AI-66-260

SECOND QUARTERLY REPORT
FOR
ALUMINUM BONDED LEAD TELLURIDE THERMOELECTRIC MODULE RESEARCH AND DEVELOPMENT

(1 August 1966 – 1 November 1966)

Contract No.: NAS5-10184

Prepared by
Atomics International
Division of North American Aviation
Post Office Box 309
Canoga Park, California 91305

for

Goddard Space Flight Center
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CONTENTS

TABLES

FIGURES

I. SUMMARY

Progress in the second quarter of this program is reported.

The Phase I 500-hour, isothermal soak test of 18 aluminum-contacted PbTe N and P elements, at 800°F in high vacuum was completed. All related examinations, tests, and analyses were also completed. The data and analysis thereof indicate very slight effect from the soak test. The contacted elements, after soaking, show thermoelectric numbers within 5% of the vendor data for the thermoelectric materials, without allowance for contact losses. It is concluded that the contacting process is satisfactory, at least for hundreds of hours at 800°F, and probably for thousands of hours.

A plan is presented for Phase II, thermal soaking testing at 400, 600, and 800°F, and periods to 2000 hours. Fabrication of 72 more test elements is essentially complete.

The Seebeck-voltage and high-temperature-resistance measuring equipment was modified to improve utility, and is now completely satisfactory.

A design has been developed for Phase III, 3-couple test modules. Conservative calculations based on assumption of a practical temperature interval (750 to 350°F), predict better than 6.6 watts/lb, 5.5% overall efficiency, and 9-ampere output. A high-vacuum test station design has been developed. Hardware is being fabricated and procured for assembly of a first 2-test-station vacuum chamber, and a 3-couple module, to check out the design. In brief, the test design features easy extrapolation to larger modules and eventual adaptability to a realistic non-magnetic space converter system.

All of the test data, experience and analysis to this point indicate that the aluminum-contacted PbTe couples are eminently suited for use in efficient, non-magnetic, space thermoelectric power supplies.

II. DISCUSSION

A. PHASE I: 500-HOUR THERMAL SOAK TEST

1. Test Plan

The 36 standard test elements made in the previous quarter had been measured physically and electrically at room temperature. Measurements were completed of Seebeck voltage and electrical resistance at a hot-junction temperature of approximately 650°F (the limit of the Seebeck device at that time), while the cold-junction temperature was in the range of 265 to 335°F, for various elements.

These elements were then divided into eight groups, as follows:

TABLE 1
TEST ELEMENT GROUPS

Element Numbers	Polarity	Process	Test Element Groups: Thermal Soak	Test Element Groups: Control
1 - 6	N	Reference	X	
7 - 12	N	Reference		X
13 - 15	N	Alternate	X	
16 - 18	N	Alternate		X
25 - 30	P	Reference	X	
31 - 36	P	Reference		X
37 - 39	P	Alternate	X	
40 - 42	P	Alternate		X

The number series 19 - 24 was reserved for a possible second alternate process, which was not developed.

In each group, one element was tensile-tested; two were mounted, sectioned and polished (one of them for delivery to NASA-Goddard); and the remainder were held as spares for further analysis if required.

The "thermal soak" elements were placed in a high-vacuum tube furnace (about 10^{-5} torr) for 500 hours at 800°F. They were then measured thermoelectrically before being subjected to destructive testing.

TABLE 2

PHASE I THERMAL SOAK RESULTS: RESISTANCE

Data From	Lower Temperature Interval			Higher Temperature Interval	
	R_C (mΩ)	R_H (mΩ)	Temperature (°F)	R_H (mΩ)	Temperature (°F)
2N – Before	0.782	3.49	293-654	Not measured	
Vendor	0.827	3.18	293-654	Not measured	
After	0.817	3.43	310-660	4.01	323-750
Vendor	0.827	3.34	310-660	3.82	323-750
2P – Before	0.525	2.32	296-655	Not measured	
Vendor	0.731	2.94	296-655	Not measured	
After	0.682	2.56	307-650	2.94	325-752
Vendor	0.731	2.99	307-650	3.66	325-752

