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RADIOISOTOPE SPACE POWER GENERATOR ANNUAL REPORT

**FOR THE PERIOD OCTOBER 1, 1976,
THROUGH SEPTEMBER 30, 1978**

by

**N. B. ELSNER, J. CHIN, H. G. STALEY,
J. C. BASS, E. J. STEEGER, P. K. GANTZEL,
and J. M. NEILL**

**Prepared under
Contract DE-AT03-76SF70060
for the San Francisco Operations Office
Department of Energy**

JANUARY 1980

GENERAL ATOMIC COMPANY

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ABSTRACT

Techniques for fabricating P-type $(\text{Cu,Ag})_2\text{Se}$ with mesh-type bonds have been developed and are being evaluated for long-term use. In addition, methods for reducing vapor suppression by the use of coatings and/or baffling continue to show gains.

The N-type alloy Gd_2Se_3 has been shown to be thermally unstable. It undergoes a sluggish cubic-to-orthorhombic phase change below 1000°C , with an accompanying degradation in mechanical and thermoelectric properties.

Fabrication studies conducted with the $(\text{Bi,Sb})_2(\text{Se,Te})_3$ alloys showed these materials to be sensitive to oxygen contamination if reproducible properties are to be obtained. Preparation of powdered material by explosive techniques was investigated. This technique appears to be useful in preparing homogeneous -325 mesh material, but it does not yield a useful amount of submicron-size powder.

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CONTENTS

ABSTRACT	iii
1. INTRODUCTION	1-1
2. SELENIDE MATERIALS DEVELOPMENT	2-1
2.1. Introduction	2-1
2.2. Fabrication of P-Type (Cu,Ag) ₂ Se Elements	2-3
2.2.1. Mesh-In-Cap and Joint Development	2-3
2.2.2. Graded Cold Shoe Bonding	2-15
2.3. Suppression of Vaporization	2-19
2.3.1. Vapor Suppression Coating Development	2-20
2.3.2. Vapor Suppression by Mechanical Baffling	2-28
2.4. Compatibility	2-42
2.4.1. Compatibility Tests	2-42
2.4.2. Summary of Compatibility Studies	2-49
2.5. Thermal Gradient Testing	2-49
2.6. Design Analysis of the P-Type (Cu,Ag) ₂ Se Element	2-60
2.6.1. Thermal Analysis	2-60
2.6.2. Thermoelectric Sleeve Vaporization Loss Model	2-74
2.6.3. Constraints on (Cu,Ag) ₂ Se Thermoelectric Generator Operation	2-76
2.7. N-Type Gd ₂ Se ₃ Bonded Element Development	2-80
2.7.1. N-Type Gd ₂ Se ₃ Thermal Stability Studies	2-81
2.7.2. N-Type Gd ₂ Se ₃ Hot-Pressing Development	2-83
2.7.3. Joining of N-Type Gd ₂ Se ₃ to Hot Cap	2-87
2.8. Bonded Selenide Couple Development	2-93
3. (Bi,Sb) ₂ (Se,Te) ₃ MATERIALS	3-1
3.1. Process Control and Materials Evaluation	3-1
3.1.1. Introduction	3-1
3.1.2. Alloy Preparation	3-2
3.1.3. Comminution and Pressing	3-2
3.1.4. Metallographic and Mechanical Property Analyses	3-3

3.1.5.	Anisotropy Measurements	3-4
3.1.6.	Thermal Conductivity	3-7
3.2.	Ultrafine Grain Material	3-7
3.2.1.	Introduction	3-7
3.2.2.	Preparation of Powders	3-8
3.2.3.	Thermal Conductivity	3-10
4.	INSULATION AND ADHESIVE CHARACTERIZATION	4-1
4.1.	Insulation Characterization	4-1
4.2.	Adhesive Characterization	4-4
4.2.1.	Shell Epon 828	4-4
4.3.	Adhesive Screening	4-8
4.4.	Characterization of Individual Adhesives	4-8
4.4.1.	Tracon 2255	4-8
4.4.2.	Thermo-Resist Glom O-N	4-13
4.4.3.	Tracon 2212	4-13
4.4.4.	Thermo-Resist TR 150-25	4-18
4.4.5.	Gulf Chemical Company Thermid "600"	4-19
4.5.	Module and Electrically Heated Thermoelectric Generator (ETG) Testing	4-27
4.5.1.	Thin-Leg Modules	4-27
4.5.2.	Tracon 2212 Module and ETG Testing	4-28
4.5.3.	TR 150-25 Adhesive Module Testing	4-33
4.5.4.	One-Watt Module Test	4-36
4.5.5.	Module Loading Tests	4-36
REFERENCES		5-1

FIGURES

2-1.	Fabrication sequence for the modified mesh-in-cap element . . .	2-4
2-2.	Schematic diagram showing different configurations of wire mesh	2-5
2-3.	Macrophotographs of hot caps with differing W-Re wire mesh orientations after plasma spraying with molybdenum	2-6
2-4.	SEM photomicrograph of the surface of a 316 SS cap ion plated with tungsten in run 1-15	2-8
2-5.	SEM photomicrograph of tungsten ion plated on W-Re wire of sample 1-15	2-9

2-6.	SEM photomicrograph of the surface of a 316 SS cap ion plated with tungsten in run 1-17	2-10
2-7.	SEM photomicrograph of tungsten ion plated on W-Re wire of sample 1-17	2-11
2-8.	SEM photomicrograph of the surface of a 316 SS cap ion plated with tungsten in run 1-19	2-12
2-9.	SEM photomicrograph of tungsten ion plated on W-Re of sample 1-19	2-13
2-10.	A 40,000 Å tungsten coating on 316 SS	2-14
2-11.	SEM photomicrograph of ion plated coatings on 316 SS of tungsten and Mo	2-16
2-12.	Metallographic cross section and macrophotograph of a vacuum hot-pressed P-type (Cu,Ag) ₂ Se element	2-17
2-13.	P-type (Cu,Ag) ₂ Se mesh in cap fabrication sequence	2-18
2-14.	900° isothermal weight loss ratio for B ₂ O ₃ + rare earth (CeO ₂ , CeO ₂ Pr ₂ O ₃ , and Y ₂ O ₃) oxide-coated P-type (Cu,Ag) ₂ Se material.	2-25
2-15.	Weight loss rates for coated and uncoated (Cu,Ag) ₂ Se P material at 850°C	2-26
2-16.	Metallographic cross sections of P-type (Cu,Ag) ₂ Se elements which were ion plated from Pyrex, Pyrex + 10% Pb ₂ O ₃ , and Pyrex + 10% Nd ₂ O ₃	2-27
2-17.	Metallographic cross section of a P-type GeO ₂ coated copper silver selenide element	2-29
2-18.	Metallographic cross section of a Pyrex + 10% Pr ₂ O ₃ coating on a P copper silver selenide element	2-30
2-19.	850°C isothermal weight loss rate for P-type (Cu,Ag) ₂ Se coated with boron nitride plus in situ Cr ₂ O ₃	2-31
2-20.	850°C isothermal weight loss rate for P-type (Cu,Ag) ₂ Se coated with carbon plus in situ Cr ₂ O ₃	2-32
2-21.	850°C isothermal weight loss rate for P-type (Cu,Ag) ₂ Se coated with in situ Cr ₂ O ₃	2-33
2-22.	Effectiveness of Cr ₂ O ₃ coating	2-34
2-23.	P-selenide material development	2-36
2-24.	Glassy barrier vapor suppression system on P-type (Cu,Ag) ₂ Se material	2-37
2-25.	Fabrication sequence for bonded P-type (Cu,Ag) ₂ Se element	2-38
2-26.	Wetting of 316 SS by Pyrex 7740 at 850°C was not improved by either grit blast cleaning or sodium silicofluoride	2-40

2-27.	W-Re wire mesh tack welded to 316 SS retained Pyrex 7740 in two 850°C bonding experiments but bowed on cooling and failed to prevent differential thermal expansion stresses from breaking the glass	2-41
2-28.	Pyrex 7740 warm pressed at 850°C to molybdenum	2-43
2-29.	Corning 1720 alumino silicate glass sleeve warm pressed to a molybdenum hot cap	2-44
2-30.	Results of 400-h compatibility tests at 900°C and 900 psi	2-46
2-31.	SEM examinations at 2000X of (Cu,Ag) ₂ Se P-type material with 900-psi contact pressure against molybdenum after 400 hours at 900°C	2-47
2-32.	SEM examinations of P-type (Cu,Ag) ₂ Se material with 900 psi contact pressure against tungsten after 400 h at 900°C	2-48
2-33.	Photomicrographs of nickel in contact with Gd ₂ Se ₃ and (Cu,Ag) ₂ Se	2-50
2-34.	Photomicrographs of polished cross sections of P-type (Cu,Ag) ₂ Se elements coated with B ₂ O ₃ + Bn	2-52
2-35.	P-type (Cu,Ag) ₂ Se element with a glassy barrier	2-53
2-36.	Photomicrographs of polished cross sections of a P-type (Cu,Ag) ₂ Se element with a glass sleeve vapor suppression barrier	2-54
2-37.	Thermal gradient life test results, Seebeck coefficient versus time	2-56
2-38.	Thermal gradient life test results, resistivity versus time	2-57
2-39.	(Cu,Ag) ₂ Se bonded element with glass sleeve after 450 h of operation at a T _h of 850°C	2-58
2-40.	Thermal gradient life test results, Seebeck versus time for test sample 6875-39-3	2-61
2-41.	Thermal gradient life test results, resistivity versus time for test sample 6875-39-3	2-62
2-42.	Thermal gradient life test results, Seebeck versus time for test sample 6875-37-1	2-63
2-43.	Thermal gradient life test results, resistivity versus time for test sample 6875-37-1	2-64
2-44.	Schematic diagram of P-selenide element	2-65
2-45.	Temperature at end of sleeve as a function of sleeve length for full contact and 0.0025-cm gap	2-67
2-46.	Percent loss in couple efficiency as a function of glass sleeve length	2-68
2-47.	Effect of shielding of P-type (Cu,Ag) ₂ Se element on couple performance	2-70

2-48.	Loss in couple efficiency and temperature at end of sleeve . .	2-71
2-49.	Temperature at end of glass sleeve	2-72
2-50.	Loss in couple efficiency as a function of glass sleeve length	2-73
2-51.	Thermal model of mesh cap design	2-75
2-52.	Model for estimating effusion rates for gases coming from between concentric cylinders	2-77
2-53.	Comparison of PbTe and $(\text{Cu,Ag})_2\text{Se}$ weight loss rates	2-78
2-54.	SEM photomicrographs of fractured surfaces of arc cast Gd_2Se_3 and as-received 3M Gd_2Se_3	2-84
2-55.	SEM photomicrographs (3000X) of fractured surfaces	2-85
2-56.	Metallographic cross section of hot-pressed N-type Gd_2Se_3 after exposure to air at 950°C	2-88
2-57.	Hot pressing die assembly used for N-type Gd_2Se_3 hot pressing .	2-89
2-58.	Schematic diagram of the die assembly used for N-type Gd_2Se_3 hot pressing	2-90
2-59.	All bonded selenide thermoelectric couple	2-94
2-60.	Schematic diagram of the all-bonded selenide thermoelectric couple	2-95
3-1.	Schematic of the self-aligning, three-point bend modulus of rupture fixture and applicable equations	3-5
4-1.	Percent of original weight as a function of temperature for Kapton insulating material	4-2
4-2.	Isothermal weight loss runs for Kapton insulating material . .	4-3
4-3.	Arrhenius plot of α for Kapton insulating material	4-5
4-4.	Percent of original weight as a function of temperature for Epon 828 epoxy	4-6
4-5.	Isothermal weight loss runs for Epon 828 epoxy	4-7
4-6.	Percent of original weight of three Tracon adhesives as a function of temperature	4-9
4-7.	Percent of original weight of two Dylon Industries inorganic adhesives as a function of temperature	4-10
4-8.	Thermogravimetric weight losses for TR 150-25 and Glom O-N adhesives	4-11
4-9.	Percent of original weight of Thermide "600" lacquer supplied by Gulf Oil Chemical Company as a function of temperature . . .	4-12
4-10.	Isothermal weight loss runs on filled adhesive Tracon 2255 . .	4-14
4-11.	Isothermal weight loss runs on Thermo-Resist Glom O-N adhesive	4-15
4-12.	Isothermal weight loss runs on Tracon 2212	4-16

4-13.	Slope (α) of isothermal weight loss runs on Tracon 2212 versus temperature	4-17
4-14.	Residual volatile material after various time-temperature variations on the cure cycle of Tr 150-25 adhesive	4-20
4-15.	Percent of original weight of TR 150-25	4-21
4-16.	As-received properties of thin-leg microwatt module 1	4-22
4-17.	As-received properties of thin-leg microwatt module 2	4-23
4-18.	As-received properties of thin-leg 1/2-W module 1	4-24
4-19.	As-received properties of thin-leg 1/2-W module 2	4-25
4-20.	Life test of thin-leg 1/2-W module 2	4-26
4-21.	Percent power output with time for modules 4A-1 and 5A-2	4-30
4-22.	Life test data for generator 6AE at 300°C	4-31
4-23.	Life test data for generator 6AE at 270°C	4-32
4-24.	Comparison of degradation coefficients for modules made from Epon 828 epoxy and Tracon 2212 epoxy and the JPL data	4-34
4-25.	Starting properties of Module 7A	4-35

TABLES

2-1.	Isothermal weight loss rates for coated P-type (Cu,Ag) ₂ Se materials at 850°C in vacuo	2-22
2-2.	Chemical composition of ion-plated vapor-suppression coatings	2-23
2-3.	Results of microprobe examinations of recent ion-plating coatings on P-type (Cu,Ag) ₂ Se material	2-24
2-4.	Results of X-ray examinations of N-type Gd ₂ Se ₃ fabrication processes	2-82
2-5.	Examination of hot-pressed N-type Gd ₂ Se ₃ material	2-86
2-6.	Effects of bond joint aids on N-Gd ₂ Se ₃	2-92
3-1.	Oxygen content	3-3
3-2.	Modulus of rupture of bismuth telluride alloys before and after controls were implemented	3-4
4-1.	Calculated 15-year weight losses for Kapton insulating material	4-4
4-2.	Results of nuclear heated thin-leg microwatt modules 1 and 2 and a GA heart pacemaker module	4-29

1. INTRODUCTION

The studies performed in FY-77 and FY-78 have been combined into this single report.

