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**DOE/JPL
ADVANCED THERMIONIC
TECHNOLOGY PROGRAM
PROGRESS REPORT NO. 43**

**April, May, June
1980**

**DOE Contract DE-AC02-76ET11291
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WORK BREAKDOWN STRUCTURE

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WORK BREAKDOWN STRUCTURE

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INTRODUCTION AND SUMMARY

The Advanced Thermionic Technology Program at Thermo Electron Corporation is sponsored by the Department of Energy (DOE) and the National Aeronautics and Space Administration (NASA) via the Jet Propulsion Laboratory (JPL).

The primary long-term goal of the DOE effort is to improve TEC performance to the level that thermionic topping of fossil fuel steam powerplants becomes technically possible and economically attractive. An intermediate goal is to demonstrate an in-boiler thermionic module in the early 1980's. A short-term goal is the demonstration of the reliability of thermionic operation in a combustion environment.

The focus of the JPL program is to develop thermionic conversion technology appropriate for nuclear electric propulsion (NEP) missions. These missions require operation at collector temperatures substantially higher than those associated with terrestrial applications.

The DOE and JPL tasks for developing thermionic energy conversion (TEC) are complementary and synergistic. Converter performance improvement is an area in which one agency's program supports the effort of the other.

This report covers progress made during the three-month period from April through June 1980. During this period, significant accomplishments include:

DOE PROGRAM

- Demonstration of over 3000 hours of stable operation (Converter No. 228: CVD Silicon Carbide No. 2) in a combustion atmosphere at a hot shell temperature of around 1650 K with a barrier index of 2.1 eV.
- TRW analysis of the hot shell-emitter temperature of Converter No. 218 (5120 hours of flame-heated operation at emitter temperatures at, or above, 1600 K) showed no life-limiting degradation mechanism.
- Development of a protective coating for the braze between the molybdenum flange and the CVD hot shell-emitter structure for the flame-heated diodes which permits extended operation at cold end temperatures up to 850 K.
- Completion of a Topical Report by C.C. Wang, "The Formation of Double Sheaths and the J-V Characteristics in the Obstructed Region."

JPL PROGRAM

- Demonstration of over 1100 hours of stable operation with Converter No. 232 (JPL Converter No. 4 - Molybdenum Emitter and Sublimed Molybdenum Oxide Collector) at a barrier index < 2.0 eV.
- Definition of oxygen transport mechanism from an oxide collector to the emitter.

1.0 PART ONE: DOE TASKS

1.1 THERMIONIC AND MATERIAL RESEARCH AND TECHNOLOGY

1.1.1 TASK I. SURFACE AND PLASMA INVESTIGATIONS

The objective of this task is to support the development of thermionic energy converters by providing experimental data and analyses relating to plasma characteristics and electrode properties.

A. Surface Characterization Chamber Experiments

Previous experiments at Thermo Electron have indicated that accurate crystal orientation ($<1^\circ$) is necessary for a low work function Zr-O-W (100) emitter and that excessive carbon diffusion from the bulk can poison the emitter surface. A W(100) crystal oriented to within $1/2^\circ$ of the (100) plan was mounted in the surface characterization chamber. An initial flash to 2400 K showed 24% carbon on the surface as determined by Auger analysis. The sample was then heated in 10^{-7} torr oxygen for two hours with 30 temperature cycles between 1500 and 2500 K. After this treatment, the carbon coverage in vacuum was only 4%.

The crystal held at 1500 K was simultaneously dosed with zirconium and oxygen (4×10^{-8} torr) for 15 minutes. Flashing to 2075 K for 10 seconds produced a work function of 2.82 eV. The elemental coverages and FERP work function versus time at 1800 K for this emitter are shown in Figure 1. The carbon coverage after 70 hours is 2%, far lower than the 47% carbon coverage after 23 hours measured for the crystal which was not cleaned in oxygen (see Figure 1, Progress Report No. 42). Thus, a two hour exposure to oxygen with temperature cycling is sufficient to reduce the carbon concentration to low levels.

An eight hour air exposure followed by a 2100 K heating in vacuum for four hours produced only minor variations in the elemental coverages and work functions of the emitter. Thus, Zr-O-W(100) emitters can be restored after prolonged air exposure. After 70 hours the zirconium coverage dropped slightly, and the work function rose to 3.28 eV. Apparently this is because zirconium and oxygen diffuse into the bulk due to insufficient bulk concentrations of these elements.

