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ADVANCED THERMIONIC TECHNOLOGY
FY1975
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Progress Report Number 7

Prepared by
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Thermionics Surface Physics Specialists Meeting

Thermo Electron participated in the Thermionics Surface Physics Specialists Meeting held at the Naval Research Laboratory (NRL) on January 15. Dr. Huffman described the technical approach of Thermo Electron to developing low work function studies and Dr. Sommer discussed the recent results in the Activation Chamber. The status and preliminary experiments with the Auger Surface Characterization Chamber were reviewed by Dr. Balestra. Mr. Rufeh summarized the converter test results.

The barium oxide experience at NRL was particularly interesting. Plans were made for a February meeting between Thermo Electron and NRL on this subject.

**TASK IA & B. ANALYSIS OF LOW WORK FUNCTION SURFACES**

**Activation Chamber Experiments**

A tungsten oxide sample was prepared by the same method used for the converter collectors. Cesium and oxygen were alternately introduced into the chamber, following the procedure for negative electron affinity (see December report). The tungsten oxide sample gave a work function of 1.47 eV at 500 K. This value is in approximate agreement with typical converter values.

Another p-type single crystal GaAs sample (supplied by RCA) was activated with cesium and oxygen in order to reproduce previous work function measurements. This experiment gave a work function of 1.1 eV at 430 K, within 4% of the previous result. Again peak thermionic emission did not coincide with peak photoemission since
the lowest value of $\phi$ was measured when the photoemission had not reached 40% of its maximum. Upon subsequent heating for more complete activation, decomposition occurred.

Experiments with (Ba, Sr, Ca)O emitters were conducted to determine the effect of substrate variations. Both "Grade A nickel" (as distinct from "cathode nickel") and platinum substrates were tried, but the results were not conclusive. The experiment with Grade A nickel was affected by a temporary slow leak in the vacuum system and the deposit on the platinum substrate was visibly patchy. These tests will be repeated.

**Dual Beam Chamber**

The Dual Beam Chamber was calibrated for Cs-beam impingement rate. A tungsten ribbon which can be flash-heated was situated where a sample normally is placed. Since optimum photoemission from cesiated tungsten occurs for monolayer coverage, the cesium arrival rate can be calculated from the time required to obtain peak photoemission from an initially clean surface. Preliminary measurements indicate that an impingement rate of $4 \times 10^{13}$ cm$^{-2}$ sec$^{-1}$ corresponds to a reservoir temperature of 100°C.

A silver diffusion tube was installed on the chamber as a controllable oxygen source. Since the pumping rate can be throttled by means of the poppet valve, oxygen pressures in excess of $10^{-6}$ torr can be obtained.

The current buss to the Cs-tube has been rewired to allow the tube to be heated by greater currents.
Surface Characterization Chamber

The Surface Characterization Chamber is now operational. A sputter-ion gun has been installed for normal incidence sputter-etching of samples. Some semiconductors (e.g., silicon) are more easily cleaned by sputtering followed by annealing, rather than by heating to just below the melting or decomposition temperature. The silver diffusion tube oxygen source is functional. By throttling the ion pump with the poppet valve, chamber oxygen pressure can be regulated in excess of $10^{-6}$ torr. The Kelvin contact potential probe was tested, using the manipulator heat-exchanger block as a sample. A contact potential difference resolution of better than 1 mV can be obtained.

The FERP gun was set up and initially operated with the aid of Dr. Lynwood Swanson, its designer. The preamplifier described in the November report is being used to detect electrons collected by the samples. Since manual scanning of the emitter/collector bias voltage produces a noisy signal, an integrating linear voltage ramp generator has been designed for automatic voltage scanning. It is presently being fabricated. A preamplifier for sensing reflected electrons from the samples is under design.

Simulated Converter Stability Tests

The stabilities of candidate semiconductor collector materials (gallium arsenide, gallium phosphide and silicon) in a converter environment have been evaluated using the simulated converter. Work function measurements were not obtained in these material tests.
A silicon sample was placed in the simulated converter (Test No. 102) apparatus and outgassed at a temperature of 525 K and a maximum pressure of $1 \times 10^{-5}$ torr. It was then heated to 525 K in the presence of one torr of cesium for 2 days. After removal, there was no apparent change in the silicon sample. These results are encouraging and indicate that silicon can be used as a collector in thermionic converter.

A gallium arsenide sample was cleaned and etched and placed in the simulated converter (Test No. 101) apparatus. The sample was outgassed at a temperature of 525 K and a maximum pressure of $1 \times 10^{-5}$ torr. It was then heated to 525 K and exposed to a cesium atmosphere (pressure range of 0.05 to 1.4 torr) for 4 days. The sample was removed from the simulated converter apparatus for examination. It had disintegrated into a black powder similar to that observed previously for gallium phosphide. Since the III-V compounds (GaP and GaAs) react under these conditions with cesium (probably to form cesium phosphide and cesium arsenide, respectively), it appears unlikely the III-V compounds can be used in a converter environment.

