pressed, followed by pressing of the Fe barrier, followed by pressing of the PbSnMnTe powder, and so forth until the final Fe powder for the shoe was pressed). The resulting element was very promising in that

Fig. 2-11. Triply segmented P element fabrication sequence

each segment and interface zone was very uniform and the PbSnMnTe cracks were minimal.

The results of the triple segmenting studies to date indicate the following:

1. The three materials, $(\text{Cu,Ag})_2\text{Se}$, PbSnMnTe-3P, and $(\text{Bi,Sb})_2\text{Te}_3$, can be successfully fabricated in one step using powder metallurgy techniques.
2. The barrier between $(\text{Cu,Ag})_2\text{Se}$ and PbSnMnTe is important in preventing these materials from reacting and preventing Cu migration into the $(\text{Bi,Sb})_2\text{Te}_3$. However, some interaction can occur without affecting thermoelectric properties. One P element was run in a gradient test for 650 h and was then examined metallographically. The Fe barrier in this element was not complete across the element and extensive interdiffusion occurred; however, the corresponding changes in $^{\circ}\text{C}$ and R were rather small.
3. Fe has been used as the barrier material because of its known long-term compatibility with PbSnMnTe and its apparent compatibility with $(\text{Cu,Ag})_2\text{Se}$.
4. When used as a simple planar barrier, the Fe barrier appears to cause stresses due to thermal expansion differences near the interfaces with the $(\text{Cu,Ag})_2\text{Se}$ and PbSnMnTe, thereby causing cracking and/or debonding. To minimize these stresses, the Fe barrier was graded as shown in Fig. 2-12. Metallographic examination of an element fabricated in this manner showed it to be sound and crack free throughout its leg.

Fig. 2-12. Triply segmented elements with a graded Fe barrier

2.2.2. Doubly Segmented P Elements

The thermal expansion differences between $(\text{Cu,Ag})_2\text{Se}$, Fe, and PbSnMnTe in the triply segmented P element are of concern as regards the long-term stability of the element during generator usage. A decision was made to switch to a doubly segmented element consisting of $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$ segments, because it might be simpler to solve the problems of the doubly segmented element than that of the triply segmented element. A successful initial effort to fabricate the doubly segmented element in one hot-pressing supported this view. Although the one-step fabrication of the doubly segmented element was simpler than the fabrication of the triply segmented element, the thermoelectric properties of the doubly segmented element were not up to par.

Figure 2-13 shows the initial fabrication sequence selected for doubly segmented P-type elements of $(\text{Cu,Ag})_2\text{Se}$ and $(\text{Bi,Sb})_2\text{Te}_3$. This sequence included a single hot-pressing step. Figure 2-12 gives an example of the P-type element resulting from this sequence. Control of the density of the $(\text{Cu,Ag})_2\text{Se}$ layer and the uniformity of the thickness of the $(\text{Bi,Sb})_2\text{Te}_3$ layer was marginal. The major drawback to the sample shown in Fig. 2-14 was the lack of an Fe barrier. Without the barrier, Cu diffused into the $(\text{Bi,Sb})_2\text{Te}_2$ during hot-pressing, ruining the thermoelectric properties of that layer. When Fe was included as a barrier to Cu diffusion, the variation in the uniformity and density of the single-step hot-pressing became more evident.

Four methods for fabricating these elements were examined:

1. Simultaneous hot-pressing of both segments without a barrier.
2. Simultaneous hot-pressing of both segments with graded zones on each side of an Fe barrier.

Fig. 2-13. Doubly segmented P element fabrication sequence

6875-110-35

Fig. 2-14. Doubly segmented P leg

3. Simultaneous hot-pressing of both segments with an Fe barrier and a graded Ni-(Cu,Ag)₂Se layer on the hot side of the barrier.
4. Sequential hot-pressing of segments with an Fe barrier.

The rationale for using Fe as the barrier layer is that it appears compatible with (Cu,Ag)₂Se at 250°C, is immiscible with Cu, and was previously used on the cold end of the ring converter with no detrimental effects over 40,000 h. Table 2-2 gives the details of the FY 79 segmented P element fabrication trials. The results show the following:

1. Single-step fabrication of (Cu,Ag)₂Se/(Bi,Sb)₂Te₃ segmented P elements can be done. Control of segment uniformity and density is, however, marginal, because of the compromise which must be made in the hot-pressing temperature.
2. A barrier layer between the (Cu,Ag)₂Se and (Bi,Sb)₂Te₃ segments is necessary to prevent thermoelectric property degradation of the (Bi,Sb)₂Te₃ due to copper contamination.
3. Fe adequately inhibits Cu movement between the (Cu,Ag)₂Se and (Bi,Sb)₂Te₃ segments in short-term isothermal tests. Long-term thermal gradient tests will be undertaken to determine the long-term stability of these materials.
4. Finely divided Fe reacts when intimately mixed with (Bi,Sb)₂Te₃ to form a new material phase. Contiguous phases of Fe and (Bi,Sb)₂Te₃ do not show a similar phase formed during hot-pressing. Long-term isothermal tests will be run to determine the stability of the Fe-(Bi,Sb)₂Te₃ interface at several temperatures.
5. Sequentially hot-pressed segmented P elements [(Cu,Ag)₂Se hot-pressed first at 800°C followed by (Bi,Sb)₂Te₃ hot-pressed at

Specimen No.	Segment	Segment Transistor Zone	Hot-Pressing Procedure	130/30 Seebeck ($\mu\text{V}/^\circ\text{C}$)	Remarks
6875-118-8	$(\text{Cu,Ag})_2\text{Se} + (\text{Bi,Sb})_2\text{Te}_3$	None	450°C in vacuum at 20,000 psi for 1 h (one-step process)	5.7	Low Seebeck values indicate Cu contamination and need for barrier
6875-118-11				6.3	Copper contamination of $(\text{Bi,Sb})_2\text{Te}_3$
6875-118-12	$(\text{Cu,Ag})_2\text{Se} + (\text{Bi,Sb})_2\text{Te}_3$	Triple-graded zone	450°C in vacuum at 20,000 psi for 1 h (one-step process)	198.0	Fe powder reacted with $(\text{Bi,Sb})_2\text{Te}_3$
6875-118-16		1. $(\text{Cu,Ag})_2\text{Se} + \text{Fe}$ (50/50)		195.0	
6875-118-24		2. Fe 3. $(\text{Bi,Sb})_2\text{Te}_3 + \text{Fe}$ (50/50)		164	
6875-125-8	$(\text{Cu,Ag})_2\text{Se}$ to $(\text{Bi,Sb})_2\text{Te}_3$	Triple-graded barrier between segments	450°C in vacuum at 20,000 psi for 1 h (one-step process)	195.0	Second phase formed in $\text{Fe}(\text{Bi,Sb})_2\text{Te}_3$ graded layer
6875-125-11		1. $(\text{Cu,Ag})_2\text{Se} + \text{Fe}$ (50/50)		153.0	Second phase formed in $\text{Fe}(\text{Bi,Sb})_2\text{Te}_3$ graded layer
6875-125-12		2. Fe 3. $(\text{Bi,Sb})_2\text{Te}_3 + \text{Fe}$ (50/50)		177.0	
6875-125-16	$(\text{Cu,Ag})_2\text{Se}$	1. $(\text{Cu,Ag})_2\text{Se} + \text{Fe}$ (50/50)	600°C in vacuum then to 800°C soak, no load for 1 h	197.0	
6875-125-24		2. Fe		201.0	
6875-125-31					
6875-127	$(\text{Bi,Sb})_2\text{Te}_3$		Cold-pressed only	232 (unbounded 171 stack 194)	
6875-125-24	1. $(\text{Cu,Ag})_2\text{Se}$	1. $(\text{Cu,Ag})_2\text{Se} + \text{Fe}$ (50/50)	$(\text{Cu,Ag})_2\text{Se}$ prepressed at 600° and 800°C	201.0	Fe barrier discontinuous at element o.d.
6875-126-1	2. $(\text{Bi,Sb})_2\text{Te}_3$	2. $\text{Fe} + (\text{Bi,Sb})_2\text{Te}_3$ (50/50)	$(\text{Bi,Sb})_2\text{Te}_3$ powder added to die with 6875-125-24 hot-pressed at 450°C	174.0