The general thrust 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 design) 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 also at vapor suppression techniques, compatibility, and joining of hot and cold end caps. Studies with Gd_2Se_3 were initiated; these studies were concentrated on an understanding of the thermal stability of Gd_2Se_3 , the various phases formed by this material, and fabrication of material by vacuum hot pressing.

The $(\text{Bi,Sb})_2(\text{Se,Te})_3$ materials were studied with respect to their use in small, rugged RTGs where the mechanical properties of the thermoelectric materials are maximized. In addition, techniques were 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 were characterized for use in these low-temperature $(\text{Bi,Sb})_2(\text{Se,Te})_3$ generators, and promising candidate materials were selected for long-term use.

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2. SELENIDE MATERIALS DEVELOPMENT

2.1. INTRODUCTION

P-type $(\text{Cu,Ag})_2\text{Se}$ is a promising high-temperature thermoelectric material that was originally developed by 3M Company and is being evaluated at GA. Its usefulness in thermoelectric converters depends on its dimensional, electrical, and thermal stability at high temperature and its compatibility with other converter component materials in a low-pressure environment. Experimental efforts have been directed at determining vaporization behavior at 900°C , partial pressures of vaporizing species versus temperature, vapor suppression coatings, thermal expansion, dimensional stability, and the high-temperature compatibility of $(\text{CuAg})_2\text{Se}$ with proposed end cap materials.

Scanning electron examination showed that as-cast P-type $(\text{Cu,Ag})_2\text{Se}$ material has a lamellar structure with occasional layers of a ductile phase, which is presumed to be copper.

$(\text{Cu,Ag})_2\text{Se}$ when comminuted and vacuum hot pressed is dimensionally unstable in subsequent use. The material increases in both length and diameter when subjected to several thermal cycles between room temperature and 500°C . Large gains have been made in reducing this dimensional instability by heat treatments during and after the vacuum-hot-pressing operation.

End cap bonding by the GA mesh-in-cap technique appears to have adequate joint strength for $(\text{Cu,Ag})_2\text{Se}$ material, but corrosive interaction occurs between the unprotected 316 stainless steel (SS) mesh and cap and the $(\text{Cu,Ag})_2\text{Se}$ material at 600°C . Compatibility studies were conducted to determine if pyrocarbon, Mo, W, W-Re, or Re were resistant

to this corrosive interaction with P-type $(\text{Cu,Ag})_2\text{Se}$ material. The application of these refractory metal coatings or carbon on 316 SS showed promise of suppressing the interaction, which would allow the high expansion stainless steels to be used with the very high expansion $(\text{Cu,Ag})_2\text{Se}$ material ($\alpha = 24 \times 10^{-6}$ in./in./°C).

Rates of vaporization for unprotected P-type $(\text{Cu,Ag})_2\text{Se}$ material at 900°C in vacuum were measured at 1×10^{-4} g/cm²-h. Knudsen cell mass spectrometer examination of heated $(\text{Cu,Ag})_2\text{Se}$ species showed Se_2 , Cu, Ag, and CuSe to be the major species. Se_2 comprises over 90% of the vapor species at 1100°C. One method of suppressing vaporization that is being evaluated is to coat the $(\text{Cu,Ag})_2\text{Se}$ material with an insulating material which is molten at 900°C, yet sufficiently viscous to relieve the thermal stresses caused by the high expansion of the $(\text{Cu,Ag})_2\text{Se}$ material. Another method of suppressing vaporization that is being examined is coating the element with a material which reacts with volatile $(\text{Cu,Ag})_2\text{Se}$ products to form a self-sealing barrier. An alternative to reacting with the products of vaporization is a reaction with the $(\text{Cu,Ag})_2\text{Se}$ in a limited manner to form a nonspalling barrier to vaporization.

Experimental work covered in this progress report describes the results of evaluations to suppress vaporization in P-type $(\text{Cu,Ag})_2\text{Se}$ thermoelectric materials. Estimations are also made, through analytical modeling, of the thermal penalties and the resulting element efficiency losses due to vapor-suppressing coatings and mechanical barriers in several select P selenide element designs.

Evaluation of N-type Gd_2Se_3 thermoelectric material is also reported in this progress summary. Descriptions are given of process evaluations to prepare the Gd_2Se_3 and hot press it into N-type thermoelectric elements. Results of microstructural examinations of these elements are presented.

2.2. FABRICATION OF P-TYPE $(\text{Cu,Ag})_2\text{Se}$ ELEMENTS

The scheme examined for fabricating P-type $(\text{Cu,Ag})_2\text{Se}$ elements is shown in Fig. 2-1. Compatibility experiments completed in FY-76 showed the requirement for a barrier coating between $(\text{Cu,Ag})_2\text{Se}$ and the 316 SS caps to prevent corrosive interaction between these materials. The work covered in this section shows a continuation of the effort to improve the mesh-in-cap joint and to extend the useful life of the P element by suppressing vaporization.

2.2.1. Mesh-In-Cap and Joint Development

Compatibility studies as reported in the last annual report (Ref. 1) show molybdenum to be an effective barrier to corrosive interaction between $(\text{Cu,Ag})_2\text{Se}$ and 316 SS. These early coatings were plasma sprayed and had the drawbacks of being both porous and thick: in addition, they significantly buried the wire mesh, which interferes with the joint strength of the mesh bond.

Methods of improving contact between P-type $(\text{Cu,Ag})_2\text{Se}$ material and the wire mesh used to bond the hot cap were evaluated. The intent of this work was to seek ways to avoid filling in of the mesh when applying a protective corrosion barrier to the hot cap. Figures 2-2 and 2-3 show W-25%Re tack welded to the hot cap to several configurations that allowed plasma spraying the hot cap with molybdenum without filling in the W-Re wire mesh. The wires of the resulting bonded hot cap joints were more satisfactorily encapsulated in the selenide material than previous wire orientations, but the drawbacks of plasma spraying remained.

Ion plating of tungsten coatings on 316 SS with W-Re wire mesh was examined. The objective of this work was to apply a thin, low-porosity barrier coating that would be as chemically effective as the plasma-sprayed molybdenum in preventing attack of the 316 SS by $(\text{Cu,Ag})_2\text{Se}$, but

Fig. 2-1. Fabrication sequence for the modified mesh-in-cap element showing (a) wire mesh formation, (b) mesh and cap ready for vacuum hot pressing, (c) vacuum hot-pressed element with mesh wires tack welded to the stainless steel cap

(a)

(b)

(c)

Fig. 2-2. Schematic diagram showing different configurations of wire mesh examined for $(\text{Cu,Ag})_2\text{Se}$ to 316 SS joint development

a

b

Fig. 2-3. Macrophotographs of hot caps with differing W-Re wire mesh orientations after plasma spraying with molybdenum

which would not interfere with the mesh-in-cap joint integrity. Figures 2-4 through 2-10 show scanning electron microscope (SEM) photomicrographs of the results of ion plating coatings of tungsten on 316 SS caps with W-Re wire mesh.

Figures 2-4, 2-6, and 2-8 show the surface of ion-plated tungsten on three 316 SS caps outside of the mesh. The low magnification (250X) photomicrographs show the machine marks in the metal. The coatings at this magnification are so smooth they are difficult to detect.

The true features of the coating are picked up at magnifications of 10,000X to 50,000X in these figures. The differences in the structures noted were due to differences in bias power settings, source-to-substrate distance, and total gas pressure. Coatings on the wire mesh and cap surfaces under the mesh for the three samples are shown in Figs. 2-5, 2-7, and 2-9. Again, the higher magnification photomicrographs are needed to observe the morphology of the coatings. The coating on the wires of samples 1 through 7 (Fig. 2-6b) show the type of leak-tight tungsten morphology, which is the target of this work. Figures 2-5c, 2-7c, and 2-9c show ion-plated tungsten coatings in the gaps between the wires on the stainless steel cap. Surfaces shadowed by the wire mesh have not yet been examined.

The results for ion-plated tungsten coatings used as a barrier against corrosive interaction with P-type $(\text{Cu,Ag})_2\text{Se}$ material show:

1. Smooth uniform tungsten coatings can be applied simultaneously to the 316 SS cap and wire mesh.
2. Porosity in these coatings depends on substrate-to-source distance, bias voltage, and argon partial pressure.

Both tungsten and molybdenum ion-plated coatings were applied to 316 SS caps. Coatings 20,000 Å thick and less could be thermal cycled

a

b

Fig. 2-4. SEM photomicrograph of the surface of a 316 SS cap ion plated with tungsten in run 1-15 showing good tungsten coverage at high magnification: (a) 250X, (b) 10,000X

a

b

c

Fig. 2-5. SEM photomicrograph of tungsten ion plated on W-Re wire at (a) 250X and (b) 10,000X of sample 1-15. The tungsten coated on 316 SS below the wire mesh is shown in (c) at 10,000X showing good tungsten coverage on surfaces shielded by W-Re wire

a

b

Fig. 2-6. SEM photomicrograph of the surface of a 316 SS cap ion plated with tungsten in run 1-17 showing good tungsten coverage at half the bias voltage used in run 1-15: (a) 250X, (b) 50,000X

a

b

c

Fig. 2-7. SEM photomicrograph of tungsten ion plated on W-Re wire at (a) 250X and (b) 20,000X of sample 1-17. The tungsten coated on 316 SS below the wire mesh is shown in (c) at 10,000X showing good tungsten coverage in shielded areas with half the bias voltage of run 1-15.

a

b

Fig. 2-8. SEM photomicrograph of the surface of a 316 SS cap ion plated with tungsten in run 1-19 showing a more porous structure than 1-15 when both substrate bias and substrate to electron beam source are reduced: (a) 250X, (b) 20,000X

a

b

c

Fig. 2-9. SEM photomicrograph of tungsten ion plated on W-Re at (a) 250X and (b) 50,000X of sample 1-19. The tungsten coated on 316 SS below the wire mesh is shown in (c) at 50,000X showing a more porous tungsten coating when both substrate bias and substrate to electron beam source distance are minimal.

(a)

(b)

Fig. 2-10. A 40,000 Å tungsten coating on 316 SS (a) failed when thermal cycled to 900°C, and (b) illustrating the integrity of the coating but the consequences of a too thick deposit

on the stainless steel without apparent damage. There was no obvious advantage in the tungsten coating over the molybdenum coating. When the tungsten coatings were too thick (greater than 40,000 Å), stresses resulting from the differential thermal expansion between the tungsten and 316 SS caused the coating to spall from the cap (Fig. 2-10) when thermal cycled to 900°C. This, of course, would only occur if a continuous coating were deposited. Other experiments showed the spalling thickness threshold during thermal cycling was qualitatively dependent on the substrate bias; the higher the bias, the thicker the coating that could be applied without spalling. This was a very limited effect, which was due to the improved adhesion of the coating as the substrate temperature and the energy of the coating atoms were increased by substrate biasing. The requirements for applying a high-quality integral coating to the stainless steel are the requirements for coating process and thickness control. Process variables affect the integrity of both tungsten and molybdenum coatings, as seen in Fig. 2-11. These variables appear to be readily controlled, making repeatability achievable.

2.2.2. Graded Cold Shoe Bonding

A technique was developed for bonding a cold shoe to $(\text{Cu,Ag})_2\text{Se}$ material. The process consists of including in the vacuum hot pressing a technique for bonding a copper plug on the end of the P selenide element. This was accomplished by blending copper powder with ground $(\text{Cu,Ag})_2\text{Se}$ material and using this as an intermediate layer between the $(\text{Cu,Ag})_2\text{Se}$ material and the powdered copper. After vacuum hot pressing, the copper was found to be intimately bonded to the P-type selenide material through the graded copper- $(\text{Cu,Ag})_2\text{Se}$ joint (Fig. 2-12). The copper was then soldered to the cold shoe with a conventional Sn 95%/Ag 5% solder. The fabrication sequence used for vacuum hot pressing P-type $(\text{Cu,Ag})_2\text{Se}$ with the graded cold shoe is shown schematically in Fig. 2-13.

1-7 10,000x W

1-23 10,000x W

1-29 10,000x Mo

1-33 10,000x Mo

Fig. 2-11. SEM photomicrograph of ion plated coatings on 316 SS of tungsten (runs 1-7 and 1-23) and Mo (runs 1-29 and 1-33) at equal magnification (10,000X) showing reduction in grain sizes due to reducing substrate biasing

a

b

Fig. 2-12. (a) Metallographic cross section of a vacuum hot-pressed P-type $(\text{Cu,Ag})_2\text{Se}$ element showing a graded copper/ $(\text{Cu,Ag})_2\text{Se}$ joint and a plasma spray molybdenum coated hot cap with a mesh-in-cap joint; (b) macrophotograph of a vacuum hot-pressed P-type $(\text{Cu,Ag})_2\text{Se}$ element soldered to a copper cold shoe with 95% Sn, 5% Ag

VACUUM HOT-PRESSED ELEMENT

Fig. 2-13. P-type $(\text{Cu,Ag})_2\text{Se}$ mesh in cap fabrication sequence

2.3. SUPPRESSION OF VAPORIZATION

Current thermoelectric generator designs using P-type $(\text{Cu,Ag})_2\text{Se}$ specify hot cap temperatures of 850° to 1000°C for target generator efficiencies. Vapor pressures of volatile species above this material are high even at 850°C . Thus, the only way these designs can be made feasible is to develop a vapor suppression system that will inhibit $(\text{Cu,Ag})_2\text{Se}$ degradation and weight loss.

Several characteristics of this material make suppression of its vaporization difficult. First, P-type $(\text{Cu,Ag})_2\text{Se}$ has a very high coefficient of thermal expansion ($23 \times 10^{-6} \text{ cm/cm-}^\circ\text{C}$). This is a factor of 2 to 6 times the thermal expansion coefficients of potential coatings that are chemically compatible with the $(\text{Cu,Ag})_2\text{Se}$ material. Second, vaporization of Se and Ag causes dissociation of the $(\text{Cu,Ag})_2\text{Se}$. Copper ions remain, which are free to migrate in a thermal gradient or electric field. This migration results in precipitation of copper on the cooler side of P-type selenide elements heated in vacuo. This effect is very pronounced at proposed thermoelectric generator design operating temperatures of 850°C and above. A third difficulty is finding chemically compatible coatings for use in suppressing vaporization. Of particular concern is the reactivity of potential coating materials with gaseous selenium.

This report summarizes most of the efforts that began in FY-76 to improve the service life of P-type $(\text{Cu,Ag})_2\text{Se}$ material by reducing its vaporization rate. Both coatings and mechanical baffling are being examined for their effectiveness in reducing vaporization. For expediency, materials have been tested at 850° and 900°C , the anticipated operating temperatures of current generator designs using this material. Other restrictions were imposed on these materials, in addition to chemical and physical compatibility, which are necessary in order to minimize thermoelectric efficiency losses due to the vapor suppression system. These include minimum thermal and electric conductivity.

