THE DEVELOPMENT OF A LOW-WORK-FUNCTION COLLECTOR FOR THERMIONIC ENERGY CONVERTERS

15 DECEMBER 1963 - 15 OCTOBER 1964

CONTRACT NONR-4012(00)-FBM

BY
W.B. HALL AND R.J. HILL

PREPARED BY:
RADIO CORPORATION OF AMERICA
ELECTRONIC COMPONENTS AND DEVICES
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PREPARED FOR:
OFFICE OF NAVAL RESEARCH
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WASHINGTON 25, D.C.
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FOREWORD

This report was prepared by the Radio Corporation of America on Contract NONR-4012(00)-FBM for the Office of Naval Research. The work was performed under the direction and technical supervision of Commander J. J. Connelly, Jr. and Commander W. Deal for the Department of the Navy.

The report covers the work performed from 15 December 1963 through 30 October 1964 at RCA-Lancaster by Thermionic Converter Engineering. The work was performed under the supervision and direction of F. G. Block, Manager. Dr. R. J. Hill was responsible for the theoretical aspects and D. B. Kaiser for the fabrication portion of the program. W. B. Hall as Engineering Leader maintained the engineering continuity of the program.
ABSTRACT

The construction and evaluation of a unique device for studying collectors of thermionic converters operating in the "Ball-of-Fire" mode are described. The test vehicle contains one emitter and a rotating disc on which six collectors are mounted. Without disturbing the vacuum condition, each collector may in turn be brought adjacent to the emitter and the electrode combination can be operated as a converter. The emitter temperature, collector temperature, cesium reservoir temperature, and interelectrode spacing may all be independently varied and measured.

A porous rhenium collector was found to be best in terms of both output voltage and output power. The stability of this kind of collector over a period of time was examined, and design recommendations are made for practical converters on the basis of the findings.
NOMENCLATURE

$T_c$  Collector temperature
$T_{cs}$  Cesium reservoir temperature
$T_e$  Emitter temperature
$S$  Interelectrode spacing
$V_d$  Internal plasma drop
$\phi_c$  Collector work function (volt)
$\phi_e$  Emitter work function (volt)
# THE DEVELOPMENT OF A LOW-WORK-FUNCTION COLLECTOR FOR THERMIONIC ENERGY CONVERTERS

## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Heading</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td></td>
<td>NOMENCLATURE</td>
<td>iv</td>
</tr>
<tr>
<td></td>
<td>LIST OF ILLUSTRATIONS</td>
<td>vi</td>
</tr>
<tr>
<td></td>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td></td>
<td>SUMMARY</td>
<td>1</td>
</tr>
<tr>
<td>I</td>
<td>INTRODUCTION</td>
<td>5</td>
</tr>
<tr>
<td>II</td>
<td>THEORETICAL ANALYSIS</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>A. Treatment of Data</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>B. Porous Surfaces</td>
<td>7</td>
</tr>
<tr>
<td>III</td>
<td>REQUIREMENTS OF TEST VEHICLE</td>
<td>11</td>
</tr>
<tr>
<td>IV</td>
<td>MODIFIED DESIGN OF TEST VEHICLE</td>
<td>17</td>
</tr>
<tr>
<td>V</td>
<td>EXPERIMENTAL TECHNIQUE</td>
<td>23</td>
</tr>
<tr>
<td>VI</td>
<td>RESULTS AND DISCUSSIONS</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>A. Silk-Screen Method</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>B. Vapor Plate</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>C. Rhenium Brazed to Molybdenum with Palladium</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>D. Pure Rhenium</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>E. &quot;270&quot; Grade Nickel</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>F. Molybdenum</td>
<td>33</td>
</tr>
<tr>
<td>VII</td>
<td>CONCLUSIONS</td>
<td>41</td>
</tr>
<tr>
<td>VIII</td>
<td>COMPENDIUM OF DESIGN AND RESULTS</td>
<td>43</td>
</tr>
<tr>
<td>IX</td>
<td>REFERENCES</td>
<td>63</td>
</tr>
<tr>
<td>Figure Number</td>
<td>Title</td>
<td>Page Number</td>
</tr>
<tr>
<td>---------------</td>
<td>----------------------------------------------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>1</td>
<td>Work Functions of Molybdenum at Various Cesium Temperatures</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>Vapor Pressure of Oxygen Over Cs₂O</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>Vapor Pressure of Hydrogen Over Cesium Hydride (Condensed) and Cesium Over Liquid Cesium</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>Photograph of Multi-Collector Test Vehicle</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>Cross Section of the Test Vehicle</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>View of Baseplate</td>
<td>21</td>
</tr>
<tr>
<td>7</td>
<td>Top View of the Test Vehicle</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>Schematic Diagram of Vacuum System</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>Diagram of Test Circuit</td>
<td>27</td>
</tr>
<tr>
<td>10</td>
<td>Photograph of Typical I-V Trace</td>
<td>28</td>
</tr>
<tr>
<td>11</td>
<td>Cross Section of Life Test Converter</td>
<td>30</td>
</tr>
<tr>
<td>12</td>
<td>Output Power Versus Cesium Pressure for Rhenium and Iridium</td>
<td>44</td>
</tr>
<tr>
<td>13</td>
<td>Characteristics of Rhenium Silk-Screened on Molybdenum</td>
<td>45</td>
</tr>
<tr>
<td>14</td>
<td>Photomicrograph of Vapor-Plated Rhenium on Molybdenum</td>
<td>46</td>
</tr>
<tr>
<td>15</td>
<td>Characteristics of Rhenium Vapor-Plated on Molybdenum</td>
<td>47</td>
</tr>
<tr>
<td>16</td>
<td>Characteristics of Rhenium Brazed to Molybdenum with Palladium</td>
<td>48</td>
</tr>
<tr>
<td>17</td>
<td>Characteristics of Pure Rhenium</td>
<td>50</td>
</tr>
<tr>
<td>18</td>
<td>Characteristics of &quot;270&quot; Grade Nickel</td>
<td>51</td>
</tr>
<tr>
<td>19</td>
<td>Characteristics of Arc-Cast Molybdenum</td>
<td>52</td>
</tr>
<tr>
<td>20</td>
<td>Effect of Spacing for Porous Rhenium Collector at 585° Centigrade</td>
<td>53</td>
</tr>
<tr>
<td>21</td>
<td>Effect of Spacing for Porous Rhenium Collector at 650° Centigrade</td>
<td>54</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS
(Continued)