6875-122-11	$(\text{Cu,Ag})_2\text{Se}$	None	450°C in vacuum at 20,000 psi for 1 h	84.0	$(\text{Bi,Sb})_2\text{Te}_3$ contamination by Cu
6875-122-16	$(\text{Bi,Sb})_2\text{Te}_3$		450°C in vacuum at 20,000 psi for 1 h	96.0	
6875-126-2	$(\text{Cu,Ag})_2\text{Se} + (\text{Bi,Sb})_2\text{Te}_3$		Unbounded stacks, 122-11 + 122-16	91.0	
6875-125-31	$(\text{Cu,Ag})_2\text{Se}$	None	450°C in vacuum at 20,000 psi for 1 h	232.0	Evidence of contamination from the hot-pressing dies
6875-122-16	$(\text{Bi,Sb})_2\text{Te}_3$		450°C in vacuum at 20,000 psi for 1 h	96.0	
6875-126-3	$(\text{Cu,Ag})_2\text{Se} + (\text{Bi,Sb})_2\text{Te}_3$		Unbounded stacks, 125-31 + 122-16	192-203	
6875-128-1-12		1. $(\text{Cu,Ag})_2\text{Se} + \text{Fe}$ (50/50)	450°C in vacuum at 20,000 psi for 1 h (one-step process)	81	Evidence of contamination in $(\text{Bi,Sb})_2\text{Te}_3$
6875-128-1-24		2. Fe		104	Evidence of contamination in $(\text{Bi,Sb})_2\text{Te}_3$
6875-128-1-35				160	
6875-128-1-36				82	

TABLE 2-2 (Continued)

Specimen No.	Segment	Segment Transistor Zone	Hot-Pressing Procedure	130/30 Seebeck ($\mu\text{V}/^\circ\text{C}$)	Remarks
6875-128-2-12		1. $(\text{Cu,Ag})_2\text{Se} + \text{Fe}$ (50/50) 2. Fe	450°C in vacuum at 20,000 psi for 1 h (one-step process)	107	Barrier layer incomplete, Cu contaminated $(\text{Bi,Sb})_2\text{Te}_3$
6875-128-2-24				72	
6875-128-2-35				140	
6875-128-2-36				146	
6875-129-1-12		1. $(\text{Cu,Ag})_2\text{Se} + \text{Fe}$ (50/50) 2. Fe	Sequential hot-pressing $(\text{Cu,Ag})_2\text{Se}$ hot-pressed at 600°C annealed for 1 h at 800°C	122	
6875-129-1-24				131	
6875-129-1-35				138	
6875-129-1-36				122	
6875-129-2-12			$(\text{Bi,Sb})_2\text{Te}_3 + \text{Fe}$ powder hot-pressed at 400°C (in vacuum) and 20,000 psi	156	
6875-129-2-24				140	
6875-129-2-35				140	
6875-129-2-36				144	
6875-130-1-12		Fe to Fe	Sequential hot-pressing $(\text{Cu,Ag})_2\text{Se}$ at 600°C annealed at 800°C for 60 min	189	
6875-130-1-24				201	
6875-130-1-35				207	
6875-130-1-36				221	
6875-130-2-12			$(\text{Bi,Sb})_2\text{Te}_3$ powder added then hot pressed at 450°C (in vacuum) at 20,000 psi	158	
6875-130-2-24				150	
6875-130-2-35				150	
6875-130-2-36				172	
6875-130-2-12		Fe		193	Wire mesh sheared in second hot-pressing
6875-130-2-24				Broke	
6875-130-2-35				154	
6875-130-2-36				193	
					Metallographic appearance good

450°C] are the most uniform segments in terms of dimensions and density. The best results were obtained when Fe was hot-pressed to $(\text{Cu,Ag})_2\text{Se}$ and additional Fe placed at the interface before the second hot-pressing.

2.2.3. Isothermal Testing of Segmented Elements

Two triply segmented P-type elements were isothermally heated at 325°C for 117 h. Samples were visually examined after 5.5, 30, and 117 h to determine if the $(\text{Cu,Ag})_2\text{Se/Fe/PbSnMnTe-3P}$ and $\text{PbSnMnTe-3P/BiSbTe}$ joints would stay together at this low temperature. These examinations necessitated thermal cycling of the elements. At the end of these tests, the joints appeared intact in spite of the thermal cycling.

Similar isothermal tests were made on two $(\text{Cu,Ag})_2\text{Se-PbSnMnTe-3P}$ segmented elements. Samples were removed from the tests after 17, 35, 78, 145, and 237 h at 475°C. An inadvertent thermal excursion above 700°C for 1 h occurred after 233 h in the chamber containing the doubly segmented samples. In spite of this thermal deviation, the $(\text{Cu,Ag})_2\text{Se/Fe/PbSnMnTe}$ joints survived the tests. One sample, however, broke during posttest handling.

An additional isothermal test was performed on four doubly segmented elements of $(\text{Cu,Ag})_2\text{Se}$ with PbSnMnTe , two with Fe interface barriers and two without barriers. This test was interrupted at 304 h to obtain a data point. Both elements having Fe barriers (of the nongraded junction variety) came apart at the Se to Fe joint during handling. The two elements without barriers continued to be tested. Testing was interrupted again at 400 h, at which time one remaining element was pulled out for metallographic examination. Testing of the fourth element was continued, and the test was interrupted at 662 h for routine measurements. Both the elements without barriers remained intact.

2.2.4. Gradient Testing

A triply segmented element without an Fe barrier was tested for 179 h, at which time a power shutdown occurred. Resistance values had begun to increase just prior to this shutdown. The test station was opened to examine the element before reheating, and a crack was discovered where the $(\text{Cu,Ag})_2\text{Se}$ was joined to the PbSnMnTe , terminating the test.

A second zero-current thermal gradient life test of a triply segmented P-type element was terminated after 660 test hours. The three thermoelectric materials from the hot to cold end of the element were $(\text{Cu,Ag})_2\text{Se}$, PbSnMnTe-3P , and BiSbTe , respectively. The T_H of the gradient was approximately 725°C , and the T_C approximately 55°C . After 50 h, a temporary power outage occurred. The power was restored and the samples brought back to test temperatures within 12 h. Figure 2-15 gives the electrical resistance and Seebeck values for this element. The slight decrease in these values was expected due to precipitation of MnTe in the PbSnMnTe-3P .

The element fractured in two sections while it was being removed from the test stand. Subsequent metallography showed the break to be in the middle (PbSnMnTe-3P) segment. This element contained a horizontal crack that propagated.

Microprobe and metallographic examinations were made of the triply segmented element that had operated for 660 h. New phases began to develop in the PbSnMnTe-3P and the $(\text{Bi,Sb})_2\text{Te}_3$. The Fe barrier between the $(\text{Cu,Ag})_2\text{Se}$ and PbSnMnTe was discontinuous. The microprobe analysis indicated that Cu was diffusing through the "leak" in the Fe barrier into the lower two segments. Cu was found in the newly formed phases and in the PbSnMnTe and the $(\text{Bi,Sb})_2\text{Te}_3$.