Figure 1. Elemental Coverages and Work Function vs Time at 1800 K

An evaporation setup is being constructed which will allow electron beam heating of ZrO_2 pellets and impingement of the released ZrO_2 vapor onto a hot W(100) crystal. This procedure should greatly increase bulk concentrations of zirconium and oxygen and enhance the emitter lifetime. A separate UHV lifetest station is also being constructed, which will allow monitoring of thermionic emission of emitters during the tests and Auger analysis after the tests.

B. Converter Theory

A Topical Report on "The Formation of Double Sheaths and the Current-Voltage Characteristics in the Obstructed Region" has been written. It has been submitted to DOE for approval. The contents of the report have been summarized in two technical papers presented at the 1980 IEEE International Conference on Plasma Science.

1.1.2 TASK II. LOW-TEMPERATURE CONVERTER DEVELOPMENT

The objective of this task is to develop thermionic diodes with improved performance at low collector temperatures (i.e., 500-900 K). Converter characteristics will be measured as a function of emitter temperature, collector temperature, cesium pressure, interelectrode spacing and, if applicable, additive gas pressure.

A. Converter No. 246: Heat Flux Diode

A heat flux diode with a tungsten emitter and a nickel collector has been designed and fabricated. This diode incorporates a heat flux collector of the design described in Progress Report No. 42. Outgassing has been initiated, and testing will begin during the next reporting period.

1.1.3 TASK III. ENHANCED MODE CONVERTER EXPERIMENTS

The objective of this task is to formulate and evaluate thermionic converter configurations which have the potential of operating more efficiently than the conventional ignited mode diode. In the ignited mode, the mechanism for supplying the ions for space charge neutralization is not efficient. Other techniques which allow the converter to operate in the unignited mode (e.g., those utilizing auxiliary discharge regions and surface contact ionization electrodes) should be more efficient in producing ions and, hence, more efficient in converting heat into electricity. Close-spaced devices that do not require ions should also be more efficient than ignited mode diodes. In the ignited mode, structured electrodes offer the possibility of significantly reducing the plasma losses. Several types of enhanced mode converters will be investigated experimentally.

Studies in the United States¹ and the Soviet Union,²³ have investigated improved converter performances with structured electrodes. At Thermo Electron, a wide range of surface topologies have been deposited on both graphite and tungsten substrates by varying the CVD parameters. One example of a CVD microstructure is shown in Figure 2. In addition to this needle-like surface, pyramidal, amorphous, and columnar structures have been formed. It should be possible to use the present CVD procedure for the first part of the deposition and then alter the parameters (e.g.; pressure, flow, substrate temperature) to provide the desired microstructure on the electrode surface.

Enhancement of converter performance would probably be associated with characteristic dimensions of the surface structure intermediate between the Debye length and the electron mean free path.⁴ If the microtopology dimensions were smaller than the Debye length, the surface structure effects would be expected to be subsumed by the sheath coupling the electrode to the plasma. Conversely, if the dimensions of the surface structure were greater than the electron mean path, no enhancement due to reduced electron reflectivity would be expected.

7910-82

Figure 2. Photomicrograph (x 100) of a CVD Tungsten Surface Deposited for WF_6

The Debye length is plotted in Figure 3 versus the charge carrier density in the plasma. Typically, the electron (and ion) densities in an ignited mode diode are around 10^{14} per cm^3 . For an electron temperature of 3000 K, the Debye length is about 4×10^{-4} cm. The electron mean free path is given in Figure 4 as a function of cesium reservoir temperature. For oxygenated converters, the cesium reservoir temperature is usually around 525 K. Assuming a cesium gas temperature of 1500 K, the electron mean free path is roughly 10^{-2} cm. Thus, the characteristic dimensions of surface microstructure of primary interest for enhanced converter performance would appear to range between 4×10^{-4} and 10^{-2} cm.