<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Title</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>Effect of Spacing for a Porous Rhenium Collector at 525° Centigrade</td>
<td>55</td>
</tr>
<tr>
<td>23</td>
<td>Effect of Temperature on Porous Rhenium Collector</td>
<td>56</td>
</tr>
<tr>
<td>24</td>
<td>Characteristics of Porous Rhenium Collector for Various Emitter Temperatures (Power) and (Voltage)</td>
<td>57</td>
</tr>
<tr>
<td>25</td>
<td>Comparison of Rough and Porous Rhenium Collectors</td>
<td>59</td>
</tr>
<tr>
<td>26</td>
<td>Power Output Versus Time for Removal of Hydrogen for Converter with Molybdenum Emitter and Porous Rhenium Collector</td>
<td>60</td>
</tr>
<tr>
<td>27</td>
<td>Characteristics of Rhenium Evaporated onto Molybdenum</td>
<td>61</td>
</tr>
<tr>
<td>28</td>
<td>Life Test of A-1194 Converter</td>
<td>62</td>
</tr>
</tbody>
</table>

LIST OF TABLES

<table>
<thead>
<tr>
<th>Table Number</th>
<th>Title</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Analysis of Cesium</td>
<td>12</td>
</tr>
</tbody>
</table>
SUMMARY

A. PURPOSE

The purpose of the subject program was the development of a low-work-function collector for converters operating in the "Ball-of-Fire" mode of the low-voltage arc. Changes in work function were to be determined by comparative measurements in actual operation of converters under identically controlled conditions. Three approaches were to be investigated: (1) the development of a material or surface which, when partially coated with cesium, produces a low work function, (2) the development of a low-work-function surface which is kept free of cesium, and (3) the addition of gas additives which, in conjunction with cesium on the base material, produces a low work function.

During the ten-month period covered by this report, the scope of the investigation was extended to include: (1) the evaluation of collectors shown in the first contractual period to be most promising against emitters shown to be most promising by the RCA in-house study, (2) the evaluation of different samples of a single collector material having different surface finishes and fabrication histories, (3) the observation of change in output voltages versus film thickness of refractory material evaporated onto a collector blank, (4) the operation of a dissimilar electrode combination in an existing converter for up to 500 hours to observe the effect of emitter contaminants on collector efficiency.

B. ACCOMPLISHMENTS

During the report period it was demonstrated that:
1. The emitter is less important than the collector in converter operation.

2. Of the materials tested to date, rhenium is the best collector material.

3. The porous form of collector material is superior to other fabricated forms.

4. Porosity is a more important characteristic than surface roughness.

5. Porous rhenium collectors are capable of the following power outputs: 5.2 watts/cm$^2$ for emitter temperature ($T_e$) of 1375° C; 4.8 watts/cm$^2$ for $T_e$ of 1350° C; and 1.4 watts/cm$^2$ for $T_e$ of 1200° C.

6. The presence of hydrogen in a converter can reduce the power output.

7. Thin films of refractory metals on a collector can mask the effects of the collector material.

8. In the 500-hour life test with $T_e$ at 1350° C, the slump in power output that occurred at 100 hours was caused by evaporation of the molybdenum emitter onto the porous rhenium collector.

The results of this investigation indicate that in the design of practical converters, the emitter should be of the same material as the collector if the converter is to function at a constant output for an extended period of time.
C. AREAS OF FURTHER INVESTIGATION

It has been determined that impurities and surface geometry affect the power output of thermionic converter collectors. These same factors govern the adsorption of cesium and, therefore, the work function for a given material. RCA proposes to clarify these effects in the following ways:

1. Both emitter and collector will be carefully outgassed in high-temperature, ultra-high vacuum to a high degree of surface cleanliness. A total clean-up within the converter prior to the introduction of cesium has never been attempted. This procedure will indicate (a) any improvement in power output by the elimination of impurities, and (b) the amount of impurity the converter can tolerate. The unique design of the test vessel enables such an outgassing process to be undertaken without the mutual contamination of both electrodes by each other during the operation. Thus the emitter may be outgassed with a blank collector opposite it, and the other five collectors may be processed in a position away from the emitter by the independent electron bombardment heater. The procedure will assure the evaluation of electrodes of the highest surface purity.

2. Impurities present in the cesium or those inadequately gettered by it will be eliminated. The present method of hydrogen removal, for example, probably does not remove all of the gas, and this residual hydrogen can cause a degradation of converter performance.

3. There is a value where porous rhenium is of optimum density for converter operation. A survey of the whole region will be made to ascertain this figure.
4. Finally, data will continue to be accumulated for the following variable parameters:
   a. Emitter temperature
   b. Collector temperature
   c. Cesium reservoir temperature
   d. Spacing

These data will show where the optimum points, both for total power and for voltage output, occur for the variable parameters. Such data are vital in the design of converters for specific temperature values and for those working over a wide range of temperatures.
THE DEVELOPMENT OF A LOW-WORK-FUNCTION COLLECTOR
FOR THERMIONIC ENERGY CONVERTERS

SECTION I
INTRODUCTION

The thermionic energy converter operating in the "Ball-of-Fire" mode is becoming increasingly important for space and terrestrial applications. The advantages of this device, now that high-temperature (1100° to 1500° C) heat sources are becoming more available, are silent operation, high power-to-weight ratios, and reasonable efficiencies.