TABLE 3

PHASE I THERMAL SOAK RESULTS: SEEBECK VOLTAGE

Data From	Lower Temperature Interval		Higher Temperature Interval	
	E_S (mv)	Temperature (°F)	E_S (mv)	Temperature (°F)
2N – Before	47.4	293-654	Not measured	
Vendor	47.0	293-654	Not measured	
After	46.8	310-660	59.4	323-750
Vendor	46.9	310-660	47.0	323-750
2P Before	35.1	296-655	Not measured	
Vendor	43.0	296-655	Not measured	
After	37.2	307-650	48.2	325-752
Vendor	42.0	307-650	55.0	325-752

2. Thermoelectric Behavior

The "before" and "after" results for resistances and Seebeck voltages of reference elements are summarized in Tables 2 and 3. As mentioned in the previous quarterly report, the aluminum contact resistance is too low to permit accurate measurement, but is believed to be 3 to 7 $\mu\Omega$ cm^2. Resistance values for N-elements should be reduced by about 2-1/2%, and for P-elements by about 6%, for comparison with vendor's values.

The N-element data are "simple" averages for six elements; the P-element data are for five elements, one having been accidentally broken.

3. Analysis of Thermoelectric Behavior

Examination of the power number, S^2/ρ, provides a valid "before and after" comparison. Table 4 indicates this for the lower temperature interval, and includes a "vendor comparison" for both temperature intervals. Instead of S^2/ρ, the approximately proportional factor $E_s^2/4R_H$ is given, because it indicates more usefully the power output capability of the standard test element, including contact resistance losses.

TABLE 4

PHASE I TEST ELEMENT POWER CAPABILITY

Calculated From	Lower Temperature Interval	Higher Temperature Interval
2-N — Before	0.161 watt, 293-654°F	Not measured
After	0.166 watt, 310-660°F	0.221 watt, 323-750°F
Vendor	0.158 watt, 310-660°F	0.212 watt, 323-750°F
2P — Before	0.133 watt, 296-655°F	Not measured
After	0.135 watt, 307-650°F	0.197 watt, 325-752°F
Vendor	0.147 watt, 307-650°F	0.207 watt, 325-752°F

A review of tabulated results indicates that the largest deviations from the vendor's data are in the 2P Seebeck voltage and resistance, which are both slightly low. However, the thermal soak tended to raise both toward the vendor data. The observed power factors are within 5% of the vendor's data (higher for the 2N, lower for the 2P).

The isothermal soak gives an exaggerated whole-body effect on the test element. The observed changes are perhaps several magnitudes greater than would be observed in a temperature gradient at $T_H = 800°F$. Therefore, even the greatest change, 10% in the 2P "hot resistance," represents a negligible effect in practice, if it is mainly in the body resistance. The corresponding 6% increase in Seebeck voltage indicates that this is the case. This concomitant increase in both Seebeck voltage and resistance at temperature, resulting in a slight overall improvement, is explained by a reduction in doping level which is favorable to the material in the measured temperature range; i.e., a shift of the figure-of-merit peak towards the lower temperatures.

The observed 2% decrease in hot resistance of the 2N elements would be discarded as experimental error, except that similar behavior of this material has been clearly detected on other AI programs.

The foregoing analysis applies only to the reference process elements. Three each, 2N and 2P elements, made by an alternate process, were also thermally soaked. As noted in the previous quarterly report, these were of very high resistance and the 2P elements showed a reversal in the resistance-temperature curve. After soak, the 2N elements were 8% higher in cold resistance and 40% higher in hot resistance; the 2P elements were 25% higher in cold resistance and 13% lower in hot resistance. The Seebeck voltages were not significantly changed. It is concluded from the sparse data that the omission of the interfacial material (used in the reference elements) resulted in formation of a thin but high resistance reaction layer at the caps. Furthermore, it is speculated that the layer is doped N-type, resulting in a carrier-depleted region in the P element; this could account for increased electrical conductivity, by degeneration, at higher temperatures.

