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TOPICAL REPORT**PRELIMINARY INVESTIGATIONS OF
THERMIONIC CONVERTERS UTILIZING HOTEMA
AND DFVLR ELECTRODES**

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TABLE OF CONTENTS

<u>Chapter</u>	<u>Page</u>
I. INTRODUCTION AND SUMMARY	1
II. EXPERIMENTAL APPARATUS	3
A. Variable Spaced Research Diode	3
B. Test Stand	3
C. Data Acquisition	6
D. Surface Characterization Chamber	6
III. Mo-Al ₂ O ₃ , Cr ₂ O ₃ EUTECTIC EMITTER BY EINDHOVEN UNIVERSITY OF TECHNOLOGY	9
A. Sample Preparation	9
B. Preoperational Diagnostics	9
C. Converter No. 277	12
D. Postoperational Diagnostics	17
IV. ZrO ₂ -Mo CERMET ELECTRODES BY DFVLR	23
A. Sample Preparation	23
B. Preoperational Diagnostics	23
C. Converter No. 261	27
D. Converter No. 268	30
E. Postoperational Diagnostics	36
V. DISCUSSION	43
VI. REFERENCES	45

I. INTRODUCTION AND SUMMARY

During 1981 and 1982, Thermo Electron received several advanced electrodes from research facilities in Europe. This report details the experimental results obtained from three thermionic converters which utilized these electrodes.

A ready way to improve thermionic performance is through improved electrodes. Among other attributes, electrodes must be stable and have a low work function at the converter operating conditions. Low collector work function translates directly into increased output voltage. A low work function emitter is necessary to provide current densities of the order of 10 A/cm^2 at low cesium pressures. The low cesium pressures, in turn, lead to an increased interelectrode gap which will facilitate fabrication.

An emitter made of a directionally solidified Mo-Al₂O₃, Cr₂O₃ eutectic was provided by Eindhoven University of Technology in Eindhoven, The Netherlands. Although the high temperature braze cycle used in bonding this electrode to the emitter substrate destroyed its characteristic needle microstructure, the converter gave good performance (barrier index of 2.04 eV). Apparently chemical species evaporated from the emitter onto the collector provided a low collector work function. The resulting low barrier indices suggest that this surface is a promising emitter.

Although the possible benefits of the extended area characteristic of the directionally solidified electrode could not be realized in this initial investigation, the results that were obtained strongly suggest that an electrode of this type has the potential of providing significantly improved thermionic converter performance. Future studies should use converters in which the high temperature braze cycle is eliminated by either: 1) utilizing a lower temperature braze or, preferably, 2) fabricating the directionally solidified eutectic coating on the emitter substrate.

Electrodes composed of a ZrO_2 -Mo cermet were provided by Deutsche Forschungs- und Versuchsanstalt für Luft- und Raumfahrt (DFVLR) in Stuttgart, Germany. Two diodes were built containing cermet emitters and collectors. Low barrier indices were obtained at low emitter temperatures using these electrodes. Unfortunately, stable performance was not observed at emitter temperatures corresponding to practical output power densities.

A brief description of the research diode and test equipment used in the experiments is given in Chapter II. Chapters III and IV detail the results obtained from the Eindhoven and DFVLR electrodes, respectively.

II. EXPERIMENTAL APPARATUS

A. Variable Spaced Research Diode

The variable spaced research diode designed at Thermo Electron is shown in Figure 1. The emitter material is typically tungsten and the collector body is nickel. Various electrode surfaces can be evaluated by spraying, bonding or vapor depositing candidate materials onto the electrode substrates. The flexible nickel bellows permit intelectrode spacing to be varied from 0.05 to 1.0 mm. A cesium pressure is established in the diode via a temperature controlled liquid cesium reservoir.

B. Test Stand

The diode is mounted in a test stand which is shown in Figure 2. Collector, emitter flange and cesium reservoir temperatures are measured with type J (Iron-Constantan) thermocouples. These temperatures are maintained with electronic temperature controllers in conjunction with resistance heaters and water-cooled heat sinks. The emitter is heated by electron bombardment. The emitter temperature is measured by sighting a cavity in the emitter body with an optical pyrometer. This cavity acts as a source of blackbody radiation. Emitter temperature is also monitored with type S (platinum, platinum-10% rhodium) thermocouples.