2.3.1. Vapor Suppression Coating Development

Three potential barriers to vaporization of $(\text{Cu,Ag})_2\text{Se}$ were explored: (1) glassy coatings, (2) reactive coatings, and (3) inert barriers. Glassy coatings were chosen as a means of accommodating the high thermal expansion of the selenide material. The thought was to adjust the viscosity of the glass such that at P element operating temperatures, the coating would undergo viscous flow rather than crack under the differential strain between the coating and substrate.

As proof of this philosophy, B_2O_3 coatings with BN, carbon, Al_2O_3 , and SiO_2 additives, to adjust the glass viscosity, were applied to $(\text{Cu,Ag})_2\text{Se}$ elements in earlier studies. The coated elements were heated at 900°C in thermal cycle tests to examine the adherence of the coatings. Coatings containing microfine carbon or finely divided BN worked best, with minimum cracking or spalling of the coatings after thermal cycling from ambient to 900°C . However, these coatings were not suitable for protection of the P-type selenide elements since their rates of vaporization were nearly as high as that of the selenide and they were also subject to hydration. This hydration would complicate handling procedures for these materials before they are encapsulated in the generator.

Glasses based on SiO_2 were also examined in earlier studies. Additives such as B_2O_3 were mixed with commercial glass to reduce the viscosity of the commercial glass. Only limited success was realized in these trials since viscosities achieved at element test temperatures were not low enough to accommodate the differential expansion between the coating and selenide materials. The coatings did stay on and did reduce vaporization to 1/3 to 1/5 of that of uncoated elements.

One of the vapor suppression systems examined in the FY-77, -78 studies reported here was selected for its potential reaction with selenium to form stable selenides that might deposit within cracks

in the coatings. Materials selected for these trials were yttrium and rare-earth-based compounds. These materials were expected to be stable and chemically compatible with the P-type selenide substrate. Compounds examined included Y_2S_3 , Y_2O_3 , Nd_2O_3 , Pr_2O_3 , CeO_2 , La_2O_3 , and $NdCl_3$.

Results from these tests are given in Tables 2-1 through 2-3 and show some encouraging results. Typical weight loss rates are summarized in Figs. 2-14 and 2-15. Some of the additives, such as yttrium compounds, initially caused an accelerated degradation of the P-type selenide material. The yttrium apparently acted as a getter for selenium and extracted selenium from the thermoelectric material. Cerium oxide and La_2O_3 acted similarly but not as vigorously as Y_2O_3 . Neodymium and praseodymium compounds reacted more slowly with the selenide and apparently formed the desired in situ barriers. Thus, vaporization rates even for nonuniformly applied $NdCl_3$ were 1/10 that of uncoated P-type $(Cu,Ag)_2Se$ material.

A significant difference in metallographic appearance was seen in samples with and without rare earth additions. Samples without the additives (Fig. 2-16a) developed internal porosity during 850°C isothermal heating, which was significantly less prominent in samples similarly tested with rare earth additives (Figs. 2-16b, 2-16c).

Other vapor suppression systems studied in these examinations included mechanical baffling and inert coatings. In both of these systems, gaps or mud cracking were expected. Mechanical interference, however, would still inhibit vaporization of the substrate, except that fraction of the surface exposed beneath cracks in the coating. Ion-plated coatings of Si_3N_4 , Al_2O_3 , SiO_2 , GeO_2 , and carbon were applied to P-type $(Cu,Ag)_2Se$ elements. The coated elements were then isothermally heated and weight loss rates were monitored. The weight loss rate for a coating from evaporated Pyrex (Fig. 2-15) shows results typical of these materials, where the weight loss rates for inert coated samples were approximately the same as that for uncoated samples. Cavitation

TABLE 2-1
ISOTHERMAL WEIGHT LOSS RATES FOR COATED P-TYPE (Cu,Ag)₂Se MATERIALS AT 850°C IN VACUO

Sample No.	Electron Beam Source Material	Gas During Coating	Estimated Weight Loss Rates (g/cm ² -h)			Remarks
			After 700 h	After 900 h	After 1100 h	
6875-19A	None	None	5.8×10^{-5}	5.7×10^{-5}	5.8×10^{-5}	Rate at 1400 h 7×10^{-5} g/cm ² -h
6875-19B	Y ₂ S ₃	Ar	3.0×10^{-5}	2.5×10^{-5}	2.1×10^{-5}	Sample appearance at 700 and 1100 h approximately the same
6875-22A	Pyrex 7740	Ar	4.4×10^{-5}	4.3×10^{-5}	4.2×10^{-5}	Not much better than control
6875-22B	Quartz	Ar	3.8×10^{-5}	3.7×10^{-5}	3.6×10^{-5}	Not much better than control
6875-24A	GeO ₂	Ar	3.0×10^{-5}	2.7×10^{-5}	1.0×10^{-5}	Mud-cracked coating but significantly less damage than control
6875-24B	Pyrex 7740 + 10% Pr ₂ O ₃	Ar	6.0×10^{-6}	5.8×10^{-6}	5.6×10^{-6}	Surface appearance 700 and 1100 h approximately the same
6875-26	Pyrex 7740 + 10% Nd ₂ O ₃	Ar	7.5×10^{-6}	5.6×10^{-6}	4.8×10^{-6}	Surface appearance 700 and 1100 h approximately the same
6875-28A	None					Plasma-sprayed 70% Pyrex 7740, 30% B ₂ O ₃ ; coating flowed and stuck to holder but still protected the P-type (Cu,Ag) ₂ Se material
6875-28B	Silicon	NH ₃	2.3×10^{-5}	--	--	

TABLE 2-2
CHEMICAL COMPOSITION OF ION-PLATED VAPOR-SUPPRESSION COATINGS

Sample No.	Electron Beam Source Material	Coating Gas	Bias Power (kW)	Chemical Composition (wt %) (Microprobe Detected)					
				Si	Al	B	O	Na	Misc.
1-35A	Pyrex 7740 + W	Ar	0.25	18	0.1	<1	22	2.0	8 (W)
1-55	Pyrex 7740	Air	0.35	30	0	<1	49	4.2	
1-35B	None (Pyrex 7740 control)	--	--	38	1.8	<1	53	4.0	0.05 (Mg)
1-37A	Quartz + W	Ar	0.80	28	0	0	30	0	16 (W)
1-37B	None (quartz control)	--	--	46	0	0	53	0	
1-41	Pyrex 7740 + 10% Pr_2O_3	Ar	0.35	32	<1	0	55	3.4	2 (Pr)
1-45	Pyrex 7740 + 5% B_2O_3	Ar	0.80	31	<1	0	46	4.0	0.05 (Mg)
1-47	Pyrex 7740 + 15% B_2O_3	Ar	0.80	27	<1	1	48	6.1	0.05 (Mg)
1-49	Pyrex 7740 + 20% B_2O_3	Ar	0.80	<1	<1	11	66	<1	
1-51A	Silicon	N gas	0.30	39		<1	<1	<1	0.25 (N)
1-51B	None (Si_3N_4 control)	--	--	60	0	0	0	0	38 (N)
1-53A	Al_2O_3 disc	Air	0.30	0	49	0	48	0	0.3 (Mg)
1-53B	None (Al_2O_3 control)	--	--	0	53	0	47	0	

TABLE 2-3
RESULTS OF MICROPROBE EXAMINATIONS OF RECENT ION-PLATING COATINGS^(a)
ON P-TYPE (Cu,Ag)₂Se MATERIAL

Specimen No.	Electron Beam Source Material	Bias Power (kW)	Chemical Composition (wt %)						
			O	B	Na or K	Si	Al	Nd	Pr
1-35B	None Pyrex 7740 standard	None	55	4	2	38	0 ^(b)		
1-65	Pyrex 7740	0.25	44	4	1.7	37	0		
1-67	Pyrex + 10% Nd ₂ O ₃	0.38 0.38	53	1.5	1.5	44	0	(b)	
1-69	Pyrex + 10% Pr ₂ O ₃	0.25	49	6.5	0.7	30	2		13
1-71	Pyrex 7740	0.50	44	1.5	1.3	41	1		
1-73	Pyrex 7740	0.35	41	1.5	0.7	39	1		
1-75	Pyrex 7740 + 15% B ₂ O ₃	0.30	55	40	1.3	32	0		
6875-31B ^(c)	Pyrex + 10% Nd ₂ O ₃	0.38	38	0	0.9	43	1	(b)	
6875-31D ^(d)	Pyrex + 10% Pr ₂ O ₃	0.25	38	2	0.9	30	1		(b)

(a) All coatings applied in $8 \text{ to } 17 \times 10^{-3}$ torr air.

(b) In the electron beam source material but not detected in the coating.

(c) Fired in He + H₂O at 850!C for 5 min after ion plating.

(d) Fired in vacuo at 800°C for 5 min after ion plating.

Fig. 2-14. 900°C isothermal weight loss ratio for B_2O_3 + rare earth (CeO_2 , $\text{CeO}_2\text{Pr}_2\text{O}_3$, and Y_2O_3) oxide-coated P-type $(\text{Cu,Ag})_2\text{Se}$ material

Fig. 2-15. Weight loss rates for coated and uncoated $(\text{Cu,Ag})_2\text{Se}$ P material at 850°C

(a)

(b)

(c)

Fig. 2-16. Metallographic cross sections (200X) of P-type $(\text{Cu,Ag})_2\text{Se}$ elements which were ion plated from (a) Pyrex, (b) Pyrex + 10% Pr_2O_3 , and (c) Pyrex + 10% Nd_2O_3 after 1243, 1159, and 1137 h, respectively, at 850°C

normally developed in the P selenide material under breaks in the inert coatings. Examples of this can be seen in the metallographic examination of these coated elements (Fig. 2-17). By contrast, cavitation rarely occurred under breaks in coatings containing reactive additives (Fig. 2-18).

Cr_2O_3 was a participant in an unusual 850°C isothermal test of inert coated P-type $(\text{Cu},\text{Ag})_2\text{Se}$ samples. One sample was carbon coated, one was boron nitride coated, and the other, a control sample, was uncoated. During intermediate examination, all three specimens showed a continuous buildup of a greenish film. X-ray examination showed this film to be Cr_2O_3 . The source of this film was suspected to be chromium from the 316 SS cap and residual oxygen. The oxygen source was either from ion-plated glass coatings or absorbed oxygen on the $(\text{Cu},\text{Ag})_2\text{Se}$ samples from ambient sample storage during an extended interruption of the test.

Figures 2-19 through 2-21 show weight loss rates for these three elements as a function of time at 850°C. The weight loss rates for these samples tend toward a common value, which is approximately 1/20 that of previous uncoated controls.

A possible explanation for the effectiveness of this coating is shown in Fig. 2-22. High mobility on the $(\text{Cu},\text{Ag})_2\text{Se}$ surface is proposed for the Cr_2O_3 coating, which allows coverage of the substrate where cracks or spalling of the coating have occurred.

2.3.2. Vapor Suppression by Mechanical Baffling

Examination of mechanical baffling as a means of reducing vaporization of P-type $(\text{Cu},\text{Ag})_2\text{Se}$ was a major effort in FY-77 and FY-78. The system examined in these studies is called the glass sleeve barrier concept. The key features of the concept are:

1. A glass sleeve is bonded to the hot cap of the element to mechanically inhibit selenium vaporization.

Fig. 2-17. Metallographic cross section (200X) of a P-type GeO_2 coated copper silver selenide element tested for 1244 h at 850°C , showing cavitation occurs where there is a break in the coating

Fig. 2-18. Metallographic cross section (200X) of a Pyrex +10% Pr₂O₃ coating on a P copper silver selenide element tested for 1159 h at 850°C, showing a break in the protective coating without a corresponding cavitation of the P selenide material under the coating break

Fig. 2-19. 850°C isothermal weight loss rate for P-type $(\text{Cu,Ag})_2\text{Se}$ coated with boron nitride plus in situ Cr_2O_3

Fig. 2-20. 850°C isothermal weight loss rate for P-type (Cu,Ag)₂Se coated with carbon plus in situ Cr₂O₃

Fig. 2-21. 850°C isothermal weight loss rate for P-type (Cu,Ag)₂Se coated with in situ Cr₂O₃

Cr OR Cr_2O_3 COATING IS APPLIED
TO THE $(\text{Cu,Ag})_2\text{Se}$ SURFACE

IF SPALLATION FROM DIFFERENTIAL
THERMAL EXPANSION OCCURS BETWEEN
THE COATING AND SUBSTRATE, Se_2 GAS
ESCAPES TEMPORARILY

HIGHLY MOBILE Cr OR Cr_2O_3 MOLECULES
MOVE TO THE COATING VOID COVERING
THE SUBSTRATE SURFACE. VAPORIZATION
OF Se_2 GAS IS AGAIN SUPPRESSED.

Fig. 2-22. Effectiveness of Cr_2O_3 coating

2. The glass allows for differential expansion between the hot cap and sleeve without fracturing the electrode joint.
3. A modified wire mesh provides an additional anchor for the glass and the maintenance of minimum electrode-element contact resistance while allowing differential expansion between the element and hot cap.

A schematic diagram of the P-type $(\text{Cu,Ag})_2\text{Se}$ element with the glass sleeve barrier is shown in Fig. 2-23. An assembled element with a glass sleeve barrier and a graded cold end is shown in Fig. 2-24.

The fabrication sequence investigated for this system is shown in Fig. 2-25. The hot cap was machined from 316 SS and then ion plated with molybdenum. The molybdenum acts as a barrier layer to prevent corrosive interaction between the P-type $(\text{Cu,Ag})_2\text{Se}$ material and the stainless steel. Two layers of W-3%Re wire mesh are then tack welded together and oriented such that the circular cut mesh protrudes into the cavity of the hot cap during hot pressing. The mesh and cap were originally tack welded to the hot cap after vacuum hot pressing, but later trials showed tack welding them together before hot pressing improved the encapsulation of the wire.

During hot pressing copper powder is mixed with P-type $(\text{Cu,Ag})_2\text{Se}$ material on the cold end to form the graded cold shoe. At the completion of the hot pressing operation, a vapor suppression coating is applied to the assembly in the ion plater. A Pyrex sleeve is then warm pressed around the wire mesh tack welded to the hot cap. This element is ready for thermal gradient testing after molybdenum opacified paper washers are slipped over the cold end of the element and a cold cap is soldered to the graded cold shoe of the element.

