FOREWORD

This is the final report covering the work performed by the General Electric Company for the United States Air Force under Contract No. AF 33 (616)-5281 entitled "Thermopile Generator Feasibility Study". This program was carried out by several components within the Company under the overall cognizance of the Aircraft Accessory Turbine Department. The contract was administered under the direction of the Aeronautical Accessories Laboratory of the Wright Air Development Center, (presently called Flight Accessories Laboratory, Wright Air Development Division) Wright-Patterson Air Force Base, Ohio. Lt. R. G. Leiby was Task Engineer during the early part of the contract, and Mr. R. N. Cooper acted as Task Engineer during the remaining portion.

The report is written in four parts, of which this is Part IV. It covers the entire period of the contract, from 1 July 1957 through 31 March 1960.

In addition to the editor of Part IV, those who contributed materially to the writing of this part of the report include: W. J. Cox, H. Kasch, L. F. Kendall, A. H. Swan, R. L. Thompson, and Dr. H. R. Wisely. Also gratefully acknowledged is the very helpful consulting assistance of Drs. R. W. Fritts and J. D. Richards of the Minnesota Mining and Manufacturing Company, the vendor of the lead telluride materials used in this work.

ABSTRACT

This report contains a detailed description and summary of a research and development study to determine means of employing thermopile generators as sources of electrical power in future air and space weapon systems. The following major areas of work were involved: 1) Materials development, 2) Junction fabrication and test, 3) Thermoelectric generator applications studies, and 4) Thermoelectric generator design.

The report consists of four parts as follows:

Part I - Summary - This presents an over-all summary of the entire program.

Part II - Materials Investigations - This contains the details of the work on materials development.

Part III - Performance Studies - This presents in detail the work on thermoelectric generator applications studies as well as the more general aspects of thermoelectric generator design.

Part IV - Generator Design - This contains the details of the work on junction fabrication and test and thermoelectric generator design for specific applications.

This is Part IV of the report and contains a detailed description of the work on junction fabrication and test and on thermoelectric generator design as applied particularly to: 1) Efforts to design, build, and test a 5 watt generator model, and 2) Preparation of specifications for a 100 watt Solar Thermoelectric Generator. The actual specifications for the 100 watt Solar Thermoelectric Generator are included as an appendix in this Part.

TABLE OF CONTENTS

Page

INTRODUCTION.. 1

DESIGN CONCEPTS

- Introduction.. 3
- Sandwich Type... 3
- Side Fin-Sandwich Type.. 9

MATERIALS SELECTION... 12

FABRICATION PROBLEMS

- Diffusion Barrier... 16
- Junction Formation.. 17
  - Electrodeposition - Iron.................................. 18
  - Electrodeposition - Nickel................................ 20
  - Vacuum Deposition... 26
  - Diffusion Bonding... 26
  - Flame Spray... 27
  - Iron Carbonyl... 27
- Sublimation and Oxidation..................................... 29
- High Temperature Glue... 35
- High Emissivity Coating....................................... 37
- Conductor Joining... 37
- Material Fabrication.. 38

MODEL THERMOELECTRIC GENERATOR

- Design Consideration.. 40
- Design Point Selection.. 46
- Design Details.. 47
- Tests... 53

TABLE OF CONTENTS (Continued)

Page

SPECIFICATIONS - 100 WATT SOLAR THERMOELECTRIC GENERATOR.............. 69

BIBLIOGRAPHY.. 73

APPENDIX A - SPECIFICATION - 100 WATT SOLAR THERMOELECTRIC GENERATOR.. 75

LIST OF FIGURES

Fig. No.	Title	Page No.
1	Sandwich-Type Thermoelectric General Construction. (a) Sandwich-Type Generator-Radiator (b) Sandwich Construction with Typical Heat Source.	4
2.	Sandwich-Type Model Thermoelectric Generator--Side View.	6
3.	Sandwich-Type Model Thermoelectric Generators--Top and Side Views.	7
4.	Typical Side Fin Type Configurations.	11
5.	Comparison of Figure Merit of Best Available Materials and Lead Telluride, n-Type.	13
6.	Comparison of Figure of Merit of Best Available Materials and Lead Telluride, p-Type.	14
7.	Surface of Lead Telluride Sample.	19
8.	Plate or Cap.	19
9.	End of Lead Telluride Rod.	19
10.	Resistance Profile of n-Type PbTe-Ni-60/40 Tin/Lead-Cu Junction.	23
11.	Resistance Profile of p-Type PbTe-Ni-60/40 Tin/Lead-Cu Junction.	24
12.	Vicor Tube Opened to Show Nickel-Plated PbTe Cylinder, Left, and Unplated PbTe Control after 24-Hour Soak at 1200 F.	25
13.	Nickel-Plated PbTe Specimen, Left, and Control Removed from Vicor Tube Showing Reaction of PbTe with Vicor.	25
14.	End Views of Nickel-Plated PbTe Specimen, Left, and Control Sample.	25
15.	Model Thermoelectric Generator--Assembly Drawing.	43

LIST OF FIGURES (Continued)

Fig. No.	Title	Page No.
16.	5-Ring Model Thermoelectric Generator--Partially Assembled.	44
17.	5-Ring Model Thermoelectric Generator--Partially Assembled.	44
18.	Major Parts of 5-Ring Model Thermoelectric Generator.	45
19.	Cylinder of Material Showing Probe Positions.	53
20.	Voltage vs Length.	54
21.	Cylinder of Material with Discontinuity.	54
22.	Resistance vs Length with Discontinuity.	54
23.	Resistance vs Length with Good Conductor on One Side of Junction.	55
24.	Resistance Profiling Device--Partially Assembled.	56
25.	Resistance Profiling Device--Completely Assembled.	56
26.	Resistance of p-Type Elements at 1100°F as a Function of Time.	60
27.	Resistivity vs Temperature--p-Type PbTe (1.0 at % Na.).	62
28.	Schematic of Test Setup Used for Single-Ring Model Tests.	64
29.	Solar Thermoelectric Generator.	71

LIST OF TABLES

TABLE NO.	TITLE	PAGE NO.
1	Performance Estimate - Sandwich Type Model Generator	8
2	Phosphate Bond Formation	33
3	Parts List for Model Thermoelectric Generator	48
4	Resistance Measurements p-type PbTe (1.0 at % Na)	58
5	Resistance Measurements n-type PbTe (0.1 mol. % PbI_2)	59
6	Summary of Progress on Single Ring Model Tests	66
7	Selected Performance Data from the Single Ring Model Tests	67

LIST OF SYMBOLS

a = Cross-sectional area of junction, cm^2

I = Current, amperes

ℓ = Length, cm

m = Ratio of external electrical resistance to internal electrical resistance of thermoelectric materials

P = Power output, watt

R = Resistance, ohms

R_j = Junction resistance, ohms

T_1 = Temperature at hot end of thermoelements, $^{\circ}\mathrm{K}$

T_2 = Temperature at cold end of thermoelements, $^{\circ}\mathrm{K}$

V = Voltage, volts

α = Seebeck coefficient, volt/K

ρ_j = Junction resistivity, ohm-cm^2

Subscripts

a = Average properties

n = n-type thermoelectric material

p = p-type thermoelectric material

INTRODUCTION

The generator design and junction fabrication phases of this contract had as their objectives two major items: 1) The preparation of specifications for a 100 watt thermoelectric generator suitable for use in space applications using currently available materials, 2) The construction of a small (approximately 5 watts net power output) model generator also using currently available materials. Progress made toward the attainment of these objectives is the subject of the material contained in this part of the report.

The intent of the preparation of the 100 watt generator specifications was to write them in such a manner that, in the opinion of the contractor, the specifications can be met: 1) By the use of materials currently available, 2) Without requiring major developments in fabrication and construction techniques. The generator was to be suitable for space applications utilizing a solar heat source. It was recognized that basing these specifications on design concepts that would not require extensive development of fabrication and construction techniques could result in calling for performance inferior to that which could be obtained after development of the appropriate techniques. However, the potential advantages to be gained should such techniques be developed would be identified.

The intent of the model generator construction program was to utilize the best design concepts developed under this contract to build a model capable of approximately 5 watts net power output. The design used was to be consistent with that required for space applications. Thermoelectric materials representative of the better ones readily available were to be used. Insofar as possible, the design concepts involved in the 100 watt generator specifications mentioned above were to be utilized. However, should some of these concepts require extensive development of fabrication techniques, it would be necessary to revert to a more conventional design since such extensive developments were beyond the scope of this contract.

The model generator was to utilize an electric resistance heater as the heat source. This is advantageous primarily from the standpoint of simplicity, but it also makes possible the accurate determination of efficiency. On the other hand, the use of an electrical heat source does not detract significantly from the demonstration of feasibility for space applications since the practical sources of heat are most likely to be solar energy or circulating fluids from a nuclear reactor. Modification of a design utilizing a simulated electrical heat source to accept these other practical sources is certainly plausible.

Some rather arbitrary service life objectives were established to serve as guides in the model generator construction program. It was desired to make the model suitable for operation in air for demonstration purposes as well as in a vacuum as required to be consistent with space applications. The service life objectives established were one year of operation in vacuum and 100 hours operation in air, both at design hot junction temperature. A generator capable of a minimum of 150 thermal cycles from room temperature to maximum operating temperature was believed to be desirable.

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The initial attempts to construct the model generator were based on the sandwich type configuration using lead telluride thermoelectric materials with bonded contacts at the junctions. This concept required the development of a number of fabrication techniques to reduce it to practice. The progress made toward the solution of these development problems is described in the material found later in this part of the report under the heading, FABRICATION PROBLEMS. With regard to the latter, in addition to the techniques described there for depositing iron on lead telluride, there is at least one other conceivable means of accomplishing this deposition, the direct casting (12) method. However, without extensive development this method was not believed to be suitable for elements of the size required here so the possibility of its use was not pursued.

Progress toward the solution of the fabrication problems involved in the sandwich type construction using bonded contacts was not sufficiently rapid to permit construction of such a model within the time and funding limits of this contract. The major difficulties were depositing iron on p-type lead telluride and providing a coating for protection of the elements against the effects of sublimation and oxidation. Therefore, it was necessary to revert to a somewhat more conventional type of construction; in particular, one that could utilize pressure contacts at the junctions between the iron diffusion barriers and the lead telluride thermoelements.

The side fin-sandwich configuration with adequate structure to provide the spring force required for pressure contacts was selected for continuation of the model generator construction program. The design of the generator based on this concept and the progress made toward its construction are described in the material found later in this part of the report under the heading, MODEL THERMOELECTRIC GENERATOR.

Specifications for a 100 watt solar thermoelectric generator have been written based on performance expectations gleaned from the model generator program. These specifications are discussed in the concluding portions of the text of this part of the report. The detailed specifications appear in Appendix A.

Items and materials used in the study, and called out in the four parts of this report by trade name or specifically identified with a manufacturer, were not originated for use in this specific study or for the applications necessary to this study. Therefore, the failure of any one of the items or materials to meet the requirements of the study is no reflection on the quality of a manufacturer's product. No criticism of any item or material is implied or intended. Nor is any indorsement of an item or material by the United States Air Force implied or intended.

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(12) Superscripts in parentheses refer to references listed in BIBLIOGRAPHY.

DESIGN CONCEPTS

INTRODUCTION

In selecting typical configurations for study, it was kept in mind that one of the inherent advantages of a thermoelectric generator is the fact that it requires, of itself, no moving parts. Hence, in considering conceptual designs of such a generator, every reasonable effort should be made to maintain this advantage by introducing as few moving parts as possible. Accordingly, the configurations studied are ones in which the generator and radiator are combined into one package and require no circulating fluids for heat transfer on the cold side. This type of configuration not only has the advantage of simplicity, but it also eliminates the problem of meteorite puncture of radiator tubes and subsequent loss of coolant.

Two basic types of configuration have been considered, the sandwich type and the side fin-sandwich type. A third type, the side fin configuration, may be considered a special case of the side fin-sandwich type. Each is discussed in the material that follows.

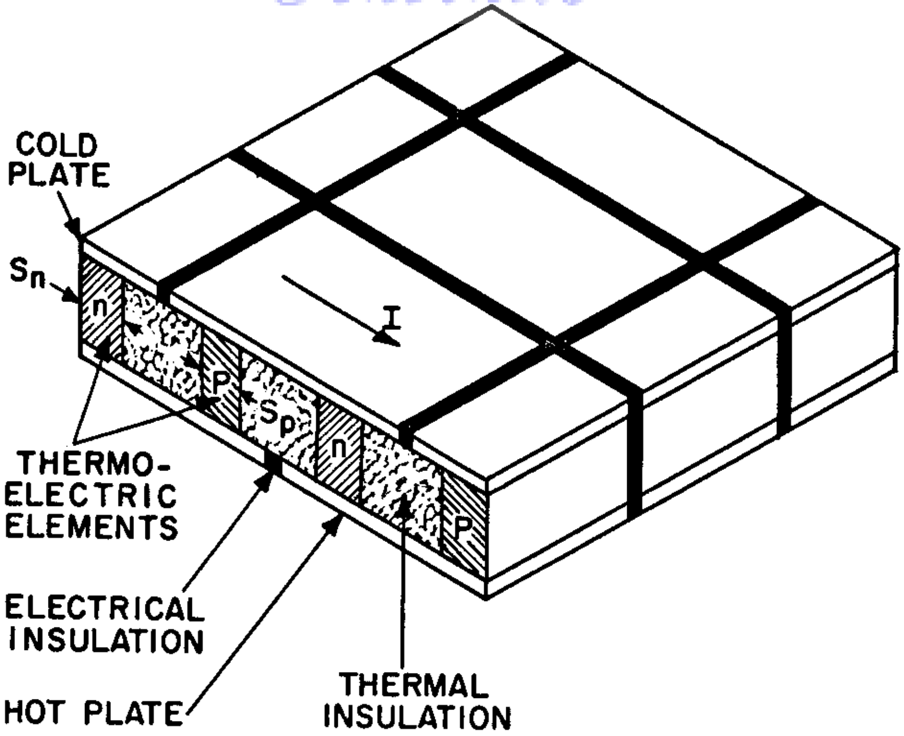
As is generally the case for thermoelectric devices, both of these basic configurations are of the modular type, i.e., they consist of a multiplicity of identical thermoelectric couples. Power level and total size of the generator are increased by adding to the length and/or width of the package, thereby increasing the total number of elements.

Depending upon details of construction, both types of configuration are flexible as to the source of heat used. Either could be adapted to accept heat by radiation from a solar collector, by direct conduction from a radioisotope or by circulation of a hot fluid utilizing solar, nuclear, or chemical energy as the primary heat source.

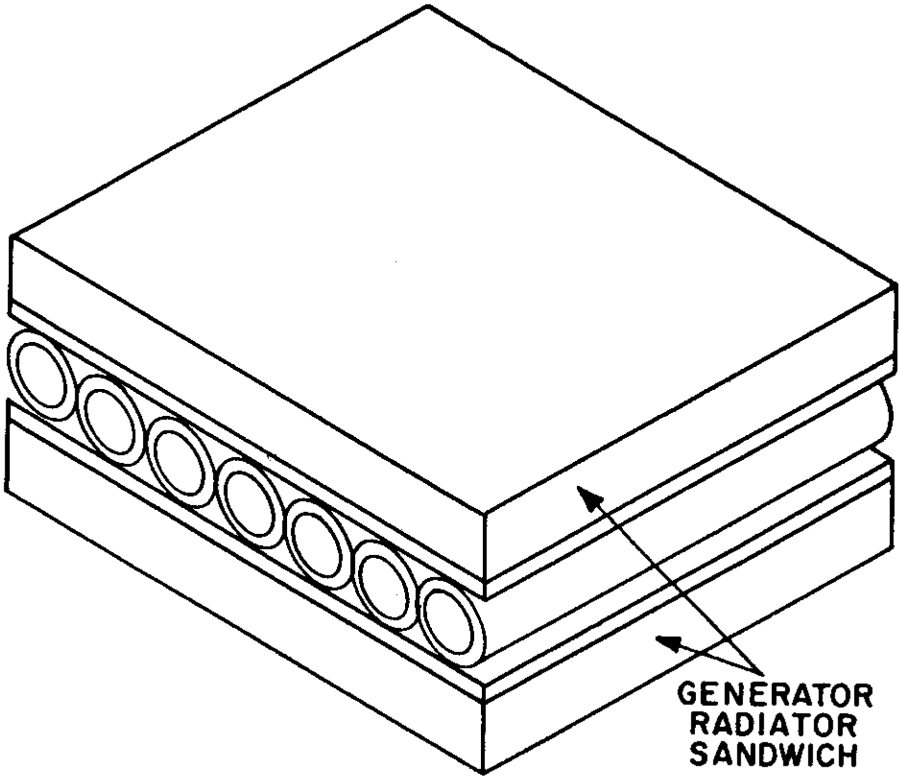
Another factor involved in the consideration of conceptual designs is the adaptability of the configuration to either bonded or pressure contact junctions, depending upon which is to be used. Either of the configurations considered here is adaptable to bonded junction construction. The side fin-sandwich type is suitable for pressure contact junctions, but a method of providing adequate contact pressure in a light weight generator of the sandwich type for space applications has not been found.

SANDWICH TYPE

The sandwich type construction is indicated in part (a) of Figure 1. The thermoelectric elements, rectangular in shape, are sandwiched between two segmented plates. These plates act as electrical conductors between adjacent elements. The hot plate also serves to collect and distribute the heat coming from the heat source, and the cold plate also serves as the radiator. The plates must be segmented in order to accommodate the electrical insulation



(a) Sandwich-Type Generator-Radiator



(b) Sandwich Construction with Typical Heat Source

Figure 1: Sandwich-Type Thermoelectric Generator Construction.

that is required between adjacent pairs of elements. Any combination of series and parallel electrical connections is possible. To minimize weight, it will usually be true that the cross-sectional area of the thermoelectric elements will be much less than the area of the radiating surface. For this configuration, increased radiator area is obtained by opening up a gap between the thermoelectric elements and filling this gap with thermal insulation or radiation shields to reduce heat leakage.

This type of generator sandwich can in turn be mounted on and electrically insulated from a surface containing the heat source. Use of a high temperature, insulating "glue" would be desirable for this purpose. A typical heat source configuration could consist of a thin mounting sheet placed across and brazed to adjacent metal tubes through which a heat transfer fluid is circulated. See part (b), Figure 1. The best spacing for these tubes would depend on the particular case. For example, instead of having the tubes immediately adjacent to one another and brazed along the sides, as shown in the figure, the tubes might be spaced further apart. Tube sheets, not shown, could also be used at intervals along the length of the tubes for structural support when the spacing between headers is large. Two generator sandwiches could be mounted on each set of tubes, one on each side, with the resulting configuration appearing as in part (b), Figure 1.

The initial work of the generator design phase of this contract was directed toward the construction of a small model generator of the sandwich type configuration. The preliminary design of this model, including dimensions, is shown in Figures 2 and 3. Initial performance estimates are listed in Table 1. A word of caution with regard to the information presented in Figures 2 and 3 and Table 1 is in order at this point. All the values given are preliminary estimates and, since this generator has not actually been constructed, have not been confirmed. Also, certain losses whose effects may or may not be significant have not been included in the preparation of the performance estimates. For example, the figures given here do not account for decreased performance due to such items as: a) Increased thermal conductivity of the insulation due to treatments necessary to bond the conductors to it, b) Junction resistance, c) Heat losses around the edges of the package, d) Any failure of thermoelectric material properties to achieve expected values.

Referring now to Figure 2, it shows, at about ten times actual size, the basic construction elements of the generator. The latter is seen to consist of alternate n and p-type rectangular elements sandwiched between blocks of insulation and connected by silver foil electrical conductors approximately 0.001 inches thick. (The thickness of the conductors in the figure is exaggerated for purpose of clarity.)

The width of the elements has been selected as 1/4 inch, and approximately 14 pairs of junctions are connected in series to form a module. The generator consists of 24 such modules, placed side by side to form a rectangular array as shown in Figure 3. Four sets of 6 modules each are permanently connected in electrical series to form four circuits. Provision can be made to connect these four circuits in turn into any combination of series or parallel arrangements.

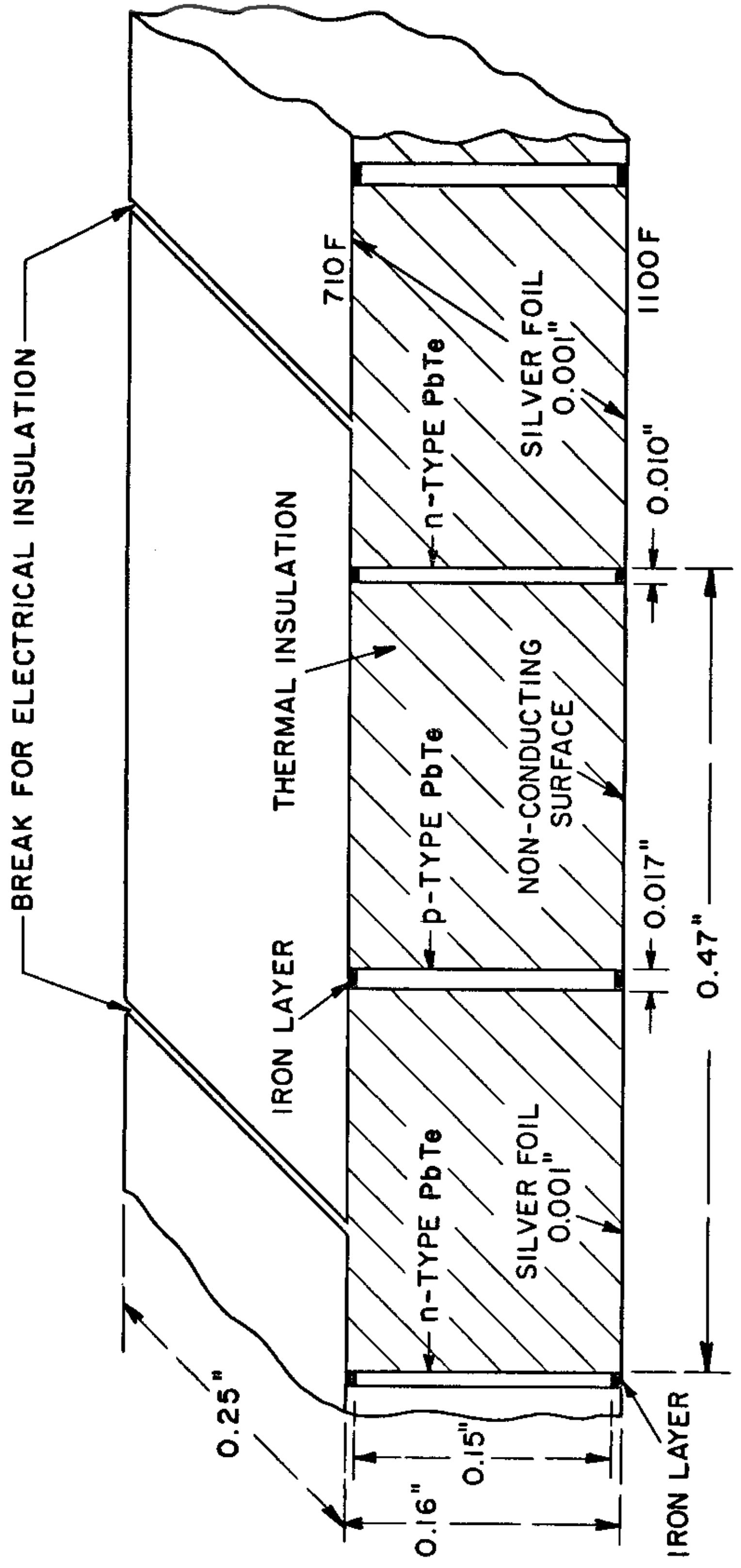


Figure 2: Sandwich-Type Model Thermoelectric Generator — Side View

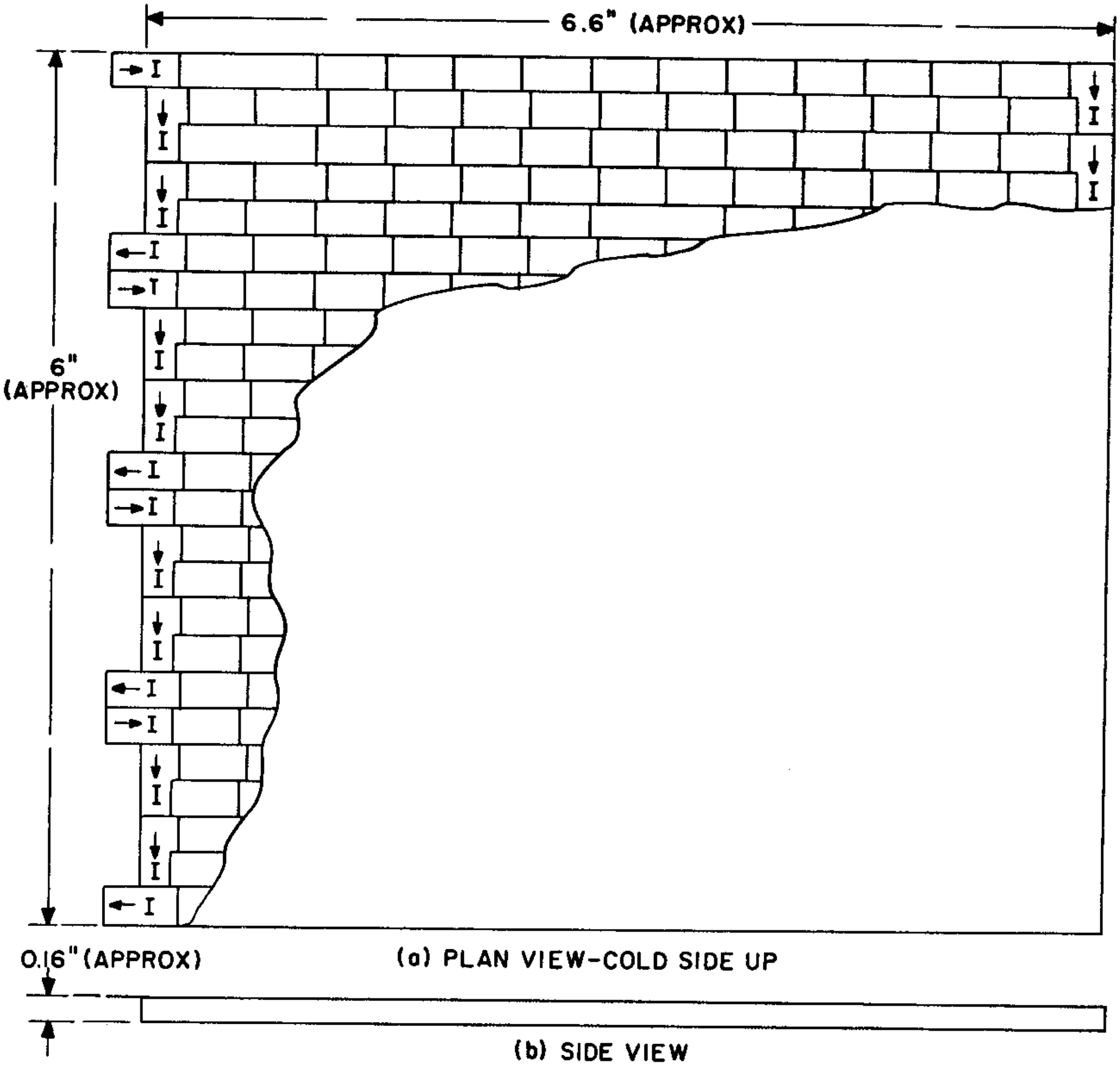


Figure 3: Sandwich-Type Model Thermoelectric Generators — Top and Side Views.