Figure 3. Dybye Length as a Function of Carrier Density in the Interelectrode Plasma

Figure 4. Electron Mean Free Path in Cesium vs Cesium Reservoir Temperature

1.1.4 TASK IV. COMPONENT HARDWARE DEVELOPMENT

The objective of this task is to develop converter hardware suitable for operation in a combustion atmosphere such as would be encountered in a thermionic-topped fossil fuel powerplant. Although the effort includes considerable materials evaluation, the focus is on the fabrication and testing of hot shell - emitter subassemblies utilizing chemical vapor deposition (CVD) of composite silicon carbide-graphite-tungsten structures.

A. Alloy Hot Shell Development

The testing of alloy hot shells in the Simulated Furnace was suspended (see Figure 5) during this reporting period. In this furnace, the domes of the hot shells were exposed to products of combustion of a liquid hydrocarbon at 1475 K. The interiors of the shells were evacuated by an ion pump. The furnace temperature and the interior vacuum of each shell were recorded on a strip chart recorder. The accumulated test hours on the specimens are shown in Table I.

Figure 5. Furnace for Hot Shell Tests

TABLE I
SIMULATED FURNACE TESTS
(9 June 1980)

806-15

Test Port No.	Hot Shell	Test Hours	Comments	Date of Initiation	Photo No.
1	446 CRES Cr-Ni Slurry Sinter	5022	Leaktight	20 Nov 1978	5
3	446 CRES Plasma Arc Sprayed with Cr_2O_3	10,490	Leaktight	31 Oct 1977	4
4	RA333	3390	Leaktight	31 Aug 1979	3
5	446 CRES Plasma Arc Sprayed with Nichrome	10,496	Leaktight	31 Oct 1977	2
6	INCONEL 671	4717	Leaktight	8 Mar 1979	1

Clock Reference 27500

The specimens were removed from the furnace for metallurgical examinations. The specimens, after removal from the furnace, are shown in Figure 6. The numbers on the photograph correspond to the photograph numbers shown in Table I.

B. CVD Hot Shell-Emitter Development

1) Hot Shell Fabrication

During this reporting period, six one-inch and three two-inch diameter CVD hot shell-emitter structures were fabricated. All units were leak tight.

Construction of a three-zone Lindberg furnace for CVD of tungsten has started. This furnace will be capable of fabricating structures up to four inches in diameter and twelve inches long. The furnace, gas supplies, chemical traps and pumps will be contained inside a twelve foot hood. All gases will be monitored and controlled by electric flowmeters.

Figure 6. Test Specimens Removed From Simulated Furnace

2) Composite Hot Shell Emitter Flange Tests

Testing at operating temperatures continued on both one- and two-inch hot shell-emitters and flange structures. These shells were heated in air by R. F. induction or flame-fired in a natural gas furnace. The test results are summarized in Table II.

Hot shell-emitter Structure No. 102 has been analyzed to determine the composition of the compounds in the flange area. Both optical and scanning electron microscopy (SEM) photographs have been taken within the flange area (see Figure 7).

A series of spots located across the region containing the "black residue" have been further analyzed by obtaining x-ray spectra from those areas and then processing the x-ray intensity data using quantitative analytical programs in a EDAX system. These data indicate that the black residue is largely composed of molybdenum with some small percentages of tungsten, copper and silicon. The photographs show that the copper is almost entirely confined to the area near the top ridge of the brazed joint between the molybdenum

TABLE II
HOT SHELL-EMITTER-FLANGE STRUCTURE TESTS

DESCRIPTION (NUMBER)	NUMBER OF HOURS	TEMPERATURE OF DOME OF SHELL	AVERAGE TEMPERATURE OF FLANGE	MAXIMUM TEMPERATURE OF FLANGE	NUMBER OF TEMPERATURE CYCLES	COMMENTS
ONE-INCH DIAMETER HOT SHELL- EMITTER (101)	110	1925 K	675 K	875 K for 20 hours	9	Black residue on flange No cracking of structure. Tungsten leak tight.
TWO-INCH DIAMETER HOT SHELL- EMITTER (102)	70	1655 K	675 K	925 K for 8 hours	1	Black residue on flange. SiC cracked and braze swelled.
ONE-INCH DIAMETER HOT SHELL- EMITTER (103)	80	1925 K	850 K	900 K for 20 hours	13	Flange coated w/Cermetal 487 SiC cracked at dome. To be analyzed. No black residue.
TWO-INCH DIAMETER HOT SHELL- EMITTER (104)	1300	1600 K	850 K	880 K for 170 hours	6	Flange coated w/Cermetal 487. Test Continu- ing. No black residue.