The entire test stand is enclosed in a bell jar and evacuated with an oil diffusion pump to a pressure of 1×10^{-6} mm Hg.

Figure 1. Standard Variable Spaced Diode

Figure 2. Test Stand for Variable Spaced Thermionic Converter

10^{-6} torr. Interelectrode spacing can be varied with three micrometer screws which can be activated from outside the bell jar.

C. Data Acquisition

An alternating current sweep supply and resistance shunts provide a variable load for the diode. Current density at different voltages can be measured as a function of emitter temperature, collector temperature, cesium pressure, and interelectrode spacing. A block diagram of the associated data acquisition system is given in Figure 3. This system permits the simultaneous testing of two converters. Five converter test stations (i.e., test stand, vacuum system, power supplies and controllers) are currently available. At any given time, a converter in a test station may be being set up, outgassed, tested, or having its data analyzed.

D. Surface Characterization Chamber

Post- and preoperational diagnostics are performed in the surface characterization chamber, shown in Figure 4. A sample admitted to the chamber can be cleaned thermally by electron bombardment from behind or can be cleaned by sputter-etching from above. Electrode surfaces can be chemically characterized by means of Auger Electron Spectroscopy.

Figure 3. Block Diagram of Test Stand Data Acquisition Equipment

Figure 4. Surface Characterization Chamber

III. Mo-Al₂O₃, Cr₂O₃ EUTECTIC EMITTER FABRICATED BY HOTEMA

A. Sample Preparation

A Mo-Al₂O₃, Cr₂O₃ eutectic sample was prepared by the High Temperature Materials Research Group, HOTEMA, at the University of Technology, Eindhoven, The Netherlands. The "directionally solidified" eutectic coating was fabricated by rapidly cooling a ceramic layer which was previously deposited by physical vapor deposition onto a molybdenum substrate. Details of this technique are given in References 1 and 2. Scanning Electron Micrographs of two metal-ceramic eutectics are shown in Figure 5. These micrographs were provided by HOTEMA.

The sample was platinum brazed in one atmosphere of hydrogen at a temperature of 2075 K. The emitter was then analyzed by Auger Electron Spectroscopy.

B. Preoperational Diagnostics

A preoperational Auger analysis was performed for the emitter of Converter 277. The emitter (EUT-01) had been brazed to the emitter body but had not been welded into the converter structure. The analysis (Table 1) showed a high concentration of carbon, even after sputtering. Additionally, the expected elements chromium and aluminum were not detected. The high temperature hydrogen brazing operation apparently

10,000x

EUT-T01

 $\text{Mo-Cr}_2\text{O}_3, \text{Al}_2\text{O}_3$

20,000x

EUT-T09

 Mo-LaCrO_3

Figure 5. Scanning Electron Micrographs of HOTEMA Metal-Ceramic Eutectics

TABLE 1
 AUGER ELEMENTAL ANALYSIS OF THE HOTEMA EMITTER OF CONVERTER 277
 BEFORE AND AFTER CONVERTER OPERATION

	Before Operation		After Operation	
Element	As Admitted	Sputtered	As Admitted	Sputtered
Mo	9.9	37.4	20.8	49.1
C	52.6	44.7	12.6	25.1
N	4.6	2.8	1.8	5.6
O	18.6	15.1	36.6	20.3
Na	2.1	-	-	-
Si	11.0	-	-	-
S	1.1	-	-	-

removed the chromium and aluminum constituents from the emitter surface. The alumina-chromia-molybdenum eutectic emitters are stable to 2000 K in 350 torr of argon gas, but heating these emitters in hydrogen or vacuum may preferentially remove the chromium and aluminum constituents.

C. Converter No. 277

Converter No. 277 contains the Mo-Al₂O₃, Cr₂O₃ eutectic emitter, provided by HOTEMA, and a molybdenum collector. The emitter and collector were outgassed in situ to a temperature of 1670 and 840 K, respectively. The diode was cesiated and current voltage characteristics were obtained at emitter temperatures of 1400, 1500 and 1600 K as a function of collector temperatures, cesium pressures and interelectrode spacings.

A cesium reservoir temperature family at $T_E = 1400$ K, $T_C = 800$ K and $d = 0.5$ mm is shown in Figure 6. The optimized performance at this emitter temperature parametric in interelectrode spacing is given in Figure 7. The barrier index at 5 A/cm² was 2.04 eV. The converter was then optimized at emitter temperatures of 1500 and 1600 K. The barrier indices at these conditions were 2.06 and 2.10 eV, respectively. These results are given in Figures 8 and 9.

