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for

COMPACT THERMOELECTRIC CONVERTER DEVELOPMENT PROGRAM - PHASE IIA (U)

RCA

**DIRECT ENERGY
CONVERSION**

CONTRACT AT(30-1)-3582

For the Period

April 1, 1966 to June 30, 1966

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Prepared for:
Sandia Area Operations Office
U.S. Atomic Energy Commission

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**COMPACT THERMOELECTRIC CONVERTER
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For the Period

April 1, 1966 to June 30, 1966

Prepared by:

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I. INTRODUCTION

A reference design for a compact converter module employing silicon-germanium thermoelectric alloys was developed during Phase I of the program. The development of this design is covered in the Phase I final report. Certain critical areas in which additional engineering work was required for full demonstration of the technology to be employed in the fabrication of compact converter modules were also identified as a result of the Phase I effort.

As described in the first quarterly report for Phase IIA, the work has been concentrated in five general areas; 1) the hot and cold heat exchanger plates, 2) the "hot stack" assembly, 3) the "cold stack" assembly, 4) the flexible connector, and 5) the thermoelement assembly.

The procurement of suitable component materials has still presented obstacles as described in the first quarterly report for Phase IIA, although the situation has now been somewhat alleviated.

Effort in all of the areas has in general proceeded as defined in Phase I. In the area of the "hot stack" assembly principal effort has been redirected toward a ductile structure rather than the composite structure defined at the end of Phase I. The decision during Phase I to proceed along composite structure line had been primarily dictated on greater ease of tooling. Further investigation during Phase IIA has indicated probable structure simplification with the ductile stack approach and primary effort is now proceeding along these lines.

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II. HOT AND COLD HEAT EXCHANGER PLATES

Fabrication techniques have been developed for the machining of hot and cold heat exchanger plates of the Phase I Reference Design. Tolerances on previous drawings have been revised to simplify such machining methods. Tubing sizes have been adjusted to accommodate available materials; see Figure 1.

The most acceptable plate sections were fabricated by means of electrical discharge machining commonly referred to as Elox machining. The advantages of this method are that the properties of the material machined are not changed by work hardening, warping of the part is minimized, and the necessity of stress relieving the material by annealing after machining is eliminated. Annealing is not recommended by the Haynes Stallite Corporation because of the geometry of the parts involved and the possibility of impairing the tensile strength and corrosion resistance due to improper control in annealing; overheating Hastelloy "B" by as little as 35°F can cause such effects.

Machining methods were also developed for fabrication by milling. The best results were achieved by using cobalt high speed steel end mills. The advantage of these tools is that they maintain a better cutting edge because they are harder (Rockwell C 68-69) than the Hastelloy materials. Cooling of the part during machining is of prime importance in minimizing warpage. However, the coolant must not be applied directly to the working surface because it has a tendency to hold chips in proximity of the cutting tool, which causes gouge marks and hard spots. Special jigs were required to permit cooling by circulation of a water soluble oil in contact with the under surface of the piece. Filler pieces were required between successive ribs to prevent walking. It was found that machining stresses are relieved somewhat and that slight dimensional changes may occur over short periods of shelf life.

Normal machining speed and feed rates were used. The depth of cut was confined to 0.008 to 0.012 inch. For cuts of less than 0.008 inch, surface hardening occurred and affected the finish and the machining rate, whereas cutting depths of more than 0.012 inch caused excessive warpage and irregularity of cut.

The performance and dimensional stability of both the milled and the Elox plates will be determined by life testing at elevated temperatures in vacuum. The results will be compared to those obtained from NaK exposure tests at similar temperatures.

A. Flat Coupon Tensile Test Specimen (TP 133), Figure 2

1. No Weld Specimens

Machining has been completed and parts have been processed and

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FIGURE 1. HEAT EXCHANGER PLATE

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FIGURE 2. COUPON TEST SPECIMEN

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placed on life test. Initial samples will be submitted for room temperature tensile tests and metallographic examination.

2. Tungsten Inert Gas Weld Specimens (TP 133)

A jig was designed which permits envelopment of the weld area in inert gas while clamping of the parts minimizes warpage of the materials during welding. Samples were welded and radiographed and are presently being machined. Parts will be referenced to identify the weld with a specific location on the radiograph. Radiographs of the materials indicate that a sound weld is obtainable using this weld technique. Inclusions and slag were prominent on some pieces while others were apparently free of such foreign materials. Some isolated areas of tungsten contamination were detectable. Warpage remained somewhat of a problem even with the use of the jig. Initial metallographic examination and physical testing of the welds will be conducted.

3. Electron Beam Weld Specimens (TP 133)

Welding of samples for use in this phase of the program has been completed. Radiographs of the welds show complete freedom from inclusions and slag. Isolated cases of sputtering were noted and are caused by the beam which on contact vaporizes sulfides present in the metal. Complete control of the procedure was obtained. Typical data recorded in welding of the materials are listed in Table I.

4. Braze Tensile Test Assembly, Figure 3

Machining requirements have been completed and parts are presently in the process of assembly in accordance with designated priority. Niore and titanium braze assemblies of nickel and Hastelloy "B" and also Niore and Gemco braze assemblies of copper and nickel are on life test. Samples will be submitted periodically for physical testing and metallographic examination.

B. NaK Containment Testing

Braze box assemblies which will be used to determine the effect of affixed brazed structures on plate performance have been prepared and are presently awaiting sealing by electron beam welding. A jig is under construction to position the pieces during welding. The use of Niore for brazing to the hot plate has been discontinued for reasons explained in another section of this report. The preference for Niore over Gemco as braze material on the cold plate has been established (See Section V). Therefore, Gemco braze will be evaluated in vacuum thermal storage tests as a back up material only.

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TABLE I
TYPICAL SETTINGS FOR ELECTRON BEAM WELDING

<u>Material</u>	<u>Sample X</u>	<u>Anode</u>	<u>Cathode Filament</u>	<u>G2</u>	<u>G3</u>	<u>Deflection</u>		<u>Focus</u>	<u>Pressure</u>	<u>Linear Speed</u>	<u>Date</u>	<u>Power</u>	<u>Remarks</u>
						<u>Hor.</u>	<u>Vert.</u>						
316 Stain- less Steel .0625 Thick	2	75 KV 6 MA	1.1 V 17.5 MA	1000V	23KV	-.IV	+.IV	70V	1 x 10-5	10"/min	7/1/66	450 W	Full Penetration
Hastelloy "B" .038 Thick	13	60 KV 7 MA	1.1 V 17.5 MA	1000V	21KV	-.2V	-.2V	70V	3 x 10-5	20"/min	7/9/66	420 KW	Full Penetration
Hastelloy "X" .0525" Thick	24	85 KV 6 MA	1.1 V 17.5 MA	1000V	25KV	-.2V	-.5V	70V	1 x 10-5	20"/min	7/11/66	5.0 W	Full Penetration
200 Nickel .062 Thick	32	75 KV 7 MA	1.1 V 17.5 MA	1000V	25KV	-.2V	-.4V	70V	-	20"/min	7/11/66	525 W	Full Penetration

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FIGURE 3. BRAZE TENSILE TEST ASSEMBLY

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Hastelloy "X" and 316L stainless steel plates have been Elox machined and are awaiting completion of a jig to be electron beam welded. Tensile specimens for NaK exposure tests will be available when needed. Specimen racks for mounting test pieces in containers are awaiting final firing. To expedite delivery of the containers they will be heliarc welded instead of electron beam welded as originally planned. These containers are presently under construction. It is expected that all NaK exposure tests will be delivered for test by the end of August.

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III. HOT INSULATOR STACK

The evaluation of the structures built and tested during Phase I and the initial stages of Phase IIA, has shown that the current hot stack design presents a major structural problem. The principal point of weakness is the composite (60-mil nickel, 40-mil tungsten, 20-mil nickel) which has exhibited extensive separations between the nickel and tungsten discs. Niore braze is not acceptable when used in connection with a diffusion limiting barrier material such as tungsten. A more detailed technical treatment of this phenomenon will be found in Section III, E.

Three different approaches are being taken in an effort to alleviate the problem:

- 1) Investigation of other brazes, specifically high nickel brazes, and substitution of other metallic members.
- 2) The substitution of "wire bundle" composites in lieu of the nickel, tungsten, nickel composite.
- 3) The substitution of a diffusion bonded ductile member in lieu of the brazed composite.

A. Investigation of Other Brazes

A selective number of high temperature brazes were investigated as a means of eliminating Kirkendall void formation in the hot stack assembly. Table II lists the name of the braze, the material composition, and the liquidus temperature of each of the alloys investigated.