For some time it has been recognized that improvements in converter efficiency and power output could be obtained by reducing the collector work function. For example, a reduction of only 0.1 volt in this work function may well increase the power output by as much as 30 percent for a converter working with an output voltage of 0.3 volt.

An investigation of material work functions and methods of reducing these functions was undertaken by RCA under Contract NONR-4012(00)-FBM. This report reviews the work performed during a ten-month period.

Since there is no standard method of measuring the work function of collector materials while they are working in a "Ball-of-Fire" converter, the approach used in the study was to measure changes in output voltage with various materials while holding all other operating parameters constant. For this purpose a test device containing a fixed emitter and a rotor with six different collectors was designed. Without disturbing the vacuum or altering any of the parameters, it is possible to operate the
device with any of six emitter-collector combinations. Any output power changes can thus be attributed directly to the collector material. This report describes the modified design of the test device and gives results obtained in tests of groups of six collector specimens compared with one another. Also described is a 500-hour life test of a converter with a dissimilar electrode combination.
SECTION II
THEORETICAL ANALYSIS

A. TREATMENT OF DATA
At present there is no satisfactory analysis that describes quantitatively the relationships of the four major parameters and the way they control converter power output. These major parameters are emitter temperature \( T_e \), collector temperature \( T_c \), cesium vapor pressure measured in terms of the reservoir temperature \( T_{cs} \), and interelectrode spacing \( S \).

The data in this investigation were obtained in terms of a current-voltage curve (I-V curve) in the power-producing quadrant for sets of specific values of the four major parameters. From the I-V curve the maximum power point was obtained by inspection and was used as the raw data. From specific I-V curves the work function of the emitter was determined using the analysis developed by Hernqvist\(^1\). The plasma arc drop, \( V_d \), was assumed in all cases to be 0.4 volt. The values of these work functions are used in comparisons between various collector surfaces.

B. POROUS SURFACES
The choice of cesium vapor pressure in a thermionic converter is a compromise between the needs of the emitter to provide a suitable work function \( \phi_e \) at \( T_e \), the similar requirements of the collector work function \( \phi_c \) which operates at \( T_c \), and the need for adequate space neutralization and least plasma drop in the interelectrode space. Figure 1 shows that for a cesium pressure suitable for an emitter of 1625° K (1350° C), the collector temperature required to produce the minimum work function occurs where back-emission
FIGURE 1. WORK FUNCTIONS OF MOLYBDENUM AT VARIOUS CESIUM TEMPERATURES

Summary Technical Report
Contract NONR-4012(00)-FBM
30 October 1964
nullifies the voltage advantage derived. In general, if useful power output is to be obtained, the collector requires a lower cesium pressure for minimum work function than does an operating emitter. A porous surface can help to obtain this lower cesium pressure. The mechanics by which a porous surface can achieve this parameter compromise are presented below.

A liquid having a contact angle less than 90° forms a concave surface in a capillary structure. It can be shown that the vapor pressure in equilibrium with the curved liquid surface is less than that above the flat surface. The relationship is:

$$\ln \frac{P}{P_0} = -\frac{2\gamma}{r\rho} \frac{M}{RT}$$

(1)

where
- $P_0$ = vapor pressure over flat surface
- $P$ = vapor pressure over curved surface
- $\gamma$ = surface tension
- $r$ = radius of pore
- $M$ = molecular weight of vapor
- $R$ = gas constant
- $T$ = temperature of the liquid

Thus as $r$ decreases, $P$ decreases. Therefore cesium present in a fine capillary structure on a collector provides a lower effective vapor of cesium at the collector surface. It is this effect which is likely to improve converter performance. A rough surface would suffice normally, provided the roughness were deep, but in a working converter the cesium is derived from outside the interelectrode gap. An interconnecting capillary structure will therefore be able to
maintain its wetted surface by replenishment more easily than a rough surface, in a manner similar to that of the liquid metal "heat pipe." It is possible, therefore, that a porous collector will be advantageous in a working thermionic converter.
SECTION III
REQUIREMENTS OF TEST VEHICLE

The test vessel must be designed to permit reliable comparison of the collector specimens with all parameters optimized for maximum power output.

For power optimization, the temperature of the emitter, collector, and cesium reservoir must be accurately measured and controlled independently of each other. Further, the spacing between emitter and collector must be adjustable in a measurable and reproducible way.

For accurate comparisons of different collectors, the environment must be kept constant from collector to collector. To ensure this condition, all specimens to be examined must be housed in one chamber and placed, in turn, opposite a single emitter for assessment. By so doing, gaseous impurities (which are always present in the residual vacuum and which may affect converter operation) will remain identical for each test. A single emitter must be used so that valid comparisons can be made. The process of changing collector specimens must be accomplished with ease and without interfering with the test vessel environment. Finally, each collector must be presented to the emitter in an identical fashion so that accurate comparisons can be made.

The cesium used for collector work function studies must be of the highest purity. It may contain only minimal amounts of impurities since these could easily nullify the effect of the adsorption of cesium.

The cesium used in the test vehicles was specially made by RCA and has low impurity values. A typical analysis is given in Table I. This analysis, however, was incapable of detecting even large amounts of permanent gases. The contaminant most likely to cause instabilities in converter
performance is hydrogen. Oxygen, if present, would not affect performance, since the vapor pressures of the oxides of cesium are extremely low (Figure 2). Even if small amounts of hydrogen do not affect the performance of a converter, it is possible for the pressure in the converter to rise after seal-off to such an extent that the converter would cease to function. It is important, therefore, to reduce the amount of hydrogen which may be dissolved in the cesium metal or may be present as cesium hydride.