Figure 7. Cross Section of Hot Shell-Emitter Structure No. 102

flange and the CVD layer of tungsten. The X-ray data show that in the region enclosed within the molybdenum flange (cf. Figure 4, Spot 1) there is a slightly higher concentration of silicon and tungsten, while the outer areas (Spots 2 and 3) have a slightly higher concentration of copper and are almost devoid of tungsten and silicon. The results of the analysis show that the black residue is composed of 90 to 98% MoO with the balance being either silicon carbide or the oxides of tungsten and copper.

Several protective coatings were deposited on hot shell-emitter Structure No. 103 around the molybdenum flange and the base of the silicon carbide hot shell. After evaluating several coating techniques, a deposit of Cermetal 487 adhered to both the molybdenum flange and the CVD silicon carbide. Hot shell-emitter Structure No. 103 was heated in air by R. F. induction and showed no signs of a black residue after 80 hours at 800 K.

After this flange test logged 20 hours at 875 K, the emitter temperature was raised from 1575 K to 1925 K. After four hours at 1925 K, the water-cooled RF induction coil burst and cooled the CVD structure to room temperature within 10 seconds. The CVD structure remained leaktight! This inadvertent test demonstrates the excellent thermal shock characteristics of the tri-layer CVD hot shell-emitter structure. The test continued at a dome temperature of 1925 K. At 80 hours, CVD Structure No. 103 developed a leak at the dome.

CVD Structure No. 104 was also coated with Cermet 487 on the flange area. It is being flame-fired in a natural gas furnace. A time profile of flange and emitter temperatures is shown in Figure 8. CVD Structure No. 104 was cycled to room temperature six times and remained leak tight. After 1300 hours of testing, there was no evidence of the black residue on the flange (see Figure 9). However, a clear deposit coated one third of the dome of the shell facing the viewport. This test will continue at an emitter temperature of 1600 K and a flange temperature of 850 K.

Figure 8. Emitter and Flange Temperature History of CVD Hot-Shell-Emitter Structure No. 104

TEST
FLANGE

PUMP

TEST
FIXTURE

JACK

2" HOT
SHELL

PROTECTIVE
COATING

TEST
FLANGE

Figure 9. Test Arrangement of CVD Hot Shell-Emitter Structure
No. 104

1.2 THERMIONIC POWER MODULE EVALUATION

1.2.1 TASK V. SYSTEM STUDIES

The objective of the system studies task is to identify the design approaches to integrate thermionic energy converters into fossil fuel applications in the most cost-effective manner. The results of these studies will help orient the design of the thermionic array module (TAM) being developed in Task VI.

Stone and Webster Engineering Corporation has devoted the last reporting period to the investigation of a TAM combustor. It is essentially a gas turbine combustor modified by adding thermionic converters to the walls. The thermionic combustor is capable of supplying hot gases to a gas turbine, an industrial process or a heat recovery boiler. Stone and Webster is refining the TAM combustor design. Preliminary studies of the thermionic combustor applied to an industrial boiler are in progress. The results of these studies will be summarized in a topical report to be issued at the conclusion of this study.

1.2.2 TASK VI. TAM MODULE DEVELOPMENT

The objective of this task is to develop combustion heated TAM thermionic converters, individually and in small arrays, which are prototypic for topping a central station powerplant. Devices with both alloy and silicon carbide hot shells will be made and tested. In order to define the transient thermal and electrical characteristics of a TAM, a four-converter array will be constructed and tested.

A. Converter No. 228 CVD Silicon Carbide Converter (CVD Tungsten As Deposited Emitter, Nickel Collector)

This converter continued on life test during this reporting period. The converter operated for a total of 3004 hours at an emitter temperature of 1650 K before failing due to a crack in the silicon carbide. The cause of the crack is not known. During the entire test period, the performance remained stable with a barrier index of 2.1 eV and a power output of 2.3 W/cm² at 1650 K.