Sample hot stack assemblies were fabricated with the following components in the sequence listed:

1) Tungsten Disc	0.460 Diameter x 0.020 Thick
2) Graphite Disc	0.380 Diameter x 0.060 Thick
3) Al_2O_3 Disc	0.470 Diameter x 0.020 Thick
4) Nickel Disc	0.460 Diameter x 0.020 Thick
5) Tungsten Disc	0.460 Diameter x 0.040 Thick
6) Nickel Disc	0.460 Diameter x 0.060 Thick
7) Hastelloy B	0.500 x 0.500 x 0.031

Braze shims were placed between the different components and the respective stacks were heated 50°C higher than the liquidus temp-

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TABLE II
HIGH TEMPERATURE BRAZES INVESTIGATED

<u>Material</u>	<u>Composition</u>		<u>Temperature Liquidus</u>
PALNI	40 Ni	60 Pd	2260°F (1238°C)
PALCO	35 Co	65 Pd	225°F (1235°C)
PALNIRO-7	8 Pd	22 Ni 70 Au	1899°F (1037°C)
Nickel-Titanium	28 Ni	72 Ti	1742°F (950°C)
Coasts Metals CM-50	1.9 B	3.5 Si 94.6 Ni	1950°F (1065°C)
Coasts Metals CM-50B	1.5 B	2.5 Si 96.0 Ni	2122°F (1160°C)
Coasts Metals CM-53	2.9 B 7.0 Cr	5.0 Si 82.1 Ni 3.0 Fe	1825°F (995°C)
Nicro	18 Ni	82 Au	1742°F (950°C)

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erature of the braze alloy in either a vacuum or a hydrogen atmosphere. Brazed sample assemblies were sectioned for microscopic examination of the six braze interfaces. Combinations that appeared promising were subjected to steady state temperatures of 900°C for hundreds of hours, and to rapid thermal cycling from 100°C to 900°C in an inert atmosphere for more than ten cycles.

None of the brazes listed in Table II could qualify for all six interfaces of a complete stack assembly. With each of the braze materials, at least one or more brazed interfaces could not meet the rigorous test requirements of a hot stack assembly. Inferior bonds were detected at the tungsten-nickel joints, the metallized ceramic interfaces, and the joints adjacent to the tungsten plated graphite.

Several hot stacks of different design were fabricated in two-step operations with two different firing temperatures and brazes. Some of the hot stack assemblies showed considerable promise and ultimately lead to the hot stack design used in the assembly of partial sub-structure PTS-11. This design consisted of the following components:

1st Braze Assembly
1150°C Firing in Vacuum

- 1) Tungsten Discs
- 2) CM-50 Braze Discs
- 3) Nickel Discs
- 4) CM-50 Braze Discs
- 5) Hastelloy B Hot Heat
Exchanger

2nd Braze Assembly
1000°C Firing in Hydrogen

- 1) Heat Distributor
- 2) Ceramic - Cold
- 3) Electrical Connector - Cold
- 4) Compensator
- 5) Pedestal
- 6) Split Couple Assembly
- 7) Ductile Insulator Assembly
- 8) First Braze Assembly

Note: NIORO Shims (0.001 inch thick) are used between each set of components.

By using a combination of high temperature braze material and ductile ceramic assemblies, it was demonstrated that thermal cycling tests could be passed successfully without damaging the conductive heat path or the thermoelectric elements.

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B. Wire Bundle Composites

As previously reported, the initial cursory look at stacks fabricated with iron bundle composites, Figure 4, looked promising. To obtain the desired thermal conductance, the initial work was concentrated mainly on developing a refractory bundle. Bundles prepared of molybdenum core wire were brazed successfully, but the preparation of adherent tungsten vapor deposited shoes was beyond existing capabilities. Another method, that of applying shoes by a pressure bonding technique, is now being considered.

Simultaneously, work has continued with the iron wire bundle. A controlled test was conducted in which solid iron discs of various diameters and thicknesses and iron wire bundle composites of varying thicknesses were brazed into structures. Table III shows a cross-section of the structure, lists the various iron members under consideration, and summarizes the results of the test.

In all cases, the solid iron discs broke the test element assemblies, whereas, the structures containing wire composites in thicknesses greater than 20 mils survived and showed no change after 14 thermal cycles to 900°C. However, one of each pair of 30 mil and 40 mil structures had surface fissures on the pellet adjacent to the hot shoe bond. These fissures were indicative of a stressed condition on the pellet surface, but they did not develop into cracks upon drastic thermal cycling.

Micro examination of the samples showed that 0.5 mil Nicro was insufficient to insure a good braze between the iron plated shoe and the adjacent member. The irregularity of the plated shoe (depressions between wires) will require a greater quantity of braze material. There was a high percentage of voids or unbonded area at the Nicro interface. It is, therefore, problematical whether the full stress was transmitted through the bundle. The test will be rerun using a greater quantity of braze to insure fully bonded interfaces. An examination of a stack containing only one 50 mil wire composite and using 1 mil Nicro, revealed a good braze. The test element survived thermal cycling. The QM-50 nickel braze (5 mils thick) made a good contact between the Hastelloy B and the iron shoe.

Thermal conduction calculations of the wire composites show that although there is an increase in the temperature drop across this composite, the increase is not excessive. More important, if molybdenum wire could be developed for use as a composite, due to a much better thermal conductivity, the temperature drop would be reduced far below the Phase I Test Module Design and would approach that of the Reference Design.

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EXPLODED VIEW

FIGURE 4. STRESS RELIEF WIRE COMPOSITE STRUCTURE

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TABLE III
WIRE BUNDLE TEST RESULTS

IRON MEMBER UNDER CONSIDERATION	No. OF TEST ELEMENTS	RESULTS AFTER BONDING	RESULT AFTER THERMAL CYCLE @ 900°C	MET LAB	ΔT @ 900°C PHASE I DESIGN AREA*
WIRE BUNDLE .460 x .020	1	1-PELLET LEG SEP.	—	HVY VOIDS 90% IN BRAZE JOINTS (NIORO) CH50 BRAZE 10-15% VOIDS	—
WIRE BUNDLE .460 x .035	2	1-LEG SURF. FISSURE	NO CHG.	"	8.8°C
WIRE BUNDLE .460 x .045	2	1-LEG SURF. FISSURE	NO CHG.	"	11.2°C
WIRE BUNDLE .460 x .055	1	NO CRACKS OR FISSURES	NO CHG.	BEST BRAZE "	13.6°C
SOLID DISC .475 x .059	1	1 LEG SEP.	—	50% VOIDS "	—
SOLID DISC .400 x .020	2	1 LEG SEP. ON EACH	—		—
SOLID DISC .400 x .030	2	1 LEG SEP. ON EACH	—		—
SOLID DISC .380 x .059	2	1 LEG SEP. 2 LEG SEP. ON OTHER	—		—

* COMPARISON

	COMPOSITE	GRAPHITE
PHASE I TEST MODULE ΔT =	7.8°C	5.6°C
REF. DESIGN ΔT =	2.9°C	2.1°C

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G. Diffusion Bonded Structures

The utilization of a diffusion bonded ductile member is being approached from two viewpoints. First, methods are being investigated for bonding the entire hot stack by diffusion bonding techniques using gold ductile members. This will entail either the development of a complex system of tooling to apply pressure at temperature, or a modification of the module configuration. In either event, methods are being developed to bond individual stacks for metallurgical systems evaluation.

The second approach is to diffusion bond a subassembly which in turn can be brazed into the stack. Tests are now being conducted to establish the diffusion bonding parameters. The subassembly will consist of tungsten foil or disc, gold pedestal, ceramic, gold pedestal, and tungsten electrical connector which can be Nicro brazed into the module, see Figure 5. Because the tungsten-gold system has an extremely limited solubility and because the quantity of nickel present is limited and controlled, no difficulties are foreseen in using Nicro braze.

There are several important advantages to utilizing gold members in the structure:

- 1) Gold has an extremely low yield strength, therefore, the stack will be ductile and any stress will be dissipated in the gold parts.
- 2) The thermal conductivity of gold is superior to that of any other material that has been considered for the stack; this will result in a minimized temperature drop.
- 3) A mass of data are available from other programs concerning the tungsten-gold bond and the possible gold-Hastelloy bond. It appears, from this information, that the introduction of a gold member is feasible and that the specified life of the device is attainable.

Successful sandwiches of the following metallurgical systems were bonded:

- a) Iron to Gold.
- b) Nickel Plated Gold to Molybdenum Metallized Ceramic
- c) Nickel Plated Gold to Bare Tungsten Discs and Foil
- d) Gold to Nickel Plated Ceramics
- e) Gold to Nickel Plated Tungsten

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FIGURE 5. DUCTILE STRUCTURE No.1

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f) Pure Nickel Disc to Bare Tungsten

These sandwiches are being subjected to storage life test for material and bond evaluation. The ultimate objective of developing these sandwiches is to develop either a fully diffusion bonded ductile structure as a first choice or a diffusion bonded composite (including the ceramic) that can subsequently be brazed into the rest of the structure. Tooling that will enable the diffusion bonding of the entire stack has been designed and is being fabricated.

The most promising hot stack composite has appeared to be one consisting of diffusion bonded, nickel plated tungsten discs to gold rings with a nickel plated ceramic in between. These sandwiches were Ni-Cr brazed in simulated full stack structures with test elements. All test elements, however, were cracked after the brazing operation. An examination showed that the gold combined with excess nickel to form large fillets, hardening the gold member, and thus causing loss of the inherent ductility of the system. To overcome this, sandwiches were bonded in which the gold, rather than the mating parts, was plated so that the amount of nickel present in the system was limited. This approach proved to be successful, no test elements were broken and this method is now being used to fabricate a module. Two other structures were successfully fabricated. In one structure the tungsten disc was replaced with molybdenum foil, while tungsten foil was used in the other. These diffusion bonded composites will be brazed into a full structure.