TABLE I. ANALYSIS OF CESIUM

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight Percent</th>
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</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.20</td>
</tr>
<tr>
<td>Ca</td>
<td>0.006</td>
</tr>
<tr>
<td>K</td>
<td>0.02</td>
</tr>
<tr>
<td>Rb</td>
<td>None detectable</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0008</td>
</tr>
<tr>
<td>Ni</td>
<td>0.02</td>
</tr>
<tr>
<td>Mg</td>
<td>0.004</td>
</tr>
<tr>
<td>Si</td>
<td>0.005</td>
</tr>
<tr>
<td>Al</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Note: Analysis was performed by spark spectrographic method. Gaseous contaminants were not investigated.

Of the several methods available for the removal of hydrogen, the following method, as described by Herold\(^3\), was used to reduce the amount of hydrogen to low values before seal-off. A tube which functions as a cold...
FIGURE 2. VAPOR PRESSURE OF OXYGEN OVER Cs$_2$O
finger when filled with liquid nitrogen (see Section V) is interposed in the vacuum line and arranged so that it is just within the temperature controlling (350° C) furnace. At the temperature of 350° Centigrade, the impure cesium in the reservoir has a vapor pressure of 7.8 torr (Figure 3), and it is distilled and condensed on the cold finger as the solid phase. The pressure of hydrogen in equilibrium with cesium at 350° Centigrade is about 400 torr. The hydrogen gas pumped past the solid-phase cesium can be adsorbed only on the surface, and less will be trapped than if the liquid phase were present, since the liquid phase is necessary for equilibrium to take place. The hydride thus formed is insoluble in the metal at this temperature, leaving most of the hydrogen to be pumped away. The process is repeated by cooling the bottom of the tube and warming the cold finger by allowing the liquid nitrogen to evaporate. Cesium condensing on the cold finger falls off and any vapor formed collects in the cooled reservoir. The distillation process can then be repeated. The lower limit of hydrogen contamination of the cesium is governed by the sticking probability of hydrogen on cesium and the surface-to-volume ratio of the solid cesium.
FIGURE 3. VAPOR PRESSURE OF HYDROGEN OVER CESIUM HYDRIDE (CONDENSED) AND CESIUM OVER LIQUID CESIUM
SECTION IV
MODIFIED DESIGN OF TEST VEHICLE

The basic approach in designing the test vessel was to use, as far as possible, only those materials that were compatible with cesium. For this reason most parts of the test vessel (shown in Figure 4) were constructed from type 304 stainless steel.

The original design of the test vehicle has been modified extensively to allow emitters to be interchangeable and to facilitate testing. The demountable aspects of the test vehicle have been extended so that spare parts can be substituted for any component which may become defective. Figure 5 is a cross section of the new test vehicle which shows the following demountable parts:

1. Baseplate
2. Spacing adjustment assembly
3. Emitter
4. Emitter bombardment heater
5. Emitter ceramic assembly
6. Combined collector thermocouple and potential probe.

The demountable approach is a new feature, and the junction between parts is obtained with a copper gasket that is deformed by compression to obtain an ultra-high-vacuum joint. Each joint was designed so that little strain occurred during compression. This technique resulted in the emitter remaining parallel with the collectors to within ±0.0005 inch.

In the later stages of the investigation it was found that gaskets made from "270" grade nickel worked as well as copper and were to be preferred on the basis of cesium compatibility.
FIGURE 4. PHOTOGRAPH OF MULTI-COLLECTOR TEST VEHICLE
FIGURE 5. CROSS SECTION OF THE TEST VEHICLE
Other features of the revised design are shown in the view of the baseplate in Figure 6. The collector outgassing heater and evaporation heater also are removable and are shown in the diagram. Figure 7 shows a view of the top of the test vehicle. The small ceramic parts of the heater and thermocouple assemblies are made from components compatible with cesium and are brazed together with a nickel-palladium alloy$^4$ which also is compatible with cesium.

The sheath of the collector thermocouple was utilized as a potential lead from the collector. The thermocouple was insulated from the sheath, and the sheath was insulated from the main test vessel by the inclusion of a ceramic-to-metal seal in the bellows assembly.
FIGURE 6. VIEW OF BASEPLATE
FIGURE 7. TOP VIEW OF THE TEST VEHICLE
The test vehicle was assembled by placing the rotor on its sapphire thrust bearing, and sliding the cross-member with its sapphire ball-race over the rotor top spindle (see Figure 5). The top cap of the rotor spindle was placed in position, and the flexible, copper, current-carrying lead was bolted to the top cap. The other end of the lead was connected to the main shell via the cross-member retaining bolts. All bolts that would be in the vacuum were slotted down one side to permit the threads to be pumped and minimize virtual leaks. The top plate gasket was put in place, and the top plate was carefully lowered into position so that the rod of the rotating mechanism was properly located. Finally, the top plate bolts were tightened half a turn at a time in a numbered sequence to prevent damage to the top plate by warping.

All stainless steel parts that would come in contact with the vacuum were electropolished and thoroughly washed immediately prior to assembly. After assembly the rotating mechanism was tested, and the final leak check was performed on the test vehicle using a helium mass spectrometer leak detector. The test vehicle was then attached via a copper compression seal to the vacuum system. (See Figure 8).

The stainless steel vacuum system consisted of a vertical tube with provision for temperature control at the bottom, to which the test vehicle was attached. Since the bottom of this tube was the coldest part of the system under operating conditions, it served as a cesium reservoir and controlled the pressure of the cesium vapor. The temperature, $T_{Cs}$, was measured by a chromel-alumel thermocouple. A copper tube was interposed above the junction between this tube and the test vehicle so that the
FIGURE 8. SCHEMATIC DIAGRAM OF VACUUM SYSTEM

Summary Technical Report
Contract NONR-4012(00)-FBM
30 October 1964
The test vehicle could be isolated from the pumps by a pinch-off. A side arm of copper containing three copper capsules of specially purified cesium was located above the pinch-off section. The entire section could be contained in a small oven.