4. Physical Behavior

The thermally soaked elements showed a 0.69% weight loss (500 hours, 800°F, vacuum) which was the same for both the 2N and the 2P elements, within experimental error. This corresponds to a rate of -1.8×10^{-5} g/cm^2-hr.

The sample sizes for the Phase I "screening test" did not permit enough tensile testing to yield significant data. The reference elements before soak pulled at 700 psi (2N) and 260 psi (2P); after soak, the corresponding values were 120 and 240 psi. The alternate process elements gave values of 2020 (2N) and 400 (2P) psi before; 800 psi (2N) after; and a broken 2P.

On metallography, the following aspects were noted:

1) The 2N's and 2P's are generally indistinguishable.

2) An interfacial phase about 0.0005-inch thick is distinguished.

3) The granular material introduced by process into the reference elements appears to be the only distinct difference – hence it appears to serve as a conducting bridge (as intended).

4) This phase grew slightly, if at all.

An electron beam microprobe analysis has been performed on a "soaked" 2P element in the region of the PbTe-Al interface. Although the results are only qualitative, they show that the interfacial layer is of higher lead content than the neighboring PbTe material. Also, there is some Te in the Al cap adjacent to the interface. Apparently, Te has diffused into the cap material from the PbTe at a faster rate than the Te diffused into the PbTe, leaving a Pb-rich zone between the element and the cap. An area typical of that analyzed is shown in Figure 1, and the photographs from the microprobe analysis can be

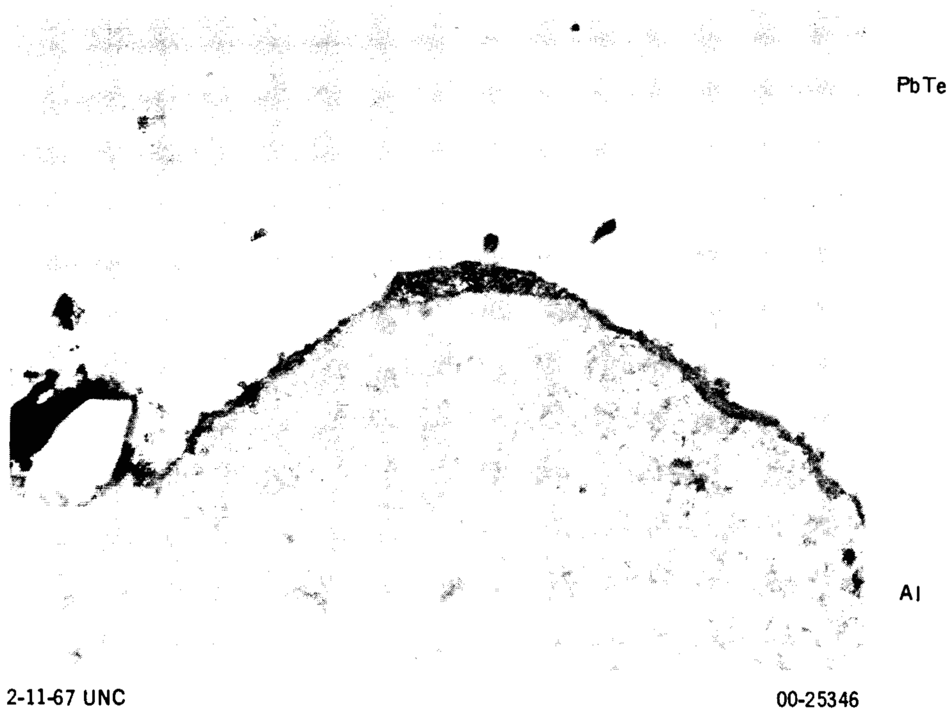

Figure 1. PbTe-Aluminum Shoe Interface Typical of that Analyzed on the Microprobe (500X)