Diffusion bonding of the full structure to the Hastelloy "B" hot plate with a refractory metal foil separating the gold ductile member from the NaK plate will also be investigated. One means of accomplishing this is to braze the foil to the Hastelloy as a pre-assembly and then diffusion bond the hot stack components and element assembly in another operation. The brazing material should be one containing no gold or other substance that would react with the NaK solution if it were to diffuse through the Hastelloy "B". This method is valid only if the foil will serve as a barrier or inhibitor to gold penetration. The rate of nickel gold penetration into the molybdenum foil was shown to be quite rapid so that subsequent effort is concentrated on the use of tungsten foil. A literature search failed to disclose valid data on rates and concentrations of nickel diffusing into tungsten and gold diffusing into the gradient nickel tungsten alloy. Sandwiches have been prepared, therefore, for storage life testing in an effort to actually determine these rates. If it appears that tungsten foil will serve as an effective barrier, full structures using the previously described system will be fabricated.

Approximately 650 hot stack samples have been fabricated and are being tested at a temperature of 800°C, and at an accelerated temperature of 900°C under both steady state and thermal cycling

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conditions. These coupons, sandwiches, and structures are representative of the metallurgical systems of the Phase I Test Module Design. The samples required to evaluate the BeO insulator will be fabricated at a later date when BeO becomes available. In the meantime, a duplicate schedule of insulator samples, using Al_2O_3 ceramics, are being fabricated and will be subjected to test and evaluation.

D. Molybdenum Wire Bundle Structure

Preliminary test results on the stress relieving characteristics of the iron wire bundle indicate a structure composed of 0.060 inch length wires is the minimum allowable length for preventing fracture of silicon-germanium test elements. The calculated temperature drop across the iron bundle is 13.2°C for hot stack application. To reduce the value of this drop, molybdenum and tungsten wires have been considered as alternates to iron wire. A comparison of the thermal characteristics of these materials clearly indicates the advantage of molybdenum or tungsten over iron:

Thermal Conductivity at 800°C (Cal/sec/Cm²/°K)

Fe - 0.070

Mo - 0.263

W - 0.283

Temperature Drop Across Wire Bundle, °C

<u>Length of Bundle, mil</u>	<u>Fe</u>	<u>Mo</u>	<u>W</u>
40	8.8	2.3	2.2
60	13.2	3.5	3.3
80	17.6	4.7	4.3

Because the fabrication process of the iron bundle structure is not easily adaptable to substitution of materials, a new process more compatible with the properties of molybdenum and tungsten and more adaptable to faster fabrication has been formulated:

- 1) Copper plating molybdenum on tungsten wire.
- 2) Stacking 12 inch lengths of the copper plated wire in copper sleeve (1/2 inch copper tubing).
- 3) Cold swaging to obtain a solidly bonded bundle of molybdenum or tungsten wires in a copper matrix. Spacing

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between adjacent wires is a function of the copper plating thickness and the degree of cross sectional area reduction due to swaging.

- 4) Slicing bundle structure to desired length (approximately 0.030 to 0.90 inch lengths).
- 5) Diffusion bonding of molybdenum or tungsten discs to the ends of the wire bundle by a hot pressing technique.
- 6) Preferentially dissolving the copper sleeve from around the bundle and the copper plate from between wires.

Work has begun on this structure and has progressed to step 4. Figure 6 shows a cross-sectional view of the molybdenum wire bundle before and after a 4 step swaging operation. The internal area reduction is 25 percent. This results in a packing density of 76 per cent with a 0.001 to 0.002 inch spacing between wires.

Preliminary pressure bonding tests on molybdenum and tungsten discs, Figure 7, shows the comparison between the interfacial zones formed by using an intermediate nickel layer and the direct bonding of the metals. A nickel strike, approximately 0.0001 inch thick, on adjacent surfaces provides a void free interface zone between both molybdenum and tungsten components. If the fabrication process proves workable, the stress relief characteristics of a prototype bundle will be tested by thermal cycling a composite structure.

E. Metallurgical Analysis of Hot Stack Bonds

A metallurgical analysis of the hot stack bonds indicated several actual and potential problem areas. The first is the interfaces created between gold or high gold alloys (Nicro) and nickel or high nickel alloys (Hastelloy series). The basic cause of this problem is the rapid rates of inter-diffusion between nickel and gold. The mode of failure in this type of joint could be:

- 1) The formation of structurally deleterious Kirkendall voids.
- 2) The diffusion of a critical quantity of gold into the Hastelloy NaK tube wall to form a nickel-gold solid solution alloy which could be attacked by NaK fluid.

Based on nickel-gold diffusion rate data from the literature and on an experimental gold penetration curve it appears probable that Kirkendall voids will form within a nickel-gold interface. This is shown below by examining the ratio of the square root of the diffusion rates of nickel into gold versus gold into nickel. This ratio is 11. A ratio of 5 or more is usually a strong indication that Kirkendall voids will form. In addition, a comparison is made

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FIGURE 6. GOLD PENETRATION INTO HASTELLOY N AND NICKEL AT 800°C

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cm 124

580x

W-W interface - Some void areas present Swaged W pellets

cm 140

580x

W-Ni-W interface - No voids within the diffusion zone.
Swaged and Ni plated W pellets

cm 125

580x

Mo-Mo interface - Continuous void zone
Swaged Mo pellets

cm 126

580x

Mo-Ni-Mo interface - No voids within the diffusion zone
Rolled Mo sheet Ni plated

FIGURE 7 - PRELIMINARY PRESSURE BONDING TEST RESULTS ON MOLYBDENUM AND TUNGSTEN DISCS (Bonding Conditions: 1030° C, 1 Hour, 30,000 psi).

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with the gold-Hastelloy "N" system. In this case the ratio is 2.

In several test modules examined, void formation as a result of diffusion was found in nickel-Nioro-nickel and nickel-Nioro-tungsten braze joints. There were no gold-Hastelloy "N" interfaces to serve as a comparison to test the prediction of less voids at this type of interface. The void area was particularly dense in the nickel-to-tungsten joints and would have resulted in mechanical failure if the ceramic-to-nickel bonds had not failed. This can be attributed to a complex diffusion phenomenon which is probably accelerated by the stress imposed on the interface due to the difference in thermal expansion between nickel and tungsten. The structure of the nickel-Nioro-tungsten interfaces consists of several zones which would require electron beam probe analysis for an accurate reconstruction of their formation. However, visual observations show a strong penetration of gold into nickel but no penetration of gold into tungsten. This is consistent with the minimal gold-tungsten solubility. Tungsten thus forms an effective barrier to gold causing most of the gold in the braze shim to diffuse into the nickel member. Therefore, the quantity of gold moving across this interface is considerably greater than it would be if there were nickel members on both sides of the Nioro braze. As a result, there is a high void density at this interface.

The interface zone is further complicated by the diffusion of some tungsten into the Nioro braze area and diffusion of some nickel-gold alloy into tungsten. The tungsten appears to lower the solubility of gold in the Nioro, causing the rejection of gold from the grain structure. As a result, a gold rich zone has been shifted from the original center of the interface into the nickel member. The high nickel structure remaining is laced with irregular shaped voids between grains. The resultant interfacial zone thus consists of several bands of voids. The relative position and intensity of these void zones appears to vary with life test conditions.

A potential problem as a result of the rapid interdiffusion of gold and nickel is the Hastelloy "B"-Nioro-nickel system. Gold penetration data on an analogous system, gold-Hastelloy "N", Figure 8, indicates that gold may come close to penetrating a 25 mil Hastelloy "N" NaK tube wall in five years. The mechanism of diffusion is a combination of grain boundary and volume diffusion. In comparison, the penetration of gold into pure, large grain size nickel is reported to be only by volume diffusion. The calculated penetration distance for a 5 to 10 a/o gold concentration line in pure nickel, Figure 8, is only 43 to 51 percent of the penetration of gold into Hastelloy over a period of five years.

The extrapolated gold penetration into Hastelloy "N" assumes a constant diffusion mechanism based on a semi-infinite diffusion couple. Since this type of bond will become non-idealized as the

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A As-packed structure 4.9x
ID - 0.433 inch
Packing Density

B After limited swaging 4.9x
ID - 0.374 inch
Area Reduction - 25.4%
Packing Density - 75.7%

C Detail of as-swaged structure 100x
Molybdenum wire diameter - .0155 inch
Copper plate thickness - .0013 inch

FIGURE 8 - CROSS SECTION OF MOLYBDENUM WIRE BUNDLE
(441 Wires in a 1/2 inch Copper Sleeve)

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diffusion front approaches the NaK interface, the gold concentration gradient will change and the time for the observed gold front to penetrate 0.025 inch could be less. A more accurate method for predicting penetration distances for actual boundary conditions typical of hot stack bonds, based on limited source and limited sink boundary conditions, is currently being investigated.