The main pumping line was extended via the cold finger and a water-cooled gooseneck section that served as a still head for cesium distillation. An ion gauge, a Vac-Ion pump, and an all-metal, ultra-high vacuum valve completed the main part of the system.

The pumping system consisted of a liquid-nitrogen U-trap, a three-stage mercury diffusion pump with a refrigerated chevron baffle trap, and a rotary, oil, backing pump.

The system beyond the chevron baffle, with the exception of the glass in the gauges and the copper parts of the pinch-off and cesium appendage, was constructed from stainless steel with copper compression seals used between all bolted sections. The entire system beyond the baffle, however, could be baked to temperatures of 425° Centigrade. Using the standard engineering practices, a vacuum typically better than $10^{-8}$ torr was obtained in the test vehicle. All filaments were flashed, and the collectors were outgassed at 700° Centigrade by electron bombardment while the temperature controlling oven was at 350° Centigrade and the emitter at 1450° Centigrade. This process was continued until the pressure in the system was reduced to the $10^{-8}$ torr scale. The emitters and electron bombardment heaters were then turned off and the oven was cooled. Using special pliers, the cesium appendage was pinched to release approximately 5 grams of cesium. The pressure rose slightly each time the copper was deformed, presumably due to occluded gas, but the pressure remained on the $10^{-8}$ torr scale.
The oven was replaced and the cesium was distilled into the cesium reservoir. The test vehicle was then operated as a converter, with the cesium being distilled up to the water-cooled gooseneck, where it dripped back to the reservoir. (See Figure 8.) The cold finger was cooled with liquid nitrogen and then warmed a few times until significant pressure changes ceased.

The test vehicle was then isolated from the pumping system by pinching off the connecting copper tubing. Since there is always the possibility of a leak developing in a pinch-off and since it was not necessary to separate the emitter from the pumping section, the unit was left intact so as not to jeopardize the successful operation of the whole device. The test vehicle at this point was ready for operation to assess the collector specimen mounted on the rotor. The oven was first heated to 325° Centigrade and the emitter temperature brought up to the desired value. The cesium reservoir temperature was adjusted by regulating the air cooling. The collector temperature rose by absorption of heat radiated from the emitter. The "Ball-of-Fire" mode of operation was initiated, and the collector temperature rose sharply as a result of heat absorption equivalent to $I\phi_c$. Using the test circuit (Figure 9) with switch S1 open, the output current $I$ was varied by adjusting the dc power supply. This operation resulted in altering the amount of heat ($I\phi_c$) absorbed by the collector and thus controlling $T_c$.

After careful adjustment and after the converter had run in a steady state for five minutes, the heavy knife switch, S1, was closed. The closing of S1 caused S2 to close a fraction of a second later, applying a pulse across the electrodes of the converter. The I-V curve traced by the oscilloscope was photographed during this procedure (Figure 10). Switch S1 was then opened (causing S2 to open and allowing the capacitor to charge) and the
To Vertical Deflection Plates of x-y Scope

Current Measuring Resistor

Thermionic Converter

dc Power Supply

Capacitor C

FIGURE 9. DIAGRAM OF TEST CIRCUIT
FIGURE 10. PHOTOGRAPH OF TYPICAL I-V TRACE
test vehicle continued to work as a converter with a fixed output. This procedure was completed within 1/2 second using a pulse cycle of 8 milliseconds. For each I-V curve, the maximum power point was found by measurement of the photographic trace.

The two bright spots in Figure 10 provide an additional check of the validity of the pulsing technique as compared with the point-by-point plotting method. The point at maximum voltage in Figure 10 is the value for the emitter-collector combination when only S1 is closed. This is a high voltage reading because the resistance of the electrical leads is not nullified by the d-c power supply. The point at lower voltage is the steady-state value when S1 is open and the converter output is governed by the d-c power supply. Since this point is on the I-V curve traced by the pulse, it shows that the steady-state value compares with the pulsed value. This provides added confidence in the method and serves as a calibration for each curve taken. All data discussed in the following section were obtained in this manner.

The life test was conducted using a small converter of simple construction, the standard RCA type A-1194. The area of each electrode is 2.48 square centimeters and the unit is contained in a kovar converter envelope. A cross section of this design is shown in Figure 11. In the past, 150 similar converters accumulated a total of 11,000 hours life on test. This experience clearly shows that the A-1194 is a reliable, well-tried test vehicle.
FIGURE 11. CROSS SECTION OF LIFE TEST CONVERTER
In the initial survey of materials it was found that the converter produced more power output with a rhenium matrix* collector than with other collector materials. For convenience the pertinent figures are assembled in Section VIII of this report. These preliminary results are plotted in Figure 12 as output power density versus cesium reservoir temperature. These results were repeated, proving that rhenium is a very efficient collector material. However, there are two main factors which detract from its usefulness in practical converters: the prohibitively high cost of the bulk material, and the comparatively high thermal-neutron-capture cross section of rhenium which affects its use in-pile. Consequently, methods of applying thin films of rhenium onto refractory metals such as molybdenum were investigated. It was necessary that the method of applying the film to the base metal be inexpensive, and the film had to retain the desirable thermionic converter properties. Various methods of applying rhenium to molybdenum were explored, and samples from each method were tested in conjunction with a nickel control reference as collectors for thermionic converters. The emitter used in these tests was rhenium-vapor-plated molybdenum. The methods and tests used are described below.