The Seebeck coefficient and resistance data showed relatively small changes. The Seebeck coefficient normally drops in PbSnMnTe elements owing to MnTe precipitation, and any changes in the Seebeck coefficient for this

Fig. 2-15. Results of test in vacuum of triply segmented P element 6875-77-6 (data uncorrected)

element were thought to be due to this effect only. Based upon (1) the amount of Cu that diffused into the lower segments and (2) the room-temperature Seebeck and resistance measurements obtained on other elements in which Cu diffused into the other segments, one might have anticipated much larger thermoelectric property changes than actually occurred.

2.2.5. Vapor Suppression in Doubly Segmented P-Type Elements

The results of thermal gradient tests with coatings and glass sleeves have shown the weak area to be the junction of the hot cap and $(\text{Cu,Ag})_2\text{Se}$ P-type thermoelectric material. When 7740 Pyrex sleeves were warm-pressed on 316 stainless steel, a joint was formed which later failed in thermal cycling. When the 7740 Pyrex was replaced with 1720 Pyrex and the 316 stainless steel with Mo, the joint formed between these materials survived modest thermal cycling tests without apparent damage. Joints between Mo and other metal components of the thermoelectric generator need to be developed.

An alternate vapor suppression system consisting of an insulator sleeve which is mechanically locked in place by a metal collar (Fig. 2-16) is being examined. This insulator sleeve is intended to be only part of the vapor suppression system. The vapor suppression system consists of (1) a vapor-deposited coating over P-type $(\text{Cu,Ag})_2\text{Se}$; (2) a locked-sleeve vapor barrier; and (3) Mo opacified paper (Fig. 2-17). The baffling factors for the vapor suppression coating should be 5 to 50; the locked sleeve, 30 to 1000; and the Mo opacified paper, 50. The total baffling factor of the system could be on the order of 7500. An engineering analysis of the vapor suppression sleeve is needed to optimize sleeve lengths, wall thicknesses, and sleeve-to-element gap.

Fig. 2-16. Doubly segmented P element showing locking vapor suppression sleeve

Fig. 2-17. Segmented P element $(\text{Cu,Ag})_2\text{Se}/(\text{Bi,Sb})_2\text{Te}_3$

2.2.6. Development of Segmented N-Type Elements

Evaluation of Gd_2Se_3 preparation begun in FY 78 continued along with evaluation of the resulting material. The objectives of the FY 79 segmented N-type element development effort were as follows:

1. To prepare and be able to reproduce Gd_2Se_3 with a known chemical and microstructural composition.
2. To determine methods of stabilizing the thermoelectric properties of Gd_2Se_3 .
3. To develop fabrication processes for hot-pressing Gd_2Se_3 and joining it to hot cap materials and other N-type thermoelectric material segments.
4. To evaluate alternative N-type Se materials.

2.2.6.1. Aging Studies of Gd_2Se_3 . As-received 3M slugs were aged to (1) obtain more information about the cubic to orthorhombic transformation of Gd_2Se_3 and (2) prepare some orthorhombic material that could be ground and vacuum hot-pressed into element-size samples. The aging studies were performed at 900°, 1000°, and 1100°C in high vacuum at pressures of 10^{-6} to 10^{-8} torr. The materials were checked by X-ray diffraction at the end of the tests to determine the percent conversion to the orthorhombic structure.

Specimens transforming from cubic to orthorhombic swelled slightly, as measured at room temperature, and their Seebeck coefficients decreased, as measured from 130° to 30°C. From a theoretical standpoint, the orthorhombic volume exceeds the cubic volume by 0.3% at room temperature. High-temperature X-ray diffraction data show that at 500°C, this volume differential reverses, and the cubic volume exceeds the orthorhombic by 0.4%. Thus, it seems feasible that the phase transformation in the material can easily contribute to stressing and cracking.

In the 1100°C aging test, two powder and two slug samples were aged for 118.9 h. There was very little, if any, conversion to orthorhombic material, and there were only small dimensional and Seebeck changes.

In the 1000°C aging tests, five slug samples were aged for 118.9 h and two powder samples were aged for 118.9 h and then for 90.0 h. After the 118.9 h-test, the samples varied between 70% and 98% orthorhombic; one slug was only 17%. The slug samples swelled, indicating the volume difference between cubic and orthorhombic at room temperature. In some slugs there was a significant drop in the room-temperature Seebeck coefficient. The two powder samples were run for another 90.0 h at 1000°C. One did not change (70%), and the other went from 85% to 98% orthorhombic.

In the 900°C aging test, the two powder samples run in the 1100°C aging test were run for 90 h at 900°C. They converted to 90% and 98% orthorhombic, and the samples had a slight reddish tinge after testing.

Table 2-3 summarizes the results of the aging tests. These results indicate that the transformation temperature for conversion of cubic to orthorhombic for $\text{GdSe}_{1.48} \pm 0.01$ is above 1000°C and below 1100°C.

Six samples have been converted from the orthorhombic to the cubic phase in the differential thermal analysis system. There was an endothermic change indicated at $1145^\circ \pm 10^\circ\text{C}$ in each case. X-ray diffraction showed that there was a 100% conversion to the cubic phase. This sharp conversion is in contrast to the cubic to orthorhombic change, which is very sluggish.

2.2.6.2. Forty-Eight-Hour Annealing Tests on GdSe_x . A series of 48-h annealing tests of cubic GdSe_x ($x = 1.350, 1.450, \text{ and } 1.493$) in a high-vacuum furnace is in progress to study the cubic to orthorhombic phase change in Gd_2Se_3 . The two lower compositions were prepared by GA, and the 1.493 composition was prepared by 3M. The $\text{GdSe}_{1.350}$ is two phase with approximately 30% GdSe , which does not change during annealing, and 70% Gd_2Se_3 .

TABLE 2-3
RESULTS OF AGING TESTS OF 3M Gd₂Se₃(a)

Specimen	Temperature (°C)	Time (h)	Change (%)			Ortho- rhombic (%)	Seebeck (μV/°C)	
			Weight	Length	Diameter		Before	After
T-14-16 slug	1100	118.9	-0.011	-0.03	+0.02	<7	-114.0	-115.2
T-4-15 slug	1100	118.9	-0.006	+0.07	-0.05	<7	-115.8	-113.6
T-5-6 slug	1000	118.9	-0.001	+0.27	+0.35	86	-113.4	-75.0
T-5-9 slug	1000	118.9	-0.007	+0.13	+0.57	98	-114.8	-65.9
6011-137-2 slug	1000	118.9	-0.028	+0.19	+0.10	>96	-101.1	-99.5
T-5-14 slug	1000	118.9	-0.043	+0.37	+0.05	73	-114.8	-92.2
N-2649-110 slug	1000	118.9	-0.174	Irregular shape		17	-110.0	-101.4
T-4-18 powder	1100	118.9	-0.030	---	---	0	---	---
	900(b)	90.0	-0.024	---	---	90	---	---
T-4-21 powder	1100	118.9	-0.065	---	---	0	---	---
	900(b)	90.0	-0.069	---	---	98	---	---
T-4-12 powder	1000	118.9	-0.015	---	---	70	---	---
	1000	90.0	-0.075	---	---	70	---	---
T-5-15 powder	1000	118.9	-0.031	---	---	85	---	---
	1000	90.0	-0.053	---	---	98	---	---

(a) All material started at 100% cubic except specimen 6011-137-2, which started at 90% orthorhombic.

(b) Had reddish tinge after 900°C test.

(c) Hot-pressed 3M material.