The collector work function was measured by the retarding plot method. Collector work function versus the

Figure 6. Cesium Reservoir Temperature Family at $T_E = 1400 \text{ K}$, $T_C = 800 \text{ K}$, $d = 0.5 \text{ mm}$ for Converter No. 277

Figure 7. Optimized Converter Performance at $T_E = 1400 \text{ K}$, and Various Interelectrode Spacings for Converter No. 277

Figure 8. Optimized Converter Performance at $T_E = 1500 \text{ K}$ and Various Inter-electrode Spacings for Converter No. 277

Figure 9. Optimized Converter Performance at $T_E = 1600 \text{ K}$ and Various Interelectrode Spacings for Converter No. 277

ratio T_C/T_R is given in Figure 10. The minimum work function was 1.53 eV at $T_C/T_R = 1.45$.

The converter output was stable under all operating conditions. In addition, the barrier index of 2.04 eV at an emitter temperature of 1400 K was reproduced after the emitter had been heated to 1650 K for a period of 4 hours. This is an indication that the eutectic emitter is stable at these temperatures.

At this point the diode was taken off test and opened for postoperational diagnostics. These results are discussed in the next section of this report.

D. Postoperational Diagnostics

Postoperational Auger analyses were performed for the emitter and collector of Converter 277 (Tables 1 and 2). The emitter contained substantial amounts of carbon even after sputtering, and the initial silicon constituent was absent after converter operation. Silicon was found after operation on the molybdenum collector, indicating a transport of silicon occurs from the emitter to the collector during converter operation. Most of the impurities on the collector were removed by sputtering, indicating these impurities did not originate in the bulk molybdenum collector.

Scanning electron micrographs were taken of the eutectic emitter after converter operation (Fig. 11). The micrographs show a wavy surface structure, with no evidence of molybdenum

needles. The stability of the needles at various temperatures and pressures should be more extensively investigated.

Figure 10. Collector Work Function versus T_C/T_R for Converter No. 277

TABLE 2
AUGER ELEMENTAL ANALYSIS OF THE COLLECTOR
OF CONVERTER 277 AFTER OPERATION

Element	As Admitted	Sputtered
Mo	4.1	37.8
S	2.1	-
C	3.0	44.5
Ca	1.5	-
N	1.3	3.3
O	28.0	13.4
Cs	25.4	1.0
Cu	1.3	-
Ni	0.7	-
Fe	1.7	-
Al	11.5	-
Si	19.3	-

400 X

1000 X

Figure 11. SEM's of $\text{Mo-AL}_2\text{O}_3, \text{Cr}_2\text{O}_3$
Eutectic Emitter After Operation

IV. ZrO₂-Mo CERMET ELECTRODES FABRICATED BY DFVLR

A. Sample Preparation

Two emitter-collector pairs were plasma sprayed at DFVLR using substrates provided by Thermo Electron. The particulars of the two electrode pairs are given in Table 3. The information contained in this Table was provided by DFVLR. The technique used to form the coatings is described in References 3 and 4. Scanning Electron Micrographs (SEMs) of emitter No. 1 and collector No. 1 are shown in Figure 12.

B. Preoperational Diagnostics

Preoperational Auger analyses were performed on the two electrode pairs upon receipt at Thermo Electron. The elemental atomic percent concentrations as determined by Auger analysis for the ZrO₂-Mo emitters and collectors are given in Table 4. The subscript on the element abbreviation is the Auger peak energy used to calculate the percent concentrations. Sputtering time was 20 minutes for the collectors and 40 minutes for the emitters. The argon pressure was 5×10^{-5} torr and the ion energy was 2 kV. A relatively small amount of methane was present in the sputtering gas, which may account for part of the carbon signal after sputtering. The primary conclusion is that molybdenum is present in much higher concentrations than zirconium for both collectors and emitters. Additional

TABLE 3
LOW-PRESSURE PLASMA ARC SPRAYED DFVLR ELECTRODES

ELECTRODE	NO.	SUBSTRATE	COATING THICKNESS (m)	BY WEIGHT (%)	
				ZrO ₂	Mo
Collector	1	Nickel	90	20	80
Collector	2	Nickel	100	20	80
Emitter	1	Tungsten	20	50	50
Emitter	2	Tungsten	25	50	50