Fig. 2-23. P-selenide material development

Fig. 2-24. Glassy barrier vapor suppression system on P-type $(\text{Cu,Ag})_2\text{Se}$ material showing a glass sleeve, a Pyrex coated element, and a graded $(\text{Cu,Ag})_2\text{Se}$ P copper cold end

W-3%Re WIRE MESH
TACK WELDED TOGETHER

316 SS HOT CAP
ION PLATED WITH
W OR Mo

VACUUM
HOT-PRESSED,
WIRES FREE

WIRE TACK
WELDED TO
316 SS CAP

PYREX SLEEVE
WARM PRESSED
INTO THE CAP
AND MESH

Fig. 2-25. Fabrication sequence for bonded P-type $(\text{Cu,Ag})_2\text{Se}$ element

One problem with the glass sleeve concept has been the joint between the sleeve and the hot cap. The first sleeves were made from 7740 Pyrex, and the hot cap was made of 316 SS. There was evidence that these joints were failing due to differential thermal expansion after several thermal cycles to 850°C. To confirm the reason for the failures, glass-to-hot-cap joints were prepared without the selenide material.

Figure 2-26 shows attempts to improve wetting of the glass to the stainless steel without the mesh by using sodium silicofluoride and also by grit blast cleaning the stainless steel. The joints failed because of poor wetting and the differential thermal expansion of the glass and stainless steel. Figure 2-27 shows two efforts to bond the glass to the hot cap through a wire mesh. The concept was to use the wire mesh to transition the thermal stresses to the glass. The photographs show the glass-to-hot-cap joint failed in spite of the adherence of the glass within the wire mesh area. Again, differential thermal expansion is thought to be the principal cause for joint failure. Bowing of the wire mesh was also noticed in these experiments. The wire mesh was flat in the "as tack welded to the hot cap" condition. The bowing was probably caused by the differential thermal expansion between the 316 SS hot cap and the W-Re wire mesh. On heating, the mesh yields and thus is bowed when recooled to ambient temperature. This bowing is thought to push the selenide and sleeve away from the hot cap during cooling. To overcome these problems, molybdenum was examined as an alternate hot cap material, since its thermal expansion is similar to that of Pyrex.

Molybdenum hot caps were substituted for the stainless steel hot caps. The molybdenum surfaces were prepared for bonding to the Pyrex by heating them in air at 550°C to form a mixed MoO_2 - MoO_3 coating on the surface. They were then heated to 1000°C in vacuo to remove the MoO_3 oxide, leaving the tenacious MoO_2 to aid in the bonding of 7740 Pyrex glass to molybdenum. The glass was warm pressed over the

Fig. 2-26. Wetting of 316 SS by Pyrex 7740 at 850°C was not improved by either (a) grit blast cleaning or (b) sodium silicofluoride

Fig. 2-27. W-Re wire mesh tack welded to 316 SS retained Pyrex 7740 in two 850°C bonding experiments but bowed on cooling and failed to prevent differential thermal expansion stresses from breaking the glass

molybdenum at 850°C and 16,300 kg/m² for 5 min. The resulting joints (Fig. 2-28) were very good; however, in one sample a crack formed in the glass, which eventually propagated around the sleeve and caused the sleeve to separate. The glass-to-molybdenum joint did not fail. The wire mesh inserted between the molybdenum and the glass appears to aid the joint by allowing accommodation of the thermal stresses that are developed.

To minimize failures in the system due to glass-glass failure, an evaluation was made of glass sleeves formed from Corning 1720, a high-temperature aluminosilicate glass. Again, a joint interface of MoO₂ was put on solvent-cleaned molybdenum by selective heating in an oxidizing furnace at 550°C for 3 min, followed by a 1000°C heating in vacuo to remove MoO₃. The glass sleeve was warm pressed over the molybdenum at 1000°C. The resulting joint (Fig. 2-29) was free of cracks and survived handling in subsequent fabrication steps.

2.4. COMPATIBILITY

Compatibility of P-type (Cu,Ag)₂Se thermoelectric material in contact with other potential thermoelectric generator materials continues to be of concern. Slab tests of (Cu,Ag)₂Se in mechanical contact with materials being tested were used to determine the compatibility of these material combinations. Similar tests were begun with N-type Gd₂Se₃ thermoelectric material. These tests are described in the following sections.

2.4.1. Compatibility Tests

Isothermal compatibility tests at 900°C were removed after 400 h at temperature. Contact loads of 6.2 MPa (900 psi) were maintained between test materials and slabs of 3M Company P-type (Cu,Ag)₂Se material

(a)

(b)

Fig. 2-28. Pyrex 7740 warm pressed at 850°C to molybdenum (a) after first cooling to ambient temperature, and (b) glass failure after remaining at room temperature for 2 days. The glass-to-metal joint remained well bonded throughout these trials.

Fig. 2-29. Corning 1720 alumino silicate glass sleeve
warm pressed to a molybdenum hot cap

throughout the test. Materials examined included quartz, tungsten, molybdenum, H-451 graphite, and a commercial borosilicate glass, Corning's "Pyrex."

There was no metallographic observable reaction between P-type $(\text{Cu,Ag})_2\text{Se}$ material and quartz, Pyrex, or H-451 graphite (Fig. 2-30). The wide difference in hardnesses made $(\text{Cu,Ag})_2\text{Se/Mo}$ and $(\text{Cu,Ag})_2\text{Se/W}$ interfaces more difficult to evaluate. A more definitive critique was made of these samples by SEM and SEM with a dispersive detector. The results of examination of TPM-Mo are shown in Fig. 2-31. X-ray dispersive detector maps of Se and Mo show a sharp boundary between Se and Mo with no interdiffusion at the interface. X-ray fluorescent spectrum examinations across this interface using a 20-kV beam at 10^{-9} A at a tilt angle of 45° located a slight amount of copper and selenium in molybdenum at location C (Fig. 2-31a), but also silicon from the polishing compound. Since the copper selenide may also have been polishing debris at the $(\text{Cu,Ag})_2\text{Se/Mo}$ interface, the existence of a diffusion layer by this test was uncertain. Since the mapping boundaries between elements were very sharp, there is a high probability no diffusion layer exists.

SEM examinations of the $(\text{Cu,Ag})_2\text{Se/W}$ interface (Fig. 2-32) show the same characteristic sharpness of the interface between the $(\text{Cu,Ag})_2\text{Se}$ and W materials as for the $(\text{Cu,Ag})_2\text{Se}$ and Mo materials. X-ray photon counts at specific locations across the interface again failed to show a significant interdiffusion layer. Locations B and D of Fig. 2-31a and location A of Fig. 2-32b show copper, selenium, and tungsten but also show silicon from the grinding compound, making the existence of a diffusion layer uncertain by this examination alone. Metallographic and element mapping examinations show no interdiffusion layer.

The compatibility of nickel with both P-type $(\text{Cu,Ag})_2\text{Se}$ and N-type Gd_2Se_3 thermoelectric materials at 900°C was evaluated. Photomicrographs of these samples after 338 h at temperature with 3.5 MPa (500 psi)

(a)

(b)

(c)

Fig. 2-30. Results of 400 h compatibility tests at 900°C and 900 psi showing $(\text{Cu,Ag})_2\text{Se}$ P-material versus (a) Corning 7740 Pyrex, (b) quartz, and (c) H-451 graphite

Fig. 2-31. SEM examinations at 2000X of $(\text{Cu,Ag})_2\text{Se}$ P-type material with 900-psi contact pressure against molybdenum after 400 hours at 900°C showing (a) locations of X-ray fluorescent localized examinations, (b) selenium mapping, and (c) molybdenum mapping.

a

b

c

a

b

c

d

Fig. 2-32. SEM examinations at 2000X and 5000X of P-type $(\text{Cu,Ag})_2\text{Se}$ material with 900 psi contact pressure against tungsten after 400 h at 900°C showing (a,b) locations of X-ray fluorescent localized examinations, (c) selenium mapping, and (d) molybdenum mapping

mechanical contact are shown in Fig. 2-33. The nickel diffused into the P-type $(\text{Cu,Ag})_2\text{Se}$ material and diffused through it in a manner similar to copper. By contrast, no interaction between the nickel and N-type Gd_2Se_3 could be detected.

2.4.2. Summary of Compatibility Studies

The results of the compatibility studies are as follows:

1. $(\text{Cu,Ag})_2\text{Se}$ material exhibits no reaction phases when held in contact at 6.2 MPa (900 psi) with quartz, Pyrex, or H-451 graphite at 900°C for 400 h.
2. Reaction phases between $(\text{Cu,Ag})_2\text{Se}$ and W or Mo, if they do occur at 900°C within 400 h at 6.2 MPa (900 psi), were not identified in metallographic, SEM, or X-ray dispersive examinations.
3. Nickel interdiffuses with P-type $(\text{Cu,Ag})_2\text{Se}$ thermoelectric material in less than 338 h at 900°C but has no noticeable reactivity with N-type Gd_2Se_3 similarly tested.

2.5. THERMAL GRADIENT TESTING

Life testing of thermoelectric elements included thermal gradient testing of elements, high-temperature isothermal testing, and compatibility testing. Thermal gradient experiments in FY-76 were zero current tests of P-type $(\text{Cu,Ag})_2\text{Se}$ elements coated with plasma-sprayed 70% B_2O_3 , 30% BN coatings. This work was continued into FY-77. P-type $(\text{Cu,Ag})_2\text{Se}$ elements that were ion plated with Pyrex, or Pyrex with and without additives, were also tested in FY-77 and FY-78. Details of these examinations are given below.

Fig. 2-33. Photomicrographs of nickel in contact with (a) Gd_2Se_3 and (b) $(\text{Cu,Ag})_2\text{Se}$ after 338 h and 500 psi at 900°C

Metallographic examination of plasma-sprayed, B_2O_3 -BN coated P-type $(Cu,Ag)_2Se$ elements after 557 h under test in a thermal gradient of $850^\circ/390^\circ C$ were completed. Figure 2-34 shows the B_2O_3 -BN protected P element remained generally undamaged, but porosity and material loss were noted in the hot cap joint. Thermal penalties from such thick coatings and the high vapor pressure of B_2O_3 limited the usefulness of this coating system.

The results of the first thermal gradient testing of the glass sleeve concept are shown in Figs. 2-35 and 2-36. This P element was run at a T_h of $900^\circ C$ but reached $975^\circ C$ for up to 48 h. The thermal excursion destroyed the Pyrex continuity but did not adversely affect the element. The hot cap partially bonded to the heater during this heating. Attempted removal of the hot cap broke the $(Cu,Ag)_2Se$ P/hot cap joint. The hot end of the P element shows very little porosity. The glass sleeve/ $(Cu,Ag)_2Se$ interface was tight on one side and had a finite gap on the other side. This was expected since the thermal expansion of the sleeve and P element differ widely. This differential thermal expansion can thus be used to preset a finite gap between the Pyrex and selenide P element at a temperature above the exposed operating temperature of the element. A discussion of the baffling effect of the sleeve is given in Section 2.6.2.

Two thermal gradient tests of P-type $(Cu,Ag)_2Se$ elements with glass sleeves were repeated. One sample was additionally ion plated from a 7740 Pyrex + 10% Nd_2O_3 evaporation source.

Thermal gradient testing of these P elements was terminated after 1458 test hours. Hot cap temperatures for both specimens were maintained at $850^\circ \pm 5^\circ C$ except for a thermal excursion in specimen 6875-39-2, which increased its hot cap temperature to $914^\circ C$ for up to 96 h at 209 test hours. Cold cap temperatures for this sample were $310^\circ \pm 10^\circ C$ for the last 1100 h of the test. Cold cap temperatures for sample 6875-39-1 were $330^\circ \pm 10^\circ C$ for the last 1000 h of the test. Cold-side temperatures for both specimens were 350° to $375^\circ C$ during the first 300 test hours.

Fig. 2-34. Photomicrographs of polished cross sections of P-type $(\text{Cu,Ag})_2\text{Se}$ elements coated with $\text{B}_2\text{O}_3 + \text{BN}$ after 557 h at a hot cap temperature of 850°C

(a)

(b)

Fig. 2-35. P-type $(\text{Cu,Ag})_2\text{Se}$ element with a glassy barrier shown (a) with Mo opacified paper and (b) with the paper removed after 497 h in a thermal gradient of 850° to 390°C plus a thermal excursion to a 975°C hot-side temperature for up to 48 h

Fig. 2-36. Photomicrographs of polished cross sections of a P-type $(\text{Cu,Ag})_2\text{Se}$ element with a glass sleeve vapor suppression barrier after a 546-h thermal gradient test at a hot cap temperature of 850°C plus a 975°C thermal excursion for up to 48 h

Thermoelectric properties measured during these tests are shown in Figs. 2-37 and 2-38. No current was run through the elements. An ion pump was used to maintain pressures in the system of $<10^{-6}$ torr, with a normal range of 2×10^{-7} to 5×10^{-8} torr. Seebeck values for both test elements stabilized out at $258 \mu\text{V}/^\circ\text{C}$ after 1000 h on test, when vacuum pressure fluctuations occurred from adding two more test elements to the same vacuum system. Similar results can be seen in an examination of the resistivity data. The resistivity shows a gradual increase for both samples and an incremental jump after 1000 h for sample 6375-39-2. Photomicrographic examinations of these samples show that a gap developed between the hot cap and element, which made the hot side of the P element cooler than read from the thermocouple and hence gave a lower apparent Seebeck value. Similarly, with the electrical contact through the wires to the hot cap, the apparent resistivity of the element increased. Figure 2-39 (element 6875-39-2) is typical of both test results.

In Fig. 2-39 there is no perceptible corrosion along the sleeve length. Porosity in the body of the material is minimal, which indicates very little selenium was lost. Copper extrusions were not evident in these samples, which is a further indication of the stability in the samples.

Electrical contact was maintained between the wire mesh and the P-type $(\text{Cu,Ag})_2\text{Se}$ material. One difference between samples 6875-39-1 and 6875-39-2 was the total encapsulation of the wires in the latter sample.

Both samples showed corrosive reaction with the hot cap and a gap between the hot cap and both the P-type $(\text{Cu,Ag})_2\text{Se}$ material and the glass sleeve. It is suspected that these gaps were generated either during heatup or as a function of time. This gap influences the α and ρ

Fig. 2-37. Thermal gradient life test results, Seebeck coefficient versus time

Fig. 2-38. Thermal gradient life test results, resistivity versus time

Fig. 2-39. $(\text{Cu,Ag})_2\text{Se}$ bonded element with glass sleeve after 450 h of operation at a T_h of 850°C

thermoelectric properties of the element since the thermocouples and voltage probes are welded to the outer hot cap surface.