An important consideration in determining if gold diffusion into a NaK tube wall could cause failure is the size of the gold reservoir available for diffusion, e.g., thickness of the braze shim. For example, a 0.001 inch thick Niore shim containing 52 a/o gold diffusing into a Hastelloy "N" plate 0.025 inch thick will at equilibrium result in a maximum gold concentration at the NaK interface of 1 a/o. For comparison purposes, if a 0.030 inch pure gold shim were used, the maximum gold concentration would be 29 a/o. However, since the critical gold concentration for NaK attack has not been determined, it is not known if a 1 a/o gold concentration can be tolerated. A 29 a/o gold concentration is almost certainly too high. Work is currently in progress on the use of gold diffusion barriers between the Hastelloy "B" NaK plate and possible gold members.

Additional attention is required by the bonds formed on both sides of the graphite shoe, i.e., tungsten-to-graphite and graphite-to-SiGe. These bonds were investigated both by micro examination and electron beam probe analysis. The latter technique was used because of the difficulty in tracing metal migration in an intermetallic impregnated body such as JTA graphite. Table IV is a summary of the electron probe analysis.

In several test structures examined, the nickel-titanium eutectic braze between tungsten and 950S graphite had penetrated the graphite and reacted with N-type SiGe. The braze alloy migrated by capillary flow through cracks and interconnected pores. Since the bonding temperature is 1225°C and the melting point of the eutectic is 950°C, the nickel-titanium alloy was highly fluid. Reaction with SiGe lowered its melting point so that in several cases SiGe had backflowed to the graphite-tungsten interface. Nickel-titanium has also been found to partially penetrate JTA graphite. Electron beam probe analysis of one sample indicated approximately four mils penetration into JTA.

A favorable result of the electron beam probe analysis was the absence of any evidence of nickel or titanium diffusion by volume, grain boundary or surface mechanism through either graphite body. A combination of crack-free, limited porosity graphite and a more sluggish braze alloy should form an adequate diffusion barrier between SiGe and the metallic bonds of the hot stack.

Work is currently in progress on the substitution of a denser grade of graphite for 950S and on a reaction study of other braze alloys for the tungsten-graphite interface.

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TABLE IV

ELECTRON PROBE ANALYSIS

Specimen	Interface	Treatment of Specimen	Observations Based on Electron Beam Probe Analysis
CM32	1) W(Ni plated) 2) Ti shim 3) 950S graphite 4) SiGe	As brazed and acceptance heat treated. Brazed-1225°C ~ 3 min. Heat treated 16 hrs, 900°C	Ni-Ti penetration into graphite CM32, 39 & 64 appears as large "clumps" of metal which are also observable by micro examination.
CM39	(Same as CM32)	Life tested Brazed & acceptance heat treated as per CM32. Life Test- 900°C, 1300 hrs.	There was no evidence of either Ni or Ti diffusion into graphite by any one of the following mechanisms: 1) Surface diffusion on the walls of the graphite pore structure. 2) Grain boundary diffusion. 3) Bulk diffusion. This applies to all graphite specimens listed here.
CM64	(Same as CM32)	Electrical reject but mechanically intact. As brazed and acceptance heat treated as per CM32.	In CM64 small islands of Ni-Ti alloy were found as a separate phase in the SiGe. Also in CM64 a high concentration of Si and Ge was found in the Ni-Ti braze interface.
CM70	1) W(Ni plated) 2) Ti shim 3) JTA graphite 4) SiGe	As brazed and acceptance heat treated as per CM32.	In CM70 Ni-Ti penetration into JTA graphite appears as "clumps" of metal which are <u>not</u> observable by micro-examination. Ni-Ti penetrated as much as 100 microns (~ 4 mil) into JTA.
CM44-1	1) W 2) Nicro shim 3) 950S graphite 4) SiGe	As brazed and acceptance heat treated as per CM32.	No evidence of Ni-Au penetration into 950S graphite. Little or no penetration of Si-Ge in 950S graphite near SiGe - 950S graphite interface. However, one "clump" of SiGe was found 20 micron (~ 1 mil) from 950S - W interface.

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TABLE IV CONT'D

NOTE: The diffusion of the braze alloy into tungsten at the graphite-tungsten interface was reported to be as follows:

CM32	Ni-Ti braze	30 micron
39	" "	60 "
64	" "	20 "
44-1	Au-Ni (Nicro) braze	180 "

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IV. COLD INSULATOR STACK

An evaluation of the structures fabricated and tested in Phase I and of those fabricated in Phase II indicates that the incidence of cracked pellets at the cold end of the couple assembly is an area of weakness. Insufficient stress compensation in the cold stack appears to be the primal cause of the problem.

Two courses of action have been taken to alleviate the improper stress compensation:

- 1) A copper and tungsten pedestal has been added to the stack between the tungsten shoe and the electrical connector. Experience on other programs has shown that pedestaling reduces stress transmission to the pellet. It is anticipated that pedestaling will also reduce stress in the Compact cold stack.
- 2) The thickness of the tungsten shoe has been increased from 20 mils to 30 mils. This added thickness will increase the rigidity of the shoe and further reduce stress transmission to the pellet.

The originally scheduled structures for the material and bond study have been held in abeyance due to the lack of BeO ceramics. A duplicate schedule has been prepared and parts are to be fabricated substituting Al_2O_3 ceramics for the temporarily unavailable BeO insulator so that the study may continue.

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V. STRESS RELIEF CONNECTOR

A preliminary evaluation of Nioro and Gemco as utilized to braze the pliant member to the simulated cold heat exchanger in the stress relief connector sandwich has been completed. Test results indicate Nioro to be the more promising braze medium due primarily to its inherent ability to wet and flow. Two groups of sandwich samples utilizing Nioro and Gemco were fabricated and subjected to tensile testing, hardness testing, and metallographic evaluation immediately after brazing and after 232 hours of steady-state life at 360°C in vacuum, Figures 9 and 10.

Metallurgically, it was observed that Nioro made an excellent initial bond between Cu and stainless steel but some small pin point voids were evident on Cu-to-Cu braze as shown in Figure 10a. These may be due to a Kirkendall effect which is initiated at the 1000°C brazing temperature. Larger sized voids were found in the Cu web to stainless steel braze when utilizing Gemco, Figure 9a. These are attributed to a wetting problem. A higher brazing temperature (1025°C) was tried. This resulted in a slightly better bond as shown in Figure 9b.

A comparison of Figures 9b and 10a, shows that the Nioro braze interfaces have smoothly rounded fillets whereas those using Gemco have ragged fillets which result in high stress concentration points and a reduction in area of thermal conductance.

Figures 9c and 10b, show Gemco and Nioro brazed interfaces, respectively, after 232 hours of steady state life at 360°C which is approximately equivalent to 2500 hours at 270°C (design operating temperature). Both bonds look very good. However, two significant points are noted, (1) the larger contact area of the Nioro brazed joint and (2) no increase in the quantity and volume of the pin point voids noticed in the initially brazed Nioro sample.

The variability in web material thickness is due to the quality of pliant member material used. As mentioned in previous reports, initial evaluations are utilizing in-house pliant member material which does not meet the specifications of incoming material. However, it is applicable for these evaluations.

Figure 10c, shows the area in which hardness readings were obtained. Both Gemco and Nioro have completely diffused through the copper-web in the lower region where it comes in contact with the braze material. Figures 11 and 12, show the initial hardening effects of Nioro and Gemco diffusion into copper-web. The higher penetration of approximately 9 mils for Nioro as compared to 4 mils for Gemco is due to the larger fillets inherent with Nioro brazing. Figures 13 and 14 show the hardening effect after 232 hours steady state life at 360°C. As can be seen, penetration of the braze material, as determined by hardness testing, has not increased significantly.

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#14

145X

INITIAL SAMPLE

Cu Web

a Gemco

Brazed at 1000°C
for 10 Min. in H₂

S.S. Slug

#15

145X

Cu Web

b Gemco Braze

Brazed at 1000°C
for 10 Min. in H₂

S.S. Slug

#9

145X

LIFE TESTED SAMPLE

232 hours Steady State at 360°C

Cu Web

c Gemco

Brazed at 1000°C
for 10 Min. in H₂

S.S. Slug

FIGURE 9 - GEMCO BRAZED PLIANT MEMBERS BEFORE AND AFTER LIFE.

#13

145X

INITIAL SAMPLE

Cu Web

a

Nioro

Brazed at 1000°C
for 10 Min. in H₂

Cu Slug

#10

145X

LIFE TESTED SAMPLE
232 hours Steady State at 360°C

Cu Web

b

Nioro

Brazed at 1000°C
for 10 Min. in H₂

Cu Slug

#9

145X

TYPICAL AREA OF KHN HARDNESS
READINGS FOR ALL SAMPLES

Cu Web

c

Braze

Slug

FIGURE 10 - NIORO BRAZED PLIANT MEMBERS BEFORE AND AFTER LIFE.