EMITTER NO. 1

COLLECTOR NO. 1

Figure 12 SEM's of ZrO_2 -Mo Cermet Electrodes (1000 X)

TABLE 4
AUGER PERCENT CONCENTRATIONS FOR DFVLR ZrO₂-Mo ELECTRODES

ELEMENT	AS ADMITTED				AFTER SPUTTERING			
	COLLECTORS		EMITTERS		COLLECTORS		EMITTERS	
	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2	No. 1	No. 1
Mo ₂₀₄₄	32.7	24.9	27.4	33.0	54.1	38.4	39.6	33.2
Zr ₁₈₄₅	-	-	-	-	4.9	7.7	10.1	9.2
O ₅₁₀	24.1	25.1	14.5	18.5	17.9	25.3	20.3	23.2
C ₂₇₃	29.5	30.9	47.2	39.8	17.9	17.3	22.9	24.6
N ₃₈₀	1.5	1.4	2.7	1.8	2.0	1.5	1.5	3.1
Ca ₂₉₁	4.9	2.8	0.9	1.3	0.9	3.2	1.9	1.7
Si ₁₆₂₀	6.8	10.2	5.7	4.5	2.0	5.3	2.8	4.0
Na ₉₉₆	-	1.8	1.6	1.2	-	0.3	-	0.5
Ni ₈₄₈	-	-	-	-	-	0.5	0.7	0.4
Fe ₇₀₃	-	-	-	-	-	0.4	-	-
Cl ₁₈₁	0.5	2.8	-	-	-	-	-	-

small amounts of impurities such as nitrogen, calcium, silicon, sodium, nickel and iron are apparently deposited on the substrates in the plasma spray process since these impurities are present even after extended sputtering.

C. Converter No. 261

Emitter No. 1 was paired with Collector No. 1 and assembled into a variable-spaced research converter. The electrodes were subjected to a high-temperature outgassing prior to assembly into the diode. The emitter and collector were held at 1725 and 1225 K, respectively, for one hour in an ultra-high vacuum chamber at 3.5×10^{-7} torr. After assembly, the emitter and collector were outgassed in situ to 1775 and 990 K, respectively. The diode was cesiated and current-voltage characteristics were obtained at emitter temperatures of 1700 and 1600 K as a function of collector temperatures, cesium pressures and interelectrode spacings.

The initial output of the diode was quite erratic. Figures 13 and 14 show cesium reservoir temperature families at the identical conditions of $T_E = 1700$ K, $T_C = 750$ K, and $d = 0.50$ mm. The family of curves in Figure 14 was generated immediately following that of Figure 13. It was not possible to correlate changes in output with emitter or collector temperature excursions. Cesium families were not reproducible for the initial 25 hours of the diode's life.

After approximately 25 hours of operation, the output became more stable. A cesium reservoir temperature family at

Figure 13. Cesium Reservoir Temperature Family at $T_E = 1700 \text{ K}$, $T_C = 750 \text{ K}$, and $d = 0.50 \text{ mm}$ for Converter No. 261

Figure 14. Cesium Reservoir Temperature Family at $T_E = 1700\text{ K}$, $T_C = 750\text{ K}$, and $d = 0.50\text{ mm}$ for Converter No. 261

$T_E = 1600$ K, $T_C = 800$ K and $d = 0.125$ mm is given in Figure 15. The converter was optimized for collector temperature and cesium pressure at $T_E = 1600$ K. This result is given, parametric in interelectrode spacing, in Figure 16. At these conditions, the barrier index was 2.20 eV at 5 A/cm^2 . The diode was taken off test and opened for postoperational diagnostics. These results are discussed in Section III-E.

D. Converter No. 268

Converter No. 268 contains emitter No. 2 and collector No. 2.

Results from the previous $\text{ZrO}_2\text{-Mo}$ cermet diode (Converter No. 261) suggested that more moderate outgassing and operating temperatures should give improved results. Prior to cesiation, the emitter and collector were outgassed to 1450 and 760 K, respectively. Initial performance measurements were made at an emitter temperature of 1400 K.