An additional simulated converter environmental test is under way with germanium. The results of this test will be given in next month's report.

**TASK II. SYSTEM STUDIES**

Studies of Strontium-90 fueled terrestrial thermionic generators have been continued. The primary technical problem is that of
economically ensuring fuel containment under accident conditions without seriously compromising generator efficiency.

TASK III. RESEARCH CONVERTER EXPERIMENTS

Tungsten Oxide Converter No. 100

A standard variable spacing converter was constructed with an arc cast tungsten emitter and a tungsten collector with a thick layer of deposited tungsten oxide. The purpose for which this converter was developed was to better define and examine the conditions under which tungsten oxide becomes a "good" collector.

Outgassing was carried out at low electrode temperatures in order to examine the behavior of the tungsten oxide coating under low temperature operating conditions (\(T_E = 1300\) K and \(T_C = 475\) K).

Data was obtained by setting the collector temperature at 500 K and varying emitter and cesium reservoir temperatures over the ranges of interest (\(T_E = 1100\) to 1400 K, \(T_R = 408\) to 577 K). The collector temperature was subsequently raised to 600, 650, and 700 K, following the same procedure. After raising the collector temperature to 800 K, the emitter temperature was raised to 1600 and 1700 K and the collector temperature was optimized.

The data showed the presence of oxygen in the converter, but the performance was not as high as that observed in previous tungsten oxide converters. The minimum collector work function was 1.45 eV at \(T_C/T_R\) values of 1.4 to 1.6. The minimum barrier index was 2.02 eV at \(T_C/T_R\) values of 1.50 to 1.55 and an emitter temperature of 1600 K. The data showed that there was little oxygen effect at
the lower collector temperatures. The performance improved as the collector temperature was increased.

There was a significant effect observed when the collector temperature was raised from 800 to 900 K (see Figures 1, 2 and 3). Review of data from the tungsten oxide Converter No. 75 (which dispensed more oxygen with a collector work function of 1.35 eV and a minimum barrier index of 1.87 eV) showed a similar improvement in performance when the collector temperature was varied through this range. The changes occur in the tungsten oxide coating at collector temperatures between 800 and 900 K and cesium pressures of one to two torr (551 to 577 K). Additional tungsten oxide collectors are being prepared for investigating the foregoing conditions in more detail.

Reflux Converter No. 98

Additional oxygen dosing and subsequent testing was carried out on the Reflux converter. This is a standard variable spacing converter (constructed with electropolished arc cast tungsten electrodes) which has a special cesium reservoir assembly which allows the admission of oxygen into the converter (see Figure 4). In December, non-oxygenated and first-dose-oxygenated data were reported which established that oxygen can reach the active area of the converter and influence the performance.

A second dose of oxygen was admitted into the converter under similar conditions and using the same procedure as the first dose except that the collector was heated to 375 K. Under the reference
Figure 1. Current-Voltage Characteristics of Converter No. 100 (Emitter Temperature of 1600 K)
Figure 2. Current-Voltage Characteristics of Converter No. 100 (Emitter Temperature of 1600 K)
Figure 3. Current-Voltage Characteristics of Converter No. 100 (Emitter Temperature of 1700 K)

CONVERTER NO. 100
TUNGSTEN EMITTER
TUNGSTEN OXIDE
COLLECTOR

$T_E = 1700 \text{ K}$
$T_C = \text{VAR K}$
$T_R = 528 \text{ K}$
$d = 20 \text{ mils}$
Figure 4. Cesium Reservoir Assembly for Reflux Converter No. 98
conditions at $T_E = 1400$ K, there was a slight improvement in performance at $T_C = 700$ K (first dose improvement was a tenth of a volt). There was however, a tenth of a volt improvement at the collector temperature of 800 K (Figure 5), indicating that heating the collector during oxygenation has a slightly different effect than leaving it cold during oxygenation. Data was obtained at a higher collector temperature, but the improvement was not so pronounced and the oxygen effect was lost. Data at the emitter temperature of 1600 K was the same as that obtained after the first oxygen dose (which showed a reduction in performance from the initial data, indicating a loss of initial oxygen along with the loss of the added oxygen.