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FIGURE 11. INITIAL HARDNESS vs. DISTANCE ALONG Cu WEB

FIGURE 12. INITIAL HARDNESS vs. DISTANCE ALONG Cu WEB

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FIGURE 13. INITIAL HARDNESS vs. DISTANCE ALONG Cu WEB

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FIGURE 14. INITIAL HARDNESS vs. DISTANCE ALONG Cu WEB

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Tensile testing of sandwich samples before and after the above mentioned life period revealed no failures in the brazed interface of either braze material. All separations occurred in the copper-webbing and ranged between 8,000 and 9,000 psi.

The following conclusions are based on the above test results:

- 1) Nioro has a greater wetting ability than Gemco, thereby forming more stress free interfaces.
- 2) The initial pin point voids noticed in the Nioro braze joint did not increase in volume or quantity after accelerated steady state life equivalent to 2500 hours at 270°C.
- 3) The effect of braze material diffusion on the hardness of the copper-web after steady state life was not significant.
- 4) The strength of brazed interfaces after steady state life exceeds that of the copper-web.

Based on the above findings, Nioro will be used in all stress relief connector sandwiches fabricated for evaluation purposes.

All tools and fixtures required for fabrication and evaluation of sandwich samples have been designed and fabricated with the exception of shock and vibration fixtures which are presently being fabricated and are due to be completed by the middle of August. Folded and slotted copper pliant member stock has been received. It is presently being inspected and processed for use in sandwich fabrication.

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VI. THERMOELEMENT ASSEMBLY AND GRAPHITE EVALUATION

A. Thermoelement Assembly

During the period covered by this report the primary aim has been to gain experience in the routine production of thermoelements for use in modules and for element life tests. Tungsten shoes in the design configuration have been limited in number because of difficulties in the source of supply. This has necessitated the use of modified configurations for coupons and test structures and the search for a second or new supplier of acceptable tungsten.

The changes in configuration required that additional bonding schedules for each configuration be determined. In setting up these bonding schedules, the temperature profile in the furnace was determined and an auxiliary thermocouple in the area of the work was installed. The furnace shows a drop of 10°C from the bottom to the top in the work area of the hot zone. The auxiliary thermocouple is used as a check and as a furnace control. A difference of more than 30°C between the furnace indicated temperature and the auxiliary thermocouple temperature is an indication that the work is not at the desired temperature and adjustments are necessary. The temperature profile is shown in Figure 15.

During this period, a major variation in the 950S graphite used in "N" thermoelements was experienced. During the previous reporting period, that covering the transfer of the bonding process from the laboratory to production, the acceptance testing (900°C , vacuum anneal, for 16 hours) showed a 70 percent yield. Acceptance dropped to 37 percent yield before the failure mechanism was determined. Metallographic and electron beam analyses indicated that the titanium-nickel braze material used in the tungsten-graphite bond moved through pores and microcracks in the 950S graphite by capillary action, reacted with the silicon-germanium to produce high contact resistance and physical failure of the graphite-silicon-germanium bond. Figure 16 shows the type of penetration that was typically observed in the tungsten-graphite bond area. Figure 17 shows a micro-crack in the 20 mil 950S barrier. Titanium-nickel braze material was found in the crack and at the silicon-germanium interface by electron beam analysis. This element was rejected for high electrical resistance across the barrier. The resistance was 13 milliohms compared to a maximum acceptable value of 0.24 milliohm. Instituting rigid inspection procedures on 100 percent of the parts at each processing step and increasing the barrier thickness from 20 mils to 30 mils raised the element acceptance level to 80 percent. The rejection rate of graphite parts rose to 70 percent. Examination of each lot of 950S material in stock showed variations in density, porosity, and resistance within each lot; about 30 percent of the material is acceptable.

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FIGURE 15. TEMPERATURE PROFILE ELEMENT BONDING SURFACE

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Tungsten

950S Graphite

210X

FIGURE 16 - TYPICAL BRAZE PENETRATION
INTO 950S GRAPHITE

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Tungsten

950S Graphite

Silicon Germanium

145X

FIGURE 17 - TYPICAL OF BRAZE DISTRIBUTION
IN HIGH RESISTANCE

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An alternate material, Speer 8826 graphite, a pressed material, was evaluated. The initial resistance is 10 percent higher than 950S and the density is 5 percent higher. The initially bonded contact resistance is 11 percent higher than the 950S graphite but still below the maximum allowable value (0.140 milliohm) for initial contact resistance. After acceptance aging (16 hours at 900°C), the resistance in elements using the 8826 graphite has increased 3.5 percent (based on 80 samples) compared to an 8.0 percent increase in the 950S graphite. Examination of the material as received has shown less variation within a lot than is experienced with 950S graphite. The rejection rate on inspected parts is 13 percent. The percent acceptance after initial aging of thermoelements is 87 percent. Based on these data, this material is now being used as the standard barrier in "N" thermoelements.

A study of the barrier contact resistance and mechanical strength of the thermoelement as related to the graphite grain orientation was conducted. Thermoelements were prepared using graphite barriers cut parallel to, at 90 degrees with and 180 degrees with the plane of compression as shown in Figure 18. The contact resistances and mechanical integrity (tensile strength) of the thermoelements were compared. The average contact resistance and tensile strength on ten samples from each orientation were the same. It was concluded that in this case orientation is not a parameter which needs control. The graphite bonded silicon-germanium thermoelements on steady state life test at 800°C have completed 2200 hours. They were evaluated for contact and total resistance at 1500 hours. Table V shows the data obtained to date on these samples. All of the samples except 15 and 17 have performed as well as the controls which are elements prepared in the laboratory during Phase I of the program. The greatest variation appears in the contact resistance value and can be attributed to the method of measurement rather than changes in the actual resistance values. The data indicate that the transfer from laboratory to production facilities has been successful.

The samples using 950S graphite in a "P" assembly as a replacement for the JTA graphite (samples 15 and 17) have both shown resistance values higher than the allowable maximum. Because failure has not been catastrophic the tests have been continued. In view of the difficulties experienced with 950S graphite and the resulting lack of sufficient elements for life testing the steady state life test will be continued to 6000 hours. At this time mechanical integrity will be evaluated. In addition to the samples covered by the data in Table V, 195 samples have been placed in steady state accelerated life testing 900°C. These samples have not undergone sufficient testing to be discussed at this time.

One of the requirements of the present program is that the module be capable of operating for a period of time in air. A screening test was run using thermoelements prepared with JTA graphite in the "P" and 950S graphite in the "N" elements. The samples (one "P" and one

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FIGURE 18. LAYOUT FOR BARRIER ORIENTATION IN 8826 GRAPHITE

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TABLE V
MILLIOHM CHANGE IN RESISTANCE FOR TIME PERIOD IN HOURS

Purpose	Item	Test	Total Resistance R_T						Contact Resistance R_3					
			0/150	150/500	500/1000	1000/1500	Net Change	Per cent	0/150	150/500	500/1000	1000/1500	Net Change	Per cent
To check Reproduction of Phase I Thermoelements	1	Phase I "N" Control	+0.20	+0.15	0.0	-0.05	+0.30	+11.3	+0.01	-0.01	+0.04	-0.02	+0.02	+11.4
	2	Phase II "N" Test	+0.20	+0.10	0.0	-0.05	+0.25	+11.2	-0.04	+0.02	0.0	0.0	-0.02	-16.5
	3	Phase I "P" Control	+0.05	+0.05	+0.02	+0.02	+0.14	+ 5.5	-0.08	+0.02	+0.02	+0.02	-0.02	-11.0
	4	Phase II "P" Test	+0.05	+0.05	+0.02	+0.02	+0.14	+ 5.5	-0.02	0.0	+0.02	+0.02	+0.02	+11.6
To determine effect of silicon weight on graphite barrier	5	Phase I "N" Control	+0.20	+0.15	0.0	-0.05	+0.30	+11.3	+0.01	-0.01	+0.04	-0.02	+0.02	+11.4
	6	0.5 gm/cm	0.0	+0.20	0.0	+0.05	+0.25	+ 9.1	-0.03	0.0	0.0	-0.02	-0.05	-16.3
	7	2.0 gm/cm	+0.20	+0.20	0.0	0.0	+0.40	+11.9	0.0	0.0	+0.05	-0.01	+0.04	+ 4.0
	8	5.0 gm/cm	+0.20	+0.15	0.0	+0.15	+0.50	+12.2	-0.02	0.0	0.0	0.0	-0.02	-16.5
To evaluate backup Furnace	9	Phase I "P" Control	+0.05	+0.05	+0.02	+0.02	+0.14	+ 5.5	-0.08	+0.02	+0.02	+0.02	-0.02	-11.0
	10	Phase II "P" Test #1	+0.05	+0.05	+0.02	+0.02	+0.14	+ 5.5	-0.02	0.0	+0.02	+0.02	+0.02	+11.6
	11	Phase II "P" Test #2	+0.05	+0.05	0.0	+0.05	+0.15	+ 6.0	-0.06	0.0	+0.04	+0.02	0.0	0.0
	12	Phase II "P" Test #3	-0.05	0.0	0.0	0.0	-0.05	- 2.5	-0.06	+0.04	0.0	0.0	-0.02	-11.0
Use of 950S in "P" thermoelement	13	Phase I "N" Control	+0.20	+0.15	0.0	-0.05	+0.30	+11.3	+0.01	+0.01	+0.04	-0.02	+0.02	+11.4
	14	Phase I "P" Control	+0.05	+0.05	+0.02	+0.02	+0.14	+ 5.5	-0.08	+0.02	+0.02	+0.02	-0.02	-11.0
	15	Test "P"	+0.50	+0.50	0.0	-0.10	+0.9	+250.	+0.22	+0.06	0.0	+0.02	+0.30	+500.
Alternate for 950S graphite JTO	16	Phase I "N" Control	+0.20	+0.15	0.0	-0.05	+0.30	+11.3	+0.01	-0.01	+0.04	-0.02	+0.02	+11.4
	17	Phase II Test	+0.65	+0.35	-0.05	-0.25	+0.70	+310.	+0.20	+0.08	-0.09	+0.05	+0.24	+209.