A cesium family at $T_E = 1400$ K, and $d = 0.5$ mm is shown in Figure 17. In contrast to the previous diode, this output was stable and reproducible. Figure 18 shows the optimum performance at $T_E = 1400$ K, parametric in interelectrode spacing. At a current density of 5 A/cm^2 , the barrier index was 2.00 eV at this emitter temperature. After 150 hours of stable operation, the performance was measured at emitter temperatures of 1500 and 1600 K. Figure 19 shows a cesium reservoir temperature family at $T_E = 1500$

Figure 15. Cesium Reservoir Temperature Family at $T_E = 1600 \text{ K}$, $T_C = 800 \text{ K}$, and $d = 0.125 \text{ mm}$ for Converter No. 261

Figure 16. Optimized Converter Performance at Various Spacings for Converter No. 261

Figure 17. Cesium Reservoir Temperature Family at $T_E = 1400\text{ K}$, $T_C = 800\text{ K}$, and $d = 0.50\text{ mm}$ for Converter No. 268

Figure 18. Optimized Converter Performance at $T_E = 1400\text{ K}$ and Various Interelectrode Spacings for Converter No. 268

Figure 19. Cesium Reservoir Temperature Family at $T_E = 1500 K$, $T_C = 800 K$, and $d = 0.5 mm$ for Converter No. 268

K, $T_C = 800$ K, and $d = 0.5$ mm. The barrier index at 5 A/cm² at these conditions was 2.08 eV. Again, the emitter temperature was raised 100 degrees. At these conditions, the barrier index was 2.30 eV at 5 A/cm². These results are given in Figure 20. As is apparent from this figure, the output degraded significantly. This degradation appeared to be irreversible. Upon returning to an emitter temperature of 1400 K the barrier index was greater than 2.30 eV, compared to the 2.00 eV recorded previously.

At this point, the diode was taken off test and opened for postoperational diagnostics. These results are discussed in Section III-E.

E. Postoperational Diagnostics

The emitters and collectors of Converter No. 261 (Emitter No. 1, Collector No. 1) and Converter No. 268 (Emitter No. 2, Collector No. 2) were analyzed by Auger electron spectroscopy. After operation, the emitters appeared uniformly gray with no obvious deposits. However, the collectors were covered with a black coating.

The postoperational Auger analysis results for the samples ("as admitted" and "sputtered") are given in Table 5. Collector No. 1 as admitted was sufficiently resistive that it was impossible to take an Auger spectrum. Collector No. 2 was heavily oxidized with impurities of cesium, carbon, calcium, silicon, nickel, magnesium, aluminum and phosphorus.

Figure 20. Cesium Reservoir Temperature Family at $T_E = 1600 K$, $T_C = 800 K$, and $d = 0.25 mm$ for Converter No. 268

TABLE 5
POSTOPERATIONAL AUGER ANALYSIS FOR ZrO_2 -Mo
CERMET EMITTERS AND COLLECTORS

Element	As Admitted				After Sputtering			
	Collectors		Emitters		Collectors		Emitters	
	No. 1*	No. 2	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
Mo ₂₀₄₄		11.4	24.0	35.7	17.3	10.0	48.5	36.3
Zr ₁₈₄₅		--	14.3	18.4	--	--	14.8	15.2
O ₅₁₀		28.0	23.7	24.7	37.9	31.5	20.5	23.5
C ₂₇₃		3.2	14.6	7.1	2.3	2.5	14.2	23.5
N ₃₈₀		--	0.9	0.6	--	--	2.2	1.5
Cs ₅₆₃		10.8	22.5	13.3	7.3	5.7	--	--
Ca ₂₉₁		7.6	--	--	3.2	5.7	--	--
Si ₁₆₂₀		11.0	--	--	--	11.3	--	--
Ni ₈₄₈		1.6	--	--	1.4	3.6	--	--
Mg ₁₁₈₀		2.0	--	--	--	1.4	--	--
Al ₁₃₈₀		4.4	--	--	30.6	9.7	--	--
P ₁₈₅₉		20.0	--	--	--	18.6	--	--

*No Auger spectrum possible due to high resistivity of surface.

The as admitted emitters were free from all impurities except cesium, carbon and nitrogen.

The sputtered collectors still contained many impurities, including cesium. The presence of cesium indicates a bulk interaction between the oxide in the collector and cesium, similar to that in the sublimed molybdenum collectors. The emitters, by contrast, contained no cesium after sputtering - indicating only surface adsorption of cesium on the emitters.