The entire structure should be fastened to a thin base plate of metal (approximately 0.002 inches thick) by means of a high temperature, electrically insulating "glue", and the complete generator can then be placed on any convenient source of heat having a flat surface.

Subject to the qualifications previously stated, various preliminary performance estimates are given in Table 1. It should be noted that the design efficiency of approximately 2.5% is rather arbitrary and was selected as follows:

It appeared (at the time the selection was made) that the possibilities of obtaining heat sources weighing on the order of 1 or 2 lb/kw of thermal output would not be too unreasonable. For such a heat source and for this design, an efficiency in the vicinity of 2 or 3% results in the minimum combined weight of generator and heat source.

TABLE 1 - PERFORMANCE ESTIMATE - SANDWICH TYPE MODEL GENERATOR

Overall thermal efficiency	2.5% 1)
Power output	5.7 watt 2)
Total generator weight (exclusive of heat source)	0.3 lb 3)
Number of circuits	4
Open circuit voltage	8.4 volt per circuit 33.6 volt maximum
Full load voltage	4.75 volt per circuit 19 volt maximum
Full load current	0.3 amp per circuit 1.2 amp maximum
Number of elements	84 pairs per circuit 336 pairs total
Hot junction temperature	1100°F
Cold junction temperature	710°F

Notes: 1) Actual efficiency would be somewhat less than this due to additional losses previously mentioned.

2) Actual power output would be somewhat less than this due to additional losses previously mentioned.

3) The weight of the thermoelectric materials plus insulation plus conductors is estimated to be about 36 lb/kw (See Figure K 5, Part III). An allowance of approximately 16 lb/kw has been made for additional items such as high temperature "glue", various coatings, base plate, etc.

Construction of a model generator of the type described above requires the solution of a number of fabrication problems. These problems are listed and briefly described below.

1. Diffusion Barrier - This problem involves the determination of the kind and thickness of material that must be interposed between the lead telluride elements and the hot and cold conductors in order to prevent harmful diffusion of the conductor materials into the lead telluride.

2. Junction Formation - The problem here is to find a technique for depositing, on the lead telluride, the diffusion barrier material that is to be interposed between the thermoelectric elements and the conductors.

3. Sublimation and Oxidation - This problem is concerned with the provision of a suitable coating for protection of the lead telluride elements against sublimation and oxidation at the temperatures and in the atmospheres specified.

4. High Temperature "Glue" - A method of fastening the basic converter assembly (consisting of thermoelectric elements, thermal insulation, and hot and cold side conductors) to a base plate (structural member) without the use of mechanical fasteners (bolts, rivets, etc.) is required.

5. High Emissivity Coating - The problem here is to produce a surface on the cold conductors (radiator) which has a high thermal emissivity.

6. Conductor Joining - This problem is concerned with the development of a technique for fastening the hot and cold side conductors to the thermoelectric elements (via the diffusion barrier material) and to the thermal insulation.

7. Materials Fabrication - The problem here is the formation of the thermoelectric materials into elements of the size and shape required by this design. These elements are small, rectangular wafers approximately 0.25 inches by 0.15 inches by 0.010 inches (n-type) and 0.017 inches (p-type) in thickness.

The work performed in attempts to provide solutions to these problems is described in the material appearing under the heading, FABRICATION PROBLEMS.

SIDE FIN - SANDWICH TYPE

The side fin - sandwich type of configuration is best introduced by first discussing the side fin type. It may then be seen that the side fin - sandwich type is the rather natural result of the combination of the side fin and the sandwich types. Both the side fin and the side fin - sandwich configurations are discussed in some detail in Appendix N, Part III.

The side fin type of construction is one in which the heat discharged on the cold side is conducted to fins extending outward from the thermoelectric elements and is then rejected to space by thermal radiation. An example of the side fin configuration is shown in part (a), Figure 4. Here the generator elements are placed around tube in the form of segmented annular discs or wafers. The internal tube contains the heat source. In the axial direction, these discs are stacked one against another with adjacent discs consisting alternately of n and p-type thermoelectric material. The axial separation between each disc is just sufficient to provide for a thin layer of electrical insulation. Cylindrical rings on the inner and outer radii of the discs are connected in the proper order to function as current carrying conductors. The direction of current flow is thus radially outward in one disc, then axial, then radially inward through the next disc, then axial, and so on. On the cold side, radiating fins (side fins) extend out on either side of the tube in order to reject the waste heat. Appropriate electrical insulation is required at the inner and outer radii.

Alternative methods of construction that may simplify the manufacture of the thermoelectric elements are shown in parts (b) and (c) of Figure 4. Four elements of either circular or square cross section can be assembled like spokes of a wheel as indicated in part (b) of the figure. To simplify the manufacture of the elements, the inner tube might be made rectangular and flat surfaces might be provided on the outer ring. The space in the corners between the elements can be filled with thermal insulation to decrease heat leakage or low emissivity coatings might be applied to the inside surfaces. Part (c) of Figure 4 shows a similar arrangement using two elements instead of four, and it is apparent that any number, consistent with the relative sizes of elements and tubes, might be used.

In the side fin configuration the axial spacing between adjacent thermoelectric elements is very small, being just large enough to accommodate electrical insulation. Actually, the principle used in the sandwich type construction to obtain increased radiator area could be used here by increasing the axial spacing between the thermoelectric elements and filling the resulting gap with thermal insulation. This combination is the side fin - sandwich type.

Either the side fin or side fin - sandwich type is ideally suited to the case where the source of heat is a circulating hot fluid such as might be obtainable from a reactor heat source. This type of configuration is also well adapted to a radioisotope heat source or a solar source utilizing a cavity focus type collector.

The structural rigidity of a cylindrical configuration makes possible the use of pressure contact junctions with either the side fin or the side fin - sandwich type of construction. However, bonded junctions are still to be preferred if the techniques for fabricating them are available.

The concepts utilized in the design of the model generator utilizing pressure contacts are basically those shown in parts (b) and (c), Figure 4. The design of this generator is described in the material found later in this report under the heading, <u>MODEL GENERATOR</u>.

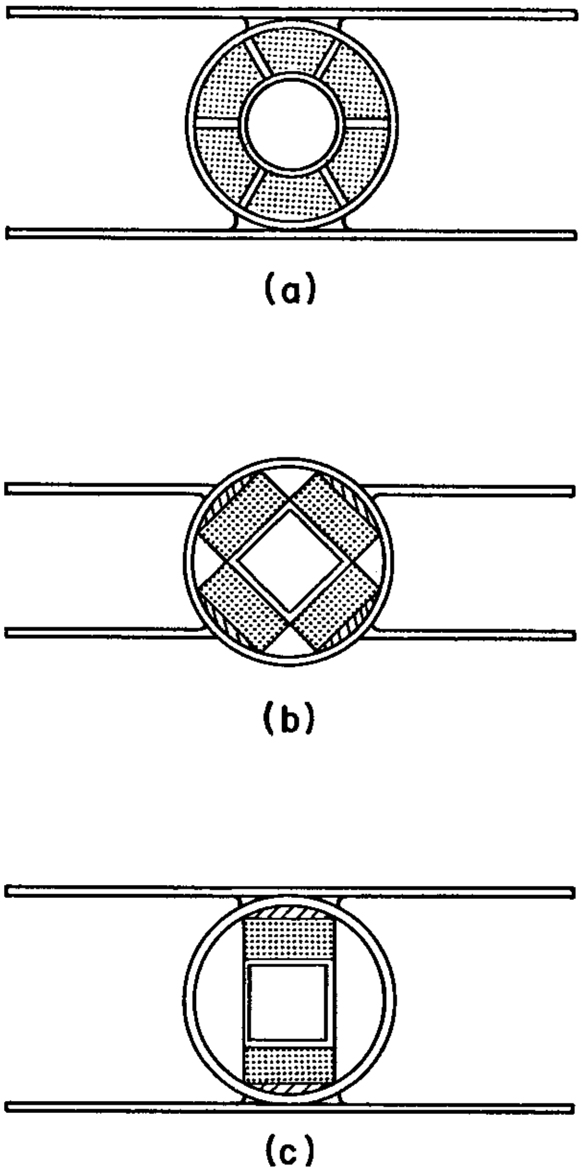


Figure 4: Typical Side Fin Type Configurations

MATERIALS SELECTION

The selection of thermoelectric materials for the generator design phase of the contract is the subject of this section.

No single property or combination of properties will serve to indicate categorically which thermoelectric material is best when weight is an important criterion of performance. However, all things considered, the Figure of Merit is probably still the material parameter having the largest single effect on performance. Also of particular importance in space applications, because of the necessity for high hot and cold junction temperatures, is the temperature at which the material displays a given Figure of Merit. The comparison of materials will, therefore, be made on the basis of Figure of Merit as a function of temperature.

In considering Figure of Merit as a function of temperature, it should be recognized that no single material exhibits the best performance over the entire range of temperatures presently obtainable, but for each different temperature range there is a material having a Figure of Merit higher than any other. Given adequate fabrication and design techniques, it is conceivable to construct an element, covering the complete temperature range obtainable, in which each material is utilized in the temperature span where it has the highest Figure of Merit. With this in mind, Figure 5 gives an indication of the maximum Figure of Merit obtainable at any given temperature using n-type thermoelectric materials having properties representative of the best materials for which data were available at the time the materials selection was made. This curve, then, represents the best Figure of Merit as a function of temperature that could be achieved by a composite element on the basis of data available in 1959. It should be noted in passing that this curve has been smoothed out to some extent; actual materials data gives a somewhat more bumpy appearance. Figure 6 is a similar plot representative of the best p-type materials available.

Also indicated on Figures 5 and 6 are the Figures of Merit(1) of the n- and p-type lead tellurides selected for the generator design phase of this contract on the basis of the best data available in 1959, the time of the selection. The n-type selected is doped with 0.1 mol. % PbI_2; the p-type with 1.0 at. % Na. These 1959 lead telluride data are based on an assumed temperature dependence of thermal conductivity. At the completion of the generator construction phase of the contract, more accurate lead telluride Figure of Merit values based on measured values of thermal conductivity became available(11). The Figure of Merit values for two n-type compositions and one p-type composition shown on Figures 5 and 6 and labeled 1960 data are based on the newer data. These values indicate that if a selection were to be made again, on the basis of the latest available data an n-type material doped with 0.055 mol. % PbI_2 is preferable to the 0.10 mol. % PbI_2 doping.

A further comment on Figures 5 and 6 is in order at this point. Although materials exist which can operate at temperatures greater than those shown, according to data available at the time of the materials selection their Figures of Merit are quite low. Therefore, the curves are not extended beyond about 1000 K.

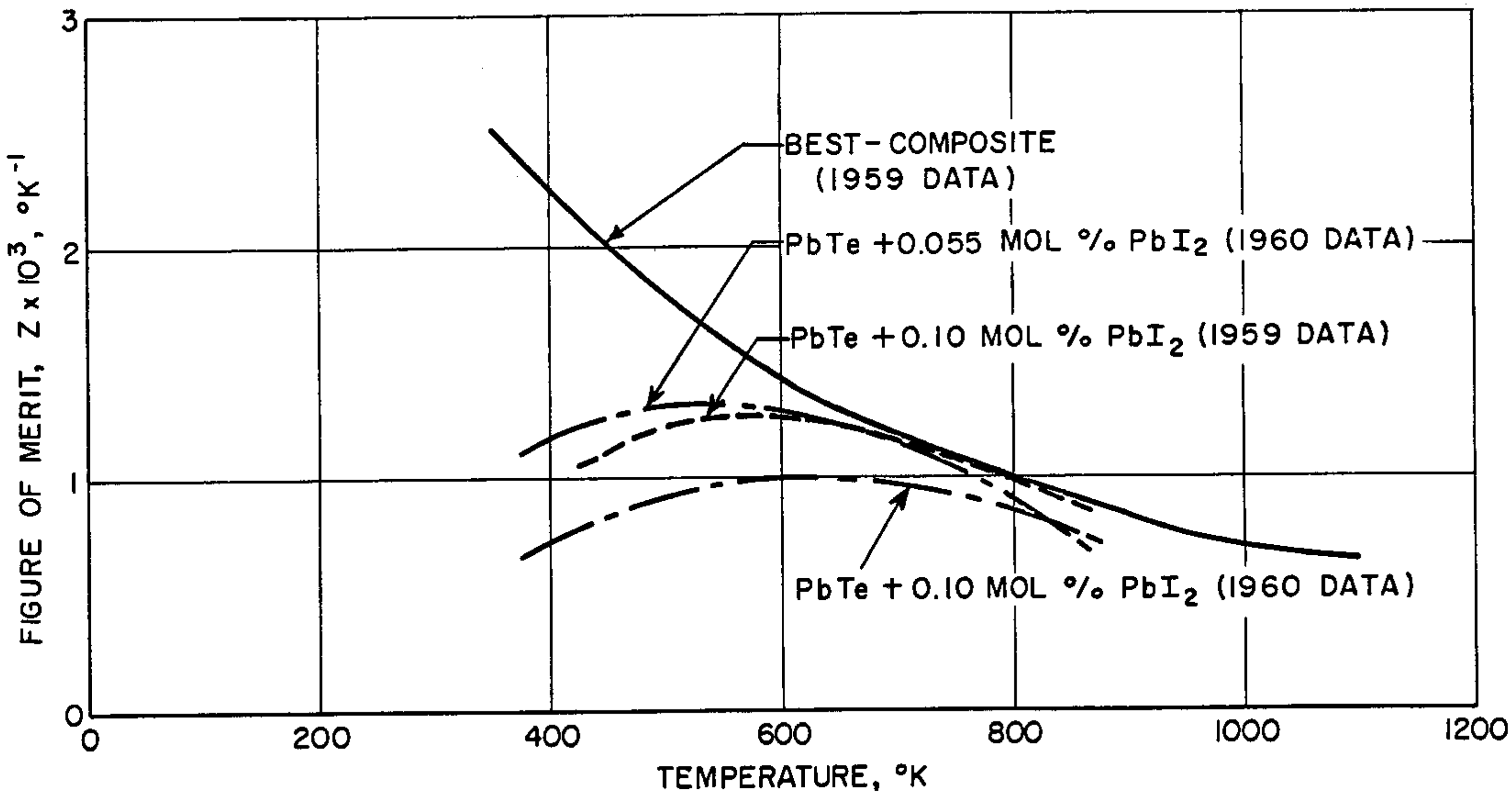


Figure 5: Comparison of Figure of Merit of Best Available Materials and Lead Telluride, n-Type.

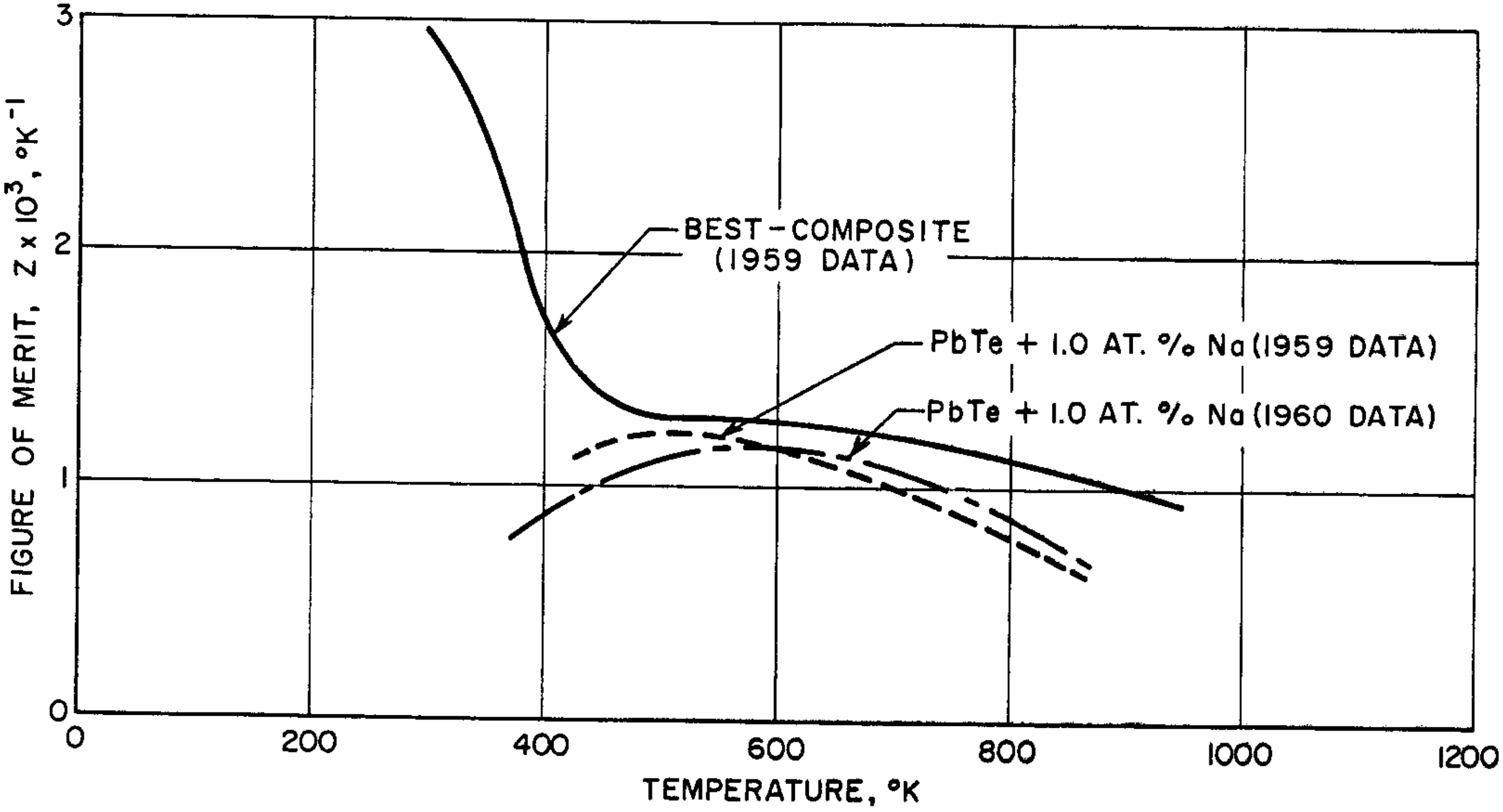


Figure 6: Comparison of Figure of Merit of Best Available Materials and Lead Telluride, p-Type.

At least two other factors in addition to thermoelectric properties should be considered in the selection of materials for generator design and construction work. These are the availability of the materials, or at least well-developed techniques for preparing them, and the degree to which the technology of their use has been developed. There are many aspects of the latter and their importance should not be underestimated because, as a class, high-performance thermoelectric materials are apt to be weak mechanically, difficult to work, and susceptible to degradation due to contamination.

On the basis of these considerations the n- and p-type lead tellurides mentioned above were selected for the following reasons:

a) They have average Figures of Merit as high or higher than any other single material within the range of temperatures (about 500 K up) of interest for space applications.

Segmented or composite elements of several materials or dopings are not, in the present state of development, believed to be practical for elements of the small sizes required in space applications. Hence, the selection of a single n-type and single p-type material was deemed necessary. Also, the fact that the curve for the best composite of n-type materials extends up to about 1100 K is, at present, rather academic because of the 950 K limitation on p-type materials. In general, it will be desirable if not necessary for the n-type and p-type elements to operate at the same hot junction temperature in light-weight generators which require small individual elements.

b) The materials selected are available in adequate quantities for experimental work as well as prototype construction from a reliable source.

c) The techniques for handling and utilizing the materials in operating devices are fairly well developed.

A number of different types of generators using these materials have been successfully built and operated. Lead telluride (n-type) has also been utilized in at least one commercially available device, the Baso pilot light shut-off valve.

FABRICATION PROBLEMS

DIFFUSION BARRIER

In order to maintain the thermoelectric properties of lead telluride it must be protected from materials that influence these properties. Unfortunately the materials normally considered best suited for conductors are not compatible with lead telluride. The following quotation from Reference (2) discusses the problem of selecting a suitable electrode material.

"In practice the necessity of using a chemically stable electrode material is the most difficult condition to satisfy. Chemical instability of the junction may take many forms:

a. The electrode material may alloy with the thermoelement in a eutectic reaction which lowers the melting point of the alloyed layer. The bonding of lead telluride to a copper base alloy is such an example:

	Melting point
Lead telluride	922°C
Copper	1083°C
Copper-lead telluride eutectic	500°C

b. The electrode material may diffuse into the thermoelement forming second phase highly conductive material which causes local short circuiting of the thermoelectric alloy.

c. The electrode material may react directly with the thermoelectric alloy to destroy its molecular form.

$$PbTe + Zn \longrightarrow ZnTe + Pb$$
$$PbTe + Cd \longrightarrow CdTe + Pb$$

To anticipate such reactions thermochemical data can be used to indicate relative stability. Where the reaction between the semiconductor and metal (or metals) of the electrode is characterized by a negative free energy change, (as given by the Gibbs-Helmholtz equation) the reaction tends to proceed with a release of energy so that the semiconductor is not stable with respect to the electrode. Where the free energy change for the reaction of the semi-conductor with electrode material is zero or positive the reaction will not proceed and the semiconductor may be considered to be stable in contact with the electrode material.

d. The electrode material may diffuse into the thermoelement where it may form donor or acceptor sites to alter the local carrier concentration.

e. The electrode material may dissolve a doping agent to effectively leach it out of the thermoelement. An example of this is the reaction observed between platinum and lead rich n-type lead telluride. At

> elevated temperatures due to the solubility of lead in platinum, the platinum electrode absorbs the excess lead from adjacent lead telluride.

"Before any material is used as an electrode, available phase diagrams and thermochemical data, already mentioned, should be consulted to ascertain what reactions or solutions may be encountered. While the above destructive processes should be considered as dangerous, it should be pointed out that many possible reactions might be avoided by operating the junction at sufficiently low temperatures to effectively arrest the rate at which the destructive interaction proceeds."

Thus it was established that, although silver or copper should be used as conductors for weight considerations, they were not suitable for direct contact with PbTe at the design temperatures. An electrode material that would serve as a diffusion barrier between the conductors and the PbTe is required. Iron or low carbon steel are recommended (2) (3) as suitable barrier materials by the lead telluride vendor. The thickness of iron required was estimated as described below.

Using Einstein's diffusion equation, a calculation was made to determine the thickness of iron required to prevent any conductor atoms from reaching the lead telluride during the period of one year. No data were available on the diffusion rates of silver or copper into iron but it was possible to set an upper and lower limit for the silver diffusion coefficient. A survey of diffusion of metals (4)(5) in iron suggests that aluminum has a high diffusion rate and that silver would probably be slower. Further, since self-diffusion is usually the slowest type of diffusion it was assumed that silver will diffuse into iron faster than it will diffuse into itself. These two diffusion rates are expected to bracket the actual case. Calculations made on the basis of the above assumptions indicated that the diffusion barrier should be between 3 and 10 mils thick to prevent silver atoms from reaching the lead telluride for one year.

A calculation was then made to determine how long it would take for enough silver atoms to diffuse through this barrier to influence the properties of lead telluride. From the data available(6) on the influence of silver on the thermoelectric properties of lead telluride it was conservatively estimated that lead telluride could tolerate 7×10^{18} atoms/cm^3 of silver. On this basis it was estimated that it would take several months after the first atoms of silver have diffused through the iron to reach this level of doping.

The above estimates are believed to be conservative, so 5 mils was selected as a reasonable thickness for the diffusion barrier.

JUNCTION FORMATION

The necessity for a diffusion barrier poses the problem, in bonded contact construction, of depositing a non-porous layer of iron of adequate thickness on the ends of the thermoelements. The bond between the iron and the lead telluride must be mechanically sound and provide adequate electrical and thermal conductances. Efforts to develop a technique for effecting such a deposit of iron on p- and n-type lead telluride are described below.

Nickel was also believed to have promise as a diffusion barrier so experiments were conducted to evaluate this possibility. This work is also described in the material that follows.

Electrodeposition - Iron

The first attempt at applying the iron diffusion barrier was by conventional electroplating techniques. Samples of both the p-and n-type lead telluride were tested. These samples were in the shape of rods 0.25 inches in diameter. It was desired to plate the end of the rod, an area of 0.049 square inches, with no more than 0.010 inch overlap on the cylindrical side wall of the rod.

It was discovered very early in the investigation that conventional iron plating baths were, in general, far too acid (p H 1.0 to 2.0) for the lead telluride. These baths set up what appeared to be a galvanic cell in the system which tended to dissolve the telluride from under the iron leaving a very poorly adherent plate. A bath of iron sulfate and potassium sulfate with a pH of 5.0 to 5.5 was used with far better results. The adherence of the samples plated with this bath was, although far better, still not good. The plate could be picked off with a razor blade with a fairly clean separation of the plate from the sample.

At this point it was decided that nickel could be used as a flash to protect the telluride from the iron bath. Several samples of both types were plated with a standard nickel chloride-nickel sulfate (Watts) plating bath with slightly more success than the iron. It was found that the surface of the lead telluride was filled with holes (see Figure 7) which could not be rinsed out well or plated all the way down. These holes, while full of plating solution, were being covered by the plate which gave rise to many small galvanic cells between the lead telluride and the plate.