B. Converter No. 239: One-Inch Diameter CVD Silicon Carbide Converter (CVD Tungsten as Deposited Emitter, Nickel Collector)

This converter is basically identical with the first three one-inch diameter converters tested. The diode has a composite CVD hot shell-emitter with an active area of 6 cm². The collector is nickel and is air cooled. The molybdenum flange and the emitter to flange braze area are coated with a silicon carbide suspension to protect them from oxidation. The cesium reservoir and tubulation are made from molybdenum and nickel, respectively. No copper was used for tubulation in order to avoid the oxidation that would occur in long-term testing.

The converter was installed in a horizontal position in the high-temperature gas and oil furnace. The converter has been operated at emitter temperatures of 1700 to 1750 K. The performance of this diode is not as good as that of the first three converters. The barrier index is 2.25 eV and the power output at 1700 K is about 2 W/cm². The poor performance appears to be due to improper electrode spacing. The spacing is fixed during construction and cannot be changed after final assembly

This converter has operated at 1730 K for 170 hours and will continue on life test at this emitter temperature.

C. CVD Silicon Carbide Array Module

During this reporting period, the design of a four-diode array module was begun. The module utilizes four one-inch diameter CVD silicon carbide converters. These one-inch converters will be similar to the first four converters tested. The converters will be completely fabricated, including outgassing and cesiation, before installation in the array fixture. They will be mounted on a single fixture which can easily be taken in and out of the furnace. The module may be operated vertically in the multiconverter test furnace or horizontally in the high-temperature furnace. Each diode within the array will have independent air cooling for both the collector and flange. The temperature of the cesium reservoirs will also be independently controlled. Initially the diodes will be connected in electrical series. However, parallel and series-parallel connections can be arranged.

Construction of the array furnace fixture, and necessary hardware will begin in the next few months. Five one inch converters will also be fabricated.

D. Postoperational Analysis of Converter No. 218

As discussed in Progress Report No. 42, a leak developed at the cold end of Converter No. 218 after 5120 hours of operation at emitter temperatures at, or above, 1600 K. During this reporting period, an extensive analysis was made of the hot shell-emitter of this converter by TRW.

Fortunately, this diode was removed from the multi-converter furnace before the electrodes could become oxidized. A small crack was found at the silicon carbide-tungsten braze interface with molybdenum flange at the cold end of the converter.

Subsequent air furnace tests described in Section 1.1.4 B2 of this report indicates that oxidation of the copper braze can be prevented by: 1) a thin nickel electroplate over the braze, and 2) a spray coating of a silicon carbide suspension over the flange-braze-hot shell area. Future flame-heated converters will be protected in this manner. In addition, the copper tube leading to the cesium reservoir will be replaced by a nickel tube. Note that Converter No. 239 incorporates these modifications.

Converter No. 218 was sectioned lengthwise and visually inspected. The ceramic-to-metal seal was in excellent condition. A full section of the diode was sent to TRW for analysis. Their metallographic, electron probe, microhardness and x-ray analyses gave most encouraging results. No life-limiting degradation mechanism was evident.

1. Metallographic Examination

The SiC surface was covered with a thin layer of glassy material (most probably, an amorphous form of silicon oxide). The microstructure of the CVD SiC was too fine to resolve by optical metallography. Other investigations have correlated such fine structure with high strength.

2. Electron Probe Microanalysis

Concentration profiles of silicon and tungsten were taken across the hot shell-emitter to determine interdiffusion of the trilayer components. Microanalysis of the SiC-graphite interface gave no evidence of interaction but showed a slight interaction with a zone width of approximately 120 microns.

3. X-Ray Diffraction Analysis

The CVD SiC is predominately β -SiC, with detectable amounts of α -SiC. The x-ray diffraction data did not show any SiO₂ reflections, implying that any SiO₂ was amorphous rather than crystalline.

4. Knoop Microhardness Determinations

Knoop microhardness measurements showed that the hardness (KHN~2600) of the dome of Converter No. 218 was within the range of values for CVD SiC shells that had not been combustion tested. Thus, no significant change in hardness took place during the 5120 hours of flame exposure.

1.2.3 TASK VII. COAL-FIRED TAM TEST UNIT

The objective of this task is to prepare plans for a TAM coal-fired test unit. The preliminary design will be formulated by taking into consideration the results of the system studies and TAM module development. The TAM test unit design will be the smallest size consistent with a realistic simulation of the temperatures, heat fluxes and slag conditions of a coal-fired steam powerplant.