A. SILK-SCREEN METHOD

A fine slurry of rhenium powder was prepared and applied to the molybdenum surface by "silk-screen" techniques. This technique is used

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*The designation "matrix" is a misnomer, strictly speaking, which has persisted throughout the growth of thermionic energy converter technology. The object was to simulate the matrix cathodes commonly used in electronic tubes in which a composite oxide is held in position by a metal matrix. The matrix collectors consist of a porous sintered metal in which cesium will be absorbed, and here the similarity occurs. The word matrix will continue to be used here.
extensively in the electronics industry to apply a thin metal coat to ceramics for use in ceramic-to-metal seals. The coat is sintered in a hydrogen furnace and produces a thin porous coating similar in structure to the thick matrices which produced the high power outputs initially. The results obtained with this collector with an emitter temperature of 1350° Centigrade (Figure 13) compare favorably with those obtained using the matrix collector at $T_e = 1375°$ Centigrade (Figure 12). The results are presented in terms of power density and output voltage.

B. VAPOR PLATE

High-temperature vapor plating produces a coherent and stable rhenium film on a molybdenum substrate and, in addition, provides a rough rhenium surface which, by the method of formation, has a high density of low-index crystallographic planes*. A photomicrograph of the surface is shown in Figure 14. Figure 15 is a plot of the power output and voltage output obtained by using this material as a collector. The point of highest power output occurs at an anomalously low cesium temperature for this material. However, it does not equal the matrix results.

C. RHENIUM BRAZED TO MOLYBDENUM WITH PALLADIUM

A rhenium sheet 0.010-inch thick was brazed to a molybdenum collector blank using palladium. Although the rhenium brazed very well, the solubility of rhenium in palladium was found to be high, and the surface consisted of patches of palladium-rhenium alloy. After converter operation, it was found that these patches had grown in size.

*Obtained from: San Fernando Laboratories
2800 Russ Building
San Francisco 4, California
presumably as a result of solid-state diffusion that occurred at the collector operating temperatures (between 500° and 600° C). The results of this test are given in Figure 16. The two runs were taken with a long time interval between them. Clearly, the contamination of the surface by palladium increased during this interval and caused a difference in power output. This method was rejected as a means of joining rhenium to molybdenum.

Phase diagrams indicate that there may be braze materials suitable for use with rhenium at high temperatures. However, it will be seen later that there is a more desirable method of joining these materials which does not involve an intermediate braze material.

D. PURE RHENIUM

A sample of pure rhenium was included as a standard rhenium comparison. The results of this test are shown in Figure 17.

E. "270" GRADE NICKEL

This material is used as a standard collector and provides a comparison between one rotor and another. The results of this test appear in Figure 18.

F. MOLYBDENUM

Arc-cast, high-purity molybdenum also was included as a blank. The results obtained with this material are shown in Figure 19.

All of these collectors were evaluated in the test vehicle under identical conditions of cesium purity, emitter temperature (T_e), collector temperature (T_c), spacing, and cesium reservoir temperature (T_{cs}). Therefore, it must be concluded from the results that the collector surface structure
has an important effect on the operation of a thermionic converter. Since each was outgassed according to the schedule outlined in Section V, and, presumably, had the same degree of contamination, it must be the mechanical surface which is important. A matrix-type surface is better than a polycrystalline or vapor-plated surface. This confirms other data obtained for molybdenum, both as matrix and polycrystalline. It should be noted that in the data for molybdenum presented in Figure 19 there appears to be a discrepancy between these results and the previously acquired molybdenum data. This difference occurred because the molybdenum collector was placed opposite the emitter and then the electron bombardment heater during their respective outgassings. Visual observations made after the test showed that the collector surface was highly contaminated. The information is included here only for the sake of completeness.

A rhenium sheet 0.005-inch thick was joined to a molybdenum blank by a high-temperature autoclave method. Since this material could be machined, a collector was fabricated from it and tested. Its behavior was identical with that of bulk rhenium, and it remained mechanically stable under collector operating conditions. It was concluded that this was the best method for applying thin, stable, dense, polycrystalline rhenium to molybdenum.

Since the porous rhenium surface fabricated by "silk screening" methods compared favorably with collectors fabricated by sintering, attention was directed to this particular collector rather than to fully dense rhenium collectors. First, the spacing was altered for a given set of conditions (viz., $T_e = 1350^\circ C$, $T_c = 585^\circ C$), and the power output was measured for various

*Parts fabricated by: Battelle Memorial Institute
505 King Avenue
Columbus, Ohio
cesium pressures. Thus, as the spacing is decreased in Figure 20, the cesium reservoir temperature is at a higher temperature to provide a higher cesium pressure for maximum power output. The same effect is obtained at different collector temperatures; for example, in Figure 21 $T_c$ is 650° Centigrade. At the higher collector temperature a higher cesium pressure is required to produce a work function equivalent to that of the collector in Figure 20. Consequently, at high pressure, large spacings will not produce optimum conditions, and will cease to be sensitive to changes in cesium pressure. The effect of spacing is demonstrated at low emitter temperatures ($T_e = 1200°$ C) in Figure 22. Further data were taken to characterize the properties of the porous rhenium collector. The results of keeping the cesium reservoir temperature constant and varying the collector temperature are shown in Figure 23. The data are consistent with the theory that optimum $T_c / T_{cs}$ is a constant. It may have been expected, however, that power output would be more sensitive to cesium vapor pressure than the results indicate.

The results for the rhenium porous collectors are summarized for various emitter temperatures in Figure 24, sheet 1, where power output versus cesium reservoir temperature is plotted. It should be noted that the performance of the molybdenum emitter compares very well with that of the rhenium emitter. Figure 24, sheet 2, shows that the favorable power outputs obtained with the porous rhenium collector are not developed by sacrificing output voltage. Even with optimum power at 1200° Centigrade emitter temperature, 0.3 volt is developed. In addition to the collector studies, some data have been obtained which indicate that porous rhenium remains stable when used as an emitter.