The next step was to fill the holes with electroless nickel which would deposit wherever the solution would flow. This was done by placing the sample in a bell jar with the electroless nickel solution on top and drawing a vacuum until all of the air in the holes was replaced with plating solution. The sample was then plated in the usual way with nickel and then with iron. The plates were far more adherent but when they did separate from the telluride the telluride split. Figures 8 and 9 show the plate or cap and the end of the rod from which it was separated. The smooth areas are the plate and the rough reflective areas are the lead telluride.

These pictures show that the bond between the plate and the lead telluride is, in more than half of the area, stronger than the lead telluride itself. This was found to be true of both the p-type and the n-type. However, in general, the p-type was worse than the n-type.

Because these results did not appear promising it was decided to investigate other methods of depositing iron on the lead telluride.

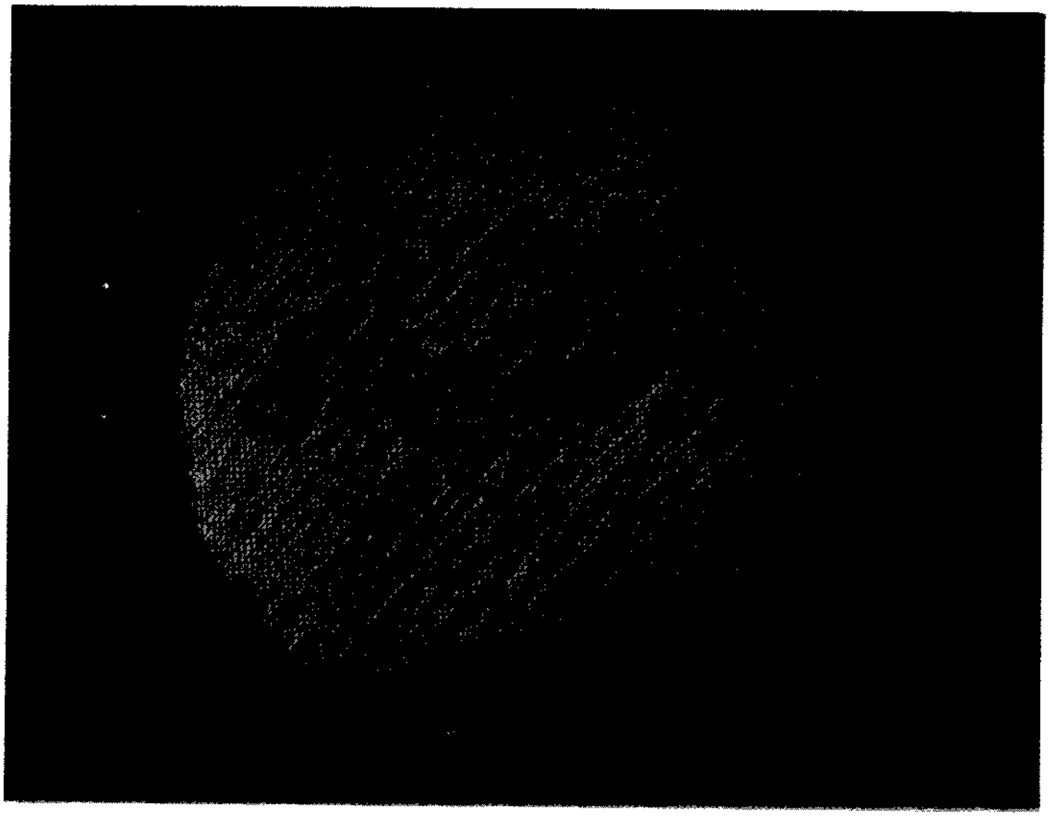


Figure 7: Surface of Lead Telluride Sample.

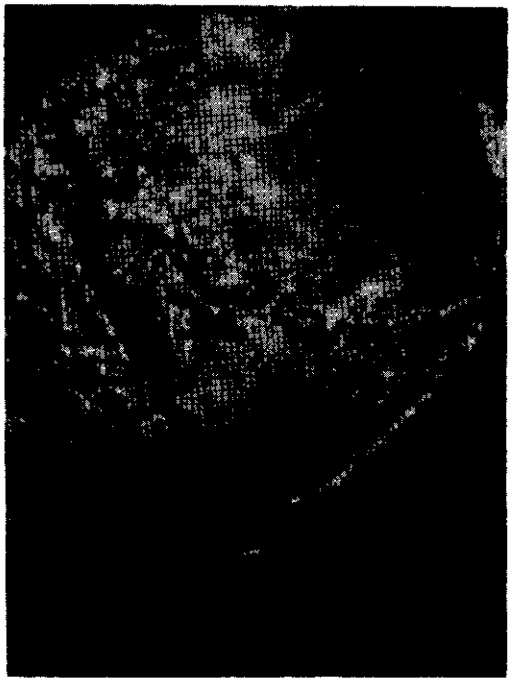


Figure 8: Plate or Cap.

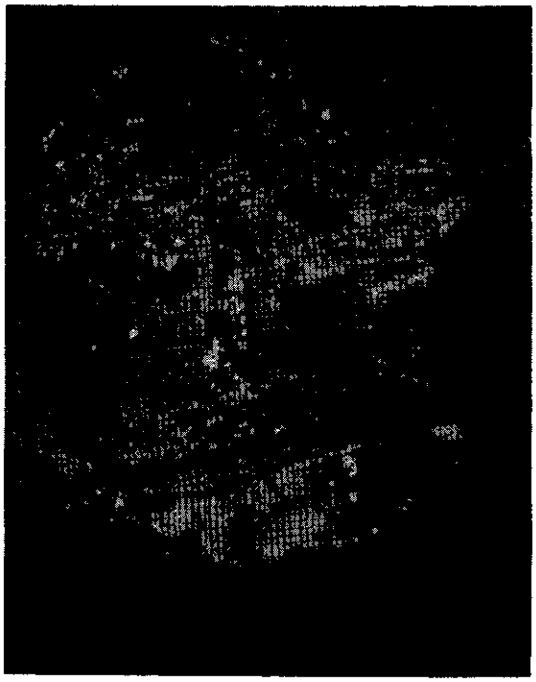


Figure 9: End of Lead Telluride Rod.

Electrodeposition - Nickel

The purpose of this experiment was to investigate the use of a layer of electrodeposited nickel as a diffusion junction barrier between the lead telluride thermoelement and the bonding agent used in the joint.

Although nickel had served well as a preparatory layer for bismuth telluride junctions, the extrapolation of its use to lead telluride operating in the neighborhood of 1100°F was unwarranted without experimental evidence. The concept of a nickel layer interposed between the bonding agent and the thermoelement has at least three aspects:

1. It must alloy in some degree with the solder or braze material to form a mechanically sound joint with adequate electrical and thermal conductances.

2. It must serve as a diffusion barrier against possible contamination by the solder at operating temperature.

3. It must be inert as far as the lead telluride is concerned and not itself contaminate the thermoelement.

It seemed most logical to investigate the third aspect first, since nickel's use as a successful barrier was dependent on its passing this chemical requirement which may be outlined as follows:

a. It must not diffuse into the lead telluride to form second-phase conductive material causing local short-circuiting of the element, or where it may form donor or acceptor sites to alter the local carrier concentration.

b. It must not alloy with the lead telluride in an eutectic reaction or react directly with lead telluride to destroy its molecular form.

c. It must not dissolve a doping agent to effectively destroy the thermoelectric properties of the material.

Contamination by these methods can most quickly be determined by exposure of the joint to operating temperatures for long periods in an inert atmosphere, and then comparing the Seebeck coefficient and resistance measurement with controls, or measurements taken before exposure.

Consequently, a program for determining the degree of contamination of lead telluride by an electrodeposited layer of nickel was proposed as follows:

1. Nickel plate each end of two 1/4" dia cylinders of PbTe (one n-type and one p-type) to a thickness of not less than 2 mils.

2. Polish each nickel-plated surface flat and smooth.

3. Soft solder (60 tin-40 lead) 1/2" long copper cylinders to each end of the PbTe pieces.

4. At room temperature measure the resistance and Seebeck coefficient and resistivity of the PbTe itself.

5. Remove copper cylinders and clean off all vestiges of solder from nickel plated surfaces.

6. Soak the nickel-plated PbTe cylinders in an environment of dehydrated argon at 1200^{o}F, atmospheric pressure, for 24 hours.

7. For use as a possible future control, soak two unplated PbTe cylinders (one n-type and one p-type) in the same environment for the same length of time.

8. Return samples to room temperature.

9. Resolder copper cylinder to each end of PbTe nickel-plated samples.

10. Repeat original Seebeck coefficient and resistance measurements.

A Watts bath was employed as a solution for electrodeposition of the nickel. The lead telluride specimen was prepared for plating by polishing the ends with emery paper and finishing with 4/0 polishing paper. The etching solution first used was identical to that used to etch bismuth telluride: 1 part HNO_3, 1 part HCl and 2 parts H_2O. A series of disappointing results with the subsequent plating process seemed to indicate a reappraisal of the etching solution. A whole series was tried with indications pointing to the fact that HCl was not only unnecessary, but actually detrimental to the etching process on lead telluride. The elimination of this acid led finally to the selection of an optimum ratio of HNO_3 to water of one to one. The plating process now consisted of a two-minute etch with the etchant at 50^{o}C followed by a distilled water wash and rinse, from which the specimen was transferred to the 50^{o}C plating solution without exposure to air. The results of this procedure varied widely throughout the experimentation. However, by control of such variables as time of etching, pH of the plating solution, current density, and time of plating fairly consistent results were usually obtained.

Microscopic inspection of the plated surfaces revealed a number of holes which in some cases extended down to the lead telluride. The porosity was a situation which could not be countenanced if the nickel was to serve as a reliable barrier over an extended period of time. Repeated attempts to obtain a non-porous surface from the bath finally led to the belief that the electroplating solution was principally at fault. As a corrective measure, a sulphamate plating solution was substituted with some success. Non-porous surfaces were then obtained quite consistently.

Obtaining a well-plated specimen of both p- and n-types, the nickel surfaces were polished smooth with 4/0 paper. This precaution was necessary so that subsequent removal of the solder could be done with assurance that solder would not remain trapped in the rough indentations of the nickel to introduce an unknown variable into the experiment. These polished surfaces were tinned with 60/40 tin lead solder and soldered to a cylinder of copper of exactly the same diameter.

Since the resistivity of the lead telluride was to be determined by profiling the thermoelement across the junction onto the copper, the excess nickel plating which inherently plates around the cylindrical edge of the specimen had to be removed. This lip of plating adheres partly to the rough surface of the lead telluride by mechanical bonding to the indentations of the surface, and hence, if not removed, could give a false picture of the tenacity of the plating bond. However, after grinding down the specimen for profiling, the plating adherence would then have to represent an alloying bond since each successful joint was subjected to an axial tensile stress of at least 250 pounds per square inch.

Two samples of successful junction assemblies ground to a constant diameter were obtained, one n-type and one p-type. The Seebeck coefficient was measured at room temperature at a temperature difference of 5^{o}C and found to fall around the nominal value for each type.

The next measurement was a resistance profile of the lead telluride sample across the junction into the copper cylinder. Although the purpose of this procedure was principally to measure the resistivity of the lead telluride, it was gratifying to observe that the interface resistance between nickel and lead telluride was so low. For two n-type junctions, it gave readings close to 1×10^{-6} ohm-cm^{2} and for a p-type, $7\text{-}8 \times 10^{-6}$ ohm-cm^{2}; Figure 10 and 11. These side results gave evidence that properly prepared nickel plating gives a low-resistance, mechanically sound joint.

In preparation for the temperature soaking experiment, the copper cylinders were removed from specimens and the vestiges of solder cleaned off the nickel. The n-type sample was enclosed in a vicor tube along with a control cylinder of lead telluride which had not been nickel-plated. "Dry, oxygen-free argon" was connected to the tube so that it renewed the gas in the tube about once every 1/2 hour. This initial experiment was continued for 24 hours at 1200^{o}F.

The results are pictured in Figure 12, with the vicor tube sawed in half longitudinally. The sublimation of the lead telluride and the oxidation of the nickel were masked by the reaction with the vicor tube. Figure 13 shows the nickel-plated couple, left, and control specimen removed from the tube. Even in sections of the periphery not reacting with the tube there has been a considerable shrinking of the diameter. The nickel surface has either combined with the tellurium or oxidized. Figure 14 shows the end views of the nickel-plated sample, left, and the control specimen.

Assuming that the oxidation had been aggravated by the presence of moisture in the argon, a drying apparatus was set up. With this set up established, another 24 hour exposure to 1200^{o}F was tried on the remaining plated specimen. To prevent reaction with the vicor tube, the plated sample and its unplated control were placed in a ceramic boat within the vicor tube. This time with apparently water free dry argon, the results were substantially the same as in the first run.

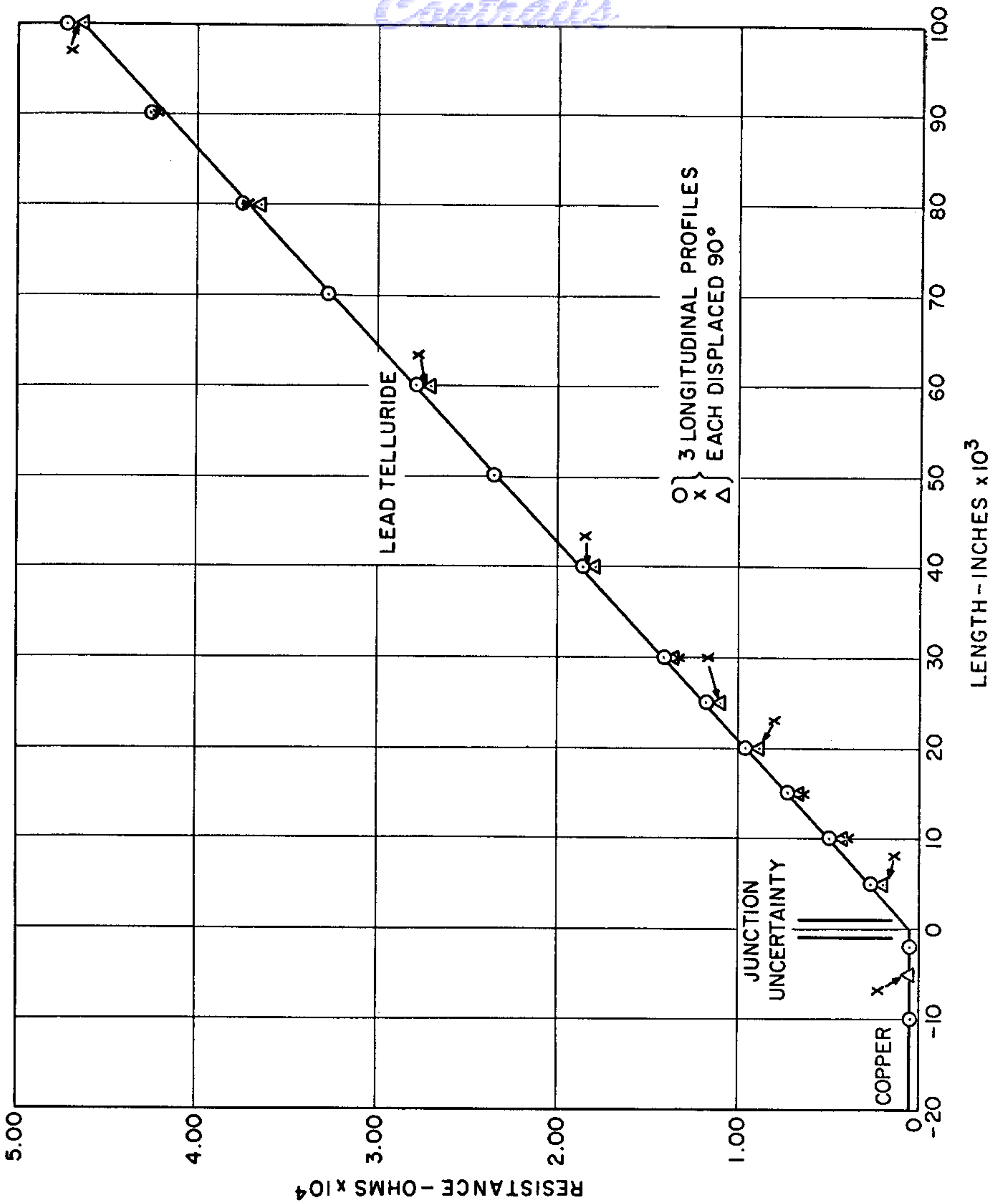


Figure 10: Resistance Profile of n-Type PbTe-Ni-60/40 Tin/Lead - Cu Junction.

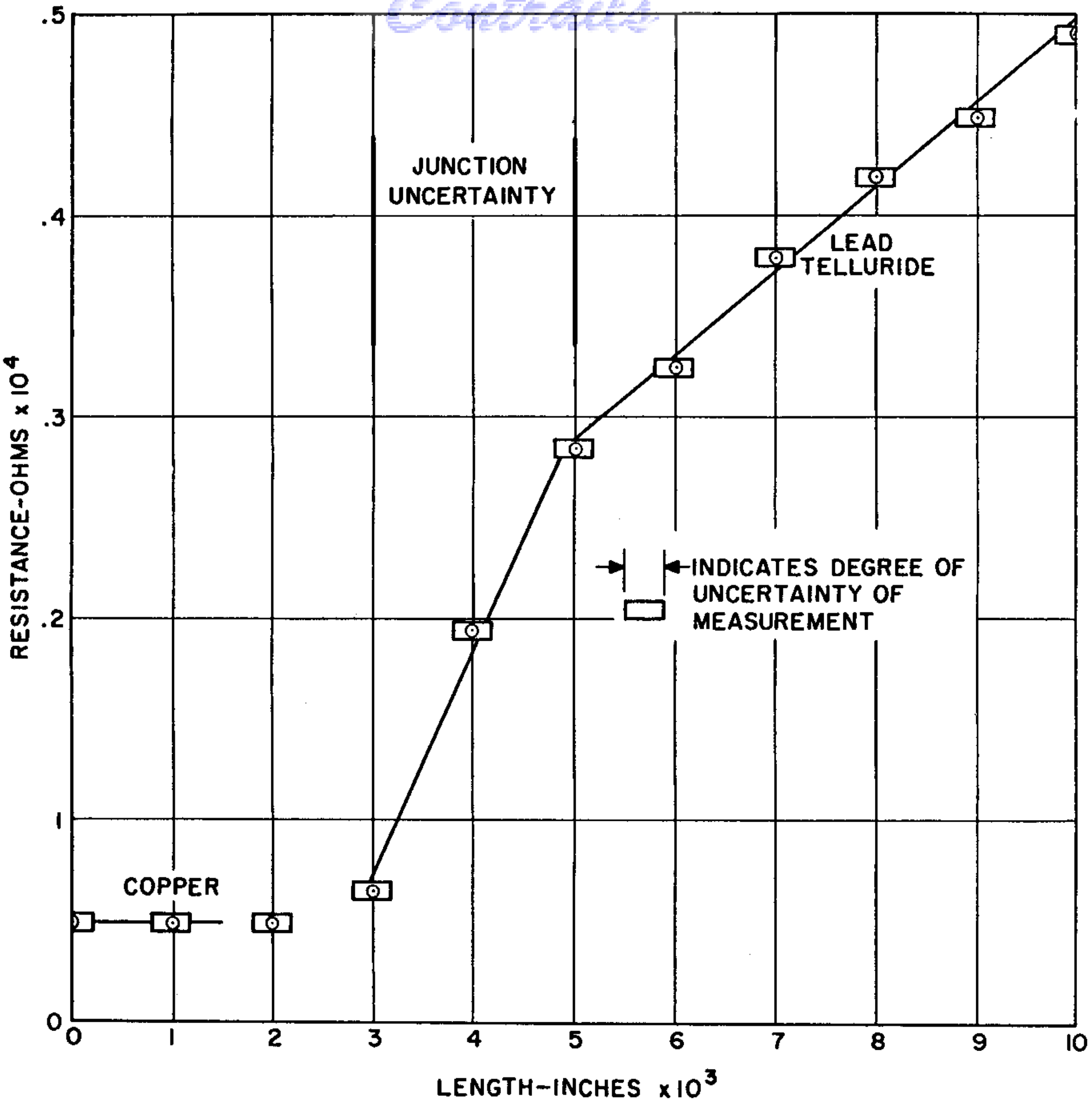


Figure 11: Resistance Profile of p-Type PbTe-Ni-60/40 Tin/Lead - Cu Junction.

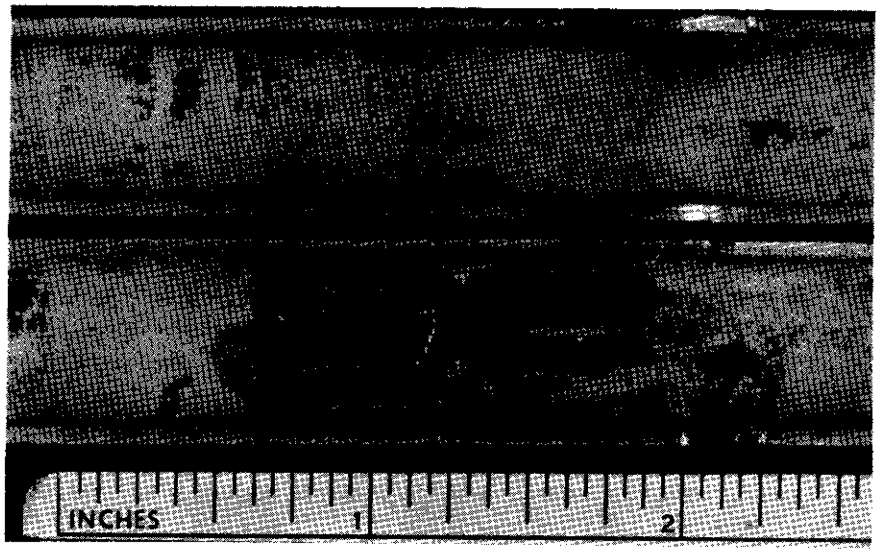


Figure 12: Vicor Tube Opened to Show Nickel-Plated PbTe Cylinder, Left, and Unplated PbTe Control After 24-Hour Soak at 1200 F.

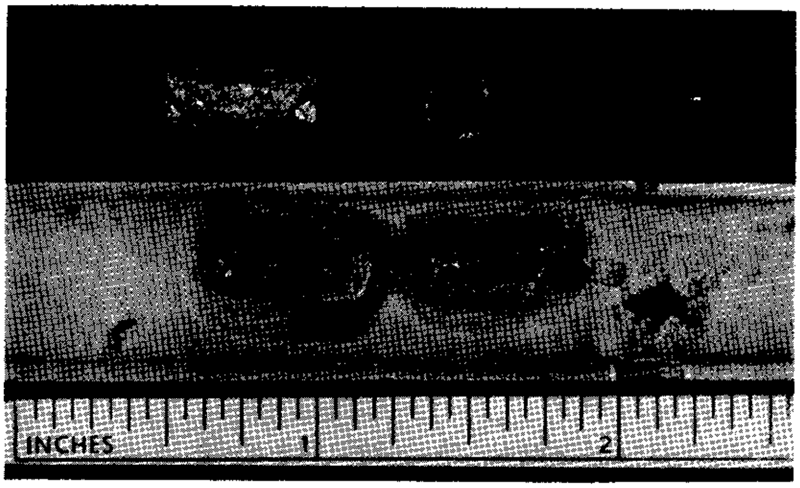


Figure 13: Nickel-Plated PbTe Specimen, Left, and Control Removed from Vicor Tube Showing Reaction of PbTe with Vicor.

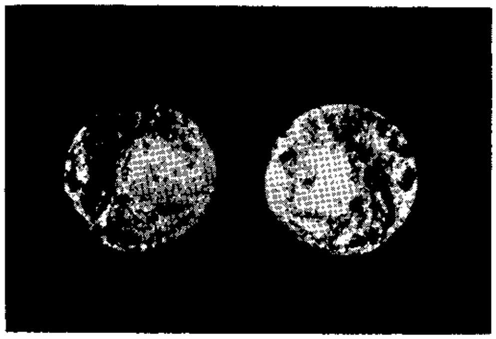


Figure 14: End Views of Nickel-Plated PbTe Specimen, Left, and Control Sample.

In appearance the plated specimen seemed to have survived the exposure. Some sublimation had occurred as indicated by the reduction in diameter, but the plated ends retained the appearance of the original nickel plate with some darkening in color. However, when an attempt was made to re-tin the apparently plated end of the lead telluride, the surface refused to wet, indicating that the nickel surface had been reduced in thickness beyond the minimum for tinning or it had alloyed with the telluride.

A final attempt was made to isolate the specimen from the contaminants in the argon atmosphere. It was coated with Eccoceram, a ceramic coating which was being investigated for protection of PbTe generating elements operated in air. After a 24 hour exposure, the observed results were even more disappointing than before. Evidently, the lead telluride, as well as nickel, had reacted with the coating compound and necked down the middle region of the specimen excessively, while the ceramic had accelerated oxidation of the plated ends. This brief excursion into ceramic-coated thermoelements was not at all conclusive; the careful pursuit of such a program could well produce successful results.

At this point, in the experiment, the results pointed to the use of too high a temperature. Discussion with those familiar with the characteristics of lead telluride helped confirm this conjecture.

It is felt that the nickel surface has a good chance of surviving a lower-temperature soaking period, perhaps in the 800-900°F region. Further experiments with a carefully prepared oxygen- and water-free argon atmosphere should be conducted to confirm this assumption. At these temperatures, the predictions point to nickel as a diffusion barrier which will at least be inert relative to the lead telluride thermoelement.

Vacuum Deposition

Several attempts were made to deposit iron on lead telluride by a vacuum deposit technique. In this process the iron is heated in vacuum so that it evaporates and then condenses on the colder lead telluride.

A thin film of iron was successfully deposited by vacuum deposition, but efforts to build up the thickness of this film by electrodeposition were not successful. The behavior of the sample during this latter process indicated that the vacuum-deposited film was quite porous. Because of these results, coupled with the fact that vacuum deposition is not capable of obtaining films of the thickness needed, except by using a second process to build up the film thickness, this investigation was discontinued.

Diffusion Bonding

This technique consisted of attempting to bond the lead telluride to the iron by actually welding them under the proper conditions. Through the application of adequate pressure at the proper temperature it is possible to form a bond between most metals that is quite strong.