Approximately 0.1 g of fresh material was weighed into W crucibles for each test. The samples were placed in the high-vacuum furnace, which was pumped to $<10^{-7}$ torr before heat-up. The temperature was measured with a Chromel-Alumel thermocouple placed in an area surrounded by the samples; the temperature varied $\pm 10^{\circ}\text{C}$ during annealing. The furnace was brought to temperature in approximately 1 h. The pressure in the furnace increased to 10^{-6} torr during heat-up, but dropped to 10^{-7} torr at temperature and 10^{-8} torr after the 48-h test. The furnace was allowed to cool after 48 h at ambient temperature. The samples were removed and reweighed, and the amount of conversion was determined by X-ray diffraction. The results, listed in Table 2-4, were good to within $\pm 5\%$ and indicate that

1. The temperature above which there is no conversion to the orthorhombic phase is between 1050° and 1075°C in the 48-h time frame.
2. The conversion kinetics are composition dependent (faster conversion as $x \rightarrow 1.50$ in GdSe_x).
3. The conversion goes through a maximum with respect to temperature.

2.2.6.3. Se/Gd Ratio Analysis. A method for determining the Se/Gd ratio was developed to check the material being made at GA and 3M. The general procedure reacts the GdSe_x with O_2 and calculates the Se/Gd ratio from the starting and final weights. The reaction is carried out in a DuPont 951 thermogravimetric analyzer. Approximately 90 ± 0.005 mg of the powdered sample is weighed. The sample holder is Pt. The sample is heated at a rate of $50^{\circ}\text{C}/\text{min}$ in flowing O_2 until most of it has reacted (650° to 700°C). The temperature is then increased to 1000°C and held. The reaction is followed to completion (5 to 6 h) by observing the weight loss.

The Se/Gd ratio is calculated by assuming that the final product is Gd_2O_3 (to obtain the amount of Gd present) and the starting product is all

TABLE 2-4
RESULTS OF 48-H ANNEALING TESTS ON GdSe_x

Annealing Temperature (C°)	Wt % Orthorhombic $\pm 5\%$		
	$\text{GdSe}_{1.35}^{(a)}$	$\text{GdSe}_{1.45}$	$\text{GdSe}_{1.493}$
600	<5	<5	—(b)
700	<5	<5	—(b)
800	<5	—(b)	—(b)
850	15	11	66
900	5(c)	37	—(b)
950	17	60	95
1000	31(c)	44	—(b)
1050	<5	30	85
1075	<5	<5	<5
1100	<5	<5	<5

(a) Two-phase with approximately 30% GdSe and 70% Gd_2Se_3 .

(b) No data.

(c) $\text{Gd}_2\text{O}_2\text{Se}$ detected.

Gd and Se (to determine the amount of Se). Table 2-5 lists the samples analyzed by this method. Several things could interfere with this analysis:

1. Impure starting products. It is assumed that the Gd and Se are pure and not contaminated during the production of Gd_2Se_3 .
2. Incomplete reaction with O_2 . The weight loss of the sample is followed until there is no significant weight loss in 1 h. Gd_2O_3 obtained from Gd_2Se_3 oxidation was analyzed by X-ray fluorescence and no Se was detected. Incomplete reaction with O_2 does not appear to be a problem.
3. Volatile Gd compounds and sample loss from the balance. No volatile Gd oxides or selenides are known in this temperature range. There was a possibility of losing samples from the sample holder because the reaction is exothermic. The heating rate was lowered to solve this problem. The quartz enclosure tube was checked after each determination for sample material which may have been ejected from the Pt sample holder.
4. Oxygen present in the sample. O_2 could be introduced during either preparation of the Gd_2Se_3 or hot-pressing the N-type element. If greater than 0.2% O were introduced during fabrication or any other process where the material is heated above 300°C , it would cause a greater than 1% error in the analysis, which would not be detected. Oxygen from air or water vapor is adsorbed by the sample in the powder form. Typical aging experiments have shown weight losses, which should be due to the reaction of adsorbed O_2 or H_2O , which would cause an error of approximately 0.2% in the analysis.

TABLE 2-5
RESULTS OF ANALYSIS OF Se/Gd RATIO

Sample	Se/Gd Ratio in Original Mix	No. of Determinations	Measured Se/Gd Ratio in Sample
6011-121(a)	1.493	4	1.491 $\pm$ 0.003
T-5-15	Unknown	2	1.478 $\pm$ 0.001
B-1(b)	1.478	3	1.474 $\pm$ 0.004

(a) GA sample.

(b) ³M sample N-2649.

Other results of the $\text{Gd}_2\text{Se}_3 + \text{O}_2$ reaction were

1. Samples exposed to air lost weight and gave off Se_2 between 350° and 450°C ; the weight loss was always small. This reaction was also observed within the mass spectrometer.
2. In the temperature range 450° to 650°C , the sample gained weight (formation of $\text{Gd}_x\text{Se}_y\text{O}_z$). The mass spectrometer study showed no loss of Se in this temperature range.
3. At approximately 650°C , the sample lost weight in an exothermic reaction. A white product (SeO_2) was given off which condensed directly to a solid in the cooler parts of the quartz tube, downstream from the sample.

The analytical method seems adequate for determining the Se/Gd ratio if care is taken during production and handling of Gd_2Se_3 .

2.2.6.4. Preparation of Gd_2Se_3 . Efforts continued on improving the technique for the preparation of N-type GdSe_x semiconductor material. Initially, three melts having different Gd/Se ratios were produced. The nominal values were sample A-1 = 1.470, sample A-2 = 1.500, and sample B-1 = 1.493. Each member of the A series had a total mass of 10 g; B-1 had a total mass of 69 g.

After the established thermal cycle for GdSe_x production was completed, the components were removed from their quartz envelopes and heated in vacuum graphite crucibles to $>1800^\circ\text{C}$. During the early stages of the thermal cycle, sample A-1 was heavily contaminated with quartz because of a shattered envelope. It was melted to determine if the quartz container contributed to the formation of the transparent red phase. It did not contribute (no red phase was found in sample A-1).

The construction of the quartz reaction vessels was modified to eliminate atmospheric contact with the elements before sealing under vacuum. Precoating the quartz vessels in a plastic material prior to breaking the quartz vessel was successful in decreasing the quartz contamination of the sample. Quartz inclusions in the Gd_2Se_3 may contribute to cracking of the elements. Quartz has been observed in the 3M material.

Weight loss calculations during melt formation indicate that the Se loss is between 0.2% to 3% depending on length of time at final temperature, mass of sample in crucible, and type of graphite used. Experiments to decrease the Se vapor pressure and/or loss during melt formation indicate that Se loss can be controlled at the 0.1% to 0.4% weight loss values.

Sample B-1 was melted in two sections owing to volume restrictions in the crucible. After melting, it was noted that a transparent red phase that was the last to solidify during cooling had collected in a relatively uniform layer in the center of the ingot, as shown below. Red phase crystals were found at the interface where the columnar grains had grown together.

Microscopic analysis showed this red phase to be distinctly different in color from the matrix, but microprobe and X-ray analyses showed this phase to have the same composition and the same cubic crystallographic structure as the matrix material. It appears that the electron microprobe is not sensitive enough to see the very small differences in composition that probably exist between the red phase and the matrix material.

The as-weighed molar ratios for compounds A-4, A-5, and A-6 were $\text{A-4} = \text{GdSe}_{1.521}$, $\text{A-5} = \text{GdSe}_{1.471}$, and $\text{A-6} = \text{GdSe}_{1.351}$. The compound

formation procedure was modified by reducing the time at 825°C from 7 days to less than 1 day. This time reduction was based on observations of the Se vapor concentration at temperature. When the Se vapor was unnoticeable, the reaction was assumed to be complete (Se vapor has a noticeable brown color).