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"N") were steady state annealed in air at 500°C. The contact and total resistance and weight loss were determined at regular intervals during the test. The data indicate that there are no measurable effects up to 100 hours in air. After 120 hours, however, the exposed graphite becomes soft and powdery. The contact resistance is not affected until after 150 hours of test. The data are shown in Figures 19, 20, and 21. This test will be repeated using a larger number of samples and 8826 graphite as an alternate for 950S.

Two screening tests at temperatures higher than 900°C were conducted in vacuum. The object of these tests was to determine element performance at 950°C and 1050°C. After 80 hours at 1050°C all samples (both "P" and "N" types) had failed mechanically. In the second test at 950°C the samples (eight "P" and "N" types) showed an average increase in contact resistance, R_2 , of 0.09 milliohm or 200 percent. This test will be continued until the samples fail mechanically.

B. Graphite Evaluation

A thorough review of graphites and their performance as a barrier layer in SiGe thermoelements is being conducted. The selection of the most suitable materials, and establishment of purchasing and inspection criteria are the objectives of this effort.

The characteristics of graphite which are known to affect bonds between SiGe and graphite include electrical resistance, density, mechanical strength, coefficient of thermal expansion and purity. Several graphites have been chosen on the basis of vendor data and have been evaluated by fabricating test elements and life testing the elements at temperatures up to 900°C in vacuum. Bondability and stability of electrical contact resistance with time at temperature are used as selection criteria. Graphites which have proven to be acceptable and which have been further evaluated include types 886S, 950S (extruded grades of low electrical resistivity) and 8826 (molded grade of slightly higher electrical resistivity) for "N" type SiGe elements; and JTA graphite (a Zr-B-Si impregnated grade) for "P" type SiGe.

A test procedure has been developed for acceptance testing of bonded thermoelements. Bonded elements are measured for contact resistance before and after exposure to 900°C in vacuum for 16 hours. Typical room temperature contact resistivities average about 0.15 to 0.2 milliohm/cm² before acceptance testing and increase by about 8 percent during the acceptance test.

While this type of acceptance test has yielded graphite bonds which have proved to be stable on life testing at 850°C, some failures of the bonds in terms of high resistances have appeared in recent element assemblies. By means of an electron beam probe, these failures have been traced to a penetration of the graphite-tungsten braze material

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FIGURE 19. ELEMENT WEIGHT CHANGE IN AIR AT 500°C AS A FUNCTION OF TIME

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FIGURE 20. CONTACT RESISTANCE IN "P" ELEMENT 500°C IN AIR AS A FUNCTION OF TIME

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FIGURE 21. CONTACT RESISTANCE IN "N" ELEMENT AFTER AGING AT 500°C IN AIR

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through the graphite and, at times, a penetration of Si and Ge through the graphite into the graphite-tungsten bond.

A re-examination of the various graphites was initiated to determine whether or not the graphite shoe itself is at fault, or whether better quality control procedures are required. This effort has taken the form of : (1) extensive surveying of vendors for types of graphite (including filled and coated graphites) and their physical properties; (2) heavy quality control (visual microscopic) inspection of graphite shoes for cracks and voids; (3) density measurements of incoming graphite to determine variability within given grades and pieces; (4) initiation of other methods of quality control inspection.

Vendors contacted during the past quarter have included:

- 1) Speer Carbon Co.
- 2) Stackpole Carbon Co.
- 3) Union Carbide Corp.
- 4) The Carborundum Co., Graphite Products Div. (formerly Basic Carbon Corp.)
- 5) Poco Graphite, Inc.
- 6) Ultra Carbon Corp. (formerly United Carbon Products)
- 7) Norton Co.

As a result of these contacts, it was determined that the production of graphite is an art, and that graphites can vary considerably from vendor to vendor. By means of minor variations in a basic recipe, the vendor can effect a major change in the properties of a given graphite. In addition, processing variables, such as extrusion or molding can cause marked differences in the electrical, thermal and mechanical properties of a given graphite. It was decided to screen vendor data and to select promising grades of graphite for further investigation.

In an attempt to develop a rapid screening technique for hidden cracks, voids, or laminations, samples of various available graphites were examined in thicknesses of 0.030 inch via X-ray transmission photography. The samples screened were:

<u>Vendor</u>	<u>Grade</u>	<u>Type</u>
Speer Carbon Co.	886S	Extruded
Speer Carbon Co.	950S	Extruded
Speer Carbon Co.	8826	Molded

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<u>Vendor</u>	<u>Grade</u>	<u>Type</u>
Speer Carbon Co.	3499	Molded
Speer Carbon Co.	39RL	Molded, highly purified form of 3499
Carborundum Co.	Graph-i-tite G	Extruded, filled and graphitized
Poco Graphite, Inc.	EP 1924 HP	Molded, high purity, fine particle size
Ultra Carbon Corp.	UT - 2 S	Molded, high purity
Union Carbide Corp.	JTA	Zr-B-Si impregnated
Union Carbide Corp.	JTO 981	Zr-Si impregnated

The photographs produced to date are included as Figures 22 to 31. An examination of these photographs reveals hidden cracks, voids, localized density differences, laminations, grain structure boundaries and inclusions. They clearly reveal the marked structural differences between the molded and extruded grades of graphites, and the lack of inclusions in the purified grades. The very fine, uniform, grain structure of EP 1924 HP graphite is notable. Fine grained structures, free from inclusions, are also shown in 39RL, UT-2S, and Graph-i-tite G. This is surprising in the case of Graph-i-tite G, in view of the extruded nature of the product. The inclusions have been analyzed by X-ray spectrometry and have been identified (as noted on the photographs) depending on the grade, as of either a ferrous or non-ferrous nature. The exact bearing that these inclusions have on the performance of a graphite in a thermoelement assembly is unknown, and must be determined by test. The initial indications are that X-ray analysis can be used as a rapid screening technique to detect hidden flaws.

Several commercial graphites, which match the coefficient of expansion of silicon carbide, are available. These are of interest because silicon carbide is formed at the interface between the silicon germanium and the graphite shoe in the initial bonding process. A coefficient of thermal expansion match should, therefore, make for a stress-free bond. Only one of the graphites has been examined, Speer grade SX4. This was available with a vapor deposited coating of silicon carbide. Sections and microphotographs of SX4, through the coating and through the graphite body itself, were made. These are shown in Figures 32 and 33. Figure 32 shows that this graphite contains rather large pores and would, most likely, not be suitable for use without the silicon carbide coating. The coating would be expected to act as the barrier material.

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FIGURE 22 - X-RAY TRANSMISSION PHOTOGRAPH OF SPEER 886 GRAPHITE

6 Kev X-Rays - 0.030 Inch Thick Specimens

4.9X Enlargement

Specimens Rejected on Basis of Visual Inspection

Note proliferation of cracks, not necessarily visible under microscope.

Note also inclusions which have been identified as non-ferrous.

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FIGURE 23 - X-RAY TRANSMISSION PHOTOGRAPH OF SPEER 8826 GRAPHITE

6 Kev X-Rays - 0.030 Inch Thick Specimens
4.9X Enlargement

Specimens Rejected on Basis of Visual Inspection

Note absence of large cracks or laminations in this molded product.

Note one barely visible crack in middle specimen.

Inclusions have been identified as iron rich.

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FIGURE 24 - X-RAY TRANSMISSION PHOTOGRAPH OF SPEER 950S GRAPHITE

6 Kev X-Rays - 0.030 Inch Thick Specimens

4.9X Enlargement

Specimens Rejected on Basis of Visual Inspection

Note cracks in this extruded product, not necessarily visible under microscope.

Note small number of inclusions which have been identified as iron rich.

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FIGURE 25 - X-RAY TRANSMISSION PHOTOGRAPH OF SPEER 3499 GRAPHITE

6 Kev X-Rays - 0.030 Inch Thick Specimens
4.9X Enlargement

Note uniform grain structure and absence of cracks or laminations in this molded product. Inclusions have been identified as non-ferrous.

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FIGURE 26 - X-RAY TRANSMISSION PHOTOGRAPH OF SPEER 39RL GRAPHITE

6 Kev X-Rays - 0.030 Inch Thick Specimens
4.9X Enlargement

Note absence of inclusions, cracks and laminations in this purified, molded product. Some faint, large-grain lines are visible in an otherwise uniform fine-grained structure.