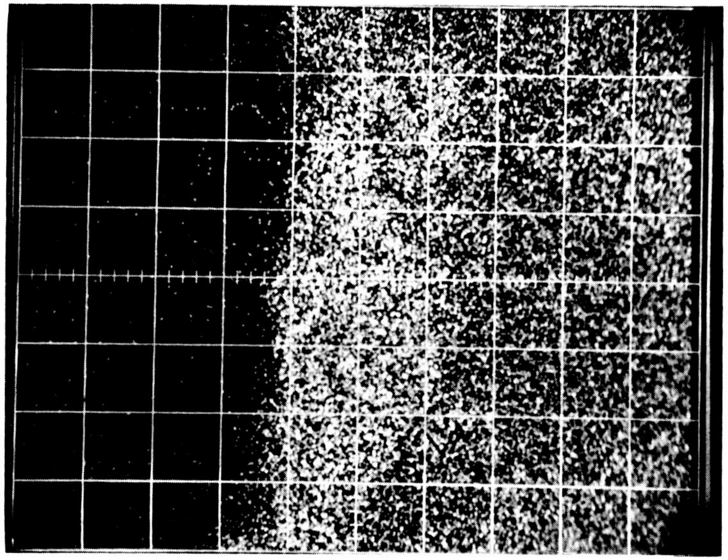

Figure 2a

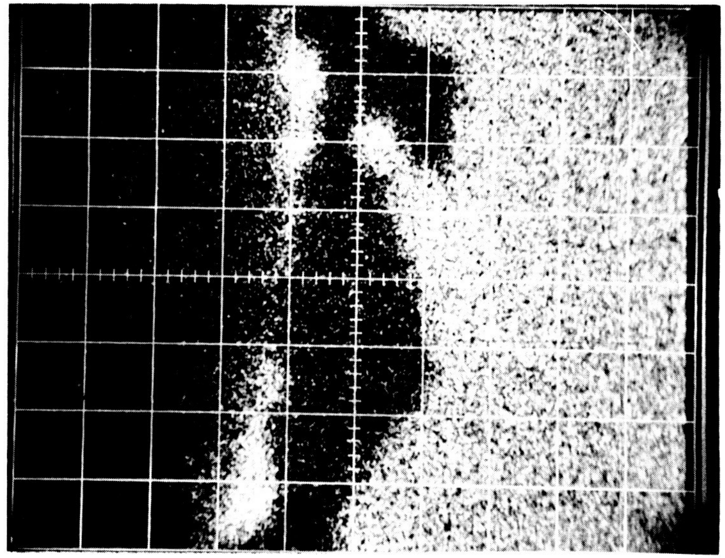

Figure 2b

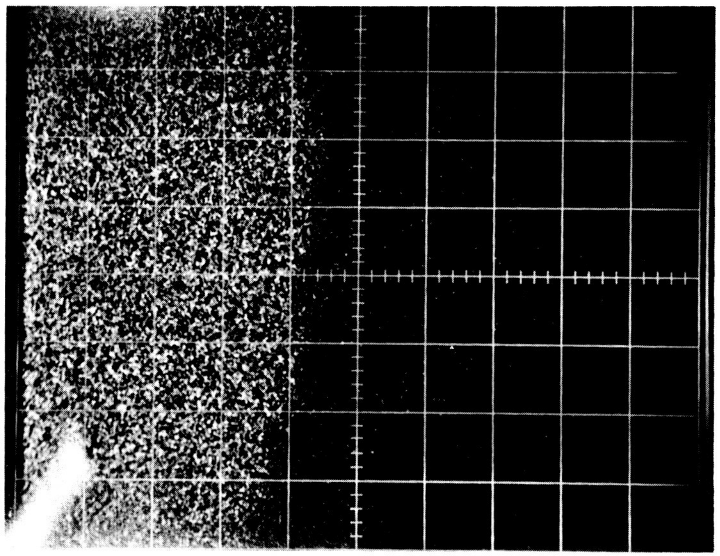

Figure 2c

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Figure 2. Microprobe Area Scans for (a) Lead, (b) Tellurium, and (c) Aluminum at the PbTe-Al Shoe Interface After 500 Hours at 800°F

seen in Figure 2. The concentration of Pb, Te, and Al is shown in Figures 2, 2b, and 2c, respectively, where the higher concentration is shown by the brightest areas in the photographs.