Samples of p- and n-type lead telluride, 1/4 of an inch in diameter, were compressed against a 5 mil iron sheet in hydrogen at various temperatures and pressures to see if this bonding technique could be applied to lead telluride. These attempts were made in a hydrogen bell jar using simultaneous application of heat and pressure. Bonding times ranged from 3 to 30 minutes, pressures from 100 to 800 psi, and the temperature was near the melting point. Pressures above 300 psi caused noticeable deformation in the hot portion of the sample. Evaporation in the hot zone was noticeable at all times. Some n-type samples were sufficiently well bonded to give contact resistances in the range between 14 and 25 x 10^{-6} ohm-cm^2, and two samples tested in tension failed outside the bond. However, no p-type samples were bonded in a manner that would permit the handling necessary for electrical and mechanical testing. Mechanical strength was simply too low. Metallographic samples of p-type joints showed intimate contact with no visible diffused region. Neither could a diffused region be seen in the n-type samples. Some samples of p-type material, after having been soldered to the copper bar which is necessary for testing junction resistance, show a fractured region beneath the surface. This technique did not appear to be adaptable for bonding the thin elements to iron; therefore, this work was discontinued.

Flame Spray

The flame spraying technique consists of passing a wire of the material to be sprayed through an oxygen-acetylene flame which melts this material and then impinges it on the surface to be coated. The sample being coated can get reasonably hot (300° to 400°C) if a heavy coating is to be applied.

It was possible to apply iron to the n-type lead telluride using this technique. The bond strength obtained was apparently adequate and the electrical resistance of the junction was approximately 10 x 10^{-6} ohm-cm^2, an acceptable value. All attempts, using conventional flame spraying techniques to deposit iron on the p-type were unsuccessful. Adherent coatings could not be obtained because of cracking of the PbTe immediately below the iron. This was apparently due to thermal shock which the brittle p-type material could not withstand, even with pre-heated samples. Samples of the p-type were sent to the Linde Company, Indianapolis, Indiana for the purpose of applying the diffusion barrier using their Flame Plating process. A coating of low carbon steel about 5 mils thick with a rough surface finish was obtained. This surface finish is not expected to be a problem since a thicker coating could have been applied and then machined to dimensions. However, there is some doubt whether this coating of itself would serve as an effective diffusion barrier for long periods of time because it may be slightly porous.

Although this method appeared to have potential merit the junction resistance and the bond strength of the p-type sample were not evaluated because the decision was made to go to the pressure contact design.

Iron Carbonyl

Thermal decomposition of the carbonyls is a method of obtaining films of certain metals including iron. The method for depositing iron is discussed briefly in Reference (7). The compound used for iron deposition is the pentacarbonyl $Fe(CO)5$; a liquid with a boiling point = 102.8°C, freezing point = 21°C, and a vapor pressure at 30°C = 40 mm Hg. Suitable precautions must be observed in its use since it is extremely poisonous, as well as flammable.

An apparatus was assembled in which the sample could be heated to a desired temperature in a bell jar containing pure argon. The purified argon entered the bell jar through an 1/8" diameter orifice directed onto the sample surface. By passing part of the argon stream through a flask containing liquid iron carbonyl, iron carbonyl vapor was transported to the sample surface. Flowmeters were used to meter both the main argon stream and the argon used to carry the iron carbonyl. PbTe in the form of 1/4" x 1/4" x 0.020" wafers was heated on a 1/4" thick piece of iron directly over the bead of a thermocouple located in a well drilled in the iron; 1/4" diameter PbTe cylinders were heated in a 5/8" thick piece of steel with the thermocouple bead in a well very close to the surface to be coated. The argon was purified by passing it first through an 18" bed of desiccant and then through a bed of zirconium chips at 750°C.

An operating cycle consisted of evacuating the bell jar, back-filling with purified argon to atmospheric pressure, and then continuing the argon flow as the heater brought the sample up to the desired temperature. Iron deposition was then started by passing argon through the iron carbonyl reservoir. When the desired deposition was attained, argon flow through the carbonyl reservoir was stopped, but the main flow was continued while the sample cooled.

The quality of the iron deposits was judged almost entirely by their appearance under the microscope. Metallic films were obtained above 625°C with argon flowing at 145 cc/min; assuming that the argon diverted through the iron carbonyl reservoir (3.5 cc/min) was saturated with iron carbonyl vapor, iron was introduced into the bell jar at the rate of 0.00034 grams per minute. This corresponds to a deposition rate of 0.001 inches per hour on a 1/4" diameter area, assuming that the density of the deposit is 7.9 grams per cm^3.

At temperatures below 600°C, deposits consisted of agglomerates of tiny iron spheres and to the naked eye looked like soot. When the total argon flow rate was much lower than about 120 cc/min, the iron carbonyl decomposed before impinging on the sample and settled as sooty clumps throughout the bell jar. Gas-borne clumps of iron also formed when the concentration of iron carbonyl was too high. Under the conditions described in the preceding paragraph, however, adherent metallic deposits were produced.

Such deposits were produced first on pieces of copper, used instead of PbTe during preliminary experiments. Under the same conditions, however, deposits on wafers of p-type PbTe were spoiled by dendritic aggregates of small iron cubes which grew perpendicular to the sample surface as deposition proceeded. New growths appeared when deposition was repeated on surfaces polished to remove the dendrites formed in a previous run. Although the problem was much less severe on cylinders of p-type PbTe, no way of eliminating it was found.

After preparing two samples to be tested for solderability and solder-joint strength, experimental work was terminated since results were not sufficiently promising for immediate application.

SUBLIMATION AND OXIDATION

Due to oxidation, lead telluride when heated in air, turns blue-grey at the melting point of lead (328°C). At higher temperatures lead oxide diffuses through the material replacing either the excess lead or the excess tellerium. The electrical properties deteriorate and the material's effectivesness as a thermoelectric element is destroyed. Lead oxidizes slowly at room temperature but this presents no serious problem and the oxide coating formed is readily removed either mechanically or by heating in a reducing atmosphere.

Sublimation of lead telluride becomes significant at 1000°F and may limit the service life of generators operated at 1100°F. The damaging effect of sublimation is the reduction of element size in the vicinity of the hot junction. The exact rate of material loss through sublimation is a function of the geometry of the generator and the temperatures of the surfaces in close proximity to the hot end of the thermoelectric elements. The only information that could be found on the vapor pressure of lead telluride was that n-type lead telluride has a calculated vapor pressure of approximately 7×10^{-4} mmHg at 600°C (8). The vapor pressure of p-type lead telluride (excess Te) is not known at 600°C, but elemental tellurium has a vapor pressure of approximately 7 mmHg at 600°C.

Current generators using lead telluride elements are protected against oxidation by operating them in neutral or slightly reducing atmospheres. Atmospheres of argon with a trace of methane have been used successfully. In generators built to date sublimation is blocked by encasing the elements in close-fitting mica sleeves of about 10 mil wall thickness.

One of the major criteria in selecting a protective coating must be its compatibility with the thermoelectric element. Many materials will damage lead telluride elements in some fashion, particularly at elevated temperatures. It has been reported (Part II, Appendix L) that encapsulation in alumina, forsterite or quartz has no adverse effects on lead telluride at elevated temperatures. However, the capsule walls described are too thick to be suitable for a low weight generator of this design.

In addition to supplying the required protection, the coating must meet the following specifications:

1. The weight of the applied coating should be equal to or less than 3.5×10^{-5} lb/cm^2 of covered area. This increases the weight of this design about 2 lb/kw of net power output.

2. The product of the thermal conductivity and the coating thickness should be equal to or less than 4×10^{-6} in.-watt/cm-K for an increase of about 2% in the heat absorbed by the generator.

3. The electrical resistivity divided by the coating thickness should be equal to or greater than 28 ohm. Then the resistance of the film will be equal to or greater than 100 times the resistance of the elements.

The first coatings that were tried, because of their ability to provide a tough impermeable coating, were:

1. Glassy coatings, such as the vitreous enamels generally used in the protection and/or decoration of metals;
2. Vitrified coatings, composed primarily of crystalline material bonded and sealed by an interstitial glass phase.

Since both of these coatings remain highly porous until they are matured (that is, those temperatures are reached when the glass softens sufficiently to form a continuous film, or interaction between particles produces a liquid phase) the firing must be done in an oxygen-free atmosphere and at temperatures below those causing excessive sublimation of the lead telluride substrate. Totally crystalline coatings may be formed in such a manner as to meet the requirement of impermeability. These may be divided into two classes:

1. coatings recrystallized from the melt of a definite compound;
2. cement-type coatings in which the pores have been filled with micro-crystals.

The first of these requires firing to the melting temperature of the compound in order to produce impermeability, hence the same precautions must be taken to prevent damaging the lead telluride substrate as are required when applying a glass coating. In the case of cement-type coatings, the bond between crystalline particles is formed at relatively low temperatures and interstitial pores may then be filled by repeated treatment with a liquid from which micro-crystals are deposited until the coating becomes impermeable.

A few exploratory experiments were performed to test the feasibility of employing the coatings on lead telluride that require high temperature firing to produce an impermeable protective surface. A vitreous enamel composition designed for use on aluminum (600°C maturing temp.) was selected as representative of the glass-type coating. A coating of vanadium pentoxide powder (m.p.690 C) bonded to the lead telluride surface with colloidal silica was chosen to test the possibility of forming a coating with a melted, recrystallized compound. Coated lead telluride fragments, along with unprotected grains of lead telluride resting on an alumina setter were fired to 700 C in a constantly flowing nitrogen atmosphere. The furnace was allowed to reach 600°C in three hours and was further heated from 600°C to 700°C in one-half hour. After holding at 700°C for fifteen minutes the power was turned off and the furnace cooled to 325°C in one hour.

As a result of this heat treatment the unprotected lead telluride grains suffered a weight loss of over 30% in one case and of nearly 60% in the sample composed of finer grains. Excessive oxidations seemed to have occurred despite the protective nitrogen atmosphere. Fragments of lead telluride that had been coated with the enamel frit (maturing at 600°C) or with the silica-bonded (m.p. 690°C) fared no better. These coatings appeared to either have run or been sluffed off at some time during the heating cycle, leaving the lead telluride unprotected.

Because of these results it was decided that emphasis should be placed on developing an impervious coating that would provide maximum protection from oxidation throughout the heating cycle and not require the high temperature production of a liquid phase to serve as a sealant.

A series of experiments were made using steel strips as the base upon which coatings were applied. These samples were fired overnight in air to 550°C and subsequently examined to observe the ability of the coating to inhibit oxidation of the iron. Among the coatings thus tested were mixtures of aluminum oxide with vanadium pentoxide blended with a solution of ammonium vanadate in phosphoric acid. After drying, these coatings were sealed more or less completely by treatment with colloidal silica in solution (Ludox obtained from DuPont). These mixtures greatly reduced, but none completely prevented, the formation of an iron oxide film on the test strips. Various commercially available high-temperature cements (such as Sauereisen nos. 31 and P-1) were similarly tested with even poorer results which may be attributed, at least in part, to some mismatch of thermal expansion.

The next approach that was tried was based on the concept of depositing a firmly bonded cement layer then making the coating impervious by precipitating crystalline material in the voids until they were filled. Sodium silicate, which is known to produce a strong and relatively insoluble bond at room temperature, was not tested because it was thought advisable to avoid a highly alkaline material. The colloidal silica solution, Ludox, provides a moderately strong bond that does not deteriorate appreciably on heating. This material has a very high drying shrinkage and cannot be used alone as a coating. Aluminum phosphate (approximately $AlPO_4.2H_2O$) dissolved in dilute hydrochloric acid or sulphuric acid was also tested as a bonding material. Alone, this liquid dried to a firm but plastic film at room temperature. As the temperature was increased the material developed drying cracks, crystallized, and became quite porous, though not water soluble. It did not produce a particularly strong bond. Coatings were prepared from Ludox and/or the aluminum phosphate solution blended with finely pulverized barites (#91 $BaSO_4$ obtained from Whittaker, Clark, and Daniels). Barium sulfate was chosen as the filler because of its high thermal expansion coefficient.

Barium sulfate, bonded with Ludox, dried at room temperature to a fairly firm coating when applied to steel or to glass. After low temperature heating the coating became permeable and was sealed by repeated applications of diluted Ludox solution. This resulted in a hard surface layer that cracked and tended to peel because of the excessive shrinkage of the colloidal silica that concentrated on the surface.

A Ludox-bonded barium sulphate coating, after drying and firing at 300°C, was alternately treated with a concentrated solution of $Ba(OH)_2$ and with dilute sulphuric acid to cause precipitation of $BaSO_4$ in the pores of the coating. This coating, though impermeable after low temperature heating, was porous following exposure to 500°C. The extremely small precipitated barium sulphate crystals had doubtless consolidated leaving voids. Although treatment again sealed the pores, subsequent overnight heating at 790°C made the coating permeable. This coating retained a fairly strong bond and could possibly be used as a protective coating for lead telluride, but the repeated treatments involving deposition of barium sulphate and heating seemed prohibitively tedious.

The most promising coating, using aluminum phosphate dissolved in hydrochloric acid as the binder, employed a mixture of barium sulfate and aluminum phosphate as a filler. With this combination a fairly hard coating was obtained but its shrinkage during low temperature firing caused it to lift from the lead telluride sample.

A coating formed from barium sulphate with Ludox added to the aluminum phosphate solution produced a hard surface but a poorly bonded under layer. When the aluminum phosphate solution was made with sulphuric acid and combined with Ludox as a bond for barium sulphate, a fairly strong coating was obtained. Treatment of the dried coating with a solution of $Ba(OH)_2$ was intended to cause precipitation of barium sulphate in the pores. Apparently, however, the sulfuric ion migrated more readily than the barium ion, since most of the precipitation seemed to occur in the hydroxide solution lying on the surface of the coating.

A viscous glass-forming aluminum phosphate solution obtained from the reaction of H_3PO_4 with $Al(OH)_3$ or Al_2O_3 is known to serve as a very good adhesive bond for more or less inert particles. The combination produces relatively strong cements capable of drying at low temperatures with little, if any, shrinkage. Subsequent crystallization of the bond, and loss of chemically combined water, makes the cement porous. Following heat treatment at 300°C the cement could be fairly well sealed by saturation with crystal-depositing solutions.

An experiment was performed in which H_3PO_4 (pre-heated to opalescence and diluted with water) was mixed with a number of materials which were applied as coatings on glass. After drying, these were heated equally to determine whether or not bond-forming reactions occurred, and if these produced insoluble bonds at lower temperatures than those required by the aluminum phosphate cements. The heat treated samples were crudely tested for bond strength by scratching with the fingernail. Bond solubility and/or the presence of unreacted acid was determined by the reaction of litmus paper placed on the surface of the water-dampened cement. As shown in Table 2 , the strongest bond and least acidity was obtained with Al_2O_3 heated at 235°C. Although MgO and CaF_2 reacted with the acid at room temperature either no bond was formed or its strength was destroyed at low heat. Fe_2O_3, however, developed some bond strength at temperatures as low as 110°C when no reaction with Al_2O_3 seemed to have occurred. Though fairly well bonded, the material was quite acidic at 235°C. In a subsequent test a mixture of Fe_2O_3 and Fe_3O_4 was moistened with dilute H_3PO_4. After heating for a short time at 165°C a coating of this mixture on glass was found to be well bonded, neutral, and apparently impermeable to water. This discovery led to a search to isolate the composition responsible for the low temperature bond.

TABLE 2

PHOSPHATE BOND FORMATION

Materials mixed with H3PO4 heated to opalescence and diluted producing a solution presumed to be predominantly HPO_3

Material	Heat Temp. °C	Treatment Time at Temp.	Results
0.9 gm Al_2O_3/cc soln.	165	2 hr.	mechanical bond only
	235	10 min.	hard, cannot be scratched, acidic.
1.5 gm Al_2O_3/cc soln.	165	2 hr.	mechanical bond only
	235	10 min.	hard bond, slightly acidic
SiO_2 (Lo-micron)	165	2 hr.	slight bonding, easily scratched
	235	10 min.	slightly harder bond
	400	10 min.	definite bonding, scratched with difficulty, soluble in H_2O, definitely acid.
ZrO_2	165	2 hr.	mechanical bond only
	235	10 min.	some bonding, easily scratched, quite acid.
ZrO_2 (CaO stabilized)	165	2 hr.	definite bonding but easily scratched, quite acid.
	235	10 min.	some bond, coating not hard
$ZrO_2 \cdot SiO_2$	165	2 hr.	bonding questionable
	235	10 min.	as above, quite acid
Fe_2O_3	110	10 min.	definite bond developed
	165	2 hr.	bond strength improved
	235	10 min.	fairly hard bond, scratches with difficulty, quite acid.
Cr_2O_3	165	2 hr.	mechanical bond only
	235	15 hr.	as above
FeO	110	10 min.	bonding questionable, much cracked, apparent reaction.
	165	2 hr.	definite bond, poor adherence to glass.
	235	10 min.	Fe_2O_3 formed, quite acid.
MgO	room	temp.	hard bond formed on drying
	110	15 min.	bond lost strength
	165	2 hrs.	poor bonding, sandy.
CaF_2	room	temp.	rapid reaction on mixing gives little bond when dry.
$BaSO_4$	165	2 hrs.	mechanical bond
	235	10 min.	as above
	400	10 min.	definite bonding, hard to scratch, neutral, not softened by H_2O

Quite different results were obtained when magnetite (Fe_3O_4) or hematite (Fe_2O_3) were mixed with pre-heated phosphoric acid or with H_3PO_4. Both acids reacted slowly with Fe_3O_4 at room temperature, and more rapidly at higher temperatures. The reaction was strongly exothermic. The reaction product obtained with H_3PO_4 remained tacky and hygroscopic after drying at 110°C. The viscous liquid resulting from a mixture of Fe_3O_4 in pre-heated acid dried to a hard mass at room temperature and, though water soluble, was not hygroscopic. When an excess of iron was dissolved in concentrated H_3PO_4, addition of water caused a granular, insoluble precipitate to form. But addition of water to a solution containing excess iron in pre-heated phosphoric acid produced flocculent precipitate that redissolved when the water evaporated. Neither acid appeared to react with Fe_2O_3 at room temperature. But, judging from the disappearance of the Fe_2O_3 color, a mixture of Fe_2O_3 in pre-heated H_3PO_4 (providing a mole ratio of $Fe^{+3}/2.7\ HPO_3$) reacted almost completely on heating at 150 C. A similar mixture of Fe_2O_3 in H_3PO_4 did not lose color when heated.

The many variables involved in the Fe_2O_3-Fe_3O_4-H_3PO_4-HPO_3-H_2O system made the experimental results difficult to evaluate on a theoretical basis. After innumerable trials it was decided that the most effective bond was obtained from a mixture in which one mole of Fe_2O_3 was added to the reacted product of one mole of Fe_3O_4 in ten moles HPO_3 (pre-heated H_3PO_4). This composition applied as a coating on glass dried at room temperature to a shiny, hard, opaque, red-colored glass free of drying cracks. When heated at 110°C, the red color (Fe_2O_3) gradually vanished. The coating became devitrified and insoluble in water (no acid reaction) when heated slowly to approximately 200°C.

The above bond material, when mixed with barium sulphate (#91, supplied by Whittaker, Clark, and Daniels) produced a well bonded cement that did not crack when applied to p-type lead telluride samples. Although the cement coating was not completely impervious to moisture penetration after firing at 300°C,(the curing temperature used), the lead telluride samples did not seem to have suffered. The cement coating was then treated with a solution of colloidal silica (ludox) to seal the pores. After drying, the cement coated specimens were heated in air from room temperature to 450°C in 3-1/2 hours. Brief examination showed no change in appearance and the samples were returned to the heated kiln. The temperature was raised to 500°C in 1 hour. Examination then showed a slight discoloration on the top of the one sample that had not been sealed with Ludox. One sample was removed from the kiln. Heating was continued overnight, with a gradual rise in temperature to 565°C. Upon removal from the kiln it was found that the lower surface of the lead telluride had been destroyed. Considerable oxidation and volatalization had occurred and the cement coating, which remained tight on the upper surfaces of the samples, was badly discolored, possibly with volatalized lead telluride. The coating at the edges of the break was light yellow in color, indicative of lead oxide (PbO) penetration.

The cause of the gross failure was not determined. The appearance of the samples suggested the possibility that a fissure had developed in the lead telluride itself, causing the cement coating to crack. Considerable thermal shock was imposed on the samples by removing them from the kiln for examination. Nevertheless, the darkened color of the remaining cement coating indicated that it had become permeable, a condition which cannot be tolerated if the coating is to provide complete protection at temperatures up to 600°C.

A mixture of magnesium oxide and sodium silicate was applied to samples of lead telluride which protected the samples from oxidation at 600°C in an air furnace. Since this coating protected the lead telluride during this severe test it appears to be promising.

It has been reported (9) that n-type lead telluride was coated with a commercial cement (ECCOCERAM - CS) and then exposed to 600°C in an inert atmosphere with no deterioration of thermoelectric properties. Samples of lead telluride were coated with thin applications of this cement to see if it could be used for this design.

Although this material proved to have relatively little drying shrinkage, cracks developed when the samples were heated to 300°F, the recommended curing temperature. These cracks doubtless resulted from differential thermal expansion. In all probability the cement filler could be altered to overcome this difficulty. After filling the cracks and obtaining apparently perfect cured samples, these were heated in air at 600°C for several hours. Weight losses of approximately 5% occurred as a result of the 600°C firing. One sample that was reheated at 600°C for six hours lost an additional 5% of its original weight. Microscopic examination of the protective coating revealed considerable lead telluride penetration. The lead telluride specimen had visibly parted from the cement envelope and much of the surface of the lead telluride had developed a vitreous layer suggestive of a lead-silicate glass. This glass, however, had apparently been unable to prevent further oxidation or sublimation.

Evaluation of the magnesium oxide and Eccoceram-CS coatings was not completed because the decision to revert to the pressure contact design involved changes that permitted the use of mica sleeves and an inert atmosphere for sublimation and oxidation protection respectively.

HIGH TEMPERATURE GLUE

An adhesive with the proper electrical, thermal and structural properties is required to bond a structural member to the generator. This adhesive or high temperature "glue" bonds the generator sandwich to a sheet of stainless steel or other temperature resistant metal capable of operating in air at a temperature of 1100 F for a minimum of 100 hours with negligible deterioration. The thickness of this metal sheet is to be approximately 0.002 inches, and it is preferable that it be fairly stiff.

Referring to Figure 2, the structural member (not shown) must be bonded to the underside of the generator sandwich. The bond is to be effected between the structural member and the silver foil conductors on the hot (1100°F) side.

The following specifications were assigned for the high temperature glue:

1. The weight of the glue should be no greater than 4.6×10^{-5} pounds per square centimeter of bonded area.

2. The thermal conductivity divided by the thickness of the glue should be equal to or greater than 0.10 watt/cm^2-K if reasonably possible.

3. The glue must bond the thin metal sheet to the generator sandwich with sufficient strength to withstand normal handling. It should be capable of withstanding a direct separating force of 1 pound per square inch when the glue is at a temperature of 1100°F.

4. The completed bond must be capable of withstanding 150 cycles from room temperature to a temperature of 1100°F and back to room temperature with negligible deterioration.

5. The completed bond must be capable of operation in air for a period of 100 hours at a temperature of 1100°F with negligible deterioration.

6. The completed bond must be capable of operation in a vacuum for a period of 1 year at a temperature of 1100°F with negligible deterioration.

7. The high temperature glue must provide electrical insulation between the thin metal sheet and the adjacent silver foil to the extent that the minimum electrical resistance between the foil and the metal sheet should be 35,000 ohms for a cross sectional area of 1 square inch. This resistance requirement varies inversely with the cross-sectional area through which it is measured. Thus, if an area of two square inches is used for measurement purposes, the required minimum resistance is 17,500 ohms. This resistance figure should apply when measured from any point on the silver foil to any point on the metal sheet.

Several commercial furnace cements were tried and found to be unsatisfactory. Then a barium sulphate base cement with a sodium silicate binder which met requirements 1, 3, and 7 listed above was prepared. The formulation of this cement is as follows:

Barium Sulphate ($BaSO_4$) #91 natural, Whittaker, Clark and Daniels	40 gms
Water Glass Soda/Silica ratio of 1/3.75 Albany Laboratories, Inc.	10 cc
Water	5 cc

To prevent blistering of the cement after application the cemented junction should be air dried for one hour, then dried at 150°F for several hours, and finally, raised to any higher temperature slowly for the first time.

At 1100°F the tensile strength of the glue is greater than 15 pounds per square inch and the electrical resistivity is 10^{11} ohm-cm. The ability of this cement to meet the remaining requirements was not verified experimentally because of the change to the pressure contact design. When this change in design was made only work on phases that are directly concerned with construction of the pressure contact design was continued.

HIGH EMISSIVITY COATING

Since thermal radiation is the only practical means for waste heat rejection in the applications of interest here, the cold side of the generator requires a high emissivity surface. An investigation was made to find a coating that, when applied to the radiating surface (silver), would have the following properties:

1. An emissivity greater than 0.9 at 710°F
2. Stability at 710°F in vacuum for one year
3. Ability to withstand 150 thermal cycles from 710°F to room temperature

A coating of black cobalt oxide mixed with a 50% Ludox, 50% water solution was found to adhere well when the silver surface had been previously coated with silver nitrate and then fired in air at about 400°C. This treatment gave the silver a rough surface which improved adhesion considerably. The total normal radiation of this coating on silver foil was measured with a radiation thermopile while the sample was at design temperature. The emissivity calculated from this measurement was found to be 0.97 ± 2%. A sample was exposed to air at 710°F for over 900 hours and showed no signs of deterioration.

This coating is felt to be completely satisfactory for its intended purpose.

CONDUCTOR JOINING

The conductor has to be bonded to the diffusion barrier on the lead telluride and should be bonded to the thermal insulation to provide support for the generator. Initially it was felt that the silver conductor could be joined to the iron diffusion barrier by soldering with a high temperature solder after the iron was bonded to the lead telluride. The first problem approached in this category was to attach the silver to the insulation.

The attempts to solder silver or flame spray silver to the insulation proved to be unsuccessful. However, it was found that a silver paint (#6808) manufactured by DuPont, which is fired on at 1400°F, adhered quite well to the insulation after the insulation was coated with colloidal silica. The silica did not influence the thermal conductivity of the insulation appreciably (room temperature measurements indicated a 15 to 20% increase) and the silver paint had 80% of the conductivity of an equal weight of pure silver.

To determine if the silver paint could be bonded to the iron diffusion barrier, attempts were made to bond the silver paint to strips of iron. When these tests were made samples of lead telluride were placed in the furnace to determine if the atmosphere used influenced the lead telluride or if lead telluride had any effect on the silver-iron bond. It was found that the silver paint would adhere well to the iron only in an oxidizing atmosphere which the lead telluride could not tolerate.