A vendor of a laboratory-sized test facility has been identified. The unit under consideration would be capable of firing 100 lb/hr of coal. A variable geometry pulverized coal burner developed by the International Flame Research Foundation could be used in this furnace. A meeting has been scheduled to define the design in more detail.

2.0 PART TWO: NASA-OAST/JPL TASKS

2.1 THERMIONIC CONVERTER EVALUATION

2.1.1 TASK VIII. HIGH-TEMPERATURE CONVERTER EVALUATION

The objective of this task is to characterize the performance of candidate emitters, collectors and converter configurations at the high collector temperatures (900-1100 K) required for nuclear electric propulsion. Variable-spaced, planar converters will be used for this task. Evaluation of each converter will include measurements of the output current density versus load voltage as a function of emitter temperature, collector temperature, interelectrode spacing and cesium pressure.

A. Converter No. 232: (JPL Converter No. 4 Molybdenum Emitter, Molybdenum Oxide Collector)

Performance details of Converter No. 232 were given in Progress Report No. 42. During this reporting period, the short-term stability of this electrode pair was evaluated. The diode parameters were set at $T_E = 1600$ K; $T_C = 750$ K; $T_R = 528$ K and $d = 0.50$ mm. At these conditions, the barrier index was 1.98 eV at a current density of 6.0 A/cm². The output of the converter remained stable for a period of 1160 hours. The collector temperature was varied above and below its set point with no deleterious effect.

After 1160 hours of operation, the output of the diode decreased precipitously. A leak was found in the emitter sleeve. Apparently, the exposure of the electrodes to the bell jar atmosphere caused a dramatic increase in collector work function.

B. Converter No. 234: (JPL Converter No. 7) Tungsten Emitter, Niobium Collector

Converter No. 234 is a standard planar, variable spaced research converter. It has a niobium collector and a chemical vapor deposited fluoride tungsten emitter. The emitter surface was electroetched to expose (110) facets. Performance data were taken at emitter temperatures of 1600 and 1650 K for a variety of collector temperatures, cesium pressures and interelectrode spacings.

The converter was fully optimized at $T_E = 1600$ and 1650 K. A typical cesium reservoir temperature family at $T_C = 800$ K and $d = 0.25$ mm is shown in Figure 10. Figures 11 and 12 show the optimized performance (parametric in interelectrode spacing) at $T_E = 1600$ and 1650 K, respectively. The barrier index at $T_E = 1600$ K was 2.26 eV, while at $T_E = 1650$ K it improved to 2.12 eV.

Figure 10. Cesium Reservoir Temperature Family at $T_E = 1650 \text{ K}$,
 $T_C = 800 \text{ K}$, and $d = 0.25 \text{ mm}$ for Converter No. 234

Figure 11. Optimized Performance at $T_E = 1600 \text{ K}$ at Various Interelectrode Spacings for Converter No. 234

Figure 12. Optimized Performance at $T_E = 1650\text{ K}$, at Various Interelectrode Spacings for Converter No. 234

The collector work function was measured by the retarding plot method. The collector work function plotted against the ratio of collector to cesium reservoir temperatures is shown in Figure 13. The minimum work function of 1.55 eV was measured at a T_C/T_R of 1.47. Pursuant to system design criteria, the diode was optimized for cesium pressure and interelectrode spacing at elevated collector temperatures. The output characteristics, parametric in collector temperature, at $T_E = 1650$ K with optimum cesium pressure and interelectrode spacing are given in Figure 14. The maximum power densities at $T_C = 800, 900$ and 1000 K were 3.2, 1.3 and 0.7 W/cm^2 , respectively.

At this point, the performance degraded substantially. In addition, the diode would ignite only at appreciably higher cesium reservoir temperatures. Suspecting a leak, the diode was taken off test to be opened and leak checked. After pinching off the cesium reservoir, the entire diode was heated to approximately 1000 K in order to remove any trapped cesium which might "plug" a leak. The diode was pumped on through the reservoir tubulation with a Veeco Model MS-17 mass spectrometer leak detector. No leak was identifiable in the diode or the cesium reservoir pinch-off.

Figure 13.