The results of the early thermal gradient tests of the glass barrier concept showed the following:

1. Loss of P-type $(\text{Cu,Ag})_2\text{Se}$ material can be minimal with an absence of gross porosity and free copper formation in 1400 h at a T_h of 850°C in vacuum and with the element operated in the open circuit mode.
2. Electrical contact with P-type $(\text{Cu,Ag})_2\text{Se}$ material can be maintained at 850°C in vacuum with mesh bonds.
3. Potential corrosive reaction with the 316 SS hot cap requires that the hot cap be ion plated with Mo, W, or W-25%Re.
4. The Pyrex 7740 - 316 SS joint was the weak link in these tests. This was expected from the results of the glass-to-metal bonding studies reported in Section 2.2.2. Thermal gradient testing of Corning 1720 - Mo joints is expected to show satisfactory performance, since these materials have similar thermal expansions.

Two relatively long-term thermal gradient tests were conducted in FY-78. One sample being tested (6875-39-3) is a P-type $(\text{Cu,Ag})_2\text{Se}$ element vacuum hot pressed and bonded to a molybdenum-coated 316 SS cap through a W 26%Re wire mesh. The bonded element was ion plated from electron-beam-evaporated Pyrex 7740 in $\text{He} + \text{H}_2\text{O}$ gas. A 7740 Pyrex sleeve was warm pressed over the hot cap at the hot end of the P element.

The test element was heated to a hot cap temperature of 850°C and held without an electrical load for 96 h. Cold cap temperatures were

approximately 375°C. A current of 100 ma^{*} was then allowed to flow through the element for the remainder of the test. Periodic temperature, voltage, and current measurements were recorded. Seebeck voltages obtained are shown in Fig. 2-40, and resistivity values are shown in Fig. 2-41. Test hours at temperature exceeded 7600 h at the end of FY-78. The step perturbations in these curves occurred when a second test was conducted in the same vacuum envelope. The second test element (6875-37-1) was preaged 3000 h at 450°C before being heated in an 850°/450°C thermal gradient. Electrical measurements from both samples were inconsistent, suggesting an electrical feedback from one test to another. The second test was turned off after 3306 h in a thermal gradient and remained in the vacuum enclosure at 450°C while test 6875-39-3 continued. Seebeck values and resistivity measurements from this test are shown in Figs. 2-42 and 2-43, respectively.

2.6. DESIGN ANALYSIS OF THE P-TYPE (Cu,Ag)₂Se ELEMENT

2.6.1. Thermal Analysis

A thermal analysis of a typical selenide-type thermoelectric element was made using the TAC2D (Ref. 2) computer program. Three areas were investigated during the study: (1) an analysis of the temperature at the end of a glass vapor-suppression sleeve as a function of sleeve length, (2) the loss in element thermal efficiency due to the glass vapor-suppression sleeve, and (3) the effect of the loss of the hot junction bond in a mesh-type joint.

The geometry used for most of these studies is shown in Fig. 2-44. It represents the type of element configuration that might be used in

^{*}This current is equal to an $i\ell/A$ ratio of 1.49.

Fig. 2-40. Thermal gradient life test results, Seebeck versus time for test sample 6875-39-3 ($il/A = 1.49$, temperature gradient = $853^{\circ}/375^{\circ}C$, 10^{-7} torr)

Fig. 2-41. Thermal gradient life test results, resistivity versus time for test sample 6875-39-3 ($i\ell/A = 1.49$, temperature gradient = $853^{\circ}/375^{\circ}\text{C}$, 10^{-7} torr)

Fig. 2-42. Thermal gradient life test results, Seebeck versus time for test sample 6875-37-1
($i\ell/A = 1.29$, temperature gradient = $850^{\circ}/450^{\circ}C$, 10^{-7} torr)

Fig. 2-43. Thermal gradient life test results, resistivity versus time for test sample 6875-37-1
($i\ell/A = 1.29$, temperature gradient = $850^{\circ}/450^{\circ}\text{C}$, 10^{-7} torr)

Fig. 2-44. Schematic diagram of P-selenide element

an "Isotec-type" light-weight selenide thermoelectric generator. The problems relating to the sleeve and the mesh joint were treated separately in the cases studied.

2.6.1.1. Glass Sleeve. When a glass sleeve is placed around an element to suppress material vaporization, the "effective" thermal conductivity of the element is lowered between the top of the element and the end of the sleeve. This decreases the temperature gradient along the element between the top and the end of the sleeve. Since more heat will flow through the portion of the element below the sleeve, the temperature gradient in that section is increased. This results in an increase in temperature at the end of the sleeve over that which would be expected at the same point along the length of an unsleeved element. The temperature increase is also a function of the area of physical contact between the sleeve and the element.

The temperature at the end of the glass vapor-suppression sleeve as a function of the sleeve length is shown in Fig. 2-45 for both full sleeve contact and a situation where there is a 0.0025-cm gap between the glass sleeve and the element. In the latter case heat conducted down the glass sleeve is transferred to the element by radiation and conduction through the gas in the gap. It is clear that the situation in which a gap is maintained is preferred. It is, however, difficult to maintain a certain gap, although this could be facilitated by including a spacer in the sleeve design that would maintain the desired gap by the use of a bead around the lower end of the sleeve. If the full contact situation is assumed, a sleeve length of 0.229 cm would maintain the element surface at 600°C.

Figure 2-46 presents the percent loss in couple efficiency as a function of the glass sleeve length for the cases in which either one element (dotted line) or both elements (solid line) have been sleeved.

Fig. 2-45. Temperature at end of sleeve as a function of sleeve length for full contact and 0.0025-cm gap

Fig. 2-46. Percent loss in couple efficiency as a function of glass sleeve length for one and both elements sleeved (for Isotec-type elements)

At this time it appears that only the P leg may require sleeving, so the design point is given by the circle on the dotted line and represents an efficiency loss of 4%.

An efficiency loss of 4% in this case means that if an unsleeved couple were operating between $T_h = 900^\circ\text{C}$ and $T_c = 150^\circ\text{C}$ with an efficiency of 10%, the same couple would be 9.6% efficient with a 0.229-cm-long vapor-suppression sleeve on the P leg.

The sleeve can be regarded as a partial thermal short that increases the apparent thermal conductivity of the P leg. The reduction in couple efficiency due to an increase in the apparent thermal conductivity of the element is plotted in Fig. 2-47.

Figure 2-48 indicates how the temperature at the end of the sleeve (solid line) and the couple efficiency (dotted lines) would change as a function of the amount of physical contact between the sleeve and the element. It can be seen that the temperature and efficiency loss change very rapidly as the initial contact is made and then more slowly as the degree of contact is increased. This is because heat transport through the glass is much greater than that through the vapor in the gap or by radiation between the surface of the element and the sleeve.

Figures 2-49 and 2-50 present the same information as presented in Figs. 2-45 and 2-46 except that in this case the model is more representative of an element in the SIG/GDS generator. In this case the efficiency loss is somewhat lower since the same thickness of glass sleeve was assumed, but the couple power is much greater. The loss in efficiency of this type of couple with a vapor-suppression sleeve should only be on the order of 2%.

Fig. 2-47. Effect of shielding of P-type $(\text{Cu,Ag})_2\text{Se}$ element on couple performance

Fig. 2-48. Loss in couple efficiency and temperature at end of sleeve as a function of percent contact

Fig. 2-49. Temperature at end of glass sleeve as a function of sleeve length

Fig. 2-50. Loss in couple efficiency as a function of glass sleeve length for one element and both elements sleeved (for SIG/GDS-type element)

2.6.1.2. Mesh Joint. A schematic of the thermal model for the initial mesh joint studies is shown in Fig. 2-51. In this study two cases were investigated. The first was the case in which there is a metallurgical bond between the hot end of the element and the cap and 0.0076-cm-diameter wires which are pressed into the element are each welded at the ends to the hot cap. In the second case, it was assumed that no metallurgical bond existed, and the majority of the heat is transferred through the mesh wires with direct heat transfer between the element and the hot cap by radiation and conduction through the vapor in the gap.

The element in this study had an overall length of 0.5 cm. It was later determined that the 0.5-cm length should be measured from the end of the element to the mesh and should not include the part above the mesh.

The study with the 0.5-cm overall element indicated a decrease in element T_h from 900° to 883°C when the metallurgical bond was lost. In the corrected length case, this change would actually be from 900° to 888°C. This indicates that there would be little loss in voltage or power due to separation of the metallurgical joint by vaporization of selenium if the mesh cap is used.

2.6.2. Thermoelectric Sleeve Vaporization Loss Model

The vapor effusion of Se_2 from a gap between the glass sleeve of the thermoelectric element and the element itself was modeled using a Clausing analysis of effusion from a long, deep rectangular slit. The validity of this model is based upon the following features of the vaporization behavior of $(\text{Cu,Ag})_2\text{Se}$.

1. The Se_2 vapor pressures dominate the vapor species, thus leading to the conclusion that $(\text{Cu,Ag})_2\text{Se}$ vaporizes incongruently leaving behind copper and silver.

$T_h = 900^\circ\text{C}$, VARIABLE GAP = 0
 $T_h = 883^\circ\text{C}$, VARIABLE GAP = 0.0025 cm

Fig. 2-51. Thermal model of mesh cap design

2. No evidence has been cited which would suggest that selenium has other than a unit vaporization coefficient from $(\text{Cu,Ag})_2\text{Se}$.
3. Two concentric close-fitting cylinders establish an equivalent of a long, narrow, deep slit, which as been analyzed by Clausing (Ref. 3, p. 87).

In the case stated above selenium will vaporize at the hottest point in the system (the bottom of the orifice formed by the element and the glass sleeve). It will not condense as an element at temperatures above about 200°C . Thus, conservatively, the system can be considered as a Knudsen cell with an orifice depth defined by the glass sleeve length, the opening between the sleeve and the element, and a slit length of the circumference of the opening. These considerations are shown in Fig. 2-52, where the Knudsen effusion equation is also reproduced.

This effusion should be manifest by shrinking of the element at the bottom of the sleeve. The element will become rich in copper and silver at this point. Selenium may be effused from the system or, if the temperature is low enough, it may be deposited in the orifice at colder points. This restriction to effusion can be termed a baffling factor.

2.6.3. Constraints on $(\text{Cu,Ag})_2\text{Se}$ Thermoelectric Generator Operation

The following documents the means by which $\dot{m}/A$ constraints are imposed upon $(\text{Cu,Ag})_2\text{Se}$ thermoelectric elements. Based on 6 years of satisfactory operation with the TRANSIT thermoelectric generator (using Bi_2Te_3), a weight loss criterion for the hottest portion of the leg of $10^{-6} \text{ g/cm}^2/\text{min}$ appears reasonable.

Figure 2-53 shows the weight loss rate, R_o ($\text{g/cm}^2/\text{min}$), as a function of reciprocal absolute temperature for $(\text{Cu,Ag})_2\text{Se}$. These data are consistent with JPL and 3M observations. If a thermal sleeve

$$1) F_W = 44.33 \left| \pi(r_2^2 - r_1^2) \right| \left(\frac{M}{T} \right)^{1/2} KP$$

$$2) K = \frac{b}{l} \ln \frac{l}{b}$$

WHERE:

F_W IS THE MASS FLUX

M IS THE MOLECULAR WEIGHT OF SELENIUM

r_1 IS THE RADIUS OF THE ELEMENT

r_2 IS THE INSIDE RADIUS OF THE GLASS SLEEVE

K IS THE CLAUSING FACTOR FOR RECTANGULAR CROSS SECTION TUBES

P IS THE PARTIAL PRESSURE OF SELENIUM AT BASE

l IS THE LENGTH OF THE SLEEVE

b IS THE GAP WIDTH

Fig. 2-52. Model for estimating effusion rates for gases coming from between concentric cylinders

Fig. 2-53. Comparison of PbTe and (Cu,Ag)₂Se weight loss rates

is placed around the element, this weight loss rate is reduced by a baffling factor BF. This baffling factor can be calculated from the following expressions:

Flow rate F_1 through a rectangular slot of width a , height b , and depth ℓ :

$$F_1 = Kab \left(\frac{T}{M} \right)^{1/2} \text{ cm}^3/\text{s} ,$$

where K , the Clausing factor (Ref. 3, p. 95), is $b/\ell \ln \ell/b$, T is the absolute temperature, and M is the mass.

and

Flow rate F_2 from free area A , sufficient to support the effusion in the baffled configuration:

$$F_2 = A \left(\frac{T}{M} \right)^{1/2} \text{ cm}^3/\text{s} .$$

Now $\alpha A = ab$, where α is a condensation coefficient; this arises because in the baffled configuration there is an immediately adjacent area A on which condensed selenium is deposited, which contributes to the effusion through slot ab . The problem is that the value of α is not known, although it is known that it will be less than 1. Thus, A will be larger than ab but, as a conservative estimate, they are taken to be equal. Hence,

$$BF \left| \begin{array}{l} \text{lower} \\ \text{limit} \end{array} \right. = \frac{F_2}{F_1} = \frac{1}{K} .$$

The measured clearance of a glass sleeve around an element was 0.002 to 0.004 cm at room temperature. Since the $(\text{Cu,Ag})_2\text{Se}$ expands more than the glass, this clearance will be less at high temperatures. In fact, manufacturing produces an interference fit at elevated temperature. Hence, to take b as 0.002 cm appears reasonable, while a depth of 0.3 cm (less than the element length of 0.5 cm) is a satisfactory choice for ℓ . This then gives $1/K = 30$.

Thus, the permissible enhancement factor, RIF, of the weight loss rate due to current flow for any given maximum operating temperature is

$$\text{RIF} = \frac{60 \times 10^{-6} \times 30}{R_o} = 1.8 \times 10^{-3}/R_o$$

From JPL studies,

$$\text{RIF} = \left[1 + 0.311 \left(\frac{T}{1073} \right)^{2/3} \frac{i\ell}{A} \right]^{4.26}$$

Given RIF and the top temperature of the segment, the permissible $i\ell/A$ can then be determined and used as a constraint for that particular segment.

2.7. N-TYPE Gd_2Se_3 BONDED ELEMENT DEVELOPMENT

Development of the bonded N-type Gd_2Se_3 element is proceeding with the following premises:

1. Gd_2Se_3 can be joined to a suitable hot cap through a mesh-type bond.

2. The joining of the hot cap and fabrication of Gd_2Se_3 elements can be accomplished without penalties to the thermoelectric properties of the material.

Fabrication development efforts in FY-78 were targeted to evaluate the above premises.