A third dose of oxygen, was admitted into the converter using the same procedure and under similar conditions as the first two doses, except that the collector was heated to 475 K (100 K higher than the second dose). Data obtained after the third-dose-oxygenation showed a light reduction in performance from that of the second-dose-oxygenation, and what little oxygen effect observed was lost quickly. These results indicate that the small hole which admits oxygen into the reservoir volume (see Figure 4) has become partially plugged, restricting the amount of oxygen reaching the active area of the converter. Steps will be taken to unplug the small hole, and subsequent oxygen dosing will be carried out at higher electrode temperatures.

Replenishing Electrodes Converter No. 99

This variable spaced converter was fabricated with an
REFLUX CONVERTER NO. 98

\[ T_E = 1400 \text{ K} \]
\[ T_C = 800 \text{ K} \]
\[ d = 5 \text{ mils} \]

\textbf{Figure 5.} Current-Voltage Characteristics of Reflux Converter No. 98
electropolished nickel emitter and collector. The converter can be operated in a conventional manner, but at any time during the testing the emitter temperature can be elevated high enough to evaporate a layer of nickel onto the collector. Figure 6 shows the nickel evaporation rate over the range of testing. This replenishing electrode converter permits one to study: 1) comparison between conventionally outgassed electrodes and virgin emitter and collector surfaces, 2) performance of nickel electrodes in a converter and 3) irreversible "burn in" effects.

Small changes in performance during the first few hours of new converter operation are usually observed. The changes are most likely due to the interaction of the freshly admitted cesium with the converter structure, gettering by the cesium of residual outgassing and interaction of these products on the collector surface. A converter with nickel electrodes can be used to observe some of these changes in a more controlled manner. After new emitter and collector surfaces have been generated, "burn in" effects can be observed repeatedly following reductions of emitter temperature. At 1500 K (266 degrees below the melting point), the vapor pressure of nickel is about $10^{-4}$ torr and the corresponding evaporation rate is $10^{-4}$ inches/hour.

Following outgassing to an emitter temperature of 1400 K and a collector temperature of 900 K (corresponding to $9 \times 10^{-7}$ torr hot and $6 \times 10^{-8}$ torr cold), cesium was introduced, the capsule was pinched off and the testing started. Performance data were obtained in the 1000 K to 1400 K temperature range, with the lower temperatures
Figure 6. Nickel Evaporation Rate versus Temperature
tested first. A surprisingly low minimum barrier index, $V_B'$ of 2.06 eV was observed at output current densities of 5 to 7 A/cm$^2$ and $T_E = 1100$ K, $T_C = 800$ K and $d = 20$ mils. This barrier index was reproduced after testing at 1300 K but increased to 2.20 eV after testing at 1400 K.

The effect on performance of replenishing the collector surface was evaluated at $T_E = 1000$ to 1500 K, $T_C = 700$ K, $T_R = 528$ K and $d = 20$ mils. With the converter output current held at 2 A/cm$^2$, the output voltage was displayed as a function of emitter temperature on a X-Y plotter. By varying emitter bombardment power and sweeping over the temperature range, time dependent changes in $V_B$ showed as hysteresis loops on the X-Y plot. Slow changes at constant $T_E$ were also recorded as current-voltage characteristics versus time.

Observations during this testing can be summarized by:

1) Maximum time dependent changes in output voltage at constant emitter temperatures were .07 eV.

2) Holding a high (1400-1500 K) $T_E$ always decreased output voltage, with the rate of change decreasing with time at temperature.

3) Holding a low $T_E$ (1100 K) always produced some "recovery" of output with time.

4) Changes, both at high and low temperatures, took several hours to complete.
5) The magnitude of the observed effects were not reproducible but depended on past treatment.

This experiment shows that some modification of barrier index is possible in a sealed, operating converter. The very slow rates of change, both at high and low temperature are quite puzzling. A possible explanation assumes that the effect is caused by additives dissolved in the cesium reservoir, with a diffusion limited release, balanced by "pumping action" in the electrode region at high nickel evaporation rates.

TASK IV. HOT SHELL EVALUATION

The assembly of the test station for evaluation of hot shell materials at Thermo Electron is under way. Initial testing is expected next month.

The evaluation of TRW's alloys as a protective cover for thermionic converters heated by combustion continued on schedule. During this reporting period two test runs (Run No. 3 and Run No. 4) were made at 2400 F for 168 hours using oxygen-rich gas mixtures. A total of eleven alloy compositions were tested which included four promising Run No. 1 materials and seven new or modified formulations. Results are tabulated in Table I. By comparison with results of Run No. 1 it is evident that all four compositions (nb-30Ti-10Al-3Cr-6V, Fe-5.5Al-22Cr-0.5Co-1.25Y, Ni-3Al, and Ni-10Pt) showed greater corrosion at 2400 F. The two best 2200 F alloys, Fe-5.5Al-22Cr-0.5Co-1.25Y and Ni-3Al, are rated only good and poor, respectively at 2400 F. The three most promising compositions based on 2400 F results are:
TABLE I
RESULTS OF RUNS NOS. 3 AND 4
(Oxygen-Rich Gas, 2400 F, 168 Hours)