Figure 14. Optimized Performance (Spacing and Cesium Pressure) of Converter No. 234 at $T_E = 1650\text{ K}$, and Various Collector Temperatures

2.1.2 TASK IX. ADVANCED CONVERTER STUDIES

In the conventional ignited mode diode, transport losses due to ionization, and coulombic and neutral atom scattering greatly reduce conversion efficiency. The objective of this task is to demonstrate improved thermionic converter performance by means of reduced potential loss in the interelectrode space. Based on previous studies, the particle thermionic converter (PTC) has been chosen for further investigations. Specifically, the electrical and thermal properties of PTC configurations will be tested as a function of particle composition and electrode spacing.

A. Particle Thermionic Converter - Converter No. 235:
Magnesium Oxide Sprayed Tungsten Emitter - Guarded
Molybdenum Collector

This converter, designed to measure the cesiated work function of magnesium oxide sprayed on the emitter, was tested. The output characteristics were much more conventional than expected. On opening the diode no magnesia was found to remain on the emitter. Apparently, these particles vaporized off the surface at the outgassing temperatures. Possibly cesium was also involved in this process.

2.1.3 TASK X. POSTOPERATIONAL DIAGNOSTICS

The variable spaced planar converters built for JPL are deliverable items. However, if it appears advisable on mutual agreement between JPL and Thermo Electron, selected converters shall be opened for postoperational diagnostics after performance testing. The objective will be to identify the degradation mode, if any, and identify the probable mechanisms of formation.

A. Collector of Converter No. 236

The collector of Converter No. 236 was mounted in the Surface Characterization Chamber (SCC). It was impossible to take an Auger spectrum (even after sputtering) because of the high electrical resistance of the collector. Moving the beam just off the dark grey collector onto the substrate produced a normal spectrum. The collector was removed from the Auger system and the resistance was found to be $>20\text{ M}$ over most of the collector. Apparently the leak in this converter caused a highly insulating layer to form on the collector.

B. Emitter of Converter No. 238

The emitter of Converter No. 238 [W(100) emitter, molybdenum collector] was examined by Auger analysis. This emitter was shiny over most of its area except for a white powdery spot in the center. Auger analysis of the main area showed W-29%, O-37%, C-29%, N-5% and of the spot area W-16%, Mo-10%, O-37%, C-33% and N-4%. This was a zero spacing converter, so the molybdenum was probably deposited on the emitter when the two electrodes touched each other during operation.

C. Oxygen Transport from an Oxide Collector

The success of converters built with molybdenum oxide collectors has stimulated renewed interest in the oxygen transport mechanism. For molybdenum oxide collector temperatures greater than 750 K, an "oxygen effect" occurs. That is, an increase of collector temperature causes an increase in emitter saturation current. This is believed to be due to an oxygen containing gas being transported across the interelectrode gap and decomposing on the emitter. The following four pieces of evidence indicate that the most plausible oxygen carrier is Cs_2O . The first stated evidence is from new data and the other three factors are from previous data.

1. Mass Spectroscopy

A sublimed molybdenum oxide collector structure (from the same sublimation run as for the collector of Converter No. 232) was mounted in front of a quadrupole mass spectrometer in the SCC. Mass spectra taken as a function of sample temperature are shown in Figure Nos. 15 - 17. The temperature was measured with an optical pyrometer with an assumed collector emissivity of 0.4. Oxygen gas is not detected for any temperature. MoO_3 is first detected at 1450 K, (at an estimated pressure of 10^{-11} torr). The occurrence of MoO_2 , MoO and Mo may be due either to actual desorption from the collector or from cracking of MoO_3 in the mass spectrometer. The seven peaks corresponding to each molybdenum oxide are due to the seven major isotopes of molybdenum, and the magnitude of each peak corresponds well with the relative natural abundance of that isotope.

On the basis of these data, one can rule out oxygen gas evolved from the collector as an oxygen carrier responsible for the oxygen effect. One can also rule out molybdenum oxides evolved from the collector since the oxygen effect occurs at 750 K and molybdenum oxides are not detected until the collector temperature reaches 1450 K.

