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Report No. TE4258-25-82

DOE
ADVANCED THERMIONIC TECHNOLOGY PROGRAM

PROGRESS REPORT NO. 47

April, May, June
1981

DOE Contract DE-AC02-81ET11291

Prepared by

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INTRODUCTION AND SUMMARY

The advanced Thermionic Technology Program at Thermo Electron Corporation is sponsored by the Department of Energy (DOE). The primary long-term goal is to improve thermionic performance to the level that thermionic topping of fossil-fuel powerplants becomes technically possible and economically attractive. An intermediate goal is to operate a thermionic module in a powerplant during the mid-1980's. A short-term goal is to demonstrate reliable thermionic operation in a combustion environment.

This report covers progress made during the three-month period from April through June 1981. During this period, significant accomplishments include:

- Continuing stable output from the combustion test of the one-inch diameter hemispherical silicon carbide diode (Converter No. 239) at an emitter temperature of 1730 K for a period of over 8500 hours.
- Determination of the elemental composition (i.e., molybdenum, nickel and cesium) through the sublimed molybdenum collector of Converter No. 262.
- Demonstration of tungsten CVD onto molybdenum flange using a reuseable graphite mandrel.

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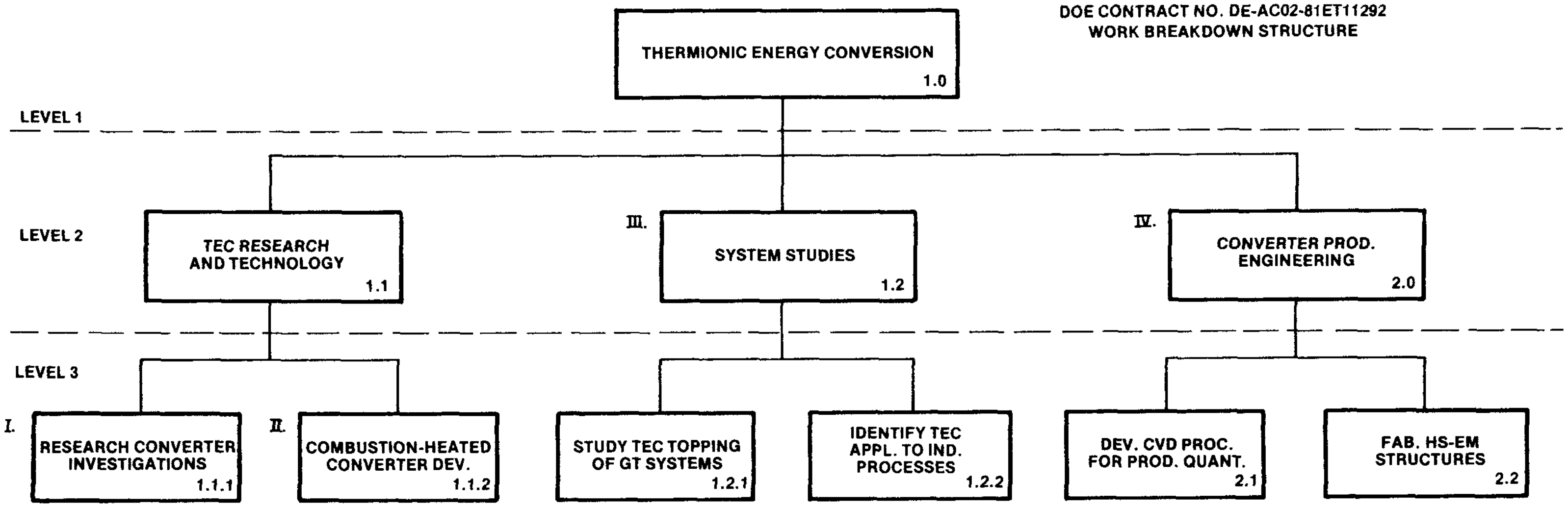
DOE CONTRACT NO. DE-AC02-81ET11292
WORK BREAKDOWN STRUCTURE



NOTE: ROMAN NUMERALS DESIGNATE LEVEL AT WHICH TASKS ARE TO BE REPORTED

I. RESEARCH CONVERTER INVESTIGATIONS

The objective of this task is to investigate electrode pair performance as it varies with emitter and collector composition, microstructure and additives, using variable-spaced research converters heated by electron bombardment. Converter characteristics will be measured as a function of emitter temperature, collector temperature, cesium pressure, interelectrode spacing and, if applicable, additive gas pressure