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FIGURE 27 - X-RAY TRANSMISSION PHOTOGRAPH OF GRAPH-I-TITE G GRAPHITE

6-Kev X-Rays - 0.030 Inch Thick Specimens
4.9X Enlargement

Note absence of cracks or inclusions even though this product is extruded.

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FIGURE 28 - X-RAY TRANSMISSION PHOTOGRAPH OF POCO EP-1924-HP GRAPHITE

6 Kev X-Rays - 0.030 Inch Thick Specimens
4.9X Enlargement

Note absence of cracks or inclusions.

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FIGURE 29 - X-RAY TRANSMISSION PHOTOGRAPH OF UT2S GRAPHITE

6 Kev X-Rays - 0.030 Inch Thick Specimens
4.9X Enlargement

Note absence of inclusions, cracks and laminations in this purified, molded product. Faint, small-grain lines are visible.

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FIGURE 30 - X-RAY TRANSMISSION PHOTOGRAPH OF JTA GRAPHITE

6 Kev X-Rays - 0.030 Inch Thick Specimens
4.9X Enlargement

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FIGURE 31 - X-RAY TRANSMISSION PHOTOGRAPH OF JTO 981 GRAPHITE

6 Kev X-Rays - 0.030 Inch Thick Specimens
4.9X Enlargement

Note absence of cracks or laminations.

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FIGURE 32 - MICROPHOTOGRAPH OF SPEER SX4 GRAPHITE

35X Magnification

This is an extruded product which matches the coefficient of expansion of silicon carbide.

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**FIGURE 33 - MICROPHOTOGRAPH OF SPEER SX4 GRAPHITE
WITH VAPOR DEPOSITED SILICON CARBIDE COATING**

145X Magnification

*Note keying of silicon carbide coating into surface pores of
the graphite.*

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An investigation is under way into the processing steps for the graphite pieces. In the past, the final slicing operation on graphite was a wet operation. Because the extent of contamination of the graphite, if any, is unknown, dry processing will be specified for test samples in evaluating new graphites. Further plans call for an evaluation of the more promising grades of graphite by bonding into element assemblies and life testing. In addition, an element assembly of special geometry is planned for simultaneously determining the SiGe to graphite junction resistance and the electrical conductivity of graphite, both at elevated temperatures of 850°C. In this assembly, the graphite wafers will be replaced by 0.5 inch long graphite blocks, each of which will carry three equally spaced voltage probes; the SiGe pellet will be instrumented with three equally spaced voltage probes; the tungsten shoes will carry the current leads and voltage probes. In testing, a given current will be passed through the test assembly and the voltage drops noted. A plot of voltage versus length will yield three straight line segments, i.e. two graphite blocks and the SiGe pellet. Discontinuities or sudden jumps between the plotted lines will yield the interface or junction resistances.

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VII. COMPONENTS AND SUB ASSEMBLIES

A. Module Construction

Partial test structure No. 10 (2 X 3 over 2 X 3 couple array) was fabricated on April 28, 1966. Visual inspection data and electrical measurements were made for each of the twelve SiGe couples. Because of the parallel electrical circuit, individual element resistance readings could not be made. Total module resistance of twelve SiGe couples in a series - parallel arrangement was 17.1 milliohms at room temperature. Thirty-six Chromel - alumel thermocouples were attached and the structure was installed in a vacuum test station. Figures 34 and 35 illustrate PTS-10 installed and wired into the vacuum test station. While operating with the hot shoe temperature at 800°C, the temperature profile along the hot heat exchanger plate indicated a range from 750°C to 930°C over a linear distance of 1.5 inches. Closer examination of temperature and electrical data indicated heat transfer problems with at least one couple hot stack. PTS-10 was cooled to room temperature after operating 70 hours.

Visual inspection of PTS-10 indicated that the nickel to tungsten metallurgical bond in four of the twelve hot stacks had separated and consequently could not conduct the normal amount of heat in the vacuum environment.

Kirkendall void formation at the NIORO brazed joint caused a break in the heat conduction path. This condition created the abnormal temperature distribution along the length of the Hastelloy "B" hot heat exchanger plate. Because of this problem, extensive investigation was undertaken with different braze materials, refractory metals, and alternate hot stack structures, which are described in section III of this report.

In addition to the heat transfer problems, two "N" elements had hair line cracks at the SiGe-to-graphite interface at the cold end of the thermoelements. This condition was apparent immediately after final brazing. After 70 hours of testing, the number of cracked SiGe elements increased to three. From visual observations and past experience in module testing it was evident that PTS-10 could not successfully pass thermal cycling tests.

As a direct result of development efforts described in section III, partial test structure #11, Figure 36, was designed and assembled. It included improvements discussed in the subsequent sections.

1. High Temperature Braze

The Kirkendall void formation in the hot stack was corrected by replacing the Nioro braze with a 94 percent nickel braze (Coast Metals #50) for the assembly of the Hastelloy "B" heat

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FIGURE 34 - PARTIAL TEST STRUCTURE NO.10 INSTALLED AND WIRED IN VACUUM TEST STATION.

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FIGURE 35 - CLOSE-UP OF PARTIAL TEST STRUCTURE NO.10 INSTALLED
AND WIRED IN VACUUM TEST STATION.

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FIGURE 36. COMPACT PARTIAL TEST STRUCTURE (12 COUPLES - 2 x 3 OVER 2 x 3)

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exchanger plate, the nickel contact plates, and tungsten lower equalizers.

2. Stress Relief

a. Hot End

Additional stress relief in the hot stack was obtained by replacing the nickel disc, insulator, and graphite stress pad with a diffusion bonded ductile gold insulator composite. Figure 37 illustrates the location of the tungsten-gold-ceramic composite which is brazed at the hot end of each SiGe couple assembly.

b. Cold End

Stress relief at the cold insulator stack was increased by use of pedestal-compensator composites of copper and tungsten. Figure 37 illustrates the location of the copper-tungsten composites which are brazed to the electrical connector and cold shoes of all "N" and "P" elements.

Based on the new design concept, Figure 37, new components were fabricated and assembled into partial test structure # 11. Figures 36 and 38 illustrate the assembly of PTS-11. After room temperature electrical measurements, the test section was instrumented with 40 chromel-alumel thermocouples and heated in vacuum to an average hot shoe temperature of 800°C for steady state life testing.

In addition to the fabrication and testing of partial test structures 10 and 11, a second approach was made to demonstrate the high temperature performance of the graphite bonded SiGe couple. Three 2-couple modules were made using elements of half cylinder geometry, bonded to ductile gold insulator stacks on round Hastelloy tubes. The basic module components in the first two modules from the hot side to the cold side were as follows:

- 1) Hastelloy X Tubing
- 2) Gold Saddle
- 3) Tungsten Pressure Pad
- 4) Gold Equalizer
- 5) Beryllium Oxide Insulator
- 6) Gold Pedestal
- 7) "N" and "P" Graphite Bonded SiGe Element Assemblies

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FIGURE 37. DESIGN CONCEPT USING DUCTILE INSULATOR COMPOSITE

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FIGURE 38 - COMPLETED PARTIAL TEST STRUCTURE NO.11 ASSEMBLY.

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- 8) Copper Connectors
- 9) Aluminum Radiators
- 10) Copper Compensator

The SiGe couples were connected in series through the aluminum radiators. One module, CA14A1 assembly, was heated in vacuum to an average hot shoe temperature of 800°C. As of June 30, 1966, the 2-couple module has an accumulated test time of 634 hours. The life test data for the first module is given in Section III, B, Module Life Testing.

The second 2-couple module, CA14A2 assembly, had 0.030 inch thick graphite shoes instead of 0.020 inch and the radiator width was increased to 3.00 inches from 1.80 inches. This module is scheduled for life test and will operate at steady state conditions with an average hot shoe temperature of 850°C.

The third 2-couple SiGe module fabricated, CA16A assembly, used the Compact Phase I Test Module water-cooled cold heat exchanger plate design. The arrangement of the components is as follows:

- 1) Hastelloy X Tubing
- 2) Gold Saddle
- 3) Tungsten Pressure Pad
- 4) Gold Equalizer
- 5) Beryllium Oxide Insulator
- 6) Gold Pedestal
- 7) "N" and "P" Graphite Bonded SiGe Element
- 8) Copper Pedestal
- 9) Tungsten Compensator
- 10) Copper Connector
- 11) Beryllium Oxide Insulator
- 12) Copper Heat Distributor
- 13) Pliant Member
- 14) Cold Heat Exchanger
- 15) Water Cooling Tube

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Figure 39 illustrates the design of the 2-couple module. By water cooling this module, the cold shoe temperature of the thermoelements can be reduced to the compact design range of 280°C. The module went on steady state life test with an average hot shoe temperature of 850°C on June 30.

Initial average temperature readings indicate that:

- 1) $T_h = 850^\circ\text{C}$
- 2) $T_c = 313^\circ\text{C}$
- 3) $\Delta T = 537^\circ\text{C}$

These temperatures simulate the specified operating conditions for "over temperature" operation.