Work was discontinued at this point when the decision was made to use the pressure contact design.

MATERIAL FABRICATION

Construction of the sandwich type model generator as described earlier requires thermoelectric elements in the form of small, rectangular wafers approximately 0.25 inches by 0.15 inches by 0.010 (n-type) and 0.017 (p-type) inches thick. The material in this section describes the processes tried for the purpose of fabricating such elements.

Initially, two basic techniques were investigated: 1) Powdering and pressing, and 2) Slicing. Additional dicing operations are involved in both methods. Investigation of the powdering and pressing technique, consisting of grinding the thermoelectric materials into powder form and then pressing and sintering into wafers, was carried out by the vendor. Samples of both n and p-type materials prepared in this manner were furnished. These samples consisted of circular wafers one-half inch in diameter and of the proper thickness. Attempts to dice them into the required rectangular shape by means of ultrasonic cutting techniques indicated that this method was feasible. However, the thermoelectric properties of the p-type wafers were considerably poorer than those of the crystalline (cast bar stock) material. Hence, some means of improving these properties was required.

Efforts at slicing the cast bar stock were carried out by the contractor at a number of different locations within the Company. Ultrasonic methods, wire cutting, sawing methods using diamond and other saws, and lathe operations using a parting tool were included in the procedures tried. Generally, it appeared quite feasible to slice the n-type material into wafers which require only a moderate amount of polishing to reduce them to the proper thickness. Samples were then successfully lapped to the proper dimension. The most successful method of slicing utilized a sawing technique with a diamond wheel in which n-type samples were sliced from 1/2 inch diameter bar stock. After lapping to thickness the wafers are then diced ultrasonically to the rectangular shape required. There is a possibility of microscopic cracks occurring in the material in the course of these processes, but inspection of random samples at a magnification of approximately 100 did not reveal any such cracks.

On the other hand, similar efforts to slice the p-type material from bar stock were largely unsuccessful. The principal problems are the extreme brittleness of the material and the presence of cracks in most samples of the bar stock. Moderate success was obtained with one set of 1/4 inch diameter samples, prepared with special care, that did not exhibit such cracks. However, the brittleness of the material and its resultant susceptibility to thermal shock makes the preparation of bar stock material devoid of cracks extremely difficult. This, plus the difficulties of handling the wafers after cutting, has resulted in the conclusion that slicing the p-type bar stock into wafers of the desired thickness is not practical.

The vendor subsequently utilized a proprietary method which results directly in rectangular wafers of the desired dimensions to prepare several samples of both n and p-type elements. Measurements indicated that with this method it is possible to obtain thermoelectric properties essentially as good as those of the crystalline material for both types.

Thus it appears that the problem of obtaining elements of the proper dimensions and properties has been solved satisfactorily. Two different methods are feasible for obtaining the n-type wafers and one suitable method is available for the p-type.

MODEL THERMOELECTRIC GENERATOR

DESIGN CONSIDERATIONS

Failure to achieve timely solutions to all of the fabrication problems involved in construction of a model generator of the sandwich type using bonded contacts necessitated a change in design concept to a more conventional type. Specifically, the lack of a technique for depositing iron on p-type lead telluride required the use of pressure contacts. They are needed at the cold junctions as well as the hot because of the high cold junction temperature (~ 700°F). Also, the fact that a coating suitable for protection of the thermoelements against sublimation and oxidation was unavailable necessitated the use of some other means for blocking sublimation. Also required is the provision of an inert atmosphere surrounding the elements to prevent oxidation during ground operation.

The sublimation problem could be reduced to a minimum by inserting the lead telluride elements in thin mica sleeves as recommended by the vendor. The ready availability of round mica tubing and of lead telluride in round bar stock form both favor the use of elements cylindrical in cross-section.

Provision of an inert atmosphere to prevent oxidation could be accomplished by enclosing that part of the model containing the elements in a hermetically sealed casing filled with the required atmosphere. The remaining major design consideration then, is provision of the pressure required for low electrical and thermal resistance pressure contacts. This is discussed in the material that follows.

The design concept considered was the side fin-sandwich configuration of the types shown in parts (b) and (c) of Figure 4 using cylindrical cross-section elements. Several alternate methods of applying the pressure required on the elements were conceived and three were given rather careful consideration. Some discussion of the requirements for establishing low resistance pressure contact junctions and the ramifications of their use are in order at this point.

The contacts to be established are between the iron electrodes which serve as diffusion barriers and the hot and cold ends of the lead telluride thermoelements. Unit pressures of about 100 psi at the junction interface are believed to be adequate although somewhat higher pressures were expected to yield better results. The mating surfaces must be clean, flat and free of gross oxide layers. Adequate alignment of the mating parts to assure contact throughout all of the available area is also required. Thin oxide films resulting from exposure to air at room temperature are believed to be removed or amalgamated during the junction seating process. In this process the assembled junction is exposed to temperatures of from approximately 700 to 1350°F in a reducing atmosphere for periods of about 10 minutes for the higher temperature to many hours if 700°F is used. This process is carried out under design contact pressure so that some plastic deformation of any high spots on the lead telluride takes place to provide better mating of the two surfaces.

One of the consequences of high temperature pressure contacts is that the elements themselves tend to become shorter with time due to the effect of sublimation in the vicinity of the hot junction and possibly also due to creep. Enclosing the elements in a thin sleeve of mica tends to decrease the rate of sublimation but 1 to 2 mils reduction in element length by the end of one year can still be expected at the design hot junction temperature of 1100°F.

The first design of a containment structure intended to provide the required contact pressure was similar to the configuration shown in part (b), Figure 4. In this design the thermoelements are fitted between an inner tube of square external cross-section containing the heat source and an outer tube to which the radiator fins (side fins) are attached. There are four elements per radial section of the generator. The total axial length of the inner and outer tubes is determined by the total number of elements desired in one envelope and the axial spacing of the elements. The pressure contact force in this design is provided by the thermal expansion of the inner tube and other parts in the vicinity of the hot junctions. This produces an outward displacement that is resisted by the outer ring which is maintained at approximately the cold junction temperature.

Further study of this design indicated several serious weaknesses. First, the manufacturing tolerances on the parts would have to be held to extremely close limits to avoid overstressing of the outer ring or failure to apply adequate pressure to the shorter elements. Second, the effective spring constant was too high to provide the spring follow-up required for adequate contact pressure if the length of the elements decreased the maximum expected amount of 2 mils per element in one year. Also the problems of assembly of a generator consisting of more than one radial section composed of four elements were expected to be considerable. Therefore, other designs that could provide a containment structure with a lower spring constant were investigated.

Individual coil springs on the cold side of each element were considered but were abandoned because again very precise manufacturing tolerances were required and the weight penalty tended to be higher than that of the designs described below.

The use of a stack of Belleville washers to provide individual spring loading for each element was considered in one design. In this design the outer tube is a relatively inflexible ring with a stack of Belleville washers inserted between each element and the ring. Four thermoelements, two n-type and two p-type are assembled in each ring in a configuration similar to that shown in part (b) of Figure 4. A square tube containing the heat source is located at the center or hub of the rings. Belleville spring design calculations indicated that sufficient flexibility was available to provide adequate follow-up for the anticipated gradual reduction in element length with time and to provide an additional allowance for manufacturing tolerances. This design was abandoned in favor of the C ring design (described later) for the following reasons:

1. The C ring design will provide flexibility or follow-up equal to that of the Belleville spring design.
2. There is less uncertainty in the manufacture and assembly of the C ring design.
3. The temperature drop between the cold junctions and the radiator was expected to be greater in the Belleville spring design than in the C ring design.
4. Parts for the assembly and test of single ring models of the C ring design could be obtained quicker than for the Belleville spring design.

The method finally selected for applying contact pressure in the model generator is the so-called C ring design. This design is based on a configuration of the general type shown in Figure 4, part (c). Two thermoelements are assembled diametrically opposite within each outer ring. This ring is split and about one-third of it removed so that it is shaped like a "C". On assembly, the jaws of the ring are pried open to allow insertion of the elements. The required loading for the pressure contacts is provided by the spring action of the C ring when it is released after the elements are in place. This design is illustrated in Figures 15, 16, 17, and 18. Figure 15 is an assembly drawing of the 21 ring, 5 watt design power output model generator. Figures 16 and 17 are two views of a partially assembled 5 ring test model, a shorter, lower power version of the 21 ring model. Figure 18 shows a collection of samples of the major parts excluding the outer casing or envelope and the fins.

As mentioned earlier, the contact pressure on the elements is applied as the result of deflection of the C ring in assembly. The design uses Inconel X for the ring material and is based on a maximum stress in the ring of about 60,000 psi at design temperature. Load relaxation in a one year period due to creep in the ring is expected to be negligible at this stress level. On this basis, the allowable initial deflection of the C ring is about 10 mils on the diameter which results in an initial loading of about 330 lb/in^2 on the junctions. The load vs. deflection curve of this ring is essentially linear. Therefore, if in a period of one year a 4 mil reduction in diameter of the internal parts takes place due to sublimation and creep, the deflection of the ring will be reduced to 6 mils and the contact pressure to 200 psi. The design objective here was to provide a minimum pressure of 100 psi at the end of one year. This would require a ring deflection of only 3 mils, so that the C ring design appears to have a suitable spring constant and adequate follow-up characteristics for a generator life of one year. To circumvent the necessity for very precise manufacturing tolerances, the initial deflection of each individual ring is established by shims inserted between the hot conductors and the heat source.

Other aspects of this model generator design are discussed later under the heading, DESIGN DETAILS.

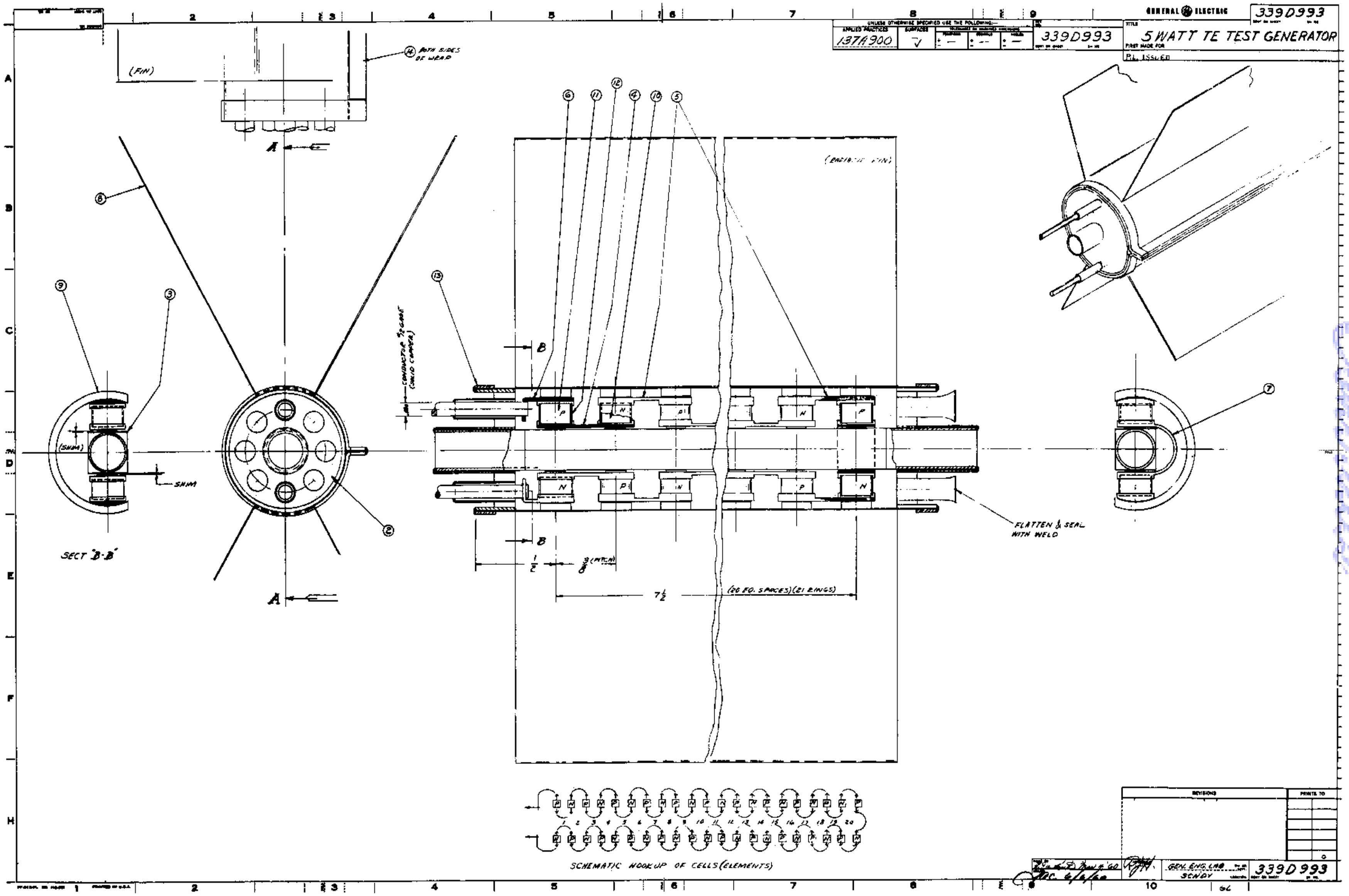


Figure 15: Model Thermoelectric Generator — Assembly Drawing.

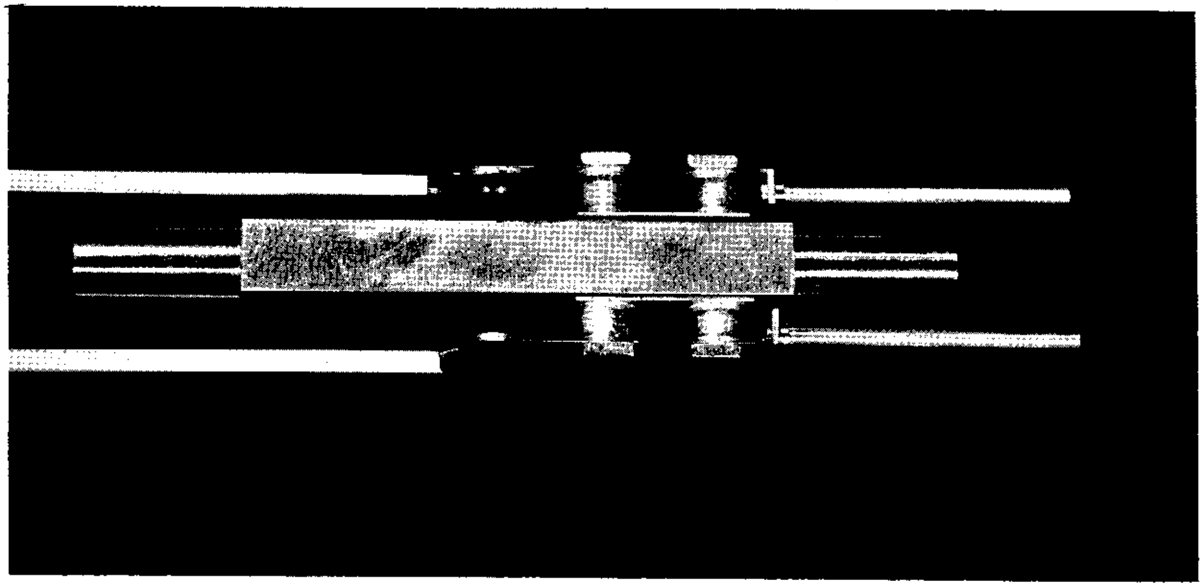


Figure 16: 5-Ring Model Thermoelectric Generator — Partially Assembled.

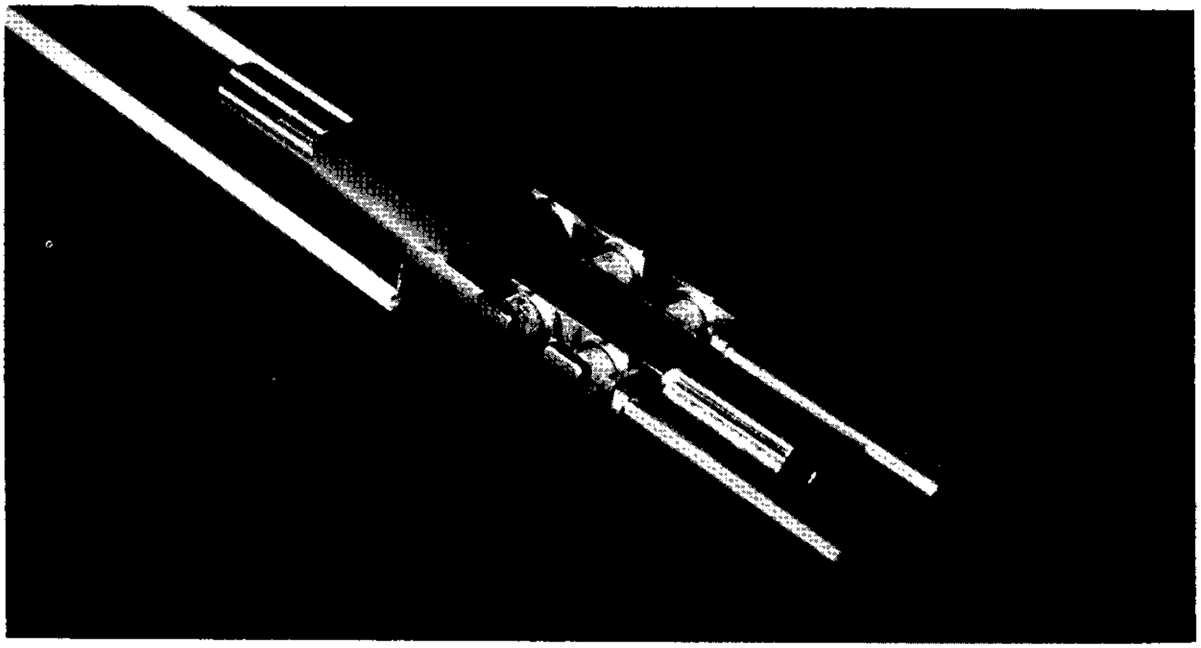


Figure 17: 5-Ring Model Thermoelectric Generator — Partially Assembled.

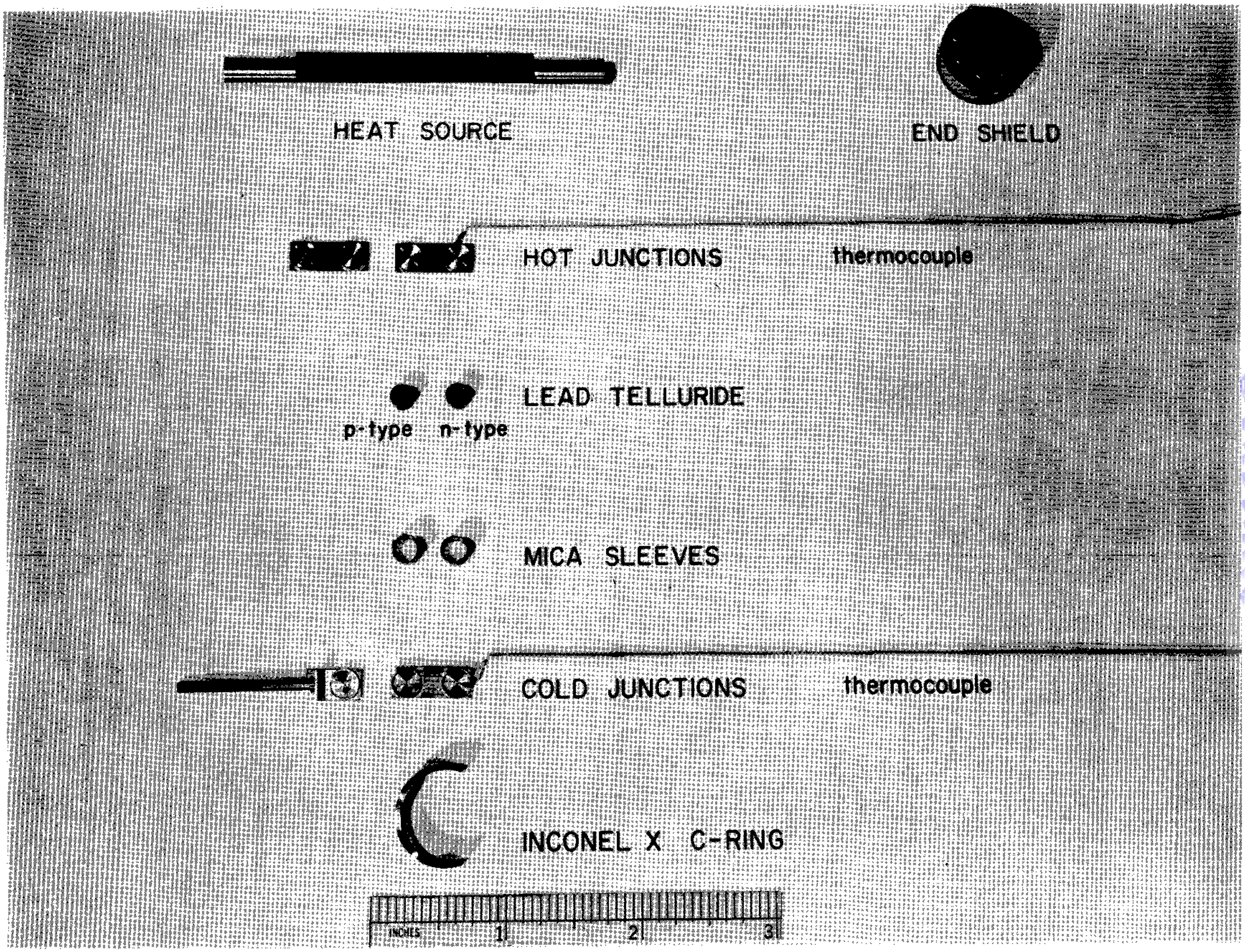


Figure 18: Major Parts of 5-Ring Model Thermoelectric Generator

DESIGN POINT SELECTION

The material in this section describes the methods and considerations involved in determining the design point for the model generator using pressure contacts.

Earlier in the contract a series of minimum weight calculations had been carried out for lead telluride at hot junction temperatures of 900, 1000, and 1100 F by using the procedures described in Part III, Appendix I. The reason for making these calculations was that the Figure of Merit of these materials declines significantly with increasing temperature in this region, and it was conjectured that this decrease might be sufficient to more than offset the otherwise beneficial effects of high hot junction temperatures. This proved not to be the case for lead telluride, however. The performance at the highest of the temperatures considered was definitely superior, so 1100 F was selected as the design hot junction temperature. Higher temperatures are not believed suitable for long service life, primarily because of sublimation.

The selection of the diameter of the elements is affected by the following considerations. The diameter must be large enough to minimize heat leakage losses by conduction through the mica sleeves. It must also be large enough to withstand the forces required for pressure contacts without danger of failure as a column. On the other hand, optimization studies (see Part III, Appendices K, L, and N) have shown that thin, wafer-like elements are best for low specific weight. The smallest diameter of elements readily available from the vendor was 3/16 inch so elements of this diameter were selected as a reasonable compromise.

On the basis of the side fin configuration with two diametrically opposed elements, as shown in part (c) of Figure 4, a calculation was made to determine the optimum balance between thermoelement weight and fin weight that would yield the minimum total weight for these two parts of the generator. These two parts constitute the major weight items if heavy containment structures required to provide pressure contact forces are neglected. For constant hot and cold junction temperatures, materials properties, and ratio of external resistance to resistance of the thermoelectric materials, fin weight turns out to be inversely proportional to the square of thermoelement length. On the other hand, thermoelement specific weight is directly proportional to the square of thermoelement length. Therefore, for each value of cold junction temperature there is an optimum element length for minimum weight per unit of power output. The initial selection of cold junction temperature was made rather arbitrarily to achieve a reasonable balance between specific weight and efficiency. This resulted in selecting a cold junction temperature of 700°K. At this temperature the optimum element length is 1/8 inch, the value ultimately used in this design.

When it became evident that Inconel-X C rings would be required to provide sufficient contact pressure, calculations of total generator-radiator weight including the heavy containment structure indicated a specific weight higher than desired. Two possible changes in the design point selection made up to this point were investigated to determine their effect upon specific weight. It was found that by reducing the cold junction temperature to 600 K, and by increasing the axial spacing between the elements (as in the side fin-sandwich configuration) to a pitch of 3/8 inch, the specific weight was reduced considerably. The resulting design for the C ring model generator then had an estimated specific weight of 70 lb/kw at a thermal efficiency of 3.4%. These figures are for an infinitely long generator with junction resistances on the order of 30 micro-ohm cm^2. If end effects are included the estimated specific weight of the 5 watt model increases to about 85 lb/kw at about 3% efficiency.

From the above, it is apparent that the design is not completely optimized, but the optimization procedures described in Part III, Appendix N were not completely developed when it was necessary to make the design point selections. However, it is believed that complete optimization would not, in this case, alter the results significantly.

DESIGN DETAILS

Introduction

The design selected for the thermoelectric generator using pressure contacts is illustrated in Figure 15. This figure is the assembly drawing and Table 3 is the corresponding parts list for a model thermoelectric generator that has a design power output of approximately 5 watts. The thermoelectric elements are connected in series as shown in the schematic at the bottom of Figure 15. At the design temperatures of $T_1 = 866$ K and $T_2 = 600$ K this model generator was expected to have approximately the following performance:

Open circuit voltage - 2.5 volts
Full load voltage - 1.3 volts
Full load current - 4.0 amperes
Full load power output - 5.2 watts
Internal resistance - 2.5 ohms

This performance estimate assumes a 10% decrease in performance due to the conductor resistance and the resistance of the lead telluride to iron junction.

Figures 16 and 17 are photographs of a test model that was partially assembled to illustrate this C ring design. To facilitate the assembly of this model for photographing the mica sleeves were not placed around the thermoelements and hence the diffusion barriers may appear to be too large in these photographs. Figure 18 shows some of the parts of this test model. The test model illustrated in Figures 16, 17 and 18 was designed for 5 rings or about one watt of power.