2.7.1. N-Type Gd_2Se_3 Thermal Stability Studies

X-ray diffraction patterns of as-received and GA-processed N-type Gd_2Se_3 were examined. The intent of this study was to determine which processes cause changes in the material that might affect its thermoelectric performance. The results thus far (Table 2-4) can be summarized as follows:

1. As-received N-type gadolinium selenide is cubic Gd_2Se_3 .
2. X-ray examination of material ground to a powder in air gave essentially the same results as examining a cut slab of material.
3. Orthorhombic Gd_2Se_3 resulted when as-received material was powdered and then hot pressed at 1000°C for 5 h at 10^{-5} torr. Partial conversion of slabs of cubic Gd_2Se_3 to orthorhombic Gd_2Se_3 also occurred after heating to 1000°C for 5 h at 10^{-5} torr. Heat treatments from 750° to 1000°C resulted in conversion of cubic Gd_2Se_3 to orthorhombic Gd_2Se_3 . X-ray fluorescence examinations showed the ratios of gadolinium to selenium in both cubic and orthorhombic forms were the same.

TABLE 2-4
RESULTS OF X-RAY EXAMINATIONS OF N-TYPE Gd_2Se_3 FABRICATION PROCESSES

Sample No.	Process Treatment	Gd_2Se_3 Cubic (%)	Gd_2Se_3 Ortho-rhombic (%)	GdSe (%)	$\text{Gd}_2\text{O}_2\text{Se}$ (%)
6011-83C	Hot pressed + 1500°C, 7 h + 1600°C, 7 h, 10^{-8} torr			92	8
6011-85D	6011-85B heated 1500°C, 7 h + 1600°C, 7 h, 10^{-8} torr	60		38	2
6011-86F	Slug heated 1600°C, 6 h, 10^{-8} torr			96	4
6011-85E	Slug heated 1600°C, 7 h, 10^{-8} torr	80		18	2
6011-78	As-received	100			
6011-80	As-received	100			
6011-80B	Cut into slab ^(a)	90+			
6011-85B	6011-80B heated 1000°C, 5 h, 10^{-5} torr	50	50		
6011-84A	As-received, argon ground	100			
6011-84B	6011-84A heated 1000°C, 5 h, 10^{-5} torr	20	50		30
6011-86H	Slug heated 1000°C, 5 h, 10^{-8} torr	60	40		
6011-82B	Hot pressed (heated 1000°C, 5 h, 10^{-5} torr) 2.4 MPa (3500 psi)		100		
6011-86I	Hot pressed (heated 1000°C, 5 h, 10^{-5} torr) 4.6 MPa (6600 psi)		100		
6011-83A	Hot pressed (heated 1000°C, 5 h, 10^{-5} torr) 4.8 MPa (7000 psi)		90-97		3-10
6011-86G	Powder heated 1500°C, 2 h + 1600°C, 4 h, 10^{-8} torr	49		50	1

^(a) Only sample not ground to a powder in air for examination. This sample was analyzed with an X-ray diffractrometer.

4. Post-heat-treatment of the orthorhombic Gd_2Se_3 at 1600°C for 2.5 h reconverted it to cubic Gd_2Se_3 . The 1600°C reversion to cubic Gd_2Se_3 resulted in a significant change in measured Seebeck values. It has not been determined whether this is a real change or a change due to partial oxidation of the Gd_2Se_3 .
5. Gd_2Se_3 heated to 1500° to 1600°C was 18% to 19% converted to GdSe , depending on the process steps before heating to 1500°C .
6. Most samples showed some $\text{Gd}_2\text{O}_2\text{Se}_3$. The largest amount of $\text{Gd}_2\text{O}_2\text{Se}_3$ (30%) resulted from heating a Gd_2Se_3 sample that had been ground and powdered in a glove box.

It is clear from this work that the control of crystal structure and chemical composition is a first priority in obtaining a bonded N-type Gd_2Se_3 element. To do this requires control of the preparation of the Gd_2Se_3 from Gd and Se. This effort is now being pursued and will continue in FY-79.

2.7.2. N-Type Gd_2Se_3 Hot-Pressing Development

Progress in the bonded N-type Gd_2Se_3 development was determined by examining hot-pressed elements with an energy dispersive X-ray analyzer (EDAX) attached to the SEM and measuring thermoelectric properties. The first Gd_2Se_3 material evaluated was received from 3M. Figures 2-54 and 2-55 show SEM photomicrographs of as-received sintered, plus 1000° , 1200° , and 1400°C samples hot pressed by GA. It was clear from the results that hot pressing at 1400°C produces material visably less porous than the as-received material. The chemical compositions of the 1200° and 1400°C hot-pressed samples as shown in Table 2-5 were essentially the same as the starting material. The density of the 1000°C hot-pressed 3M material was

A

(a)

4 μ m

(b)

Fig. 2-54. SEM photomicrographs (3000X) of fractured surfaces of (a) arc cast Gd_2Se_3 and (b) as-received 3M Gd_2Se_3

(a) as-received sintered material

(b) ground 3M material hot pressed at 1000°C

(c) ground 3M material hot pressed at 1200°C

(d) ground 3M material hot pressed at 1400°C

Fig. 2-55. SEM photomicrographs (3000X) of fractured surfaces
2-85

TABLE 2-5
EXAMINATION OF HOT-PRESSED N-TYPE Gd_2Se_3 MATERIAL

Sample No.	Hot Pressing Conditions			Density (g/cm^3)	Room- Temperature Seebeck ($\mu\text{V}/^\circ\text{C}$)	Resistivity ($\text{m}\Omega\text{-cm}$)	Composition (wt %)	
	Temperature ($^\circ\text{C}$)	Pressure [MPa (psi)]	Time (min)				Gd	Se
6011-80A ^(a)		None		6.90	-111	9.43	--	--
6011-80A ^(a)		None		--	-108	--	56.91	43.09
6011-81A	1000	2.1 (3100)	30	5.24	--	--	--	--
6011-82A	1000	1.6 (2330)	300	6.78	-68.5	--	54.44	45.45
6011-111-2	1200	1.8 (2600)	1	6.87	-100	11.95	56.91	43.09
6011-112-6	1400	1.8 (2600)	1	7.15	-115	15.5	56.55	43.45
6011-108B ^(b)		None		7.20	-116	--	58.70	41.30

(a) As-received N elements from 3M.

(b) Vacuum-cast material from Gd and Se.

significantly lower than that of as-received samples. Attempts to measure the resistivities of 1000°C hot-pressed samples without ion-plated contacts failed.

The thermoelectric properties of the 1200° and 1400°C hot-pressed samples were reasonably close to those of the starting material. The density of the 1400°C hot-pressed material was very close to that of cast material. This higher density qualitatively decreased the friability of this material.

One concern in Gd_2Se_3 hot pressing is how much $\text{Gd}_2\text{O}_2\text{Se}$ will form during N element fabrication. Metallographic and X-ray examinations were used to determine the $\text{Gd}_2\text{O}_2\text{Se}$ content. An N-type Gd_2Se_3 element was hot pressed at 1000°C, 68.9 MPa (10,000 psi) for 5 h at 10^{-5} torr. After hot pressing, the element was heated to 950°C in air for 16 h. A metallographic cross section of this thermally aged sample (Fig. 2-56) shows a dense 30- μm layer formed on the edge of the sample. X-ray examination showed the presence of $\text{Gd}_2\text{O}_2\text{Se}$. The oxide layer appears to be in intimate contact with the Gd_2Se_3 .

Die tooling was modified to allow hot pressing at 25.2 MPa (3660 psi) at higher temperatures (i.e., above 1200°C). Higher pressures were found necessary for higher density, more uniform hot-pressed N-type Gd_2Se_3 . Figures 2-57 and 2-58 show the hot-pressing die used for this study. The vacuum hot press is evacuated to 1×10^{-6} torr at the beginning of the hot-pressing cycle and drifts upward to approximately 10^{-5} torr at peak temperatures.

2.7.3. Joining of N-Type Gd_2Se_3 to Hot Cap

Experimental trials thus far have shown Gd_2Se_3 can be bonded to a hot cap through a mesh-type joint. Some weakness in the joint was noted; experiments are now in progress in which an attempt is being made to overcome this problem.

0.01 cm

Fig. 2-56. Metallographic cross section of hot-pressed N-type Gd_2Se_3 after exposure to air at 950°C for 16 h showing the formation of a $30\text{-}\mu\text{m}$ oxide layer

Fig. 2-57. Hot pressing die assembly used for N-type Gd_2Se_3 hot pressing

Fig. 2-58. Schematic diagram of the die assembly used for N-type Gd_2Se_3 hot pressing

Other fabrication trials have shown Gd_2Se_3 is readily hot pressed. Thermoelectric properties, however, are changed after hot pressing. A major goal of the bonding trials was to minimize thermoelectric property penalties resulting from joining of the element to the hot cap.

Hot-pressing temperatures were raised to minimize material changes. A high-temperature hot press was refurbished and fitted with POCO graphite dies for N element hot pressing. Pressing temperatures were raised to 1150°C . Molybdenum hot caps replaced the 316 SS hot caps. The W-Re wire mesh was diffusion bonded to the molybdenum hot cap prior to hot pressing the element.

Fine powders were added to Gd_2Se_3 in the hot joint to improve joint resistance to microcrack propagation. Materials evaluated included nickel, gold, titanium, cobalt, and graphite. One percent by weight addition of Ni, Au, Ti, Co, and carbon were added to separate batches of ground Gd_2Se_3 . The Gd_2Se_3 additive mixes were hot pressed at 1200°C and 17.9 MPa (2600 psi) for 1 min. Hot-pressed samples were then examined by metallography and measurements were made of Seebeck values, microhardness, density, and modulus of elasticity. The results of these trials, except for gold, are summarized in Table 2-6. Gold was too fluid at 1150°C and flowed out of the joint area. Room-temperature Seebeck values and resistivities of these elements showed titanium caused an unexpected change in Seebeck values. Nickel appeared to be the best of the materials examined. It had the least effect on the thermoelectric properties, was chemically compatible, and caused the best qualitative improvement in resistance to mechanical shock fracture of the Gd_2Se_3 . A 1% addition of the low-density, high-volume carbon was too much for a fair evaluation of this additive. Further examination of additives to Gd_2Se_3 to aid both hot cap joining and toughness in the final hot-pressed N-type element are in progress.

TABLE 2-6
EFFECTS OF BOND JOINT AIDS ON N-Gd₂Se₃

Sample No.	Gd ₂ Se ₃ Material Source	1% Additive	Density (g/cm ³)	Ambient Seebeck (μV/°C)	Hardness (DPH)	Modulus of Elasticity [MPa (ksi)]	Remarks
104-1	3M N element	Ni	7.34	-89.3	504	496 (72)	Post-cooling micro-cracks stopped by Ni
104-2	3M N element	Ti	7.02	+26.0	502	434 (63)	Multiphased
104-3	3M N element	Co	7.46	-131	486	510 (74)	Post-cooling micro-cracks stopped by Co
105-4	3M N element	C	6.78	-146	493	482 (70)	Too much carbon in this sample for a fair evaluation
106-7	3M N element	None	6.70	-102	--	427 (62)	Applied pressures successfully modified to minimize post-cooling micro-cracking

2.8. BONDED SELENIDE COUPLE DEVELOPMENT

An all-bonded selenide couple was completed and installed in the life test. The couple (Figs. 2-59 and 2-60) was tied together with a laser-welded nickel collector (current strap).

The P element has a 316 SS hot cap with a molybdenum barrier coating. This cap is bonded to the P-type $(\text{Cu,Ag})_2\text{Se}$ element through a W-Re mesh. A Pyrex 7740 sleeve and an ion-plated glass + Nd_2O_3 layer form the vapor-suppression barriers of the P element. The graded P-type $(\text{Cu,Ag})_2\text{Se}$ -Cu element cold end is diffusion bonded to a nickel cold shoe through a gold layer.

The N element has a nickel hot cap that is bonded to the N-type Gd_2Se_3 element through a W-Re wire mesh. The nickel cold cap was diffusion bonded to the N element with a gold layer at the interface. The Gd_2Se_3 was ion plated with Ni prior to the diffusion bonding operation.

Molybdenum opacified paper washers were placed around both elements between the hot and cold caps. Instrumentation of the couple is complete. Life testing is beginning at $T_h = 840^\circ\text{C}$ and $T_c = 400^\circ\text{C}$. Initial testing is open circuit for instrumentation diagnostics and thermal stability examinations.

Fig. 2-59. All-bonded selenide thermoelectric couple

Fig. 2-60. Schematic diagram of the all-bonded selenide thermoelectric couple

Blank

2-96

3. $(\text{Bi,Sb})_2(\text{Se,Te})_3$ MATERIALS

The purpose of effort in this area was to provide background information on the fabrication of high-quality reproducible $(\text{Bi,Sb})_2(\text{Se,Te})_3$ powder metallurgy material and evaluate possible improvements in its fabrication. This section is broken down into two tasks. Section 3.1 deals with the efforts to investigate the effects of manufacturing process control and with evaluation of materials. Section 3.2 discusses the studies to produce fine-grain material with the goal of lowering thermal conductivity.

3.1. PROCESS CONTROL AND MATERIALS EVALUATION

3.1.1. Introduction

The goal of this work was to provide a higher quality reproducible product for both N-type and P-type thermoelectric material. The reproducibility was measured with respect to the Seebeck values, resistivity, density, and strength. Attempts were made to characterize the anisotropy of the pressed material; however, additional effort is required. Particular attention was paid to the results of P-type pressing because of the resultant swelling of hot-pressed pucks. For some applications, this swelling is tolerable; however, where high strength is required, pore-free material is highly desirable. It was suggested and later confirmed that O_2 contamination from a number of sources was responsible for this problem. These sources were then eliminated, as was the swelling.

3.1.2. Alloy Preparation

It was noted in some initial batches that small particles of non-alloyed material were floating on the molten semiconductor ingots. Investigation showed that this material was present only when a certain type of tellurium was used. Subsequent to batches BTN-17 and BTP-19, all elements used in mixes were precleaned in a hydrogen atmosphere at temperatures above the melting point of the respective material in an effort to reduce oxide formation. Also, the tellurium contained oxygen, and high-purity tellurium was subsequently used.

3.1.3. Comminution and Pressing

The processing of the various ingots after melting consisted of breaking the quartz vessel, obtaining the weight of the ingots and the Seebeck coefficient, and then placing the ingots in a dry box for grinding. Grinding consisted of passing pieces of the ingot through a small hammer mill for pulverizing, followed by sieving either by hand or with a sonic sifter. In an effort to determine the effectiveness of the dry box deoxygenation system, samples of the ground material were sent out for neutron activation analysis for oxygen. Early results indicated that oxygen levels were considerably higher than expected. As a result, the dry box was upgraded and an oxygen analyzer was installed that maintained the O_2 level to ~ 1 ppm. Modifications in the use of the entry port were initiated to decrease the chances of box contamination.