During the melt formation step, the time at temperature was reduced from 5 to 10 min to 2 min. It was hoped that this time reduction would lessen the loss of Se vapor. However, as in the case of A-4, which had a high initial Se concentration, considerable amounts of Se were lost. Based on weight loss calculations, the final Se/Gd molar ratio was 1.49 ± 0.03 . Chemical oxidative determination (COD) studies determined the Se/Gd molar ratio to be 1.459 ± 0.003 . In the case of A-5, the weight loss calculations indicated a Gd/Se molar ratio of 1.44 ± 0.03 with a COD molar ratio of 1.452 ± 0.002 . The amount of Se loss for A-5 was within experimental error of the thermogravimetric analysis. Therefore, there was no change in molar ratio. COD studies confirmed this, giving a ratio of 1.355 ± 0.001 . Table 2-6 gives the Se/Gd molar ratios.

A new Thermox oxygen analyzer was installed in the present O monitoring line of the glove box. The new analyzer is based on measuring the O potential between two Pt electrodes as O diffuses through a hot alumina barrier. Although the two systems now in use are based on different methods, they do agree closely with each other in the ranges of O found in the dry box. For example, a reading of 1.0 ppm on the electrochemical device will find a corresponding reading of 0.8 ppm on the more highly sensitive Thermox analyzer.

2.2.6.5. Vapor Species Above Gd_2Se_3 . Se_2 has been observed to vaporize from N-type Gd_2Se_3 in two unexpected temperature ranges, 200° to 500°C and 700° to 900°C. The results of studies discussed below show that the amount vaporized from fine powder is greater than that from small chunks. Vaporization occurs only after the Gd_2Se_3 has been exposed to air, and

TABLE 2-6
Se/Gd MOLAR RATIOS OF COMPOUNDS A-4, A-5, AND A-6

Compound	Se/Gd Molar Ratio		
	As Weighed	Melt Formed	COD Determined
A-4	1.521 $\pm$ 0.006	1.49 $\pm$ 0.03	1.459 $\pm$ 0.003
A-5	1.471 $\pm$ 0.006	1.44 $\pm$ 0.03	1.452 $\pm$ 0.002
A-6	1.351 $\pm$ 0.006	1.35 $\pm$ 0.03	1.355 $\pm$ 0.001

experiments indicate that the amount of vaporization is dependent on the amount of time the Gd_2Se_3 has been exposed to air. Phase transitions in Gd_2Se_3 were examined with a differential thermal analyzer (DTA). Se was noted condensing in the cooler parts of the DTA apparatus after runs to 1000°C . The evaluation of the nature of this vaporization led to the mass spectrometric-Knudsen cell studies reported below.

The Knudsen cell was constructed of Mo, and temperatures were measured with Pt - Pt 10% Rh thermocouples. The cell was temperature and pressure calibrated by observing the Ag signal deflection at its melting point out of the Knudsen cell. The mass spectrometer was a CEC 21-703, high-temperature, 60°C magnetic deflection instrument. The sample studied was 3M N-2649 Gd_2Se_3 in the form of small chunks and fine powder.

Two series of tests were run. The first was on small chunks of Gd_2Se_3 and the second on fine powder. These tests showed that the only vaporizing species was Se_2 , which vaporized in two temperature regions, around 400°C and 800°C . As expected, Se_2 was seen above 1200°C . Table 2-7 summarizes the results.

Chunk Gd_2Se_3 (26 mg) was put into the Mo Knudsen cell, and the vapor pressure of Se_2 as a function of time and temperature was observed (Fig. 2-18). The sample was cooled to room temperature and reheated to 900°C , and no Se_2 was observed. The sample was cooled, removed from the mass spectrometer, and weighed, and the weight loss was 0.19%. The weight loss could have been off by a factor of two because of the sensitivity of the balance. The sample had a slightly reddish tinge after the run.

The sample was exposed to air for 4 h with the Knudsen cell uncovered. The cell was covered, put back into the mass spectrometer, and reheated to 900°C , and the Se_2 was vaporized in the two temperature ranges. The amount vaporized was approximately 2% of the original amount vaporized. The amount vaporized was determined by summing the time and vapor pressure data for the two runs.

TABLE 2-7
SUMMARY OF RESULTS OF Se₂ VAPORIZATION FROM Gd₂Se₃

Sample Size	Vaporization Range		Se ₂ in Vaporized Original Heat-up (wt %)	Wt % of Original Vaporized Se ₂ After 4-h Exposure to Air
Chunks	402 - 480	739 - 900	0.19	2.0
Powder	222 - 516	687 - 900	0.42	11.0

Fig. 2-18. Vaporization of Se_2 from Gd_2Se_3 chunks: 3M N-2649 sample weight = 26 mg, weight loss = 0.19%

The tests on the chunks were rerun on 204 mg of finely powdered Gd_2Se_3 . The results are plotted in Fig. 2-19. The sample was cooled and then reheated to 900°C . The pressure was identical to the Se_2 pressure when the first heat-up was terminated. The sample was cooled and weighed; the weight loss was 0.42%, which is over twice as much as that of the chunk sample. The sample had a definite red color.

The sample was exposed to air for 4 h with the Knudsen cell uncovered. The cell was covered, put back into the mass spectrometer, and reheated to 900°C , and the Se_2 was vaporized in the two temperature ranges. The amount vaporized was approximately 11% of the original amount, compared with 2% for the chunks.

The vaporizing behavior of Gd_2Se_3 is summarized as follows:

1. The greater amount of Se vaporized from the powdered Gd_2Se_3 indicates that surface area plays a part in vaporization.
2. Failure to vaporize Se_2 after cooling and reheating (in the mass spectrometer) indicates that there is no precipitation of Se from Gd_2Se_3 during cooling from 900°C .
3. Vaporization of Se_2 after exposure of Gd_2Se_3 to air shows that surface-adsorbed oxygen (O_2 or H_2O) is a problem. The oxygen reacts with the Gd_2Se_3 , apparently substituting for the Se. The Se in turn is easily vaporized.
4. The smaller amount of Se vaporized after exposure to air and reheating indicates that the time that Gd_2Se_3 is exposed to air is a factor.
5. The results show that Se_2 will be vaporized from the N leg if it is exposed to air before heat-up. They also indicate that extreme

Fig. 2-19. Vaporization of Se_2 from Gd_2Se_3 powder: 3M N-2649 sample weight = 204 mg, weight loss = 0.42%

care should be exercised to keep powdered Gd_2Se_3 from being exposed to air.

6. The Se condensate observed in previously run modules and generators is probably not just from the $(\text{Cu},\text{Ag})_2\text{Se}$ but from the Gd_2Se_3 in the early part of life. Unless efforts are made to contain this Se (such as by coatings), it must be contended with in generator design.

2.2.6.6. Gd_2Se_3 Stabilization. Gd_2Se_3 exhibits the undesirable trait of transforming from a cubic to an orthorhombic structure. Alloy additions to $\text{GdSe}_{1.5}$ may stabilize the cubic phase but have little effect on thermoelectric properties. Work done at GA in the early 1960s was directed at $\text{CeSe}_{1.5}$. This alloy is cubic in the as-fabricated condition but transforms to another phase after short periods at selected temperatures. Additions of Sr, Ba, and Ca alloys were individually made; all three elements were successful in stabilizing the cubic phase.