A. Investigations of Zr-O-C on Tungsten

The detailed studies of Zr-O-W(100) and Zr-O-C-W(100) have been concluded. A paper containing the results has been written and accepted for publication.(1)

The coadsorption of zirconium and carbon monoxide on polycrystalline tungsten was briefly investigated to determine the role of crystal orientation. A 0.25-in. diameter polycrystalline tungsten sample was mechanically polished and electropolished and inserted into the surface characterization chamber. Heating to 1400 K produced a surface containing 37 percent carbon. This surface was exposed to CO and then zirconium and CO simultaneously and finally annealed at 1700 K (see Method 4 in Progress Report No. 46).

The resultant work function was 3.94 eV. Subsequent heatings in oxygen (10^{-7} torr, 2 min., $T_W = 1500$ K) followed by 2100 K vacuum anneals produced an interesting pattern (see Figure 1). Zirconium surprisingly appeared to readily diffuse in and out of the bulk polycrystalline tungsten, similar to bulk diffusion in W(100). Also, the zirconium and carbon appeared to move together, in contrast to the usual pattern of zirconium diffusing with oxygen on W(100). The large bulk carbon concentration may enhance formation of a Zr-C complex.

The work function after the 2100 K anneals was relatively insensitive to the carbon concentration, always staying in the range of 3.45 to 4.01 eV. After the last 2100 K anneal, two distinct peaks were evident in the FERP spectrum, indicating two different crystal faces with different work functions.

The sample was cleaned of bulk carbon by high temperature oxygen treatments. Subsequent simultaneous zirconium and carbon monoxide doses produced a minimum work function of 3.14 eV. Some nitrogen (8 - 11%) was present in these latter experiments. It may be possible to reduce the work function below 3.1 eV by elimination of the nitrogen and careful control of all elemental concentrations.