Using the method developed by Hernqvist, the collector work function ($\phi_c$) was determined for various cases. The calculation was done without taking

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Summary Technical Report
Contract NONR-4012(00)-FBM
30 October 1964
-35-
into account the voltage drop in the emitter assembly in order to measure the useful power developed outside the converter and not impractical power outputs at the electrode surfaces. In all cases the I-V curve chosen for the calculation was the one which produced the optimum power in the series and, consequently, the arc drop $V_d$ was taken to be 0.4 volt. The calculations show that for porous rhenium with $T_e = 1350^\circ$ Centigrade

$$\phi_e = 1.60 \text{ volts}$$

compared with that for polycrystalline rhenium measured under the similar conditions:

$$\phi = 1.66 \text{ volts}$$

when the emitter temperature was $1200^\circ$ Centigrade

Porous rhenium $\phi_c = 1.63 \text{ volts}$

Polycrystalline rhenium $\phi_c = 1.68 \text{ volts}$

Less importance is placed on the absolute magnitude of these values than on the difference between them. This same difference in work function between the two types of rhenium at both emitter temperatures, however, manifests itself in terms of increased output power.

One answer to the question of why a porous collector should behave so well might be that the surface area is increased and more electrons are collected. It is known that rough surfaces covered with a monolayer of cesium have low reflection coefficients for low-energy electrons. However, although the surface of the vapor-plated rhenium collector is undoubtedly rough (see Figure 14), the power output of this collector compares unfavorably with that of the porous collector (see Figures 13 and 15). In a
further series of investigations designed to confirm this observation, a polycrystalline rhenium collector was roughened by fine sandblasting to produce a surface similar in terms of roughness to a porous collector. The two collectors were then compared in the test vehicle, using an arc-cast molybdenum emitter. The results are given in Figure 25. The work functions were calculated in the same manner as before:

Porous rhenium $\phi_c = 1.73$ volts

Rough rhenium $\phi_c = 1.68$ volts

The difference of 0.05 volt in converter work function between the two surfaces is similar to that between porous and essentially smooth rhenium. These results show quite unequivocally that it is the porosity of the rhenium that produces the increased performance, possibly by a mechanism such as the one proposed in Section II.

Previous work at RCA has shown that hydrogen may be removed from an operating thermionic converter by the use of a heated palladium thimble exposed to the hydrogen and cesium vapor on one side and to the atmosphere on the other. This earlier work indicated that the presence of hydrogen was not beneficial to the converter operation, and, in fact, power output increased as the hydrogen was removed.

It has been suspected for a long time that the unique method of processing the converter, especially the liquid-nitrogen cold-finger technique of freezing the cesium to remove any hydrogen impurity, contributes to the high power output. Hydrogen cannot be removed from the cesium by a simple distillation technique because of the gettering action of the condensing cesium. A palladium thimble was incorporated into the test vehicle to confirm that hydrogen is a critical constituent and that it has a deleterious effect on the converter output.

Summary Technical Report
Contract NONR-4012(00)-FBM
30 October 1964
During processing, the cold finger employed for the removal of contaminant gases was used in such a way that some of the hydrogen present would remain within the converter after pinch-off. Then, during actual operation the palladium thimble was heated to 460° Centigrade with its inside surface exposed to the cesium vapor, characterized by a reservoir temperature of 300° Centigrade, and any hydrogen partial pressure formed from the decomposition of \( \text{CsH}_1 \). It can be seen from Figure 3 that if hydrogen is present, it will be at a relatively high pressure at the working cesium temperature. Thus, the hydrogen will be pumped away to the atmosphere through the palladium thimble. The power output versus time, which was determined for a converter using a molybdenum emitter and porous rhenium collector, is plotted in Figure 26. Although the output power is by no means the best possible for the converter, it nevertheless demonstrates the improvement in performance when hydrogen is removed during the first three hours of operation.

The thickness of foreign material deposited onto a collector, which gives the surface the properties of the foreign material, was determined. This information is needed to determine the life of a collector being constantly contaminated by evaporation from the emitter. It is also useful when collectors of exotic materials are made by the evaporation of this material onto a more common substrate.

Rhenium was evaporated from a filament onto outgassed molybdenum collectors within the test vehicle in controlled amounts prior to the admission of cesium. The amount of rhenium on the collector was estimated using standard vapor pressure data and assuming the sticking coefficient of the impinging rhenium atoms on molybdenum at room temperature to be unity. The surface produced would be a film of microcrystals of random orientation due to the slow diffusion rate of the high-melting-point
Two surfaces were formed on adjacent molybdenum collectors, one estimated to be a monolayer ($\theta = 1$ for $3 \times 10^{14}$ atoms/cm$^2$) and the second to be two layers ($\theta = 2$). These collectors were compared with a bare outgassed molybdenum collector, and the results are shown in Figure 27. It is clear that the surface assumes the properties of the evaporated species at approximately $\theta = 2$ in a thermionic converter, and that a monolayer is likely to produce a complex surface having neither the properties of the substrate nor the adsorbate. It is likely that a collector will cease to function according to its original surface after approximately one monolayer has been evaporated onto it from the emitter. Conversely, if collectors for use in cesium vapor are made by evaporating thin films, then the substrate should be coated with at least two monolayers. In practice this means that very thin layers are sufficient.