Accordingly, a GdSe alloy containing Sr was prepared. The alloy examined was purposely restricted to temperatures $\leq 1000^\circ\text{C}$. It was prepared by placing the raw materials in an evacuated vial and slowly bringing the vial up to 1000°C . Starting with the elements and limiting the temperature to 1000°C made it possible to determine the equilibrium phases that would form. The problem with melting the materials and then subjecting them to low-temperature aging studies is that the kinetics of the low-temperature transformations may be extremely sluggish, and long times are required before equilibrium is achieved.

The results obtained indicate that it is possible to stabilize the $\text{GdSe}_{1.5}$ compound in the cubic structure. After extended aging of the vial at 1000°C , the alloy was granular and contained both dark and light orange material. X-ray diffraction showed that the light orange material was cubic with a lattice parameter which was slightly larger than that of $\text{GdSe}_{1.5}$. The dark material was multiphase and contained some cubic material.

Microprobe analysis of the light orange granules indicated there was ~7 wt % Sr in the $\text{GdSe}_{1.5}$.

2.2.6.7. NdSe_x Alloy Preparation. An alternative to stabilizing Gd_2Se_3 is to select an alternate rare earth selenide which has no known cubic to orthorhombic transformation. Nd_2Se_3 is one such promising alloy. Hence, an $\text{NdSe}_{1.470}$ alloy was prepared by weighing the elements into a quartz reaction tube, which was in a glove box. The tube was evacuated, sealed, and slowly heated to 1000°C . It was then aged at this temperature for 5 days. Analysis of the product showed that it was 90% NdSe_2 and 10% NdSe and an unknown. The differences in the reaction rates during formation of Gd_2Se_3 and Nd_2Se_3 from their elements must be resolved before a full evaluation of Nd_2Se_3 as a thermoelectric material is possible.

2.2.6.8. Fabrication of Segmented N-Type Elements. Figure 2-20 shows the segmented N elements. The Gd_2Se_3 segment was hot-pressed in a vacuum at 1400°C and 4500 psi for 1 min and then slow-cooled without pressure. The end of the element was grit blasted with Al_2O_3 powder and ion plated for 2 min with PbTe at a bias power of 500 W and an electron beam power of 600 W. This produced a 15,000-Å coating. Previously hot-pressed PbTe-2N was placed on top of the Gd_2Se_3 which was in contact with the ion-plated PbTe in a die and was warm-pressed together at 450°C in H followed by hot-pressing in a vacuum at 600°C for 45 min.

2.2.6.9. Examination of Gradient-Operated Gd_2Se_3 Element. A Gd_2Se_3 element fabricated by 3M and evaluated by Jet Propulsion Laboratory (JPL) at a T_H of 800°C and a T_C of 240°C was forwarded to GA for evaluation. The element was whole, but contained cracks. JPL stated that the vacuum station developed a problem at 2000 h. This problem was fixed, and the sample was operated an additional 2000 h. A very thin white layer on the sample indicated that it had probably oxidized slightly; this layer was easily removed. On the cold end, the soft Pb layer had been pushed up around the element.

Gd_2Se_3 VACUUM HOT-PRESSED
 Gd_2Se_3 SURFACE ION-PLATED WITH PbTe
 PbTe HOT-PRESSED SEGMENT (WITH Ni COLD CAP) DIFFUSION-
 BONDED TO ION-PLATED PbTe

Fig. 2-20. Segmented N element $Gd_2Se_3/PbTe$

After the element was axially sectioned, three pieces of bulk material were selected for X-ray diffraction: the hot end, just below midway down the element, and the cold end. The results showed that the hot end was orthorhombic, the midway sample both orthorhombic and cubic, and the cold end cubic. The as-received 3M material was cubic, and isothermal studies performed on 3M material shows that it transforms to the orthorhombic structure at temperatures below 1200°C. Thus, the results obtained on the gradient-operated element are in agreement with prior GA isothermal studies. This phase change (along with accompanying dimensional changes) could contribute to cracking of the N-type element.

2.2.6.10. Isothermal Testing of an N-Type Segmented Element. An N-type element with Gd_2Se_3 and PbTe-2N segments was heated at 475°C for 185 h. The specimen was removed from the test and visually examined after 92 h. After 181 h, a thermal excursion occurred in which the temperature remained above 700°C for 1 h and temporarily reached 720°C. This thermal perturbation had no visual effect on joint integrity.

2.3. SELENIDE COUPLE TESTING

The all-bonded selenide thermoelectric couple described in Ref. 2-1 was placed in an ion-pumped bell jar, as shown in Fig. 2-21. The couple was kept in the thermal gradient, open circuit for 550 h. It was then kept at a current of 100 mA for 2800 h, which corresponded to an iL/A of 1.22 A/cm. Figures 2-22 through 2-24 present the hot-and cold-side temperature histories of these elements. The hot-side temperatures varied less than 2°C during any 48-h test period.

Both elements of the couple were removed from the test. The P element was intact at shutdown, but the hot cap failed when the couple was removed from the station (it was slightly stuck to the heater). The N element cold-side bond failed during couple removal.

Fig. 2-21. Couple and test station setup

Fig. 2-22. Life test data for Se couple 6875-65

Fig. 2-23. Life test data for Se couple 6875-65 $(\text{Cu,Ag})_2\text{Se}$ P leg

Fig. 2-24. Life test data for Se couple 6875-65 Gd_2Se_3 N leg

Metallographic analysis was performed on each element. The N element (Fig. 2-25) appeared to be structurally sound and the mesh bond intact. Some porosity was evident in the hotter one-third of the element. Since an as-fabricated element showed a similar distribution of porosity, it is thought the porosity in this element was initially present because of the way it was pressed. The cold-side bond was $\text{GdSe}_{1.5}$ diffusion-bonded to Au. The materials separated cleanly at the interface. The $\text{GdSe}_{1.5}$ was not ion plated first, and the diffusion bond was apparently weak.

The P element (Fig. 2-26) showed considerable vaporization at the hot junction (its T_H was 850° to 900°C). The glass sleeve around the $(\text{Cu,Ag})_2\text{Se}$ was not tightly bonded to the cap, and as a result the vaporizing species could easily escape. (The thermal expansion between the quartz sleeve and the stainless steel cap was quite large.)

REFERENCE

- 2-1. Elsner N. B., et al., "Radioisotope Space Power Generator Annual Report for the Period October 1, 1976 Through September 30, 1978," General Atomic Report GA-A15683, January 1980.

#6011-134-5

Fig. 2-25. N leg from 3000-h test couple

6875-65-1

Fig. 2-26. P leg from 3000-h test couple

3. (Bi,Sb)₂(Se,Te)₃ MATERIALS

3.1. MODULE TESTING

The Mo-contacted 1-W generator module was tested in Ar at $T_H \sim 350^\circ\text{C}$ and $T_C \sim 90^\circ\text{C}$ for 5000 h. Figure 3-1 is a plot of the output of the module at periodic times. There was no degradation in power; however, when the hot-side temperature was increased to 375°C , a system leak developed, which caused a delay in module testing.

3.2. THERMID 600 HIGH-TEMPERATURE ADHESIVES

3.2.1. Cure Cycle

The laquer version of Thermid 600 relies on the vaporization of the solvent and melting for its cure. Preliminary attempts at an acceptable cure cycle indicate that the temperature of the cure, not the time at temperature, is more important in vaporizing the solvent. Figure 3-2 shows the percent solvent loss after cures at various temperatures. These cycles were done above the melting point of the resin ($\sim 200^\circ\text{C}$). A cycle in which the solvent can vaporize below the resin melting point was sought to see if solvent evaporation is more effective. Above the resin melting point some solvent remains entrapped at the temperatures of interest for curing, i.e. below 300°C .