B. PHASE II: EXTENDED THERMAL SOAK TEST

1. Test Plan

The results of the Phase I soak test have been used to guide the planning for the next test. The objectives are two: to obtain longer term results at the same temperature (800°F); and to investigate the temperature effect by exposing the test elements to different temperatures, under otherwise identical conditions. The small but significant weight loss experienced at 800°F suggests that this is a reasonable maximum test temperature to use without encapsulation.

The minimum temperature that might be considered for testing is the anticipated cold junction temperature in practice, or 350 to 400°F. It is not expected that the PbTe body will show significant change at this temperature; however, some effect on the aluminum contact is plausible, and would be very important to identify.

The extended soak, therefore, is planned to include three isothermal temperatures: 400, 600, and 800°F. At each temperature, nine elements each of 2N and 2P will be soaked. Three elements of each type will be withdrawn at 500, 1000, and 2000 hours. For controls, nine elements of each type will be made. The total element requirement for this test will therefore be 72 (cf. 64 originally planned).

Measurements and destructive tests will be performed as in Phase I. Two of each group of three elements will be destructively examined.

2. Status

At the end of this report period, all 72 element bodies had been formed; 24 2P's and 12 2N's had been contacted and measured thermoelectrically. At this writing, all 72 are contacted and all except 24 have been measured. The data for insertion in the furnaces is set at November 14, 1966.

The thermoelectric measurements on these elements include: (1) room-temperature resistance; (2) Seebeck voltage and resistance at 650°F to 300°F (approximately); (3) the same at 750°F to 335°F (approximately). The variability in the lower temperature is a function of thermal contact in the measuring device.

C. INSTRUMENTATION — SEEBECK DEVICE IMPROVEMENT

The test device which was built during the first quarter was limited in upper temperature by safe capacity of the heater (one heater cartridge was burned out, initially). Consequently, the Phase I test elements, before thermal soak, were measured at $T_H = 650°F$, maximum.

The heater was rebuilt with more complete insulation. Also, the face which contacts the test element was plasma-sprayed with Al_2O_3, and polished. Formerly, single-crystal mica had been used. These two changes greatly reduced (3X) the required heater power. In addition, the mass of the heater block was trimmed so as to improve speed of response. Heating and cooling time were also decreased, by a factor of about four. The inspection rate has been increased from 3 elements per day to 8 elements per day.

Mica sheet is still used between the test element and the water-cooled heat sink, because it gives approximately the desired temperature increment. This device now functions satisfactorily in every respect, and the design is thought to be worthy of copying for other programs.

D. PHASE III: SMALL MODULE TESTS

The efficient execution of this program calls for overlap of phases. Specifically, the small-module testing cannot wait upon full completion of the Phase II thermal soak tests of individual elements. The results from Phase I are sufficient to allow preliminary design of the small-modules and their test stations.

The program scope calls for the testing of 18, 3-couple modules — not simultaneously — in 6 test stations, at 3 different temperature conditions. It is intended to build the test stations in 3 pairs, each pair having a single heat source at a controlled temperature, and each pair contained in a single high-vacuum system.

Since the time of the program proposal, Atomics International (AI) has refined its testing techniques, and also has detailed further the requirements of this program. Therefore, the proposed test module and station differ considerably from what was originally conceived and proposed.

The principal new features of the present small-module test design are as follows:

1) The couples will be attached to a flat-plate "hot wall," which will be radiantly heated by an electrical heater.

2) Heat rejection from the cold junctions will be radiative, through integral fins which serve also as electrical straps.

3) The basic row-of-couples design allows simple mechanical and electrical repetition; i.e., a long module is a direct, linear extrapolation of a short one. Easy replacement of a defective couple is also provided.

4) The 3-couple test assembly will give an accurate exemplification of the power density and efficiency of a complete, full-size converter.