A life test was conducted to examine the effect, if any, of the evaporation of material from a molybdenum emitter onto a porous rhenium collector. The A-1194 test converter described in Section V was used for this test. The results are plotted as power output and voltage versus time up to 500 hours in Figure 28. With the emitter operating at 1350° Centigrade, the vapor pressure of molybdenum was calculated to be $4.2 \times 10^{-11}$ torr$^{-10}$. If a sticking probability of one for the molybdenum vapor on porous rhenium at 510° Centigrade is assumed, the top scale of Figure 28 indicates the number of monolayers deposited versus time. It should be noted that this assumption for the value of the sticking probability is high for two reasons: (1) because of the high collector temperature ($T_e = 510°$ C), and (2) the porous rhenium is coated with a partial monolayer of cesium for efficient converter operation. Bearing these facts in mind, the reduction of converter output by 9 percent after 120 hours compares favorably with the information obtained from the evaporation experiments. A collector is likely to be contaminated by evaporants from the emitter unless precautions are taken to prevent contamination.

Summary Technical Report
Contract NONR-4012(00)-FBM
30 October 1964
A low-work-function collector has been developed for use in the construction of practical power-producing converters. The collector must be designed to produce optimum power output, and if the collector is to remain efficient during operation, the emitter must be fabricated from the same material. When both collector and emitter are fabricated from the same material, the collector surface is protected against evaporative contamination, which would reduce power output in long-term operation.

The results obtained in this research show that a porous rhenium collector, which can be cheaply made by a silk-screening technique, produces a higher power output than any of the collectors examined. A rhenium emitter should be used with this collector to assure continued efficient collector operation. There is reason to believe that a suitable rhenium emitter can be fabricated in the same way as the collector.

Finally, investigations have shown that hydrogen should be removed from the converter, since it has a deleterious effect on converter operation.
SECTION VIII
COMPENDIUM OF DESIGN AND RESULTS
FIGURE 12. OUTPUT POWER VERSUS CESIUM PRESSURE
FOR RHENIUM AND IRIDIUM

Collector Material - Rhenium Re
Iridium Ir
Emitter Material - Molybdenum
Emitter Temperature - 1375° C
Collector Temperature - 525° C

Summary Technical Report
Contract NONR-4012(00)-FBM
30 October 1964
FIGURE 14. PHOTOMICROGRAPH OF VAPOR-PLATED RHENIUM ON MOLYBDENUM
(Magnified 552X)
FIGURE 15. CHARACTERISTICS OF RHENIUM VAPOR-PLATED ON MOLYBDENUM
Runs made at different times

Te - 1350°C
Tc - 575°C
Spacing - 0.016 inch

FIGURE 16. CHARACTERISTICS OF RHENIUM BRAZED TO MOLYBDENUM WITH PALLADIUM (Sheet 1 of 2)
FIGURE 16. CHARACTERISTICS OF RHENIUM BRAZED TO MOLYBDENUM WITH PALLADIUM (Sheet 2 of 2)
FIGURE 17. CHARACTERISTICS OF PURE RHENIUM
FIGURE 18. CHARACTERISTICS OF "270" GRADE NICKEL
FIGURE 19 CHARACTERISTICS OF ARC-CAST MOLYBDENUM
FIGURE 20. EFFECT OF SPACING FOR POROUS RHENIUM COLLECTOR AT 585° CENTIGRADE
Summary Technical Report  
Contract NONR-4012(00)-FBM  
30 October 1964

FIGURE 21. EFFECT OF SPACING FOR POROUS RHENIUM COLLECTOR AT 650° CENTIGRADE
FIGURE 22. EFFECT OF SPACING FOR A POROUS RHENIUM COLLECTOR AT 525° CENTIGRADE
FIGURE 24. CHARACTERISTICS OF POROUS RHENIUM COLLECTOR
FOR VARIOUS EMITTER TEMPERATURES (POWER)
(Sheet 1 of 2)

Summary Technical Report
Contract NONR-4012(00)-FQM
30 October 1964
FIGURE 24. CHARACTERISTICS OF POROUS RHENIUM COLLECTOR FOR VARIOUS EMITTER TEMPERATURES (VOLTAGE)
(Sheet 2 of 2)
FIGURE 25. COMPARISON OF ROUGH AND POROUS RHENIUM COLLECTORS
FIGURE 26. POWER OUTPUT VERSUS TIME FOR REMOVAL OF HYDROGEN FOR CONVERTER WITH MOLYBDENUM EMITTER AND POROUS RHENIUM COLLECTOR
FIGURE 27. CHARACTERISTICS OF RHENIUM EVAPORATED ONTO MOLYBDENUM

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SECTION IX
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Cleveland 4, Ohio
Attn: Wm. J. Leovic

Consolidated Controls Corporation
Bethel, Connecticut
Attn: Mr. David Mends

General Electric Company
P. O. Box 846
Atomic Product Division
Vallecitos Laboratory
Pleasanton, California
Attn: H. Sutton

General Electric Company
Power Tube Division
1 River Road
Schenectady 5, New York
Attn: Mr. D. L. Schaefer
<table>
<thead>
<tr>
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</tr>
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<tbody>
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<td>1</td>
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<tr>
<td>200 South 33rd Street</td>
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<td>Philadelphia 4, Pennsylvania</td>
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<td>Start</td>
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<td>2</td>
<td>Lecture</td>
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<td>3</td>
<td>Lab</td>
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<tr>
<td>4</td>
<td>Quiz</td>
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<tr>
<td>5</td>
<td>Review</td>
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<td>6</td>
<td>Project</td>
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<tr>
<td>7</td>
<td>Midweek</td>
</tr>
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<td>8</td>
<td>Workshop</td>
</tr>
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<td>9</td>
<td>Field Trip</td>
</tr>
<tr>
<td>10</td>
<td>Exam</td>
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<td>11</td>
<td>Final</td>
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The course revolves around the theme of 'Innovation and Practice', involving a blend of theoretical learning and hands-on activities. Each week builds on the previous one, ensuring a comprehensive understanding of the subject area.
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