<table>
<thead>
<tr>
<th>Spec Number</th>
<th>Alloy Composition</th>
<th>Visual Rating</th>
<th>Metal Surface Recession, cm X 10^-4</th>
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<tr>
<td>Ni-10-3</td>
<td>Ni-10Pt</td>
<td>Fair</td>
<td>28.2</td>
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<tr>
<td>F1-3</td>
<td>Fe-22Cr-5.5Al-0.5Co-1.25Y</td>
<td>Good</td>
<td>12.8</td>
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<tr>
<td>Ni-3-3</td>
<td>Ni-3Al</td>
<td>Poor</td>
<td>104.0</td>
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<td>N-1</td>
<td>35Ni-35Co-25Cr-5Mo</td>
<td>Good</td>
<td>12.5</td>
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<tr>
<td>Fe-1-1</td>
<td>Fe-35Ni-20Cr-3Al-0.2Y</td>
<td>Good</td>
<td>4.4</td>
</tr>
<tr>
<td>N-3</td>
<td>Ni-3Al-1Y</td>
<td>Poor</td>
<td>14.5</td>
</tr>
<tr>
<td>N-2</td>
<td>46Ni-46Co-5.5Al-1.5Y</td>
<td>Good</td>
<td>8.2</td>
</tr>
<tr>
<td>Cr-1</td>
<td>Cr-26Fe-8Al-0.05C</td>
<td>Very Good</td>
<td>0.9</td>
</tr>
<tr>
<td>C2-4</td>
<td>Cb-30Ti-10Al-6V-3Cr</td>
<td>Poor</td>
<td>177.0</td>
</tr>
<tr>
<td>Co-1</td>
<td>Co-25Cr-1.5Y</td>
<td>Very Good</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe-2-1</td>
<td>Fe-35Ni-20Cr-3Al</td>
<td>Very Good</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Chromium base: Cr-26Fe-8Al-0.05C
Cobalt base: Co-25Cr-1.5Y
Iron base: Fe-35Ni-20Cr-3Al

Preliminary attempts to cold roll these alloys showed that the chromium base alloy is too brittle, the cobalt-base alloy can be rolled with difficulty, and the iron base alloy offered no problem. The immediate efforts now are: 1) preparation of samples of the best alloy compositions for long-term (672 hours) testing at 2200 F and 2400 F in oxygen-rich gas mixture; and 2) preparation of one pound ingots of the two best workable alloys: (Co-25Cr-1.5Y, and Fe-35Ni-20Cr-3Al, for rolling into sheet materials for high temperature mechanical tests at TRW and for delivery to Thermo Electron for further evaluation.
## ERDA CONTRACT AT(11-1)-3056
**ADVANCED THERMIONIC TECHNOLOGY**

### SUBMITTED PROGRAM MILESTONES FY75

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<tr>
<th>Milestone Description</th>
<th>Target Date</th>
<th>Actual Date</th>
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<td>1. Submit technical program plan for approval</td>
<td>July 20, 1974</td>
<td>July 18, 1974</td>
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<tr>
<td>4. Complete test station for hot shell evaluation</td>
<td>December 1974</td>
<td></td>
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<tr>
<td>5. Preliminary study of BaO/SrO surface completed</td>
<td>January 1975</td>
<td>Nov. 27, 1974</td>
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<td>6. Submit topping cycle report</td>
<td>April 1975</td>
<td></td>
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<td>7. Low temperature parametric data mapped</td>
<td>May 1975</td>
<td></td>
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<td>8. Summary report on low work function collectors</td>
<td>June 1975</td>
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## TASK BREAKDOWN

**PERIOD ENDED 1/26/75**

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<th>Task No.</th>
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<th>Total to Date</th>
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<td>Experimental Surface Physics</td>
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<td>280,377</td>
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<td>Plasma Theory</td>
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<td>18,026</td>
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<td>29,846</td>
<td>140,134</td>
<td>110,288</td>
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Sub Total | $67,869 | $470,621 | $1,014,522 | $543,901

Fixed Fee (6.897%) | 4,681 | 32,459 | 69,972 | 37,513

Total | 72,550 | 503,080 | 1,084,494 | 581,414

Open Commitments | --- | 130,788 | --- | (-130,788)

Total Including Commitments | $72,550 | $633,868 | $1,084,494 | $450,626

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20
## TASK BREAKDOWN

**PERIOD ENDED 1/26/75**

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<td>$92,891</td>
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