5) The module will contain no ferro-magnetic materials.

6) The test chambers will use metal gasket seals, will contain no organic materials, and will be connected to ion pumps with 1-inch diameter, straight, non-valved tubing. A vacuum of less than 10^{-6} torr will be obtainable.

7) The electrical heater is re-entrant, so that the heater cartridge will be external to the vacuum system, and will be replaceable.

8) The thermal shunt through the heater support structure is calculated to be less than 3%. This allows an accurate direct determination of overall converter efficiency by ratio of electric power out/in.

The proposed design is sketched in Figure 3. (One layer of thermal insulation is omitted for viewing.) Mechanical attachment of the couples to the hot wall, and the support for the fins, is accomplished by the "tension-stud rocker assembly" shown in the insert. This technique has been used successfully in several devices at AI since 1961. Effectively, it produces accurate, uniform compliant mechanical loading of each element.

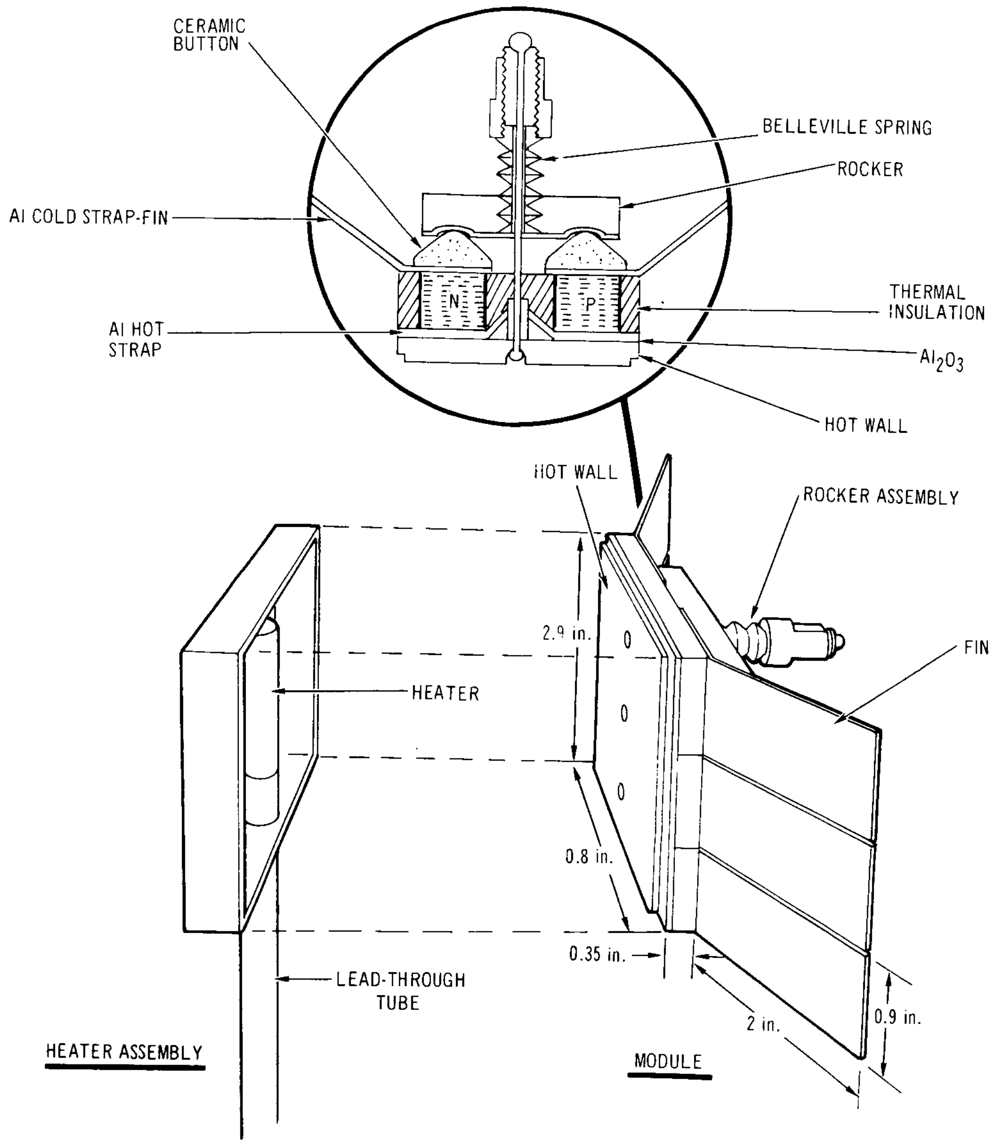

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Figure 3. Small Module Test Schematic

The module design features listed above represent a feasible system for using aluminum-contacted couples in a space thermoelectric converter; they incorporate some realism without, however, sacrificing any requirements of the test. This design extrapolates directly, also, to the 10-watt demonstration module specified for Phase IV of the program.

The originally proposed module test design invited the criticism that the elements would be tested under conditions which were ideal for the elements, but which could not later be provided or simulated in a converter. The new design does not have this objection in any important detail, nor does it have any feature which appears to jeopardize experimental "purity."

Although power density and efficiency are not of prime interest in this program, they have been cursorily examined for the test design. Assuming T_H and T_C will be approximately 750 and 350°F, and referring to Table 4, it is estimated that each couple will deliver at least 3/8 watt. The small module will deliver at least 1-1/8 watts and weigh about 0.17 lb, including hot wall and fins. This gives a power density of more than 6.6 watts/lb. The overall efficiency will lie in the range 5-1/2 to 6-1/2% (16 to 20% device efficiency). The output current will be of the order of 9 amperes to a matched load.

1. Status

Flanges, gaskets, and a glass viewing port for one vacuum chamber are being procured. All other parts and materials for one test station and the 3-couple modules are on hand. Shop fabrication of parts for one module is in progress.