Previous environmental test experience had demonstrated the need for a mock-up of thermoelectric devices to check fixtures and holding devices during hot shock and vibration tests. Detrimental resonances can be induced into thermoelectric devices which create an order of magnitude increase in stress in some areas. To provide such a preliminary test tool, a mock-up of equal mass and volume was designed and fabricated. Hollow steel was substituted for the insulator stacks and elements. The proper design of hot and cold heat exchanger plates and pliant copper members were used in fabricating the mock-up of the twelve (12) couple partial test structure. Figure 40 is a photograph of the mock-up.

B. Module Life Testing

Two test structures were placed on operational life test during the quarter. The first was a twelve couple partial test structure, PTS-10, which was extensively thermocoupled to determine temperature distribution of the module and heat exchanger plates. This structure developed a heat transfer problem after 70 hours, and was shut down for visual analysis. The second test structure was a two couple linear test structure, CAL4A1. This had completed approximately 600 hours of satisfactory operation by the end of the reporting period, and is being continued on life test. Details of the operation of these two structures follow.

1. Partial Test Structure - 10

Partial Test Structure (PTS)-10 was placed on life test on May 13, 1966. This test module was extensively thermocoupled, to determine the temperature uniformity of the hot and cold heat exchanger plates, as well as the temperature profile from hot heat exchanger to cold heat exchanger through the insulator stacks and thermoelectric elements. This was the first Partial

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FIGURE 39 - LINEAR TEST STRUCTURE NO. CA16A-3.

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FIGURE 40 - MOCK-UP FOR EVALUATING HOT SHOCK AND
VIBRATION FIXTURE AND TEST PROCEDURE.

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Test Structure placed on life using the all-brazed water cooled cold heat exchanger. This was also the first Partial Test Structure using a hot heat exchanger plate with 0.150 inch inside height and thus the first module test for the thinner heater required for this construction. Thermocouples were so located that in addition to providing the desired temperature readings the voltage and resistance of each element pair and couple pair could be determined.

The Partial Test Structure was operated at a hot heat exchanger temperature of 1500°F (816°C). It operated with a load resistance approximately equal to the internal resistance of the test module, except for brief periods of open circuit operation to allow measurement of open circuit parameters.

As indicated in another part of Section VII, B, a heat transfer problem was encountered in at least one hot stack, which made precise evaluation of temperature profiles impossible. However, enough temperature information was obtained to indicate that the new all brazed cold heat exchanger plate is satisfactory for providing desired temperature uniformity and a temperature level on the hot side of the cold heat exchanger plate. The new heater design also appears satisfactory for providing uniformity of hot heat exchanger temperature. There is, however, an undesirable amount of direct radiation of heat from the exposed ends of the heater to the cold heat exchanger plate. This will be corrected in the next Partial Test Structure by a slight redesign of the heater and use of thermal insulation to shield the cold heat exchanger plate.

2. Linear Test Structure # CA14A1

Two-couple Linear Test Structure # CA14A1 was placed on life test on June 3, 1966, and as of June 30, 1966 had completed 634 hours of operation at a nominal hot shoe temperature of 800°C. Operation is satisfactory. The module is operating in a "hydro-carbon free" life test station pumped by a vac-ion pump. Vacuum is approximately 10^{-7} Torr.

The primary purpose of this test is to evaluate the performance of the 20 mil graphite bond at the hot end of the SiGe couples. At 600 hours there was no indication of degradation in these bonds. Degradation would be indicated by a change in the temperature profile, an increase in test structure resistance, or a change in power output when the NaK tube temperature is held constant.

Table VI shows the temperature profile at zero hours and at 600 hours. Figure 41 shows test structure resistance, open circuit voltage, and matched load power output, with the NaK tube temperature held constant to within $\pm 8^\circ\text{C}$. Note that these data are

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FIGURE 41. MODULE No. CA14A1 LINEAR TEST STRUCTURE
MODULE RESISTANCE, VOLTAGE, AND POWER vs. TIME

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TABLE VI

TEMPERATURE PROFILE - LINEAR TEST STRUCTURE NO. CA14A1

	<u>0 Hours</u>	<u>600 Hours</u>
T NaK	925	916
T Saddle	844	832
T _h Shoe	802	795
T _c Shoe	419	418

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not normalized. The data in Table VI and Figure 41 show no significant change in the condition of the graphite bond.

A second objective in life testing this structure is the evaluation of the leakage resistance of the BeO ceramic insulators. A plot of this resistance versus time for the two-couple structure is shown in Figure 42. To obtain an indication of whether materials evaporating from the hot portion of the test structure will deposit on the cold ceramics and cause leakage across the insulator, two BeO ceramics were suspended on wires and mounted parallel to and about half an inch away from the hot shoe ceramics. The resistance versus time characteristics of these ceramics are also plotted in Figure 42.

The objective specification for the Compact module calls for a leakage resistance not less than 100,000 ohms for a 288-couple structure, or approximately 3×10^7 ohm for the two-couple structure under test. Thus, it is obvious from Figure 42 that additional work must be done to improve the level of module leakage resistance. The plot of leakage resistance of the two separate "outrigger" ceramics, however, does not show any degradation with time. This probably means that the observed leakage resistance of the test structure is caused by an initial surface condition of the ceramics rather than deposition of materials on the ceramics during operation. The indicated method of improving test structure leakage resistance is, therefore, some form of cleaning of the insulator surfaces.

Two additional 2-couple test structures have been fabricated and are being prepared for life test. Both include 30 mil rather than 20 mil graphite bonds, and one utilizes a water cooled heat exchanger on the cold side. These test structures will be evaluated at higher hot shoe temperatures than the present test structure. It is expected that life tests with both modules will begin about 30 June 1966. Another 12-couple partial test structure (PTS-11) of improved construction is being prepared for life test and is expected to begin operation about the middle of July.

3. Shock and Vibration Testing

In preparation for shock and vibration tests at operating temperature of Partial Test Structures, a series of tests was run to determine a suitable heater configuration. It was found that the regular graphite heater will withstand the required shock and vibration if the space between the heater and the heat exchanger plate is completely filled with sheet mica. When heated, the mica defoliates and effectively presents relative motion between heater and heat exchanger.

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FIGURE 42. MODULE No.CA14A1 LINEAR TEST STRUCTURE
LEAKAGE TO GROUND vs. TIME

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C. BeO Ceramics

During the past quarter considerable progress has been made on the BeO metallizing program. As a direct result of a series of metallizing ink evaluation tests the vendor was able to submit a small, 150 piece, shipment of metallized periodic kiln fired BeO which successfully passed RCA metallizing adherence tests (zero failures in 10 samples). These ceramics were metallized by laboratory personnel utilizing production facilities. A lot of tunnel kiln fired ceramics metallized at the same time and under similar conditions had 4 failures in 10 samples in RCA metallizing adherence tests.

A supplier of metallized BeO parts has submitted to RCA, at our request, samples of BeO ceramics metallized with four different metallizing inks, single and double coated and fired at 2300°F (1260°C), 2400°F (1320°C), 2500°F (1370°C), and 2700°F (1480°C). These results indicated that double coatings resulted in better metallizing adherence and that ceramics fired at lower temperatures had better adherence values than those fired at higher temperatures. A new test submitted by this vendor involves BeO ceramics from two sources double coated with three different inks and fired at 2300°F (1260°C), 2400°F (1320°C), and 2500°F (1370°C). Evaluation tests are now in progress.

On May 21, 1966 RCA ran a series of metallizing experiments using outside metallizing facilities and proprietary metallizing inks. BeO ceramics were single and double coated at RCA Harrison, RCA Lancaster and an outside vendor and fired at 1350, 1450, and 1550°C. The best metallizing adherence results were obtained at 1350°C. Additional tests are scheduled for August at 1250, 1300 and 1350°C on BeO ceramics supplied by two vendors.

D. Tungsten Investigation

The status of activity for procurement of tungsten discs with suitable mechanical properties is as follows:

1. Company "A"

A number of tungsten disc samples were received from Company "A" during the reporting period, metallographically examined, and tested by use of the 3-point bend test used by RCA.

This material was found to possess large recrystallized grains, and cracks. Its bend strength was less than half that of acceptable Company "D" material. This tungsten disc sample was judged to be the lowest quality submitted by any tungsten vendor to date.

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2. Company "B"

Company "B" has not reported any improvement in tungsten rod grain structure to date, following efforts to duplicate acceptable grain structure. Since production material is urgently required, a trial order of three hundred 0.040 x 0.424 x 0.460 inch, six hundred 0.030 x 0.142 x 0.460 inch, and six hundred 0.030 x 0.262 x 0.460 inch "rectangles" was placed with Company "B". Their product, as currently produced, comes closest of any vendor to meeting RCA specifications.

3. Company "C"

No word has yet been received from Company "C" concerning their success in developing the desired grain structure in their tungsten rod product.

4. Company "D"

A recent rod sample received from Company "D" shows the same microstructural characteristic that earlier first-quality material possessed. Disc samples have been ordered for further metallographic inspection and mechanical test. It appears possible that the process for producing high-quality tungsten discs is again being used by Company "D", perhaps having been "rediscovered".

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