An acceptable low-temperature cure cycle was found by making a weight loss run on the uncured resin. Figure 3-3 shows the results of this run. This run showed maximum weight losses at approximately 125° and 180°C . An isothermal run showed 43% weight loss at 125°C in 6 h. The sample was then heated to 180°C , where it lost another 6%. Next, it was heated above its melting point to 250°C , where 1.5% was lost in less than 1 h. There was no

Fig. 3-1. 5000-h test on Mo-contacted 1-W $(\text{Bi,Sb})_2(\text{Se,Te})_3$ generator module:
 $T_H \sim 350^\circ\text{C}$, $T_C \sim 90^\circ\text{C}$

Fig. 3-2. Percent weight loss at 350°C (samples cured for 2 h at 225°C and 1 to 4 h at temperatures between 250° and 350°C)

Fig. 3-3. Weight left as a function of temperature for uncured Thermid 600 adhesive (heating rate = 1°C/min)

further weight lost at this temperature after 3 h. Figure 3-4 shows the results of weight left as a function of temperature for Thermid 600 cured for 6 h at 125°C, 2 h at 180°C, and 1 h at 251°C. Isothermal weight loss experiments were run on material using the low-temperature cure cycle to check long-term stability.

3.2.2. High-Temperature Vaporization Properties of Thermid 600

A series of isothermal weight loss runs on cured Thermid 600 are in progress. Figure 3-5 shows the results of the 425° and 450°C runs. These results along with those of the runs in progress will be used to predict weight losses at lower generator temperatures.

3.3. MODULE LOADING TEST

Zero, 25%, 50%, and 75% of design loads between the heat source and module were applied in full 75-mW tests at 300°C. Figure 3-6 shows the results of the tests. The 50% and 75% loads show degradation. An open circuit developed when the module was raised to 300°C at full design load. Examination of the module showed two loose connector tabs on the hot side. Both were on outer rows, on opposite edges.

These accelerated life, loading tests indicate that the degradation of the GA $(\text{Bi,Sb})_2(\text{Se,Te})_3$ modules below ~300°C is a physical phenomenon. The problem seems to be in the ability to apply an even force to all the connector tabs. As a solution to the problem, a module will be potted with Thermid 600, sanded down to the tabs, and checked for its loading properties.

3.4. RTG-2A DIAGNOSTICS

RTG-2A was defueled at Los Alamos Scientific Laboratory (LASL) and underwent diagnostic analysis at GA according to the test plan described in Appendix A whenever feasible. As predicted from the voltage measurements

Fig. 3-4. Weight left as a function of temperature for Thermid 600 cured for 6 h at 125°C and 2 h at 180°C (heat rate = 2°C/min)

Fig. 3-5. Results of isothermal weight loss runs on Thermid 600 adhesive cured at 325°C for 4 h

Fig. 3-6. Results of loading tests on a 75-MW module ($T_H = 300^\circ\text{C}$)

between the leads and case, the short between the module and the base was at couple No. 8. The short disappeared when the "ear" became electrically (and mechanically) isolated from the base, as shown in Fig. A-5. The short returned once, but never again. When the module and base were separated, residual strain in the Cu-Be base was apparently relieved and caused the short to open. Attempts were made to recreate the short with 100-V tests in air and in vacuum, but to no avail.

The module was X-rayed after it was cut down to the one-slice-thick range, as shown in Fig. A-9. Some heavy-density matter was apparent at the interface of couple No. 8 between the Au tab and the Cu-Be base. The X-ray shows that this matter is not touching either surface. After being X-rayed, the one-layer-thick slice separated in the epoxy near the Au tab interface. Optical examination showed a black pimple on the Au tab and a corresponding black hole in the epoxy.

Photographic evidence agreed with the X-ray radiograph, which indicated foreign matter at the interface. Scanning electron microscope analysis showed the hole to contain Bi, Te, and Au. Apparently, one or more particles of $(\text{Bi,Sb})_2(\text{Se,Te})_3$ were entrapped in the epoxy, and as the 100-V test was repeated, the distance between the particles was not sufficient for insulation. This RTG ran 7000 h as an ETG before fueling and exhibited the shorting in Xe after the RTG was pinched off for several days. The majority of the module removed from RTG-2A was reworked. Just prior to applying the Au tabs, a slight crack was noted on one element.

All failure diagnostics involving RTG-201 and RTG-2A were completed, and the following changes were incorporated: (1) the insulation on the hot and cold ends was increased, as shown in Fig. 3-7; (2) the mating surfaces were individually final-machined to each module; and (3) the mating metal surfaces in contact with the module were chemically polished. A new RTG-2A module was fabricated and successfully passed module performance tests. The module was mounted on its new base; 3-mil Kapton was bonded to the base. The electrical resistance to the base was checked at 100 V before the module

3-MIL KAPTON IS EPOXIED IN PLACE WITH A TOOL; EPOXY IS ONLY ON BOTTOM SIDE. MODULE IS THEN EPOXIED TO BASE. FUEL CANISTER IS LOADED ON MODULE WITH MICA AND KAPTON IS PLACED AT INTERFACE. NO EPOXY IS USED ON THE HOT SIDE.

Fig. 3-7. Schematic of module, base, and fuel canister showing upgraded insulation

was bonded in place; a metal block simulating a module was used to perform this test.

3.5. RTG-201 DIAGNOSTICS

RTG-201 is presently configured as an ETG without the two outermost foils and has accumulated ~150 h of life test and is exhibiting stable performance. It is the first unit to be subjected to high-temperature, 50-V, vacuum and high-temperature, 50-V, Ar tests. RTG-201 was subjected to this test after the fuel canister was positioned in place and the tie wires secured.

A small decrease in the resistance between the power leads and the case was observed in Ar and in vacuum at the upper operating temperature; however, the resistance (10^7 to 10^8 ohms) was well above the specification level of 105 ohms, which is attributed to the ionization of water in the Kapton, epoxy, or mica at elevated temperatures.

Following the above test, the unit was placed in the ETG configuration without the outer two foils and placed on burn-in to determine if there were any resistance changes with time. The unit in the ETG configuration at the typical operating temperature (up to 120 mW output) exhibits infinite resistance between the leads and the base. The reason for the difference between the ETG burn-in and the prior test is the operating T_H of the unit. In the test in vacuum and in Ar the unit reached a higher temperature, and the difference in the T_H caused the decrease in the resistance of the Kapton and/or mica.

The procedural specification is being modified so that the elevated temperatures* in the 50-V, vacuum, Ar test are the same as operating temperature.

* Temperatures in excess of the typical operating temperature are achieved during module checkout and vacuum degassing after fueling.

RTG-201 will be shut down in the near future, its outer shields epoxied in place, and life testing as an ETG continued until shock and vibration testing is performed.

3.6. SPECIFICATIONS AND PROCEDURES

Fourteen procedural specifications were upgraded to provide more vigorous control and inspection of the units during assembly.

APPENDIX A
TEST PLAN FOR LOCATING SHORT AT THE COLD SIDE INTERFACE
OF RTG-2A

A.1. BACKGROUND

RTG-2A developed a short after being fueled and pinched off (at LASL). The RTG was subsequently opened, and the short was determined to be on the cold side. The resistance of the short was ~1300 ohms as measured with a conventional laboratory volt-ohm meter.

The following items are considered significant with regard to RTG-2A and its possible relationship to the short:

1. The unit has PET cloth and epoxy at the interface between the Cu-Be base and the module.
2. The interface insulation is the same as that of all the units except for RTG-102 and RTG-201.
3. The module and base were originally in RTG-1. This RTG was inadvertently opened, and the module and base were fitted with a new fuel canister when it was designated RTG-2A.
4. The same module and base have been subjected to shock and vibration testing three times: the first time as an ETG for RTG-1, the second time as RTG-1, and the third time as an ETG for RTG-2A.