TABLE 3

PARTS FOR MODEL THERMOELECTRIC GENERATOR

NAME	PART NUMBER FROM FIGURE 15	QUANTITY REQUIRED
Thermoelectric elements		
n-type - 0.1 mol % PbI_2	10	21
p-type - 1.0 atomic % Na	11	21
Mica Sleeves	12	42
Conductor (with diffusion barriers)		
Output leads	6	2
Cold side	5	20
Hot side	4	20
Hot side jumper	7	1
Heat Source	3	1
C-Rings	9	21
Casing and Radiator	8	1
End Shields	2	2
Bands and Cleats	13,14	2
Thermal Insulation (Fibrous Potassium Titanate)		
Electrical Insulation (0.0015 inch mica)		

Thermoelectric Elements

The vendor could supply 3/16 inch diameter lead telluride in pieces one inch long which had to be cut to the design length of 1/8 of an inch. It was possible to cut the elements to .125 ± 0.0005 inches using a 3 inch diameter x 0.006 inch thick carborundum wheel (Carborundum Resin Bond, C240-PRR7) for slicing the elements and then lapping to size with polishing paper (Behr-Manning 600A - Tufbak). The elements are cut with less damage due to chipping at the edges if they are rotated as the cutting wheel passes through. The n-type (0.1 mol % PbI_2 doping) was easily cut and polished while about 25% of the p-type (1.0 atomic % Na doping) was lost due to shattering while cutting or to excessive chipping of the corners while polishing.

The pressure contact design requires that the elements faces be parallel and as flat as possible. The polished elements were checked with a comparator and the maximum total deviation observed in flatness was 0.0002 inch. Measurements made to determine how parallel the faces were indicated no measurable deviation from being parallel. These results indicate that if care is taken the lead telluride can be cut to satisfactory tolerances.

Mica Sleeves

The mica sleeves were purchased from the Mica Insulator Company of Schenectady, New York and are designated 6T Isomica Tubes. These tubes were supplied in six inch lengths and 3/16 of an inch in diameter with about a 0.008 inch wall. Because of the nature of these mica tubes the tolerances are ± 0.010 inch on the diameter and ± 0.0015 on the wall thickness. These tolerances could result in excessive clearance unless the sleeves are selectively fitted to the thermoelements. If the sleeves are too small for the elements they can be expanded a few mils by forcing over a tapered mandrel. The sleeves were cut about 0.002 inches shorter than the lead telluride by simply mounting the tube on a mandrel in a lathe and cutting to length with a razor blade. Because the mica sleeves contain traces of water they must be degassed by placing in a 1200°F furnace for several hours before assembly.

Conductors

Copper was selected as the material for both hot and cold conductors because it presented the best balance of conductivity, weight and availability. For minimum system weight the product of the electrical resistivity and the density must be as low as possible. Beryllium and silver are as good or better than copper in this respect but they are not as readily available; therefore, copper was selected.

The weight considerations make a thin conductor desirable but this would increase the generator's internal resistance. Initially the conductors were designed so that they would increase the generator's resistance about five percent. In the final design, the copper thickness was increased because of machining problems, so that the final conductor design resistance is about three percent of the design generator resistance.

The use of copper meant that a diffusion barrier of some metal that is compatible with lead telluride would have to be used. Iron or low carbon steel were recommended by the vendor (2) (12) and since steel also has good mechanical properties at 1100°F it was selected for the diffusion barrier.

The thickness of the diffusion barrier had been previously estimated for silver conductors and this calculation was corrected for copper. The thickness obtained by this calculation was 0.005 inches but the final design specified a 0.010 inch thickness because of the machining problems associated with a 0.005 inch conductor. The diffusion barrier was extended through the copper conductor because it was found that copper has inadequate creep resistance at the design temperature.

Heat Source

The generator was designed with a liquid metal heat source in mind so a tube that would not have excessive pressure drop was selected. For low weight the tube should be small but to keep the pressure drop low and because of machining problems the tube was made 0.250 inches square with a 0.210 inch bore. Inconel-X was used for the tube because of its superior mechanical properties when properly heat treated.

After the tube is rough machined the following heat treatment is used:

1. Heat to 1150 C for 3 hours in air.
2. Allow to air cool.
3. Heat to 845 C for 24 hours in air.
4. Allow to air cool.
5. Then heat to 705°C for 20 hours in air and air cool.

The tube is then machined to the final dimensions.

For the model generator the heat source is simulated with a nichrome wire heater. This heater is made from 0.020 nichrome wire wound on a 0.125 inch ceramic tube and then cemented into the Inconel-X tube with Saureisen Furnace Cement #31.

C Rings

Inconel-X was the material selected for the C rings because it is a good material for springs operating at high temperatures.

To prevent distortion of the rings during the final finishing operation it is necessary to rough machine the rings to a complete circle and then give them the same heat treatment mentioned above for the heat source. Using this procedure the C rings distorted only about one mil during the final machining and cutting operations.

Casing and Radiator

The casing or tube that encloses the generator is made from 0.001 inch stainless steel that has a flash plating of silver on both sides. This silver plating is done so that the casing can be fastened to the Inconel-X C rings by a diffusion bonding technique. The bonding will be done by putting the casing and C rings into a fixture to apply sufficient contact pressure and then placing this assembly in a hydrogen furnace at 650°F. An inert arc weld is made along the casing seam and then around the ends to fasten the casing to the end shields.

The radiator will be made from 0.004 to 0.005 inch silver that has been coated with the high emissivity coating, described earlier in this report (see High Emissivity Coating under FABRICATION PROBLEMS), and it will then be attached to the casing by a diffusion bonding technique similar to that used for the rings.

End Shields

The ends of the tube that house the generator are sealed with an aluminum oxide disc containing Kovar sleeves through which the power and thermocouple leads pass. This aluminum oxide disc is vacuum brazed to the individual Kovar sleeves and to the outer Kovar ring with silver using titanium hydride as a flux. These shields are then inert arc welded to the casing as mentioned above.

Bands and Cleats

The bands and cleats are made from stainless steel and are provided to prevent burning through the 0.001 inch tube wall while it is being inert arc welded.

Electrical Insulation

An electrical insulation must be provided to prevent shorting of the generator through any of the C rings or along the heat source. The first insulations used were ceramic materials which could be directly applied to the inside of the C ring and the outside of the heat source. An aluminum phosphate base and then a magnesium oxide base insulation were tested during the single ring model tests and were found to be unsatisfactory in a reducing atmosphere.

Mica (General Electric Company specification #A14A3A5) was found to be satisfactory in a reducing atmosphere and was therefore selected for the electrical insulation even though it cannot be directly attached to the Inconel-X. A sheet of this mica about 0.001 to 0.0015 inches thick is inserted between the cold conductors and the C rings and between the hot conductors the heat source during assembly.

Insulation

The thermal insulation used is DuPont's fibrous potassium titanate which can be packed into the assembled generator before it is welded. The insulation must be degassed before assembly because traces of water vapor will accelerate the oxidation of the lead telluride. It is recommended that the insulation be baked in a vacuum furnace at 1100°F just prior to assembly.

Assembly

The metal components must be thoroughly cleaned and the mica and thermal insulation degassed just prior to assembly. The order of assembly is as follows:

1. Place all the hot junctions on the heat source with a layer of mica between and then wire in place.

2. Place the lead telluride in the mica sleeves before inserting in the hot junctions. Make certain that flakes of mica do not stick to the ends of the thermoelements.

3. Assemble the lead telluride and the cold junctions on the heat source and wire in place so that the wires used will fall between the C rings.

4. Diffusion bond the 0.001 in stainless sheet to the series of Inconel-X C rings in a fixture which will give the proper pitch to the C rings.

5. Place the generator sub-assembly into the tube by inserting through the open side of the C ring and tube assembly and then rotating the generator sub-assembly into place.

6. With a special tool spread each C ring so that it is deflected 0.010 to 0.012 in. from the unstressed position and then insert mica on the cold side and steel shims on the hot side to maintain this deflection.

7. Remove the wires that held the sub-assembly together.

8. Pack with the thermal insulation and then arc weld the seams and solder the thermocouples and power leads to the end shields.

9. Degass the entire generator again before filling with argon and sealing.

10. Attach the radiator with the high emissivity coating by diffusion bonding.

It should be noted here that technical difficulties encountered in the model generator construction program showed progress to the point that the 5 watt generator could not be completed within the time or funding available under the contract. These difficulties included the problems encountered in the single ring model test program (see Single Ring Models, page 63) and the high junction and element resistances that appeared in the resistance measurements work (see Resistance Measurements, page 53). Some difficulties were also encountered in the fabrication processes required for assembly of the model. For example, the diffusion bonding technique required to fasten the 0.001 inch stainless steel casing to the Inconel X rings has not been perfected. Initial attempts resulted in bonding over a relatively small portion of the total area available and were not considered adequate.

The status of the model generator construction program is that the design as described above is complete and some, but not all, of the parts have been fabricated. Some of the details of assembly and of sealing the casing have not been proved experimentally.

Resistance Measurements

As the generator construction phase of this contract began, it was evident that certain experimental data would be required to define the construction details and techniques. This section is primarily concerned with the design, operation and results of a device constructed to evaluate electrical resistances between conducting electrodes and semiconductor thermo elements

To be specific, the junction resistance should involve a dimensional factor. For the purposes of this section the junction resistivity shall be defined as

$$\rho_J = R_J \quad a$$

where R_J is the resistance across the junction, and a is the cross sectional area of the junction. The junction resistivity will certainly depend upon the junction thickness. Usually this would be difficult to measure. The thickness is dependent upon the forming technique and in general kept to a minimum, hence for comparative results, it is not necessary to explicitly specify the thickness in the expression.

Equipment Design Principles

To understand the measurement described here, consider an homogeneous cylinder of material as shown in Figure 19. A uniformly distributed current, I, is injected over the surface of one end as indicated, passes though the sample and is removed from the surface of the other end. This condition establishes equipotential planes perpendicular to the axis of the cylinder and uniformly distributed over the length of the cylinder. Consider now two voltage probes, one fixed at g and the other variable at h a distance ℓ from g. The voltage measured between g and h is linearly dependent upon ℓ. The constant of proportionality is $I \frac{\rho}{a}$ Thus we have

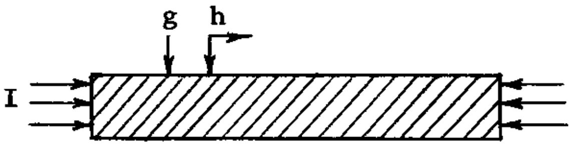


Figure 19: Cylinder of Material Showing Probe Positions

$$V_{gh} = I \frac{\rho}{a} \ell$$

$$\rho = \frac{V_{gh}}{I} \frac{a}{\ell} = R_{gh} \frac{a}{\ell}$$

where V_{gh} is the voltage measured between g and h, ρ is the electrical resistivity of the material, a is the cross sectional area of the material, and R_{gh} is the resistance of the material between points g and h. A plot of V vs ℓ is shown in Figure 20.

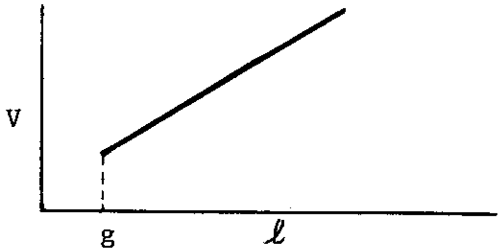


Figure 20: Voltage vs. Length

The slope is proportional to the resistivity of the material.

Consider now the effect of a discontinuity perpendicular to the axis of the cylinder at point d as shown in Figure 21.

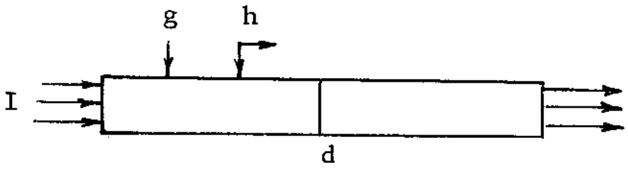


Figure 21: Cylinder of Material with Discontinuity

Then the profile of the sample might look like that shown in Figure 22, a plot of R vs. ℓ

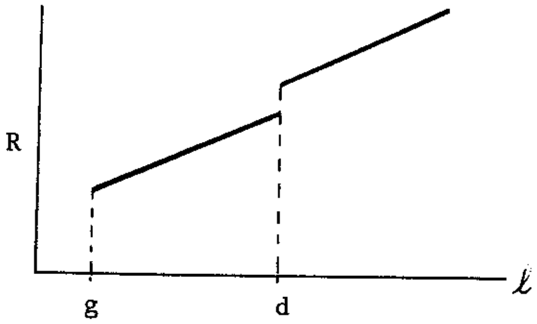


Figure 22: Resistance vs. Length with a Discontinuity

An ohmic junction can usually be expected to produce just such a discontinuity and the magnitude of the discontinuity is considered the junction resistance.

When the material on one side of the junction is a good conductor (low resistivity) then the slope of the line on that side will be small and the profile will be more like that in Figure 23.

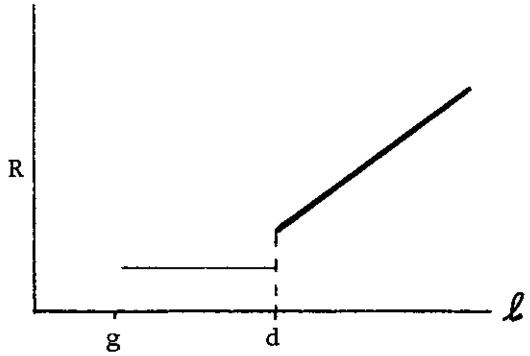


Figure 23: Resistance vs. Length with Good Conductor on One Side of Junction

Equipment Design Details

To measure the resistance of pressure contacts several requirements had to be satisfied.

1. A variable longitudinal mechanical pressure adjustment was required to ascertain the dependence of junction resistance on mechanical pressure.

2. A controllable temperature was required to determine the relationship between junction resistance and temperature over the range of anticipated operating temperatures for the generator.

3. The accurate measurement of the position of the junction relative to the probe was required to establish ℓ within a tolerance of ± 0.001 inch.

4. Control of atmosphere surrounding all parts at elevated temperatures was required to avoid oxidation.

5. A suitable semiconductor resistivity measurement technique was required (i.e. one which did not introduce thermal errors).

Figure 24 shows the jig that evolved to meet these requirements:

The pressure control was achieved by means of a coil spring with its compression controlled by a screw adjustment. The spring and screw assembly was

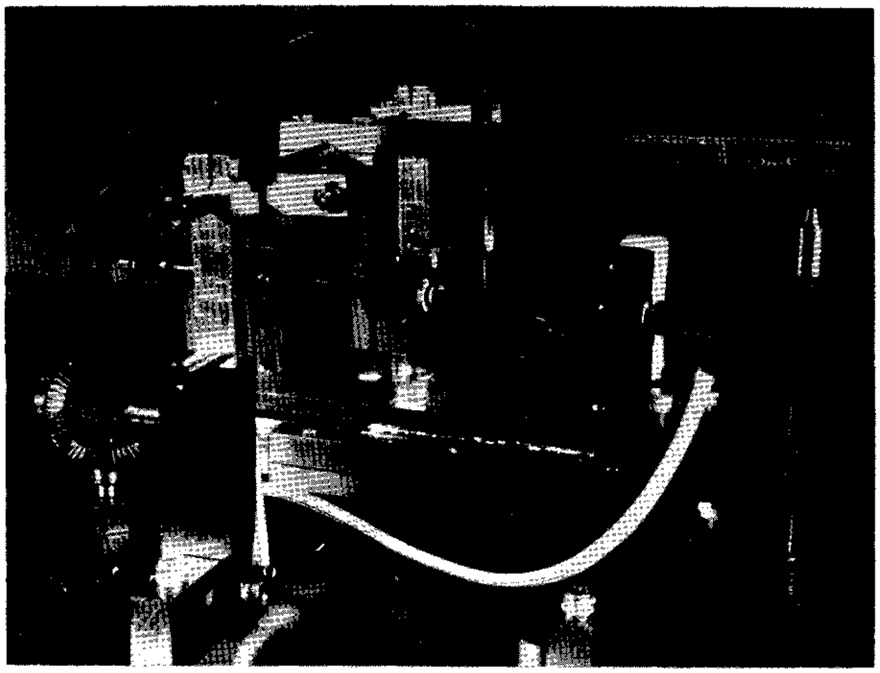


Figure 24: Resistance Profiling Device — Partially Assembled.

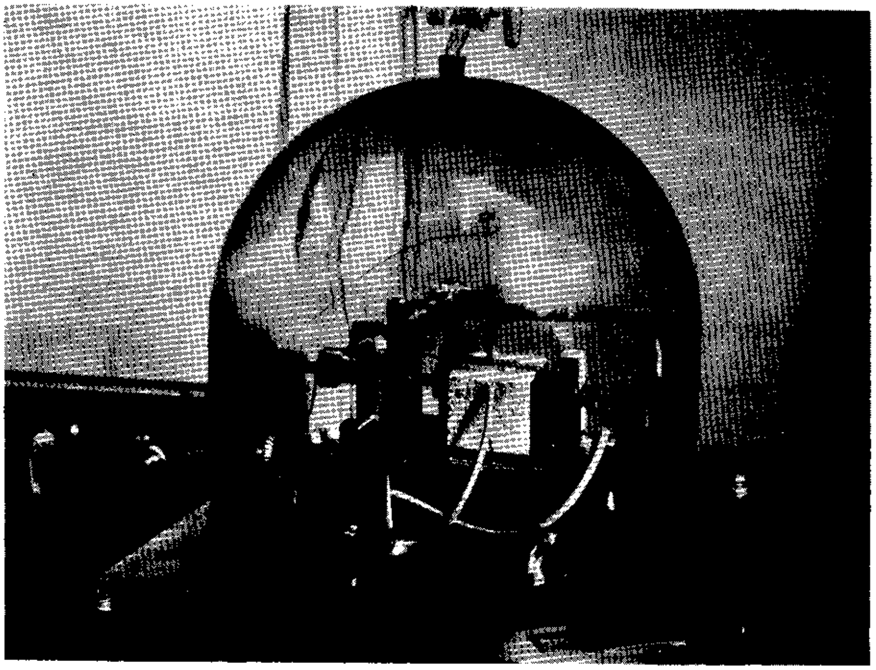


Figure 25: Resistance Profiling Device — Completely Assembled.

calibrated and the pressure was calculated from the measured compression of the spring.

The thermoelement and junctions were surrounded by a heater element not shown in Figure 24, but in place in Figure 25. The element and surrounding insulating block had an access slot along one side to allow free movement of the probe from one end to the other of the sample. The temperature was measured by a thermocouple, spot welded on the electrode, a short distance from the junction.

A micrometer operated platform having one horizontal degree of freedom and supporting the sample holding assembly, was driven from under the base plate by means of a mitre gear.

Data carefully taken in the region around the junction could be used to locate the junction to within ± 0.001.

The entire assemble was built on a base plate of a vacuum system and could be covered with a bell jar as shown in Figure 25. The chamber containing the assembly could be evacuated and back-filled with the desired gas.

An ac measurement technique similar to that described by Dauphinee & Mooser(10) was used to make the resistance measurements. This device gave the resistance directly by a comparison method.

Resistance Measurements Results

As stated in the introductory remarks, this effort was aimed at developing and evaluating a junction technique suitable for use in the proposed generator. Methane reduced pressure contact junctions had been used in the Snap III-B thermoelectric generator as well as in the Baso gas control element, but little specific data was available on this type of junction.

Tables 4 and 5 are a summary of the results of these investigations. The data are presented in a more or less chronological order for each type with the p-type in Table 4 and the n-type in Table 5.

The P-1 measurements indicated a time dependence in the formation of a low resistance junction. It was felt that the junction formation might be expedited by exposure for a short duration (10 min.) to a higher temperature (1350°F). The P-2 measurements were the first to include this procedure. A thermocouple error in the P-2 series yielded somewhat lower temperatures than desired. This was discovered and corrected after the series was completed.

The P-3 series was intended to give extended time-at-temperature data. In this series a rather unexpected result became apparent. The material resistivity appeared to increase with time. This was a rather significant change and the remaining tests on the p-type material were attempts to learn more about this new problem. The magnitude of the change is graphically illustrated in Figure 26.

TABLE 4. RESISTANCE MEASUREMENTS
p-type PbTe (1.0 at % Na)

Sample and Measurement Designation			Time from Heat Up	Measurement Temperature	Junction I Resistivity ohm in^2	Junction II Resistivity ohm in^2	Material Resistivity ohm in	Comparative Value From Materials Data (1) ohm in	Remarks
P	1	1	48 hr	1110 F	4.3×10^{-5}	1.1×10^{-4}	4.25×10^{-3}	2.13×10^{-3}	Samples 1 - 4 were measured in 15" Hg of CH_4. All pressure contact junctions were loaded with 200 psi unless otherwise indicated.
P	1	2	68 hr	1110 F	2.76×10^{-5}	2.86×10^{-5}	4.91×10^{-3}	2.13×10^{-3}	
P	1	3	68 hr	620 F	5.8×10^{-3}	1.24×10^{-4}	3.58×10^{-3}	1.40×10^{-3}	
P	2	1	Immed.	1060 F	3.05×10^{-5}	3.81×10^{-5}	2.44×10^{-3}	2.22×10^{-3}	Processed at 1300 F for 10 minutes prior to measurement.
P	2	2	Immed.	587 F	3.17×10^{-5}	2.59×10^{-5}	1.11×10^{-3}	1.25×10^{-3}	
P	2	3	Immed.	80 F	----	----	2.07×10^{-4}	1.45×10^{-4}	
P	3	1	52 min	1100 F	3.67×10^{-5}	3.9×10^{-5}	2.67×10^{-3}	2.18×10^{-3}	Processed at 1350 F for 10 minutes prior to measurement.
P	3	2	3 hr 42 min	1100 F	2.91×10^{-5}	3.3×10^{-5}	3.12×10^{-3}	2.18×10^{-3}	
P	3	3	6 hr 37 min	1100 F	2.6×10^{-5}	3.2×10^{-5}	3.38×10^{-3}	2.18×10^{-3}	
P	3	4	24 hr 12 min	1100 F	1.98×10^{-5}	2.21×10^{-5}	4.16×10^{-3}	2.18×10^{-3}	
P	3	5	47 hr	1100 F	3.6×10^{-5}	2.08×10^{-5}	4.52×10^{-3}	2.18×10^{-3}	
P	3	6	71 hr	1100 F	4.7×10^{-5}	1.6×10^{-5}	5.8×10^{-3}	2.18×10^{-3}	
P	4	1	2 hr 37 min	1100 F	----	----	2.77×10^{-3}	2.18×10^{-3}	Sample was cut fresh from 1" ingot, as received, using diamond saw - dry. No junction data taken on this sample.
P	4	2	2 hr 52 min	600 F	----	----	1.2×10^{-3}	1.3×10^{-3}	
P	4	3	3 hr 37 min	1100 F	Electrode to electrode resistance		= 1.55×10^{-2} ohms	----	
P	4	4	4 hr 37 min	1100 F	Electrode to electrode resistance		= 1.60×10^{-2} ohms	----	
P	4	5	21 hr	1100 F	Electrode to electrode resistance		= 1.89×10^{-2} ohms	----	
P	5	1	Immed.	1100 F	1.84×10^{-5}	3.12×10^{-5}	2.62×10^{-3} (1.47×10^{-2} ohm)*	2.18×10^{-3}	Chamber was evacuated to 4×10^{-4} mm Hg and backfilled to 15" Hg with Argon, heated to 1350 F, cooled, evacuated, refilled with Argon, heated to 1350 F.
P	5	2	50 min	1100 F	Electrode to electrode resistance		= 1.51×10^{-2} ohms	----	
P	5	3	1 hr 15 min	1100 F	Electrode to electrode resistance		= 1.54×10^{-2} ohms	----	
P	5	4	17 hr	1100 F	Electrode to electrode resistance		= 1.89×10^{-2} ohms	----	
P	5B	1	Immed.	1100 F	Electrode to electrode resistance		= 1.64×10^{-2} ohms	----	Sample was fitted with a mica sleeve similar to that proposed for the generator. Junctions were formed at 1350°F for 10 minutes.
P	5B	2	1 hr 30 min	1100 F	Electrode to electrode resistance		= 1.69×10^{-2} ohms	----	
P	5B	3	5 hr 10 min	1100 F	Electrode to electrode resistance		= 1.81×10^{-2} ohms	----	
P	5B	4	7 hr	1100 F	Electrode to electrode resistance		= 1.84×10^{-2} ohms	----	
P	5B	5	35 hr	1100 F	Electrode to electrode resistance		= 2.17×10^{-2} ohms	----	
P	5B	6	71 hr	1100 F	Electrode to electrode resistance		= 2.29×10^{-2} ohms	----	
P	6	1	0	620 F	3.2×10^{-5}	5.9×10^{-5}	1.46×10^{-3}	1.40×10^{-3}	This sample was run at increments of 100°F for 24 hour periods. Three profiles were taken during each 24 hour period, and the temperature was raised to the next step immediately after the third profile
P	6	2	7 hr	620 F	----	----	1.56×10^{-3}	1.40×10^{-3}	
P	6	3	24 hr	620 F	----	----	1.50×10^{-3}	1.40×10^{-3}	
P	6	4	0	700 F	----	----	1.64×10^{-3}	1.72×10^{-3}	
P	6	5	7 hr	700 F	----	----	1.78×10^{-3}	1.72×10^{-3}	
P	6	6	24 hr	700 F	----	----	1.85×10^{-3}	1.72×10^{-3}	
P	6	7	0	800 F	----	----	2.22×10^{-3}	2.09×10^{-3}	
P	6	8	6.5 hr	800 F	3.9×10^{-5}	5.7×10^{-5}	2.14×10^{-3}	2.09×10^{-3}	
P	6	9	23 hr	800 F	----	----	2.09×10^{-3}	2.09×10^{-3}	
P	6	10	0	900 F	----	----	2.39×10^{-3}	2.28×10^{-3}	
P	6	11	7.5 hr	900 F	----	----	2.34×10^{-3}	2.28×10^{-3}	
P	6	12	24 hr	900 F	----	----	2.25×10^{-3}	2.28×10^{-3}	
P	6	13	0	1000 F	----	----	2.57×10^{-3}	2.28×10^{-3}	
P	6	14	7 hr	1000 F	----	----	3.14×10^{-3}	2.28×10^{-3}	The power was off for a weekend shut down between measurements 14 and 15.
P	6	15	7 hr	1000 F	----	----	3.14×10^{-3}	2.28×10^{-3}	
P	6	16	23 hr	1000 F	----	----	2.86×10^{-3}	2.28×10^{-3}	
P	6	17	0	1100 F	----	----	2.64×10^{-3}	2.16×10^{-3}	
P	6	18	8 hr	1100 F	----	----	3.30×10^{-3}	2.16×10^{-3}	
P	6	19	24 hr	1100 F	----	----	3.83×10^{-3}	2.16×10^{-3}	
P	6	20		1000 F	----	----	4.10×10^{-3}	2.28×10^{-3}	Immediately after the last measurement at 1100 F, the temperature was reduced in steps of 100°F with a profile taken at each step.
P	6	21		900 F	----	----	3.66×10^{-3}	2.28×10^{-3}	
P	6	22		800 F	----	----	3.12×10^{-3}	2.09×10^{-3}	
P	6	23		700 F	----	----	2.60×10^{-3}	1.72×10^{-3}	
P	6	24		600 F	----	----	2.36×10^{-3}	1.40×10^{-3}	

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*Electrode to electrode resistance.