After comminution the powder was sealed in a screw cap jar, weighed, and then pressed into pucks. To ensure that oxygen did not enter into the puck, the die assembly was kept in a plastic bag during removal from the dry box for loading into the press.

After pressing, the Seebeck and density values were measured and the pucks were sintered. For low-oxygen-content P-type powders (<200 ppm for the ground powder), the Seebeck values changed little between hot pressing and sintering. Large changes in density were noted in those pucks whose powders had high O₂ contents, as discussed below.

3.1.4. Metallographic and Mechanical Property Analyses

As part of the quality assurance program, neutron activation analysis studies for oxygen content were performed on various representative powder samples. The results (Table 3-1) clearly indicate abnormally high oxygen levels in the BTP-16 and BTP-21 samples versus the other two batches. A comparison of the density values for the sintered pucks supports and typifies the high oxygen content, i.e., lower than average densities are consistent with the excessive oxygen levels.

TABLE 3-1
OXYGEN CONTENT

Sample Identification	Relative O ₂ Levels	Average Puck Density (g/cm ³)	
		As-Pressed	Sintered
BTP-16	4.3	6.81	5.66
BTP-17	1.7	6.79	6.78
BTP-20	1.0	6.79	6.78
BTP-21	3.2	6.79	6.48

Metallographic studies also support the contention that high oxygen content is a main source of nonuniformity in physical and thermoelectric properties for these materials. Mechanical strength tests using a modified fourpoint loading technique (similar in concept to ASTM C651-70) provide further comparative information. The results showed

that BTP-20 samples failed at a flexural strength of 5113 ± 575 units. The BTP-16 samples fractured at values below the sensitivity of the instrument as set up.

In further mechanical testing, a three-point modulus of rupture jig (Fig. 3-1) was utilized to more evenly load the specimens. Modulus of rupture test data generated with this jig on material processed before and after the tight controls were implemented are shown in Table 3-2. More importantly, materials fabricated under the tighter controls have shown excellent strength in slicing and dicing in production.

TABLE 3-2
MODULUS OF RUPTURE OF BISMUTH TELLURIDE ALLOYS
BEFORE AND AFTER CONTROLS WERE IMPLEMENTED

Type	Average Modulus of Rupture [MPa (psi)]		Young's Modulus [MPa (ksi)]
	Before	After	
N	68.4 (9930)	90.4 ± 5.2 (13,120 $\pm$ 760)	9646 (1400)
P	54.7 (7940)	70.8 ± 11.4 (10,270 $\pm$ 1650)	8268 (1200)

3.1.5. Anisotropy Measurements

To further the characterization of pressed and sintered $(\text{Bi,Sb})_2(\text{Se,Te})_3$ alloys, the measurement of the Bacon anisotropy factor (BAF) (Ref. 4) was investigated. The BAF is a measure of preferred orientation of the material structure. The degree of preferred orientation is important because these alloys are anisotropic. Through powder metallurgy techniques, however, this effect is controlled on a macroscale, thereby controlling thermal conductivity, electrical resistivity, strength, and possibly other properties. A BAF value of 1.0 represents an isotropic material; values greater than 1.0 represent the degree of anisotropy.

MODULUS OF RUPTURE, S:

$$S = \frac{3Pl}{2bd^2}$$

YOUNG'S MODULUS, E:

$$E = \frac{Pl^3}{4ybd^3}$$

WHERE: P = LOAD AT FRACTURE
 l = SPAN LENGTH
 y = DEFLECTION AT FRACTURE
 b = SPECIMEN WIDTH
 d = SPECIMEN THICKNESS

Fig. 3-1. Schematic of the self-aligning, three-point bend modulus of rupture fixture and applicable equations

The BAF results across the diameter of the face, parallel to the pressing direction, of a half-moon specimen of N-type $(\text{Bi,Sb})_2(\text{Se,Te})_3$ were: edge 1.35, middle 1.72, and edge 1.11. The center was highly anisotropic and the edge near the mold surface was the least, as expected. Since the thermoelectric elements are cut perpendicular to the pressing direction, the heat flow rate, for example, would probably be the least for the material taken near the middle and the greatest for material taken near the edge. In this work it is possible that the light beam is looking at too small an area, and the BAF numbers are not indicative of the general area.

The BAF measurements were made with a micropolarimeter, which was developed at GA for use on pyrolytic carbon (Ref. 5). In this method, light from a He-Ne laser is directed onto the specimen through an oil objective. The polarization direction of the incident beam and the light reflected from the specimen are rotated by a rotating half-wave plate. The reflected light from the specimen is sensed by a pin diode, whose output is fed to an amplifier and oscilloscope. A computer program is used to calculate the BAF.

A correlation of BAF with other properties of bismuth telluride would be a useful quality control on nondestructive evaluation techniques. In measuring the BAF, the diameter of the laser beam through the optics of the micropolarimeter was found to be too small for the grain size of the $(\text{Bi,Sb})_2(\text{Se,Te})_3$ material. The beam diameter was enlarged to about 1 mm by the removal of the 16X oil-immersion optics. Although this resulted in undesirable reflections off the various surfaces, it was possible to obtain readings at some places on the polished specimen surface.

In summary, this nondestructive technique appears very promising and could be applied to other anisotropic thermoelectric alloys. Further developmental effort is needed to adapt the necessary computer codes and experimentally verify the readings with the observed material properties.

3.1.6. Thermal Conductivity

The thermal conductivity of the material discussed in Section 3.1.5. was measured on a specimen of square cross section with the Colora apparatus at a mean of 170°C. Although this specimen geometry was not ideally suited for the Colora apparatus, an estimate of the thermal conductivity ratio of $\lambda_{\perp}/\lambda_{\parallel} = 1.16$ with respect to the pressing direction was obtained. The degree of orientation measured by this method is an average for the specimen area. In contrast to this, the micropolarimeter can analyze a small area to provide a profile of BAF values.

The thermal conductivities for both N- and P-type material at 170°C were within 7.5% of each other as measured parallel to the pressing direction (nominal values of 0.010 W/cm-°C were obtained). The sample geometry dictated the measurement in the parallel direction or perpendicular to the direction of the thermoelectric element. However, the measurement in this direction should give a good overall indication of the material quality.

In the Colora method, a cylindrical specimen is placed between two silver platens, which are in contact with two boiling liquids having a suitable boiling point difference of about 20°C. The time needed to evaporate a given volume of liquid from the "cold" side of the specimen determines the quantity of heat flow through the sample. The apparatus is calibrated for a selected liquid pair with a series of known standards.

3.2. ULTRAFINE GRAIN MATERIAL

3.2.1. Introduction

A study was initiated to evaluate ultrafine grain $(\text{Bi,Sb})_2(\text{Se,Te})_3$ material. As the grain size is reduced, it is anticipated that the

mechanical strength will increase and possibly the lattice thermal conductivity (K_L) will decrease. By the introduction of planar defects and reduction of the grain size below current levels, a further reduction in thermal conductivity might occur.

3.2.2. Preparation of Powders

Several techniques were surveyed for producing the ultrafine grain powder ($\sim 1 \mu\text{m}$): each of these techniques is discussed below. The only successful technique was with the Bahco classifier.

Attempts were made to sonically sieve $(\text{Bi,Sb})_2(\text{Se,Te})_3$ powder, which had previously been reduced to ≤ 325 mesh (mesh opening is $45 \mu\text{m}$), through a $5\text{-}\mu\text{m}$ sieve. Little or no material passed through the sieve, even though it appeared (from SEM analysis) that a significant amount of the material should pass through the screen. Variations of pulse amplitude, sift amplitude, and sifting time did not affect the mass of material passing the $5\text{-}\mu\text{m}$ sieve. However, optimum conditions were established for increasing the mass of material passing through the 325 mesh ($45 \mu\text{m}$) screen.

SEM photographs of ≤ 325 mesh material indicated that most particles were substantially smaller (i.e., 1 to $10 \mu\text{m}$) than the $45\text{-}\mu\text{m}$ nominal screen size would indicate. Apparently the particles reaggregate and are prevented from easily passing the $5\text{-}\mu\text{m}$ sieve.

Another technique, called vortex grinding, consisted of spinning roughly ground material at high speed in an inert gas vortex, formed by high-pressure gas rotating in a cylinder. The particles in this case grind against each other. While this technique is successful for hard materials, the softer $(\text{Bi,Sb})_2(\text{Se,Te})_3$ alloys did not readily reduce in size below $5 \mu\text{m}$.

Conventional ball milling and roller milling were also studied; powder of $\leq 1\text{-}\mu\text{m}$ size was not obtained.

The Bahco classifier yielded the most promising technique for obtaining the ultrafine grain material. In this technique significant amounts of $\leq 5\text{-}\mu\text{m}$ powder were obtained such that a conventional puck could be pressed. The only drawback was that the classification was performed in air and not inert gas; thus, there was a chance for oxygen pickup. If further work is carried out with this classifier, it could be encased in an argon box.

Powder preparation directly from the melt was also investigated. Since the $(\text{Bi,Sb})_2(\text{Se,Te})_3$ alloys are very volatile at their melting points, the alloys are prepared in sealed vials to prevent loss of constituents. Thus, if powder is to be prepared it is necessary to start from the liquid sealed in the vial. A novel technique was developed that readily produced powder; unfortunately, the powder was slightly coarser than desired (approximately 325 to 200 mesh). In this approach, the sealed vial is dropped into a liquid and allowed to hit the bottom of the tank and crack. After a small amount of liquid enters the vial, it quickly vaporizes and causes the vial to explode. The shock wave produced causes the molten material to solidify as very fine particulates. The whole quench process is over in less than a second. The quenching media evaluated were water, liquid nitrogen, and liquid helium.

Quenching with water produced material having a wide range of particle sizes predominantly in the 325 to 200 mesh category. X-ray analysis indicated that the material was mainly crystalline with little, if any, amorphous characteristics. Liquid helium quenching yielded results similar to those for water. Liquid nitrogen gave very coarse material; apparently the low heat capacity of nitrogen prevents a strong enough explosion from developing in the short period of time available.

3.2.3. Thermal Conductivity

One of the pucks prepared with powder from the Bahco classifier was vacuum hot pressed and subjected to thermal conductivity measurements. A conductivity check of $0.008 \text{ W/cm}^\circ\text{C}$ was obtained at 170°C , which is approximately 20% below pucks pressed with conventional material.

4. INSULATION AND ADHESIVE CHARACTERIZATION

The goals of this task were to investigate the stability of the insulating and adhesive materials used in the construction of $(\text{Bi,Sb})_2(\text{Se,Te})_3$ thermoelectric modules at normal and above normal temperatures. The principal investigative method used was a thermogravimetric analyzer (TGA), which measures weight loss, under free vaporization conditions, as a function of temperature and time.

4.1. INSULATION CHARACTERIZATION

The insulation used in module construction is a polyamide film, Kapton. Small pieces of the material were run on the TGA. Figure 4-1 shows the results of an experiment where the weight loss of Kapton was measured from room temperature to 480°C at a heating rate of $2^\circ\text{C}/\text{min}$. A small weight loss around 70°C has been shown, in previous experiments, to be caused by a loss of water. The weight loss is catastrophic above 400°C , which is well above the normal operating temperatures of 180° to 270°C for these modules.

An experiment was run to show if the loss of water is reversible. Several pieces of Kapton were heated to 300°C for 24 h and then put in an ambient room environment for 4 weeks. A TGA run showed a weight loss around 100°C , indicating that the loss of water is reversible.

A series of isothermal weight loss runs were made in order to make long-term weight loss predictions. Figure 4-2 shows the results of 100-h experiments at 300° , 325° , 350° and 375°C . These data were

Fig. 4-1. Percent of original weight as a function of temperature for Kapton insulating material (heating rate = 2°C/min)

Fig. 4-2. Isothermal weight loss runs for Kapton insulating material

put into a form that gave the best straight lines. The least-squares slope (α) of these lines is plotted in Figure 4-3 as a function of the reciprocal absolute temperature. This plot was used to predict a values for lower temperatures, which were used to calculate the 15-year weight losses listed in Table 4-1. These predictions indicate that Kapton is an extremely stable material at temperatures below 300°C and can safely be used at higher temperatures for short periods of time.

TABLE 4-1
CALCULATED 15-YEAR WEIGHT LOSSES FOR KAPTON INSULATING MATERIAL

	200°C	220°C	240°C	260°C	280°C	300°C
Weight loss, %	0.01	0.06	0.30	1.10	4.10	14.80

4.2. ADHESIVE CHARACTERIZATION

4.2.1. Shell Epon 828

Epon 828, the epoxy used in $(\text{Bi,Sb})_2(\text{Se,Te})_3$ module construction, was run on the TGA using the same techniques as those used in the Kapton insulating material tests.

A weight loss experiment, as a function of temperature, was run on the cured epoxy to obtain a general idea of the weight loss characteristics of the material. The results are shown in Fig. 4-4. Appreciable weight loss occurred at temperatures above 200°C.

Results for TGA isothermal weight loss runs that were carried out at 175°, 200° and 225°C are plotted in Fig. 4-5. The curves were used to calculate the following 100% vaporization times: 175°C, 11.4 years; 200°C, 2.6 years; and 225°C, 126 days. These temperatures are around the hot-side temperatures encountered in $(\text{Bi,Sb})_2(\text{Se,Te})_3$ thermoelectric generators. These results indicate that epoxy vaporization could occur

Fig. 4-3. Arrhenius plot of α for Kapton insulating material
 $[\alpha = (1 - W/W_0)/\Delta T]$

Fig. 4-4. Percent of original weight as a function of temperature for Epon 828 epoxy (heating rate = 2°C/min)

Fig. 4-5. Isothermal weight loss runs for Epon 828 epoxy

from the very end of the hot side of modules made from Epon 828. A successful effort was made to find a substitute adhesive that was less volatile but still compatible with module construction.

4.3. ADHESIVE SCREENING

A series of adhesives have been screened as a replacement for Epon 828 epoxy in module construction. Manufacturers' recommendations for curing their products were followed in the screening tests.

Figure 4-6 gives the results of three epoxys supplied by Tracon, Inc.: 2212, 2255, and 2272. Epoxys 2212 and 2255 gave encouraging results and further tests were made.