5. RTG-2A was run as an ETG for ~7000 h before the third shock and vibration test was performed.
6. The first 100-V resistance check on RTG-2A was performed in Ar after ~7000 h of life testing and $>10^8$ ohms were measured.
7. Right after fueling but before final welding, the 100-V test measured $>10^8$ ohms. This test was performed in Ar.
8. RTG-2 exhibited the first signs of shorting when the 100-V test was performed after welding and under vacuum.
9. RTG-2 was back-filled with Xe, the feed-throughs were cleaned, and the short disappeared.
10. RTG-2 was pinched off in Xe.
11. After the welds were X-rayed, RTG-2 exhibited a short that has remained.
12. RTG-2 was opened and the heat source removed.
13. The ratio of the voltage measurements between the two pins to the case indicates that couple 5, 6, 7, or 8 is where the module shorted (Fig. A-1).

A.2. DIAGNOSTIC PLAN

A.2.1. Determination of Shorted Couple

The hot side of the module is exposed and the Au tabs are readily accessible. As previously performed on an RTG, the Au tabs are

progressively removed to locate the shorted couple. The hot side is heated with a heat lamp for a few seconds, and the voltage output is simultaneously monitored between the base and the negative terminal. No voltage is obtained when the Au tab of the affected couple is removed (Fig. A-2).

Determination of the shorted couple starts with the tenth Au tab from the negative terminal. After the tenth Au tab is removed, the ninth Au tab is removed, followed by the eighth tab. Theoretically, no voltage should be obtained when the seventh, sixth, or fifth Au tab is removed. Since Au tabs join two elements on the cold side, only the shorted couple can be determined, and it will not be possible to isolate the shorted element. Resistance probing of the module is of little value since the short is ~1300 ohms and the resistance of one thermoelectric leg is 1 ohm.

A.2.2. Separation of Cu-Be Module Platform from Base

A diamond blade saw-cut is performed as shown in Fig. A-3. This allows the module to be analyzed more conveniently in the scanning electron microscope.

A.2.3. Removal of One Side "Ear"

As shown in Fig. A-4, most of the ear is removed with the diamond cutoff wheel. Approximately 5 mils of this ear remain. The cut is performed on the side of the shorted module.

A.2.4. Isolation of Segments of Cu-Be Platform

As shown in Fig. A-5, the 5-mil Cu-Be slice is electrically isolated from the rest of the platform by lapping off the corner. Isolation of the two pieces of Cu-Be will be determined by probing from the top of the module to each of the Cu-Be segments (Fig. A-6).

TEST PROCEDURE

1. DIGITAL VOLTMETER WAS CONNECTED TO THE BASE ASSEMBLY AND A MODULE POWER OUTPUT LEAD
2. THE HEAT LAMP RAISED THE MODULE HOT-SIDE TEMPERATURE ENOUGH TO PRODUCE AN OUTPUT VOLTAGE WHICH WAS READ BETWEEN THE BASE AND OUTPUT LEAD
3. EACH TIME A GOLD TAB WAS REMOVED THE MODULE WAS REHEATED AND VOLTAGE OUTPUT READ
4. AFTER REMOVING THE LAST TAB THE VOLTAGE DROPPED TO ZERO, INDICATING THAT THE SHORT WENT OPEN

Fig. A-2. Measurement technique employed to isolate module electrical short (this procedure was used on RTG2 and is recommended for RTG2A)

Fig. A-3. Cross section of module on base

Fig. A-4. Removal of one side "ear"

Fig. A-5. Isolation of Cu-Be slice from platform

Fig. A-6. Probing from top of module to isolate two Cu-Be pieces

A.2.5. Shorting Direction

After isolation, it is possible to determine if the module short is between the 5-mil piece on the side and the horizontal platform. If the short is in the direction of the platform (as expected), then the 5-mil Cu-Be piece is removed by lapping or grinding. With this 5 mils of material removed, the interface between the module and platform is inspected as described in Section 2.6.

If the short is in the direction of the 5-mil-thick Cu-Be segment (this is possible but not expected), then the horizontal platform is removed by grinding and the interface is inspected as described in Sections 2.6 and 2.8. Further sectioning of the module to isolate the affected couple is performed in a manner similar to that described in Sections 2.7 and 2.9.

A.2.6. First Inspection of Interface

The interface is first inspected visually with the optical microscope to note any probable shorted areas. This interface is examined with the scanning electron microscope in the passive and active modes. In the passive, or conventional, mode, the scanning electron microscope inspects the interface topography and determines the composition of any metallic impurities that may be at the surface. In the active mode, a voltage is applied between the module and the Cu-Be segment to which it shorted.

With the proper attachments, the scanning electron microscope can detect and photograph the current while under the applied voltage. However, it is necessary that the short be present at the surface and not be covered with epoxy.

A.2.7. Slicing of the Module

As shown in Fig. A-7, it is planned to section the module and the Cu-Be platform vertically. This slice is made at the third row in from the shorted side of the module. This sectioning operation leaves a slice that is two rows wide, and the shorted couple is still bonded to the Cu-Be segment. For handling convenience, the slice is also shortened as shown in Fig. A-8.

A.2.8. Second Inspection of Interface

Since the slice can be readily observed from two directions, intensive lighting can be used to highlight any particulates at the interface; hence, this evaluation is performed first. The scanning electron microscope passive and active mode examinations described in Section 2.6 are performed, and radiographs of the joint are made.

A.2.9. Sectioning of the Slice

It is desirable to isolate the affected couple physically, but this reduction in area should be limited to about two couples. This sectioning can be accomplished by mounting the two-layer-thick slice in wax and removing the two couples from the wax after cutting (Fig. A-9).

A.2.10. Third Inspection of Interface

With the couples further isolated, the interface can be inspected from all four sides, and intensive lighting can be used to help locate any particulates in the epoxy. After the visual examination, the same type of passive and active scanning electron microscope analysis is performed, as noted in Section 2.6. Radiographs are made if they can be of benefit.

Fig. A-7. Vertical section of module and Cu-Be platform

Fig. A-8. Shortening two-row slice

Fig. A-9. Cutting two-layer slice

A.2.11. Exact Location of Short

After the above analyses and examinations have been performed, the shorted area may be visible with the optical or scanning electron microscope. If it is apparent that a metal particle is causing the short, methyl chloride can be used to soften the epoxy and remove the Cu-Be segment. The exposed epoxy surface is then examined to find the shorted area. The techniques used are (1) visual inspection, (2) use of a fine probe to "feel" around the surface until the short is located, and (3) use of a scanning electron microscope in the passive and active modes.

If it is apparent that metallic particles are not causing the problem, the couples are mounted in wax and lapped very slowly. At 1/2-to 1-mil intervals, the surface is monitored for continuity of the short and examined on the scanning electron microscope in the active mode to observe any current flow. If it is suspected that the short is caused by a combination of particulates and some thin conductive film, then the lapping technique is the most likely to be pursued. Once the short is located, its composition is determined with the scanning electron microscope.

A.2.12. Mechanism of Short Formation

After the short is isolated and characterized, attempts are made to determine how the short developed. This analysis includes determination of the epoxy creep properties; 100-V resistance measurements performed in air, Ar, Xe, and vacuum; and determination of possible contaminating materials in the PET cloth and epoxy. The analysis may include tests which cause a short under the hypothesized conditions.

A.2.13. Documentation

Detailed procedures, sequence of events, data, records, and photographs are obtained and incorporated in a report on RTG-2A.

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