A comparison of the elemental compositions of the sputtered electrodes before and after converter operation is given in Table 6. The collectors after operation show heavy oxidation and large impurity concentrations which obscure the molybdenum and zirconium signals. The impurities of calcium, silicon and nickel are apparently desorbed from the emitter onto the collector during converter operation.

The phosphorus, aluminum and magnesium impurities either diffuse from the bulk collector or are absorbed from the gas phase from an unknown source during converter operation. The carbon concentration on the collectors is greatly reduced after operation. This is similar to the small carbon concentrations found on sublimed molybdenum collectors and is apparently caused by carbon combining with the bulk oxygen and desorbing as CO or CO₂.

The emitter elemental concentrations are nearly equal before and after operation, except for the removal of some

TABLE 6
COMPARISON OF ZrO_2 -Mo ELECTRODES BEFORE AND AFTER CONVERTER OPERATION
(ALL SURFACES SPUTTERED)

Element	Collectors				Emitters			
	No. 1 Before	No. 1 After	No. 2 Before	No. 2 After	No. 1 Before	No. 1 After	No. 2 Before	No. 2 After
Mo ₂₀₄₄	54.1	17.3	38.4	10.0	39.6	48.5	33.2	36.3
Zr ₁₈₄₅	4.9	--	7.7	--	10.1	14.8	9.2	15.2
O ₅₁₀	17.9	37.9	25.3	31.5	20.3	20.5	23.2	23.5
C ₂₇₃	17.9	2.3	17.3	2.5	22.9	14.2	24.6	23.5
N ₃₈₀	2.0	--	1.5	--	1.5	2.2	3.1	1.5
Ca ₂₉₁	0.9	3.2	3.2	5.7	1.9	--	1.7	--
Si ₁₆₂₀	2.0	--	5.3	11.3	2.8	--	4.0	--
Na ₉₉₆	--	--	0.3	--	--	--	0.5	--
Ni ₈₄₈	--	1.4	0.5	3.6	0.7	--	0.4	--
Fe ₇₀₃	--	--	0.4	--	--	--	--	--
Cs ₅₆₃	--	7.3	--	5.7	--	--	--	--
Mg ₁₁₈₀	--	--	--	1.4	--	--	--	--
Al ₁₃₈₀	--	30.6	--	9.7	--	--	--	--
P ₁₈₅₉	--	--	--	18.6	--	--	--	--

No. 1 refers to Converter No. 261; No. 2 refers to Converter No. 268.

impurities. This result suggests stability of the emitter cermet material at high temperatures for short periods (1700 K, 10 hours for Converter No. 261 and 1600 K, 2 hours for Converter No. 268). The ZrO_2 -Mo cermet electrodes thus look promising as permanently oxidized emitters providing that impurities can be prevented from depositing onto the collector.

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V. DISCUSSIONS

Two converters with $\text{ZrO}_2\text{-Mo}$ cermet electrodes produced by a low pressure plasma spray technique at DFVLR were fabricated and tested. The first of this pair of diodes was outgassed and operated at high temperatures and did not show improved thermionic performance. The second of the two was outgassed and operated at more moderate temperatures. An encouraging barrier index of 2.00 eV at $T_E = 1400$ K was recorded. Additionally, pre- and postoperational diagnostics confirmed that elemental concentrations on the emitter were nearly equal before and after operation. However, these electrodes did not give stable performance at emitter temperatures corresponding to practical output power densities.

The $\text{Mo-Al}_2\text{O}_3$, Cr_2O_3 eutectic emitter developed by HOTEMA exhibited stable performance at emitter temperatures up to 1650 K. The barrier index at $T_E = 1400$ K was 2.04 eV. The minimum collector work function as measured by the retarding plot method was 1.53 eV. This low work function may be related to the presence of oxygen (which was verified by postoperational diagnostics) on both the emitter and collector. These results suggest that an emitter of this type has the potential of providing significantly improved thermionic converter performance.

SEMs of the emitter after a high temperature braze cycle show that the fine metal needles formed by the HOTEMA process had been destroyed. Thus the possible benefits of this extended area electrode structure on increasing thermionic output could not be realized in the initial investigation.

In future studies, the high temperature braze cycle used in bonding the HOTEMA emitter to the substrate can be avoided by either: 1) using a lower temperature braze or 2) fabricating the directionally solidified eutectic coating on the emitter substrate. The latter route is preferable since it would avoid the possibility of the braze contaminating the emitter surfaces.

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