TABLE 5. RESISTANCE MEASUREMENTS
n-type PbTe (0.1 mol. % PbI_2)

Sample and Measurement Designation	Time from Heat Up	Measurement Temperature	Junction I Resistivity ohm in^2	Junction II Resistivity ohm in^2	Material Resistivity ohm in	Remarks
N 1 1	Immed.	1100 F	1.3×10^{-5}	7.8×10^{-6}	1.23×10^{-3}	
N 2 1	Immed.	590 F	7.45×10^{-6}	1.7×10^{-5}	3.73×10^{-4}	
N 2 2	Immed.	1056 F	2.34×10^{-5}	2.62×10^{-5}	1.09×10^{-3}	
N 3 1	Immed.	1100 F	Electrode to electrode resistance		= 7.90×10^{-3} ohms	This sample was fitted with a mica sleeve and measured electrode to electrode. Following measurement #7 the sample was cooled, the chamber opened, and the mica sleeve removed so that the junctions could be profiled in measurement #8 and #9.
N 3 2	.5 hr	1100 F	Electrode to electrode resistance		= 7.92×10^{-3} ohms	
N 3 3	1.5 hr	1100 F	Electrode to electrode resistance		= 7.92×10^{-3} ohms	
N 3 4	2.5 hr	1100 F	Electrode to electrode resistance		= 7.95×10^{-3} ohms	
N 3 5	17.5 hr	1100 F	Electrode to electrode resistance		= 7.85×10^{-3} ohms	
N 3 6	26 hr	1100 F	Electrode to electrode resistance		= 7.75×10^{-3} ohms	
N 3 7	41.5 hr	1100 F	Electrode to electrode resistance		= 7.76×10^{-3} ohms	Sample was cooled for one day then heated and profiled for 67 hours.
N 3 8	Immed.	1100 F	$(<10^{-6})$	$(<10^{-6})$	1.6×10^{-3}	
N 3 9	6 hr	1100 F	$(\sim 10^{-6})$	1.1×10^{-5}	1.66×10^{-3}	
N 3 10	0	1100 F	3.3×10^{-5}	$(<10^{-6})$	1.36×10^{-3}	
N 3 11	2 hr	1100 F	2.2×10^{-5}	$(<10^{-6})$	1.37×10^{-3}	
N 3 12	23 hr	1100 F	9.0×10^{-6}	$(<10^{-6})$	1.34×10^{-3}	
N 3 13	67 hr	1100 F	6.2×10^{-6}	$(<10^{-6})$	1.36×10^{-3}	

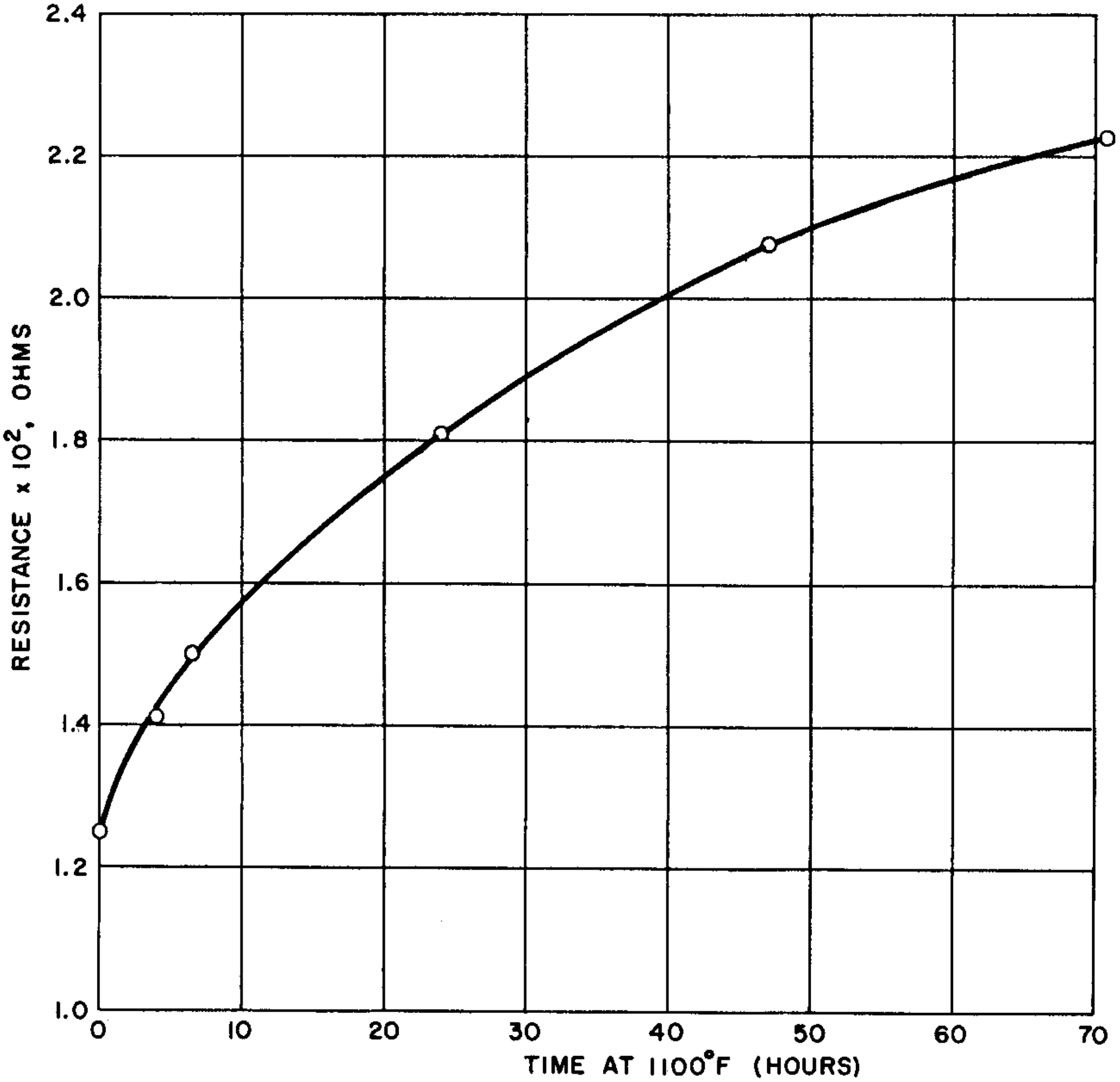

Figure 26: Resistance of p-Type Elements at 1100°F as a Function of Time.

The P-4 series was intended to deduce that the effect was related to the preparation of the material surfaces. The particular type of abrasive finishing paper which was used was reported to have given trouble in Hall measurements made by the vendor. The P-4 sample was cut with a diamond saw, but not finished with any abrasive paper. The results indicate that the use of the abrasive paper per se was not the source of the problem. This is not to say that some other aspect of the condition of the sample ends could not be responsible, however, it was felt that this was unlikely and that other possibilities existed which seemed more feasible.

Accordingly, the next tack was to consider the effect of the atmosphere. In the P-5 series, argon was substituted for methane to ascertain its effect on the material and junctions. This variation seemed to have little effect on the problem of increasing material resistivity. Heretofore it was believed that the methane served as a reducing agent on the oxides at the interface between the thermoelectric material and the electrodes. A remarkable result of this series was that the junctions formed just as well in argon as in methane.

It was evident from examination of the probe that sublimation of the thermoelectric material was occurring. X-ray examination of the sublimate indicated excess telluride. This suggested a need to protect the thermoelement from sublimation during these measurements. Close fitting sleeves of mica for this purpose had been planned for use in the generator and were on hand. The P-5B series of measurements were run to test this procedure. The results indicate that the mica sleeve was not successful in occluding the flow of vapors away from the sample. That is, there was evidence of leakage in the system and the resistivity continued to increase with time at temperature.

Feeling that it might be necessary to tolerate the increasing resistance, and considering that in practice only a small portion of the sample would be at the maximum temperature, the P-6 series of tests evolved to determine the rate at which this effort occurred at various temperatures over the range of proposed operation. The results have been plotted on Figure 27 to illustrate the magnitude of the change at each temperature and its permanence. The numbers on the figure indicate the sequency of measurement and correspond to the measurement designations listed in Table 4 for the P-6 series.

The remarks column of this table indicates the procedure followed in making these measurements.

Subsequent investigation by the vendor(11) of possible causes of this apparent increase in resistivity have led to the conclusion that oxidation may be the source of the difficulty. Samples of the p-type PbTe heated to 1300°F in sealed capsules under a variety of atmospheres for a period of 70 hours have shown no increase in resistivity. Another test in which a sample was sealed in air in a capsule of about 10 times the volume of the sample and exposed to temperatures of 1200°F again indicated no increase in resistivity. However, samples heated to high temperatures in a continuous flow of a gas containing traces of oxygen exhibited marked increases in resisitivity. Evidently the limited supply of oxygen in the capsules sealed in air was insufficient to

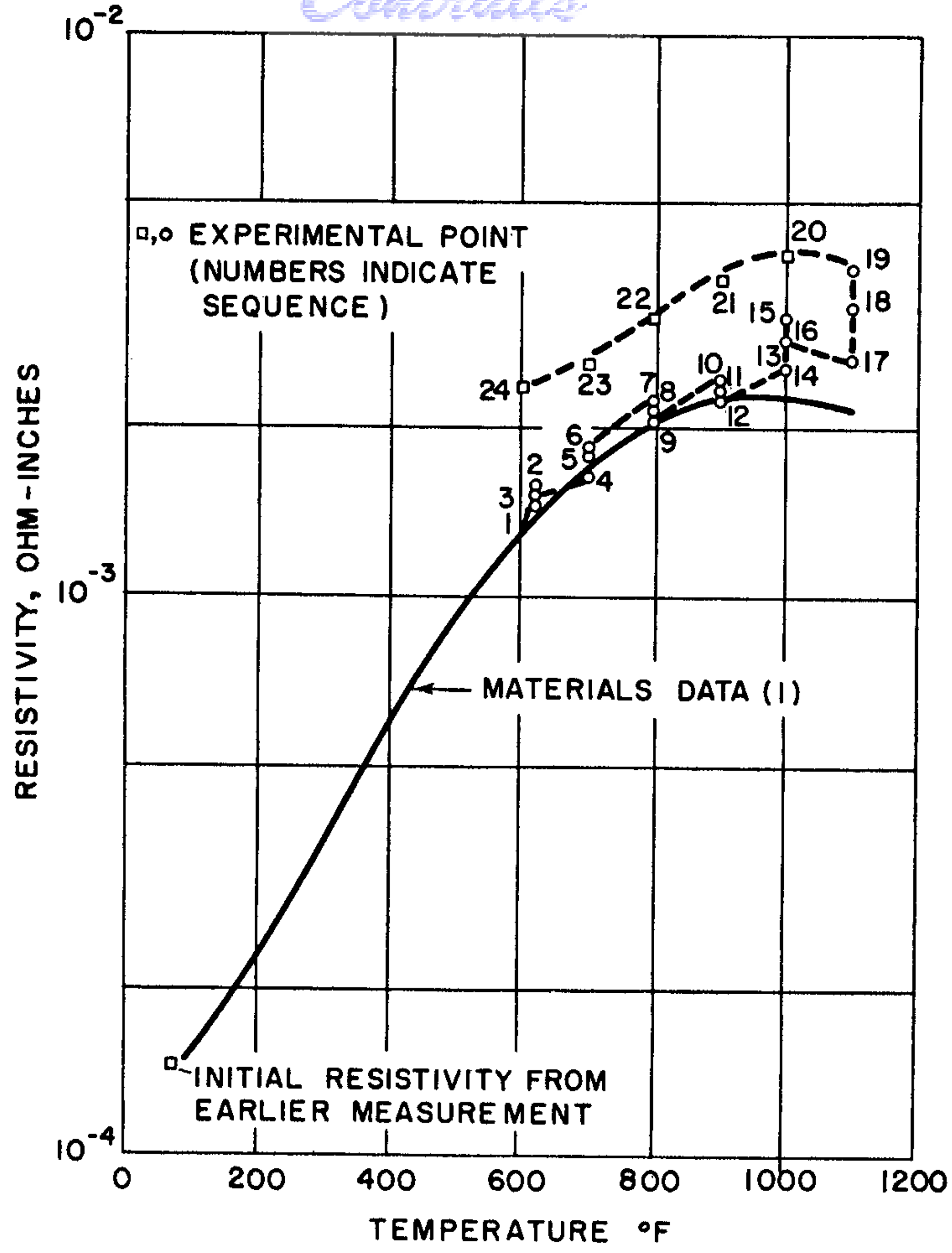

Figure 27: Resistivity vs Temperature — p-Type PbTe (1.0 at. % Na).

cause enough oxidation to result in a detectable increase in resistivity. On the basis of the tests performed by the vendor, it seems possible that the increase in resistivity found in the resistance profiler measurements described above may be due solely to oxidation. Traces of oxygen in the large volume of gas enclosed in the bell jar or evolved from the various heated parts of the experimental device itself may have been present in each experiment.

Less effort has been applied to the measurements of n-type material and junctions, because the junctions, in general, were better than those of the p-type and the n-type material resistivity did not appreciably deviate from the vendor's data even over extended time at temperature tests.

The junction resistivity measurements shown in Tables 4 and 5 are so erratic that to draw any conclusions is difficult. However, one might speculate that pressure contact junction resistivities on the order of 250 x 10^{-6} ohm cm^2 could be expected for the p-type. The n-type junctions are certainly better, perhaps by a factor of two or more. The question of what effect possible oxidation of the lead telluride as mentioned above has had on these junctions is, at this writing, unanswered.

Single Ring Models

Tests of single ring models of the 5 watt generator design were required to evaluate the construction and assembly problems as well as performance before attempting to build the final generator. These models were not sealed so they were tested in a chamber that could provide various types of atmospheres. A schematic of the test chamber is shown in Figure 28.

At the start of the test program an attempt was made to perform the junction seating process (required to reduce the high initial junction resistance) in this test cell. However, it was not possible to get the cold junction to the recommended temperature (700 F) for this procedure. Then the test models were placed in a hydrogen furnace at 1100°F for about 50 hours to see if the junction resistance could be reduced. Other work (See Figure 26) showed that the apparent resistivity of the p-type lead telluride almost doubled when the entire element was at 1100°F for 70 hours. Because of this the test cell was modified so that the cold junction could be maintained at about 700°F and thus it was hoped the junction resistance could be reduced in the test cell.

Whatever method was used for junction resistance reduction, after the single ring model was mounted in the test cell the following procedure for starting tests was used:

1. The test cell was pumped down at room temperature to about 10 microns pressure.
2. The generator was heated to about 200°F and pump down again to about 10 microns.
3. The operating atmosphere was introduced. If a reducing atmosphere was used a constant flow of the gas was purged through the system and burned at the outlet.
4. The generator was raised to operating temperature over a period of about 1/2 an hour.

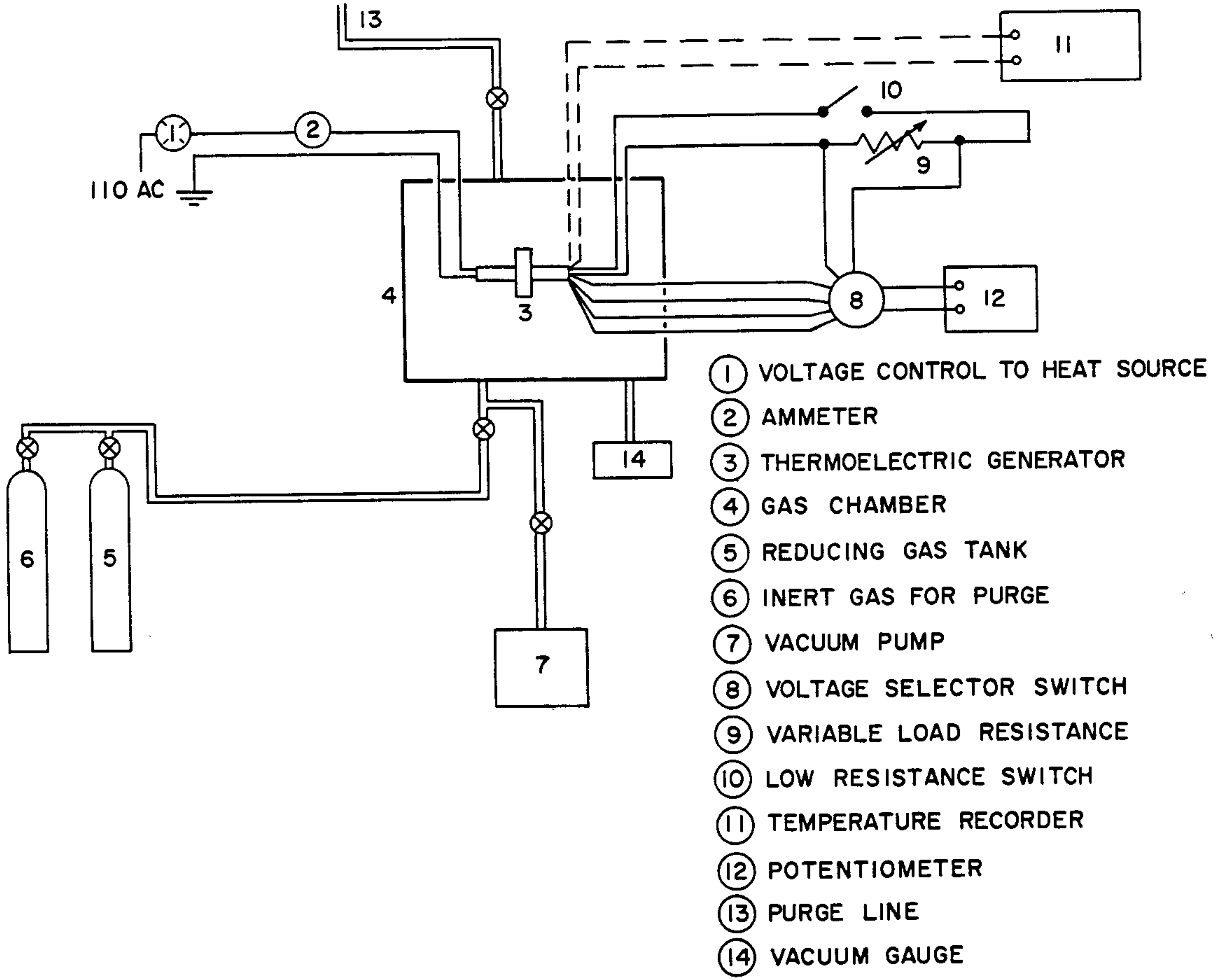

Figure 28 : Schematic of Test Setup Used for Single-Ring Model Tests.

5. The generator was operated at various temperatures and necessary data were recorded.

6. For shutdown the system was purged with argon after turning off the input power to heater.

The system was pumped down initially to avoid traces of oxygen and water vapor in the system during operation. To remove these contaminants from the gases introduced to the system various techniques were used. When the gas was hydrogen (commercial dry hydrogen distributed by the General Electric Company) a Deoxo catalytic purifier followed by a tube of Drierite, $Ca\ SO_4$, was used. For operation in methane (C. P. grade of Matheson Inc.) an absorbant, Ascarite, followed by a tube of Drierite was used to remove traces of oxygen, water vapor and carbon dioxide. Argon of 99.995% purity (Linde Air Products Inc.) was readily available and this was used with only the Drierite tube in the gas supply line.

After the junction resistance was reduced as much as possible the following data were recorded:

1. The hot junction temperature (T_1)

2. The cold junction temperature (T_2)

3. The variable load resistance (R_v) using a Kelvin Double Bridge.

4. The open circuit voltage (V_{oc}), closed circuit or full load voltage (V_{cc}) and the drop across the variable load resistance (V_R), using a Rubicon Precision Potentiometer.

From this recorded data the power out (P), the current (I) and the resistance ratio (m) were calculated.

A summary of the tests performed in the single ring model test stand is presented in Table 6. During this period of testing it was determined that copper has inadequate resistance to creep at the design temperatures so the design of the diffusion barrier was modified on Model C4. The modification was to make the iron barrier project through the copper and thus support the compression load between the thermoelements and the C. rings. This and other minor modifications apparently solved the problem of initial relaxation of the internal parts that had reduced the contact pressure to unacceptable levels in earlier tests. In the course of these tests it was also determined that mica was the most satisfactory electrical insulation for operation in a reducing or inert atmosphere at the design temperatures.

Performance Results

Table 7 is a more detailed presentation of performance data from the single ring model tests with a comparison of the measured values and those calculated from the vendor's data.

TABLE 6

SUMMARY OF PROGRESS ON THE SINGLE RING MODEL TESTS

Model #	Date Started	Total Hrs. @ Temp.	Temperature °F		Voltage		Operating Atmosphere	Current amps.	m R/r	r ohms	P watts	Remarks
			T_1	T_2	Open Circuit	Closed Circuit						
1	2/1/60	1	1100	476	.29	.062	CH_4	1.21	.25	.20	.075	This was a 2 couple solid ring design with radiator attached. A couple is defined as one n-type and one p-type junction. The internal heater burned out after one hour of operation.
2	2/12/60	 1	1100 1100	650 650	.241	.025	CH_4		.115	.45 .50	.0029	This unit is a 2 couple solid ring design. Discontinued testing because of the high internal resistance.
C1	2/10/60	60	1100	1100			H_2			.15		All of the following "C" ring models have one couple and are without a radiator. Attempted to lower the junction resistance by heating the entire unit in a hydrogen furnace.
C1		150	1100	1100			H_2			.15		When the unit was removed from the furnace it was discovered that the internal components had relaxed. The unit was reshimmed but this did not lower the internal resistance, so tests were discontinued.
C2	3/7/60											The control relay on the hydrogen furnace failed and the generator was ruined.
C3	3/15/60	46	1100	1100			H_2			.027		A short was discovered in the electrical insulation (Barium Sulphate base) on the "C" ring so mica shims were inserted to complete the test.
C3		1	1100	615	.1306	.0616		1.8	1.04	.0328	.11	
C3		13	1100	615	.1355	.0686		1.19	1.03	.056	.0815	When removed because of the high internal resistance, it was discovered that the internal components had relaxed enough so that the "C" ring was undeflected.
C4	3/23/60	1	1100	1100			H_2			.029		The electrical insulation on the "C" rings was changed to an Aluminum Phosphate base insulation. The hot and cold junctions were redesigned to prevent creep at operating temperature.
C4		65	1100	1100			H_2			.015		This insulation also failed and this is assumed to be the reason for the small internal resistance.
C4			1100	560	.1606	.080	H_2	2.05	1.01	.038	.166	Transferred to operating chamber after mica insulation was inserted to prevent short circuit through the "C" ring.
C4		15	1100	560	.1589	.0789		2.07	.975	.039	.163	The unit relaxed .003" out of an initial deflection of .007".
C5	6/8/60	1	1100	720	.115	.059	15% H_2 85% N_2 by Vol.	1.9	1.05	.0295	.112	Used a .0015 mica for electric insulation on both hot and cold sides. The initial "C" ring deflection was .007 inch. The test cell was modified and used for the reduction of junction resistance.
C5		7	1100	640	.1347	.0737		2.47	1.2	.0248	.152	
C5		20	1100	660	.1356	.0658	"	2.24	.945	.0312	.147	Here the generator was removed and reshimmed so that the "C" ring deflection was .015.
C5		26	1100	640	.129	.072	"	2.38	1.27	.0238	.172	
C5		34	1100	645	.1263	.0705	"	2.24	1.25	.0250	.157	

TABLE 7

SELECTED PERFORMANCE DATA FROM THE SINGLE RING MODEL TESTS

MEASURED VALUES														VALUES CALCULATED FROM VENDOR'S DATA				
Model No.	Atmosphere	Total Hrs. @ Temp.	Temperature °F T_1	Temperature °F T_2	Voltage Open Circuit	Voltage Closed Circuit	Current amps.	r_p ohms	r_n ohms	$(\alpha a)_p \times 10^4$ V/°K	$(\alpha a)_n \times 10^4$ V/°K	m	P watts	$(\alpha a)_p \times 10^4$ V/°K	$(\alpha a)_n \times 10^4$ V/°K	r_p ohms	r_n ohms	P watts
C4	H_2	15	1100	560	.1587	.0789	2.07	.0328	.0053	3.22	2.07	1.0	.164	2.73	1.82	.009	.0032	.32
C5	15% H_2 85% N_2 by Volume	7	1080	640	.1347	.0735	2.47	.0174	.0074	3.1	2.2	1.2	.152	2.78	1.85	.0094	.0032	.28
C5	"	20	1095	950	.0457	.0255	.777	.0182	.00785	2.97	2.47	1.26	.02	2.62	2.0	.0104	.0048	
C5	"	26	1100	640	.129	.072	2.38	.018	.0058	2.90	2.15	1.26	.172	2.78	1.85	.0094	.0032	.28

The maximum power output for any of the single ring models was approximately 60% of the design power output. This loss is due to the high value of measured internal resistance as shown in Table 7. Other work (see Resistance Measurements Results) indicated that this apparent high value for the internal resistance is due primarily to high resistance at the lead telluride and iron junction. During the testing the contact pressure was increased and various gases were used in the chamber to determine their influence on the junction resistance. The contact pressure was increased to approximately 400 psi (by increasing the C ring deflection) with no significant increase in performance. Also three different atmospheres (argon, hydrogen, and a forming gas of 15% by volume hydrogen and the rest nitrogen) were used with still no increase in performance.

At this writing, there is no available knowledge of an established method for reducing the junction resistance beyond the levels apparent from these tests. Therefore, present expectations for the performance of the model generator indicate a net power output of approximately 3 watts instead of the design power of 5 watts.