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Figure 15. Quadrupole Signal vs Mass Number for a Sublimed Molybdenum Oxide Collector Heated to Temperatures of 760, 857, and 1076 K

Figure 17. Quadrupole Signal vs Mass Number for a Sublimed Molybdenum Oxide Collector Heated to a Temperature of 1525 K

2. Auger Spectroscopy

Postoperational analysis of Converter No. 210 (tungsten emitter, sublimed molybdenum oxide collector) showed no molybdenum on the emitter. The detectability limit was 1% of a monolayer. This result also supports the conclusion that molybdenum oxides evolved from the collector are not responsible for the oxygen effect.

3. Thermochemical Analysis

A thermochemical analysis for a tungsten-tungsten oxide converter reported in Progress Report No. 20 is summarized and presented in tabular form in Table III. The elemental species concentrations are 1000 moles W, 1000 moles Cs and 100 moles O. The data show that 89-99% of the gas is cesium, with the remainder almost entirely Cs_2O . The formation of Cs_2O is enhanced by lower temperatures (800 K) and higher total pressures (2 torr). The data imply the Cs_2O pressure at the emitter side may be 2-10 times smaller than at the collector. Smaller Cs_2O pressures at the emitter are

TABLE III
THERMOCHEMICAL DATA ANALYSIS
Adapted from TECO Report No. 20, Feb. 1977

<u>T(K)</u>	<u>P(torr)</u>	<u>Partial Pressures (Percents of Total Pressure)</u>							
		<u>Cs</u>	Cs O	Cs	CsO	WO	<u>O</u>	O	WO
800	0.23	92	8	4×10^{-3}	*	*	*	*	*
	0.76	89	11	1×10^{-2}	*	*	*	*	*
	2.3	89	11	4×10^{-2}	*	*	*	*	*
1500	0.23	99	0.7	2×10^{-4}	3×10^{-4}	9×10^{-5}	3×10^{-6}	2×10^{-6}	6×10^{-7}
	0.76	98	2	7×10^{-4}	3×10^{-4}	3×10^{-5}	1×10^{-6}	6×10^{-7}	2×10^{-7}
	2.3	94	6	2×10^{-3}	4×10^{-4}	9×10^{-6}	3×10^{-7}	2×10^{-7}	6×10^{-8}

* Less than 10^{-10} percent of total pressure

Thermochemical data analysis for tungsten-tungsten oxide converter. The elemental species concentrations are 1000 moles tungsten, 1000 moles cesium and 100 moles oxygen.

expected because of Cs_2O decomposition on the emitter and formation of free oxygen and tungsten oxides. Some of the tungsten oxides vaporize, but the majority stay in the solid phase at 1500 K. In summary, the thermochemical calculations indicate that Cs_2O is the most predominant oxygen containing gas for the given concentrations of W, Cs and O.

4. Experimental Observations

Converter experiments indicate that the temperature of the oxygen effect is relatively independent of a) whether the collector is tungsten oxide or molybdenum oxide, and b) whether the sublimed molybdenum oxide is deposited at a substrate temperature of 1025 or 1225 K. These data are consistent with the hypothesis that the temperature of the oxygen effect corresponds to the desorption temperature of Cs_2O and that the substrate acts merely as a source of oxygen to form Cs_2O .

The foregoing four pieces of evidence strongly support the conclusion that the oxygen carrier in oxide converters is Cs_2O , although one cannot completely rule out such gases as H_2O , CO or CO_2 .

2.2 CYLINDRICAL CONVERTER DEVELOPMENT

2.2.1 TASK XI. CYLINDRICAL CONVERTER COMPONENT DEVELOPMENT

The objective of this task is to develop the technology required to construct cylindrical converters, excluding the electrode surfaces. This task includes electrode insulation, seal-bellows subassembly and thermoelectric lead components.

Due to program priorities established by JPL, no significant effort was expended on this task during this reporting period.

2.2.2 TASK XII. CORRELATION OF DESIGN INTERFACES

The objective of this task is to provide technical coordination between Thermo Electron and other contractors as well as with government agencies in order to assure overall compatibility of design, materials and interfaces between the thermionic conversion and other subsystems. This effort will be continuously updated.

In this task, technical coordination between Thermo Electron government agencies and other contractors is provided. Thus the overall compatibility of the various subsystems is ensured.

In view of the difficulty in obtaining a long life electrical insulation of the heat pipe and thermionic converter emitter structure, an alternative coupling mechanism was investigated. A computer analysis has been initiated to model radiation coupling between the emitters and the reactor heat pipes.

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