Figure 4-7 gives the results on two inorganic adhesives supplied by Dylon Industries: C-3 and C-10. Both adhesives showed good weight loss properties but were too coarse to be used in module construction. No further work was done on these adhesives.

Figure 4-8 gives the results on two adhesives supplied by Thermo-Resist, Inc: Glom O-N and TR 150-25. Both showed promise and further work was done.

Figure 4-9 gives the results on an adhesive supplied by Gulf Oil Chemical Company: Thermid "600." The results on the lacquer version of this adhesive indicate possible use. Further characterization of this product is still in progress.

4.4. CHARACTERIZATION OF INDIVIDUAL ADHESIVES

4.4.1. Tracon 2255

Tracon 2255 is a filled epoxy. Weight loss experiments showed that the ratio of filler to epoxy is 4 to 1. The residue from one of these runs was analyzed by X-ray diffraction and was found to be Al_2O_3 .

Fig. 4-6. Percent of original weight of three Tracon adhesives as a function of temperature (heating rate = 2°/min)

Fig. 4-7. Percent of original weight of two Dylon Industries inorganic adhesives as a function of temperature (heating rate = 2°C/min)

Fig. 4-8. Thermogravimetric weight losses for TR 150-25 and Glom O-N adhesives (heating rates = 5°C/min and 2°C/min, respectively)

Fig. 4-9. Percent of original weight of Thermide "600" lacquer supplied by Gulf Oil Chemical Company as a function of temperature (heating rate = 5°C/min)

Isothermal weight loss runs were made at 250°, 275°, and 300°C. The results are shown in Fig. 4-10. The results are plotted as the percent of epoxy left. The original epoxy was only 20% of the total adhesive weight.

4.4.2. Thermo-Resist Glom O-N

This adhesive is also a filled epoxy. Weight loss experiments showed that the ratio of filler to epoxy is 3 to 2. X-ray diffraction analysis showed that the filler was Al_2O_3 .

Isothermal weight loss runs were made at 225°, 250°, and 275°C. The results are shown in Fig. 4-11. The weight loss characteristics were almost identical to those of Tracon 2255. Both are adequate with respect to weight loss at anticipated generator temperatures. Tests also showed that the two filled epoxies will adhere to $(Bi,Sb)_2(Se,Te)_3$. Both are pastes and cannot be applied to thin layers in the present methods of module construction.

4.4.3. Tracon 2212

Tracon 2212 is a liquid epoxy system, similar to Epon 828. Isothermal weight loss runs were made at 250°, 275°, and 300°C. The results are shown in Fig. 4-12. These data were put into a form that gave the best straight lines. The least-squares slope (α) of these lines is plotted in Fig. 4-13 as a function of the reciprocal absolute temperature. This plot was used to predict α values for lower temperatures, which were used to calculate the following 100% vaporization times: 175°C, 389 years; 200°C, 36.6 years; and 225°C, 4.5 years. In these calculations free vaporization (no baffling) was assumed, which is a worst case assumption. Comparison of these times with those calculated for Epon 828 indicates that at the same temperatures as those of the typical generator hot side, it would take ten times longer for 100% vaporization of Tracon 2212.

Fig. 4-10. Isothermal weight loss runs on filled adhesive Tracon 2255

Fig. 4-11. Isothermal weight loss runs on Thermo-Resist Glom 0-N adhesive

Fig. 4-12. Isothermal weight loss runs on Tracon 2212

Fig. 4-13. Slope (α) of isothermal weight loss runs on Tracon 2212 versus temperature

Experiments showed no evidence of adverse interaction between Tracon 2212 and the Kapton insulating material used in module construction. The results for a weight loss experiment in which Tracon 2212 had been cured on a piece of Kapton were identical to those for an experiment with the cured epoxy by itself. This would indicate no chemical reaction had occurred between the two materials.

A series of three-point bending tests were made on slices of $(\text{Bi,Sb})_2(\text{Se,Te})_3$ thermoelectric material bonded together using Epon 828 and Tracon 2212 epoxies. The slices made from Tracon 2212 were found to be, on the average, 19% stronger.

The thermal conductivity of Tracon 2212 was measured at 170°C to be 0.0023 W/cm-°C. The reported value for Epon 828 was the same.

Three working thermoelectric modules were fabricated using Tracon 2212 epoxy. In general, in comparison with Epon 828, Tracon 2212 was easier to work with because (1) it is less viscous, which makes it easier to apply and more bubble-free; (2) it has a longer pot life (24 h versus 2 h) at room temperature; and (3) it comes premeasured in bags and is easily mixed.

Tracon 2212 was found to be completely compatible with the module manufacturing procedures. There was no loss of material due to slices failing during the cutting operation, as opposed to large losses during this step using Epon 828. The module tests are reported in Section 4.5.

4.4.4. Thermo-Resist TR 150-25

This material is a polyamide-type adhesive that relies on the vaporization of material during curing. In the screening test on TR 150-25 (Fig. 4-8), which was cured following the manufacturer's instructions, considerable volatile material was left. Severe bubbling

was also noted during the curing cycle. This adhesive shows promise of extending the generator hot-side temperature well above 200°C if these two problems could be overcome.

A tentative solution of the bubbling problem was to pre-cure the adhesive in all of the module fabrication steps below the bubbling temperature, with a final cure at high temperature of the constrained full module. This proved successful when a module was constructed from TR 150-25.

Tests were run which showed that the volatile material can be greatly reduced by increasing the final cure time and temperature. A number of samples were cured at various temperatures and times. All of the samples were cured for 2 h at 150°C and then at higher temperatures. The results of these runs are shown in Fig. 4-14. The percent volatile material left was determined by heating the cured adhesive to 350°C in the TGA. Figure 4-15 compares the results for TR 150-25 cured following the manufacturer's procedures with those for TR 150-25 cured by methods developed under this task.

A working module was fabricated using TR 150-15 adhesive. Some difficulties were encountered with the short pot life of the air-exposed material. Some slices also fell apart during cutting operations. The completed module performed well during testing (see Section 4.5).

4.4.5. Gulf Chemical Company Thermid "600"

Thermid "600" is a polyamide system that relies on vaporization of solvent and a melting step for curing. It has the same bubbling and residual volatile material problems as TR 150-25. If these problems can be solved, the adhesive shows promise well above 300°C. Work on Thermid "600" is in progress.

Fig. 4-14. Residual volatile material after various time-temperature variations on the cure cycle of TR 150-25 adhesive

Fig. 4-15. Percent of original weight of TR 150-25 cured following the manufacturer's procedures and those developed by GA

Fig. 4-16. As-received properties of thin-leg microwatt module 1

Fig. 4-17. As-received properties of thin-leg microwatt module 2

Fig. 4-18. As-received properties of thin-leg 1/2-W module 1

Fig. 4-19. As-received properties of thin-leg 1/2-W module 2

Fig. 4-20. Life test of thin-leg 1/2-W module 2 ($T_h = 248^\circ\text{C} \pm 6^\circ\text{C}$
 ΔT corrected to 185°C)

4.5. MODULE AND ELECTRICALLY HEATED THERMOELECTRIC GENERATOR (ETG) TESTING

4.5.1. Thin-Leg Modules

Two microwatt and two 1/2-W thin-leg modules were supplied to GA for evaluation. These modules have the potential advantage of a higher voltage output, for a given size, than conventional modules. One of the microwatt modules was returned for repair because a lead had broken off. Some of the as-received properties of the four modules, as a function of ΔT , are shown in Figs. 4-16 through 4-19.

Thin-leg microwatt module No. 1 was life tested for 2000 h at a hot-side temperature of 105°C. There was no power degradation. The internal resistance showed an approximate 1% increase.

Thin-leg 1/2-W module No. 2 was life tested for 1875 h at a hot-side temperature of 250°C. The results are shown in Fig. 4-20. The output power had decreased by 12% and the internal resistance had increased by 13% when the test was terminated. It was surmised that the Ni metallic contacts on the hot side reacted with the $(\text{Bi,Sb})_2(\text{Se,Te})_3$ alloys, causing the degradation.

It was desirable to evaluate the thin-leg modules with respect to operating efficiency. Therefore, attempts were made to fabricate the thin-leg modules into existing GA pacemaker RTG hardware. The leads on these modules were too fragile and as a substitute test, both GA modules and thin-leg modules were evaluated under the conditions in a vacuum bell jar. Two PuO_2 fuel capsules were used for these evaluations. The efficiency measurement in this evaluation is only a comparative test but is indicative of the performance that could be obtained in an RTG configuration.

Nuclear heat sources were attached to both of the thin-leg microwatt modules and vacuum data were obtained. One of the same heat sources was attached to a GA heart pacer module for comparison. The data are summarized in Table 4-2.

Analysis of the data on the thin-leg microwatt modules indicates that there is an excessive amount of parasitic heat loss. This can be attributed to the much larger volume fraction of nonthermoelectric material used in the construction of the thin-leg modules as compared to the GA modules. The differences between the performance of the two thin-leg microwatt modules can probably be attributed to lack of control in manufacturing tolerances in the construction of the modules.

4.5.2. Tracon 2212 Module and ETG Testing

Two 1/4-size and one full-size 75-mW modules were fabricated from Tracon 2212 epoxy for testing. The tests were designed to duplicate tests run earlier on modules fabricated with Epon 828 epoxy. One 1/4-size module (SA-2) completed over 850 h of accelerated life testing at a T_h of 300°C. The results are shown in Fig. 4-21 and are compared with a module using Epon 828, which was of a similar configuration and was operated at the same temperature. The results show essentially no power degradation in either case. Visual examination of the hot side showed much less epoxy vaporization in the module made from Tracon 2212.

The full-size 75-mW module was installed in an electrically heated generator fitted with thermocouples for measuring hot- and cold-side temperatures. It finished accelerated life tests of 760 h at a hot-side temperature of 270°C and 520 h at a hot-side temperature of 300°C. These runs are shown in Figs. 4-22 and 4-23. A least-square fit of each set of data is also plotted. Degradation coefficients of 4.95×10^{-4} at 270°C and 1.48×10^{-3} at 300°C were calculated from the data. These compare with 5.4×10^{-4} at 270°C and 1.8×10^{-3} at 300°C calculated

TABLE 4-2
RESULTS OF NUCLEAR HEATED THIN-LEG MICROWATT MODULES 1 AND 2 AND A GA HEART PACER MODULE

	Thin-Leg Module 1	Thin-Leg Module 2	GA Module
Nuclear heat (source number)	757	754	757
Original Pu-238 (loading), g	0.18	0.18	0.18
Open-circuit (voltage), v	1.91	2.82	0.354
Matched-load (voltage), v	0.955	1.41	0.177
Current, mA	0.0595	0.068	1.83
Power, mW	0.057	0.096	0.324 ^(a)
Cold-side temperature, °C	23	23	23
Calculated resistance, Ω	16,050	20,735	97.7
Length, cm (in.)	1.219 (0.480)	1.219 (0.480)	1.369 (0.539)
Cross-sectional area, cm ² (in. ²)	0.158 (0.0246)	0.174 (0.0270)	0.119 (0.0185)

(a) In a typical pacemaker RTG configuration, this module would produce 0.4 mW.

Fig. 4-21. Percent power output with time for modules 4A-1 (Epon 828) and 5A-2 (Tracon 2212) showing very little degradation in both cases

Fig. 4-22. Life test data for generator 6AE at 300°C

Fig. 4-23. Life test data for generator 6AE at 270°C

from previous runs at these temperatures using a generator with a module fabricated with Epon 828. The degradation coefficients were 10% and 18% less at 270° and 300°C, respectively. The degradation coefficients are plotted versus $1/T$ (K) in Fig. 4-24. Also included are data from JPL (Ref. 6) run on similarly constructed modules made with Epon 828 epoxy. Fifteen-year module degradations, which do not include isotope heater decay, calculated from these coefficients and extrapolated to 210°C were 5.8% for the Epon 828 JPL data, 1.2% for the Epon 828 GA data, and 1.4% for the Tracon 2212 GA data.

Based upon its overall superior performance, it was concluded that Tracon 2212 epoxy was an acceptable substitute for Epon 828 epoxy in 75-mW $(\text{Bi,Sb})_2(\text{Se,Te})_3$ thermoelectric modules.

4.5.3. TR 150-25 Adhesive Module Testing

A 1/4-size 75-mW module was fabricated using TR 150-25 adhesive. No significant modification had to be made in the module fabrication procedures except in the curing cycle. The starting properties of the module (7A) were measured and are plotted in Fig. 4-25. These properties were similar to those for previously run modules that were made using epoxy adhesives. The module was life tested for 500 h at a hot-side temperature of 300°C. There was a 7% decrease in the open-circuit voltage during the test and no change in the internal resistance. $(\text{Bi,Sb})_2(\text{Se,Te})_3$ -type modules typically degrade by an increase in resistance with no change in open-circuit voltage. The module showed flow of thermoelectric material on the hot side after the run. Partial shorting of the legs could have occurred. The flow was caused by an excess stress on the module in the test fixture by a factor of approximately three. The flowed material was cleaned off and the module rechecked. The thermoelectric properties returned to those measured at the start of the life test.

Fig. 4-24. Comparison of degradation coefficients for modules made from Epon 828 epoxy and Tracon 2212 epoxy and the JPL data

Fig. 4-25. Starting properties of Module 7A

4.5.4. One-Watt Module Test

A 1-W $(\text{Bi,Sb})_2(\text{Se,Te})_3$ module, which has molybdenum contacts, was put on accelerated life test. The test is being run in 1 atm of argon. The module completed 2600 h at a hot-side temperature of 325°C with no degradation. The module is now on test at 350°C and has completed 4200 h with no degradation.

4.5.5. Module Loading Tests

The purpose of this task was to investigate the behavior of thermoelectric modules under various loading conditions. Previous module life tests showed unexpectedly low degradation rates. One of the main differences between these tests and the generator configuration is in the method of the loading of the heat source to the module. In the module tests, the heat source was allowed to ride freely on the module with only the heater weight applying force. The generator loading is set at 1.4 MPa (200 psi) during construction by tensioning holddown wires at room temperature.

A module having one-quarter the area of a normal 75-mW module has completed 530 h at a hot-side temperature of 300°C, at various loads in a test fixture, with no degradation. The loads varied from no load to approximately four times the generator load. This result indicates that possible adverse metallurgical reactions and the absolute load on the contacts are not contributing to the thermoelectric degradation. The possibility that the greater surface area of the full module contributes to the degradation (i.e., uneven loading forces) is now being investigated.

It should be noted that the degradations observed are only at very high accelerated temperatures and the amount of degradation at the lower operating temperatures is hardly measureable

5. REFERENCES

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