SPECIFICATIONS - 100 WATT SOLAR THERMOELECTRIC GENERATOR

INTRODUCTION

In preparing the specifications for the 100 watt solar thermoelectric generator, which appear as an appendix in this Part, the main objectives were to: 1) Make them as realistic as possible, and 2) Keep them reasonably flexible in order to not restrict unnecessarily the opportunity for design ingenuity on the part of anyone endeavoring to meet the specifications.

In order to meet the first objective, liberal use was made of the experience gained on this contract, both that gained in system and optimization studies and that gained in endeavoring to construct and test the 5 watt generator model. In connection with the second objective, specification of design details was completely avoided, and only some very general ground rules for design concept were spelled out where it was felt that the evidence of their desirability was extremely strong. Examples of such general ground rules are the specification that this generator be constructed for use with a circular, parabolic solar collector and that the heat flow between the cold junctions and the radiator not require the use of any moving parts or circulating fluids.

DESIGN CONSIDERATIONS

In order to make the specifications for weight, volume, and efficiency realistic, it was felt necessary to base them on the use of specific materials and a specific design concept, although the specifications themselves, except for the few restrictions just mentioned, do not spell out either materials or detailed design concepts.

Of first consideration was the choice of thermoelectric materials. Lead telluride was selected, as it was for the 5 watt generator model, and for the same reasons. These reasons have been discussed previously in this Part. Selection of lead telluride in turn means that absorber temperatures of about 900^{o} K would be required. It is, moreover, doubtful if temperatures much less than this would give satisfactory performance even if materials other than lead telluride were involved.

Of second consideration, because of its influence on generator design, was the type of collector on which to base the design. That is, should it be a circular, parabolic collector or a cylindrical parabolic collector. For absorber temperatures in the neighborhood of 900^{o} K, considerations such as those carried out in Appendix O of Part III of the report indicate that a circular (i.e. spherical) parabolic solar collector is required in order to achieve reasonable collection efficiency. (See Figures O-7 and O-8 of Appendix O for example). Indeed, this evidence seems so conclusive that it was decided to incorporate in the specifications the requirement that a circular collector be used.

Consideration was then given as to whether the absorber design should be one in which the collector focuses its energy through an aperture into a cavity, or whether it should focus on an absorber surface having selective absorptivity and emissivity characteristics. From these considerations, (again see Figure O-8 of Appendix O, Part III, for example) the aperture type absorber was selected as being most promising. The specifications do not specify, however, the type of absorber that must be used, it being felt that this was placing undue restrictions on the design.

Another consideration then involved selection of the design concept for the generator itself, i.e. whether it should, for example, be of sandwich type construction, or one incorporating side fins. Because it will result in less weight, a side fin construction was selected; indeed, it was decided to pattern the design very closely to that of the 5 watt generator.

The resulting design concept on which performance estimates were then made is indicated in Figure 29. The energy of the sun is reflected from a circular, parabolic collector through an aperture in the end of a cylindrical tube. The thermoelectric elements are mounted in the annular space around this tube, (or ring) and held in place by an outer ring. Side fins extend outward to reject the waste heat. The inner and outer rings, thermoelectric elements, side fins, appropriate electrical conductors, and insulation constitute the thermoelectric generator for which the specifications are written. The solar collector is considered to be a separate piece of equipment, just as is the equipment for regulation, orientation, voltage regulation, and energy storage that would be necessary for a complete system. The specifications, therefore, do not cover these latter equipments, although they include some requirements which they must meet and on which the generator performance estimates are based.

The generator design concept is thus seen to be essentially identical to that of the 5 watt generator previously discussed. In estimating its performance, studies were made both of the design incorporating two elements per ring (See 5 watt generator discussion) and a solid ring design incorporating 4 elements per ring. The same criteria were used for allowable stresses, deflections, etc. as were used in the 5 watt generator design. Use of pressure contacts was also assumed.

The diameter of the inner tube or ring of Figure 29 will be considerably greater than that used for the 5 watt generator design. A typical value, for example, might be around 2 inches as compared to the 3/16 inch used in the 5 watt generator. This occurs because collector and orientation system inaccuracies require fairly large aperture diameters in order to obtain reasonable collection efficiencies. As was discussed in Appendix N, Part III, the larger the diameter of this inner ring, the more the generator will weigh per unit of net power output. Consequently, for generators of large output, a lighter weight system will probably result if several modules of the kind shown in Figure 29 are arranged together rather than having a single large, generator-collector combination. For example, for the 100 watt generator for which the specifications were written, four modules each of 25 watts output, seems a reasonable number for the design concept used here.

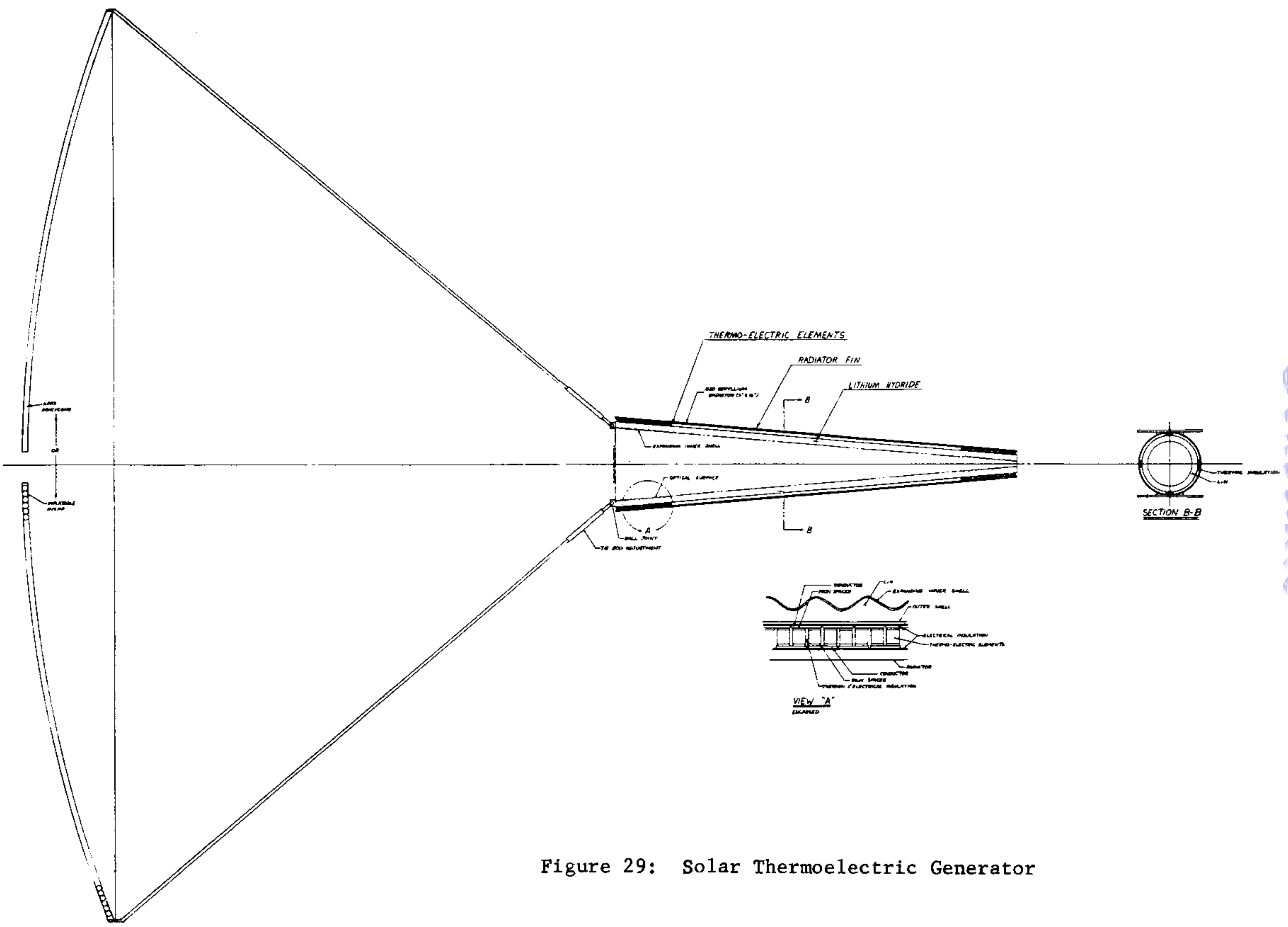

Figure 29: Solar Thermoelectric Generator

With fairly large ring diameters, studies indicate that use of the solid ring construction with four elements per ring will have less weight than the split ring, 2 element per ring design, and this is, therefore, the kind shown in Figure 29. In connection with this figure, it should be mentioned that the fin arrangement shown there might result in an excessive temperature drop between the cold junctions and the base of the fin. Consequently, a more probable fin arrangement is that shown in Figure N-3b of Appendix N, Part III, wherein the base of each fin is brought close to the thermoelectric elements.

A possible problem in connection with this design concept which should be mentioned, is that of insuring an even distribution of heat flux along the length of the generator cylinder. A high reflectivity surface on the inside of the inner cylinder will undoubtedly be required, and it may also be necessary to vary this along the length, making it highly reflective at the inlet and highly absorptive at the end furthest from the aperture.

SUMMARY OF ANTICIPATED PERFORMANCE

From the studies mentioned above, it is expected that the following performance figures for the 100 watt solar thermoelectric generator are realistic, and these are the requirements given in the specifications.

Minimum output - 100 watts
Maximum weight of generator - 20 pounds
Maximum envelope volume of generator - 3400 cubic inches
Minimum generator efficiency - 2%

In connection with the envelope volume, this is fairly large because it includes the space between fins. However, this volume, compared to the volume requirements of the collector, is still very small and should not provide a restriction on the complete system.

It should be re-emphasized that the above figures comtemplate the use of pressure contacts. They also include an allowance for the high junction contact resistances encountered in efforts to build the 5 watt generator. Consequently, if this junction problem could be wholly or partially solved, the anticipated performance would improve significantly.

BIBLIOGRAPHY

1. Fritts, R. W., Design Parameters for Optimizing the Efficiency of Thermoelectric Generators Utilizing p-Type and n-Type Lead Telluride, Communications and Electronics, January, 1960.

2. Fritts, R. W., unpublished notes on Joining Techniques, presented at, A Course on Thermoelectric Materials and Devices, New York University, 1959.

3. Fredrick, R. E., et al, Contacting Semi-Metallic Electrical Conductors, U.S. Patent No. 2,811,569, October 29, 1957.

4. Jost, W., "Diffusion", Academic Press, 1952.

5. Barrer, R.M., "Diffusion in and Through Solids", University Press, Cambridge, 1951

6. Fritts, R. W., et al, Thermoelectric Generators, U.S. Patent No. 2,811,571, October 29, 1957.

7. Powell, C. F., Cambell, I. E., Gonser, B. W., "Vapor Plating", John Wiley & Sons Inc., page 60, 1955.

8. Brady, E. L., Preparation and Properties of Lead Telluride, General Electric Company, Report No. 53RL822, March, 1953.

9. Klein, P. General Electric Company Electronics Laboratory, Syracuse, New York, Personal Communication.

10. Dauphinee, T. M., Mooser, E., Apparatus for Measuring Resistivity and Hall Coefficient of Semiconductors, Review of Scientific Instruments, July, 1955.

11. Richards, J. D., Minnesota Mining and Manufacturing Company, Personal Communication.

12. Fritts, R. W., et al, Electrically Conductive Compositions and Method of Manufacture Thereof, U.S. Patent No. 2,811,720, October 29, 1957.

APPENDIX A

PRELIMINARY SPECIFICATION

GENERATOR, THERMOELECTRIC, SOLAR, 100 WATT

26 August 1960

PRELIMINARY SPECIFICATION

GENERATOR, THERMOELECTRIC, SOLAR, 100 WATT

1. SCOPE

1.1 SCOPE.- This specification covers a 100 watt thermoelectric generator suitable for use with a concentrating, circular, parabolic solar collector as the source of heat. The generator shall be designed, fabricated, and ground tested to demonstrate the feasibility of using such a generator with solar collectors as the source of heat. The solar collectors are separate equipment not a part of the generator specified herein.

2. APPLICABLE DOCUMENTS

2.1 The following documents, of the issue in effect on the date of invitation for bids, form a part of this specification.

SPECIFICATIONS

Military

MIL-S-5002	Surface treatments (Except Priming and Painting) For Metal and Metal Parts in Aircraft
MIL-D-5028	Drawings and Data Lists; Preparation of Manufacturers' (for Production Aircraft, Guided Missiles, Engines, Accessories, and Other Auxiliary Equipment)
MIL-F-7179	Finishes and Coatings; General Specification for Protection of Aircraft and Aircraft Parts
MIL-S-7513	Systems, Sets and Components, Method for Obtaining Assignment of Nomenclature and Approval of Nameplate Identification and Description for Aeronautical and Supporting Ground Equipment

STANDARDS

Military

MIL-STD-130	Identification Marking of U S. Military Property

PUBLICATIONS

Air Force-Navy Aeronautical Bulletins

143	Specifications and Standards; Use of

3. REQUIREMENTS

3.1 Components.- The 100 watt solar thermoelectric generator shall consist of a number of identical, self-contained, modules whose combined power output is equal to or greater than 100 watts of electrical energy under conditions specified in paragraph 3.6.3. The number of such modules shall be anywhere in the range of one through four inclusive. The modules shall be physically separate in the sense that each shall operate from its own solar collector.

3.2 Selection of specifications and standards.- Specifications and standards for necessary commodities and services not specified herein shall be selected in accordance with Bulletin 143, except as provided in 3.2.1 and 3.2.2.

3.2.1 Commercial parts.- Commercial parts having suitable properties may be used where, on the date of invitation for bids, there are no suitable standard parts. In any case, commercial utility parts like screws, bolts, nuts, cotter pins, etc. having suitable properties may be used provided:

a. They can be replaced by the standard parts (MS or AN) without alteration.

b. The corresponding standard part numbers are referenced in the parts list and, if practical, on the contractor's drawings.

3.2.2 Standard parts.- With the exception in 3.2.1, AN and MS standard parts shall be used where they suit the purpose. They shall be identified on the drawings by their part numbers.

3.3 Protective treatment.- When materials are used in the construction of the 100 watt solar thermoelectric generator that are subject to deterioration when exposed to climatic and environmental conditions likely to occur during service usage, they shall be protected against such deterioration in a manner that will in no way prevent compliance with the performance requirements of this specification. The use of any protective coating that will crack, chip, or scale with age or extremes of climatic and environmental conditions shall be avoided.

3.4 Design.- Each module specified in paragraph 3.1 shall contain, but not be limited to, the functional elements listed in paragraphs 3.4.1 through 3.4.7.

3.4.1 Absorber.- The function of the absorber is to absorb a portion of the thermal energy focused upon it by the solar collector.

3.4.2 Energy distributor.- The function of the energy distributor is to distribute to the hot junctions of the thermoelectric elements the thermal energy absorbed by the absorber.

3.4.3 Thermoelectric elements.- The function of the thermoelectric elements is to convert to electrical energy a portion of the thermal energy delivered to them by the energy distributor.

3.4.4 Radiator.- The function of the radiator is to reject, by means of thermal radiation, the waste heat from the module. The waste heat flow between the thermoelectric elements and the radiator shall not require the use of any moving parts or circulating fluids.

3.4.5 Electrical conductors.- The function of the electrical conductors is to electrically interconnect the thermoelectric elements and deliver this energy to two terminal posts.

3.4.6 Terminal posts.- There shall be two terminal posts located at a convenient position on each module whose function shall be to receive the electrical energy from the conductors and deliver it to an external load when suitable connections are made from the load to the terminal posts.

3.4.7 Mounting flange.- The function of the mounting flange is to provide a means of mechanically connecting the module to a matching flange which is in turn connected to struts which are in turn connected to the solar collector supplying the heat energy to each module. The flange connection shall be by means of bolts, the number and size of which shall be sufficient to satisfy all appropriate requirements of this specification.

3.5 Construction.- The generator shall be so constructed that no parts will work loose or fail in service or under the strains, jars, vibration, and other conditions that can be predicted to be incident to shipping, storage, installation, and testing operations.

3.6 Performance

3.6.1 Environment.- It shall be an objective to design and construct the generator to withstand the environmental conditions specified in paragraphs 3.6.1.1 through 3.6.1.8.

3.6.1.1 Temperature.- Minus 20° to plus 180°F at any time and for extended storage for periods up to six months.

3.6.1.2 Pressure.- 14.7 to 0 psi at any time.

3.6.1.3 Humidity.- All conditions of relative humidity within the temperature limits specified in paragraph 3.6.1.1

3.6.1.4 Gravity.- Zero gravity.

3.6.1.5 Meteorites.- Meterorite particles encountered at altitudes of 100 miles or greater above the earth.

3.6.1.6 Radiation.- Ionizing radiation encountered at altitudes of 100 miles or greater above the earth.

3.6.1.7 Vibration.- Continuous vibrations in all three mutually perpendicular planes within a frequency range of 20 to 2,000 cps equal to 0.05 inches double amplitude, or 20G, whichever is less.

3.6.1.8 Acceleration.- Linear acceleration of 10G along the longitudinal axis and 2g along any axis perpendicular to the longitudinal axis as well as instantaneous deceleration along any axis.

3.6.2 Reliability.- It shall be an objective to design and construct a generator having a reliable, trouble-free life expectancy which is a minimum of one year.

3.6.3 Design operating conditions.- Design operating conditions shall be as specified in paragraphs 3.6.3.1 through 3.6.3.6.

3.6.3.1 Solar collector characteristics.- It shall be assumed that each solar collector, when operating, shall have a reflectivity of 0.9 and a ratio of diameter to focal length of 1.85. Each collector shall also be assumed to have a slope at every point on its surface which deviates 16 minutes from the slope of a perfect parabola at that point. The direction of this deviation, moreover, shall be assumed always to be such as to decrease the radius of curvature at each point.

3.6.3.2 Solar collector area.- The total projected solar collector area normal to the sun which is required to achieve the performance given in paragraphs 3.6.4 and 3.6.5 under the conditions specified in paragraphs 3.6.3.1, and 3.6.3.3 through 3.6.3.6, shall not exceed 110 square feet. The number of solar collectors and total projected area required shall be specified by the contractor.

3.6.3.3 Orientation characteristics.- It shall be assumed that during operation the generator and the collector to which it is connected will be oriented toward the center of the sun with an accuracy of ± 0.1°.

3.6.3.4 Solar constant.- It shall be assumed that the solar constant is 65 watt/ft^2.

3.6.3.5 Pressure.- Environmental pressure shall be a vacuum.

3.6.3.6 Temperature.- It shall be assumed that the effective temperature surrounding the generator is 300° K.

3.6.4 Generator power output.- The measured net power output of the generator, when corrected to conform with the conditions of paragraphs 3.6.3.1 through 3.6.3.6, shall be equal to or greater than 100 watts with an output voltage equal to or greater than 12 volts.

3.6.5 Generator efficiency.- The measured generator efficiency, when corrected to conform with the conditions of paragraphs 3.6.3.1 through 3.6.3.6 shall be equal to or greater than 2%. This efficiency is defined as the ratio of the net power output from the generator to the net heat input to the generator.

3.6.6 Life endurance.- The generator shall be capable of operation for a minimum of 25 hours at or above hot junction design temperature and rated load under the environmental conditions of paragraph 4.3.1.

3.6.7 Thermal cycling.- The generator shall be capable of withstanding at least 100 cycles of warm-up and cool-down between the environmental temperatures and hot junction temperatures equal to or greater than the design value under the environmental conditions of paragraph 4.3.1.

3.7 Interchangeability.- All parts having the same manufacturer's part number shall be functionally and dimensionally interchangeable. The drawing number requirements of Specification MIL-D-5028 shall govern changes in the manufacturer's part numbers.

3.8 Dimensions.- The total envelope volume of the generator shall not exceed 3400 cubic inches. This volume shall be determined by summation of the individual envelope volumes of each of the modules referred to in paragraph 3.1.

3.9 Weight.- The total weight of the generator shall not exceed 20 pounds.

3.10 Finish.- Finish requirements shall be in accordance with Specifications MIL-S-5002 and MIL-F-7179.

3.11 Identification of product.- Equipment, assemblies, and parts shall be marked for identification in accordance with Standard MIL-STD-130.

3.12 Nomenclature and type designations.- Nomenclature and type designations shall be in accordance with Specification MIL-S-7513, subject to the approval of the Air Force.

3.13 Workmanship.- All workmanship shall be of high quality and consistent with the standards normally expected for military, aircraft equipment.

4. QUALITY ASSURANCE PROVISIONS

4.1 Classification of tests.- The inspection and testing of the 100 watt solar thermoelectric generator shall be classified as follows:

Acceptance tests.

4.2 Acceptance tests.- Acceptance tests shall consist of:

Individual tests.

4.2.1 Individual tests.- Each of the modules referred to in paragraph 3.1 shall be subjected to the following tests as described under paragraph 4.4, Test methods, of this specification:

a. Examination of product.
b. Environmental tests.
c. Reliability tests.
d. Functional tests.

4.3 Test conditions.

4.3.1 Atmospheric conditions.- Unless otherwise specified, all tests required by this specification shall be made at an atmospheric pressure of 28 to 32 inches of mercury, a temperature of 80° plus or minus 40° F, a relative humidity of 80% or less, and wind velocities less than 5 miles per hour. Where tests are made under conditions substantially different from the above values, proper allowance shall be made for changes in instrument readings and other effects on the performance being measured.

4.4 Test methods.

4.4.1 Examination of product.- Each module referred to in paragraph 3.1 shall be visually inspected by the contractor to ascertain that all non-functional requirements of Section 3 have been met. No performance tests are required, and no measurements are required other than those necessary to establish conformity with paragraphs 3.7, 3.8, and 3.9.

4.4.2 Environmental tests.- No specific environmental tests are required, since the objective of the 100 watt solar thermoelectric generator is to demonstrate feasibility, and the ability to withstand the environmental conditions of paragraphs 3.6.1.1 through 3.6.1.8 is a design objective and not a requirement.

4.4.3 Reliability tests.- No reliability tests are required, since the objective of the 100 watt solar thermoelectric generator is to demonstrate feasibility, and the ability to achieve the reliability of paragraph 3.6.2 is a design objective and not a requirement.

4.4.4 Functional tests

4.4.4.1 Generator power output.

4.4.4.1.1 Test Assembly.- The generator shall be assembled into a system consisting of a solar collector, an orientation mechanism, and a means of applying electrical load and shall be ground tested under conditions which conform as closely as possible to the conditions specified in paragraphs 3.6.3.4 and 4.3.1.

4.4.4.1.2 Prior tests.- The solar collector shall have previously been tested to insure that over the range of possible absorber designs to be used, it delivers to the absorber an amount of energy equal to or greater than would be delivered by a solar collector having the characteristics specified in paragraphs 3.6.3.1 and 3.6.3.2. The orientation mechanism shall also have previously been tested to insure that it meets the requirements specified in paragraph 3.6.3.3. The solar collector and orientation mechanism and a dummy absorber shall, moreover, have been calibrated by means of previous testing so that the net energy input to the absorber under test conditions can be accurately determined from test data.

4.4.4.1.3 Test data and instrumentation.- Test data to be taken during the test shall include, but not be limited to, the following:

a. Solar flux density as measured by a pyrheliometer.
b. Output voltage and current as measured by conventional instruments.
c. Absorber surface temperatures by means of at least five thermocouples distributed over the surface of each module.

d. Hot junction temperatures by means of at least five thermocouples placed at various points on each module.
e. Cold junction temperatures by means of at least five thermocouples on each module placed opposite the hot junction thermocouples, i.e. on or near the same thermoelectric elements.
f. Radiator surface temperatures by means of at least five thermocouples distributed over the radiator surface of each module in the same vicinity as the cold junction thermocouples.
g. Ambient temperature.
h. Ambient pressure.
i. Wind velocity.

All instrumentation shall be calibrated at one month intervals before, during, and after the tests, and the calibration data for each instrument shall form a part of the test data.

4.4.4.1.4 Corrections.- It will generally be impossible to duplicate exactly the design conditions of paragraphs 3.6.3.1 through 3.6.3.6. Moreover, functional testing will not be carried out under the conditions of paragraph 3.6.3.5 because it is not considered practical to do so. Therefore, the measured performance shall be corrected by theoretical means to obtain the performance conforming to these design conditions. The method of making such corrections shall be prepared by the contractor and submitted to the Air Force for approval prior to carrying out the tests.

4.4.4.2 Generator efficiency.

4.4.4.2.1 Test assembly.- Test assembly shall be as specified in paragraph 4.4.4.1.1.

4.4.4.2.2 Prior tests.- These shall be as specified in paragraph 4.4.4.1.2.

4.4.4.2.3 Test data and instrumentation.- This shall be as specified in paragraph 4.4.4.1.3.

4.4.4.2.4 Corrections.- Corrections shall be applied to the performance data as specified in paragraph 4.4.4.1.4.

4.4.4.3 Life endurance tests.- The generator shall be operated at or above hot junction design temperature and rated load for a period of at least 25 hours.

4.4.4.4 Thermal cycling tests.- At least 100 cycles of warm-up and cool-down shall be conducted between the environmental temperatures and hot junction temperatures equal to or greater than the design value. These tests shall be conducted with the load resistance which gives maximum power output.

4.4.4.5 Response time for warm-up.- The time shall be determined for the generator to reach operating temperature and rated output from the environmental test temperature condition. The electrical load shall be at that value which has previously been determined to give maximum power output. Items b) through g) of paragraph 4.4.4.1.3 shall be continuously recorded. Items a) and i) shall be recorded immediately before and after the test and at five minute intervals during the test. Item h) shall be recorded immediately before and after the test.

4.4.4.6 Response time for cool-down.- The time shall be determined for the generator to reach the environmental test temperature from operating temperature and rated power upon abrupt shading from solar radiation. Items b) through g) of paragraph 4.4.4.1.3 shall be continuously recorded. Items a) and i) shall be recorded immediately before and after the test and at five minute intervals during the test. Item h) shall be recorded immediately before and after the test.

4.4.4.7 Voltage characteristics.- Output voltage at design operating temperature shall be determined as a function of load current over the range from a load current of zero to a load current equal to twice the value which gives maximum power output.

5. PREPARATION FOR DELIVERY

5.1 Preparation for delivery.- The 100 watt solar thermoelectric generator shall be preserved, packaged, and shipped in accordance with the contractor's commercial practice.

6. NOTES

6.1 Intended use.- Use of these specifications is restricted solely to the design, construction, and initial feasibility testing of a 100 watt solar thermoelectric generator. In particular, these specifications are not to be construed as applicable to flight prototype or production versions of this generator.

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