E. PROGRAM FOR NEXT QUARTER

1. Phase II

The extended thermal soak test will start November 14, 1966. The 500-hour and 1000-hour samples will be withdrawn during the quarter. All measurements and tests will be completed on these (36) elements and on 12 of the control elements.

2. Phase III

One vacuum chamber with two test stations will be set up and leak checked.

One test couple will be installed and operated briefly to check temperature distribution, and to determine if adjustment of fin area is required.

One three-couple module will be assembled and installed in a test station. All operational factors will be checked out.

If the previous tests are completed satisfactorily, fabrication of two additional vacuum chambers, four more test stations, and five more 3-couple modules will be started. At least one more module will be placed in operation.

3. Phase IV

Design of the demonstration 10-watt module will be started, incorporating any modifications indicated by Phase III experience.

F. NEW TECHNOLOGY

A statement will be prepared and transmitted separately by G. A. Koris of the AI Patent Group, in response to this contractual requirement.

G. CONCLUSIONS

The Phase I 500-hour thermal soak test gave apparently accurate, consistent, and meaningful thermoelectric behavioral data. The metallographic analysis added some basic information concerning the nature of the aluminum contact. It is recommended that the original plan for extended thermal soak testing (Phase II) is still valid.

The specific thermoelectric data indicate very slight changes in properties in 500 hours at 800°F in high vacuum. Thermoelectric power number (S^2/ρ) measured after test, is within 5% of the vendor's material data, even without allowance for the aluminum contact resistance. This early result is so encouraging that it is recommended to proceed with small-module testing, using the reference process for contacting.

Consideration of alternate processes should be dropped.

The Seebeck voltage and high-temperature measuring instrument developed for this program is satisfactory and requires no further modification.

All of the test data, experience, and analysis to this point indicate that the aluminum-contacted PbTe couples are eminently suited for use in efficient, non-magnetic, space thermoelectric power supplies.

The experimental results from this program have been furnished to Program AF33(615-3770), Light Weight, High Power Density Thermoelectric Module Development, which plans use of aluminum contacts in the PbTe stage of the module.