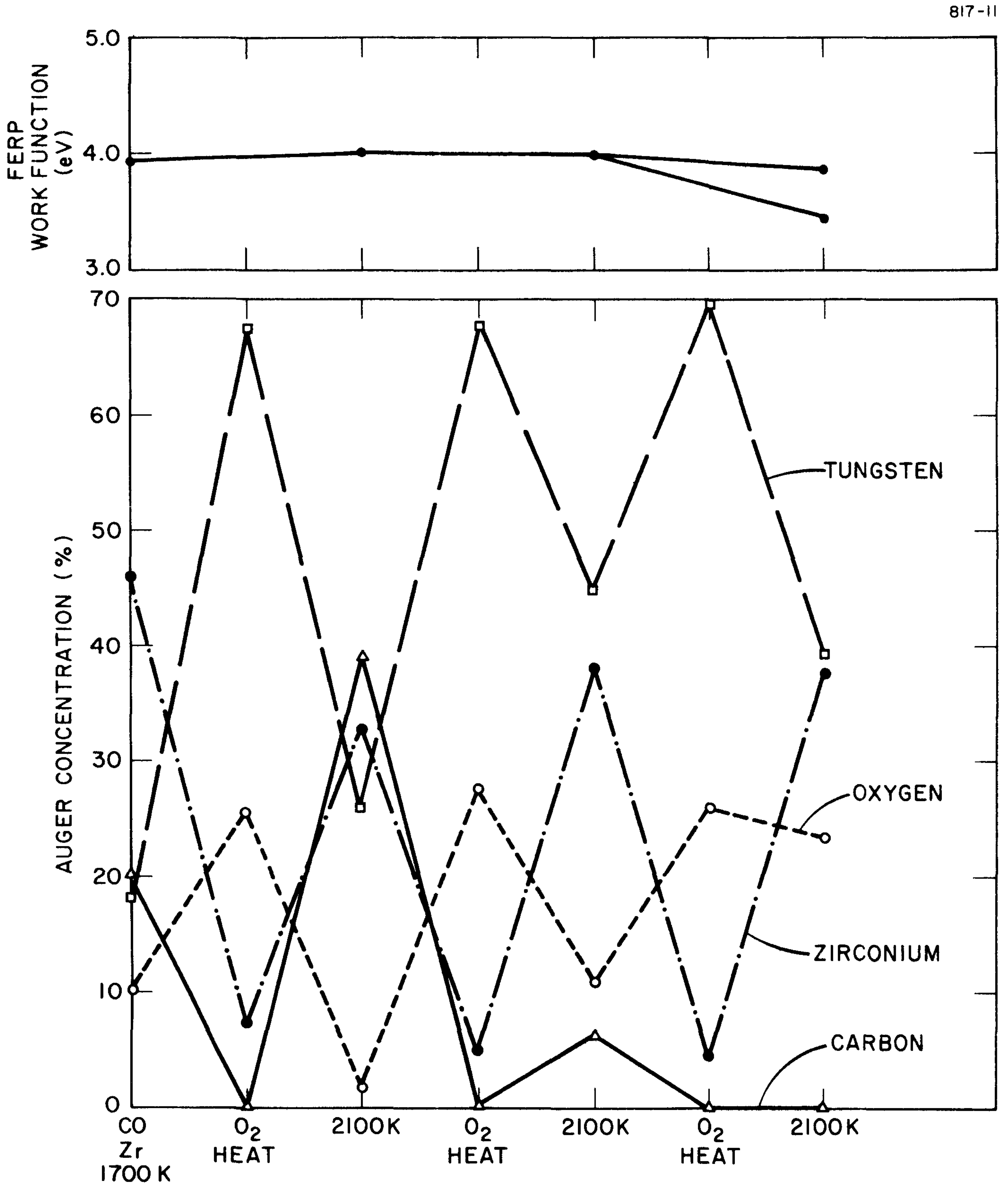


Figure 1. Auger Percent Concentration and FERP Work Function for Polycrystalline Tungsten after Various Treatments

B. Postoperational Diagnostics

Postoperational Auger analysis was performed for Converter No. 223 (molybdenum emitter, tungsten oxide collector). The purpose was to determine whether any tungsten oxides from the collector had evaporated onto the emitter. The percent concentrations for the emitter and collector as admitted and after sputtering are shown in Table I. No tungsten is present on the emitter, indicating that oxygen transport from the collector to the emitter via tungsten oxides is unlikely. However, a high concentration of molybdenum is present on the collector, indicating transport of molybdenum or molybdenum oxides from the emitter to the collector. The converter possessed a barrier index of 2.16 eV, even with this high concentration of molybdenum on the collector. After sputtering the collector, the tungsten substrate becomes partially evident, as expected.

A sample of molybdenum oxide as deposited and the molybdenum oxide collector of Converter No. 262 were sectioned, etched, and polished. These samples were sent to Photometrics for analysis of the Mo-Ni interface. For both samples, the molybdenum immediately

TABLE I

AUGER POSTOPERATIONAL ANALYSIS
CONVERTER NO. 223

ELEMENT	EMITTER (MOLY)		COLLECTOR (W_xO_y)	
	AS ADMITTED	SPUTTERED	AS ADMITTED	SPUTTERED
Mo	39.0	76.1	33.5	65.3
O	40.6	8.4	40.1	14.9
C	6.1	15.4	6.2	12.5
Cs	14.2	-	20.0	-
W	-	-	-	7.3

adjoining the nickel was deposited in the absence of intentionally added oxygen. A SEM picture (back-scattered mode) of the interface region for the as deposited sample is shown in Figure 2. Both the nickel and the molybdenum appear smooth with no granular structures. The molybdenum and nickel signals (Energy Dispersive Spectroscopy) along the indicated horizontal line are also shown in Figure 2. The interaction region where both metals are present is 2 to 3 μm wide.

SEM pictures and elemental concentration scans were also made for the collector of Converter No.262 in the interface region (see Figure 3). Cesium has remarkably penetrated through 4 to 5 mils of molybdenum/molybdenum oxide during the operating time of the converter (21 hours). Since no cesium is present in the nickel, we conclude that cesium can readily penetrate through molybdenum/molybdenum oxide but not through the nickel substrate.

Pronounced structure is present both in the molybdenum layer and in the interfacial region. The granules in the molybdenum layer (1 - 10 μm in diameter) are composed of molybdenum and cesium. Oxygen may be present in the granules so a MoO_3-Cs complex may be

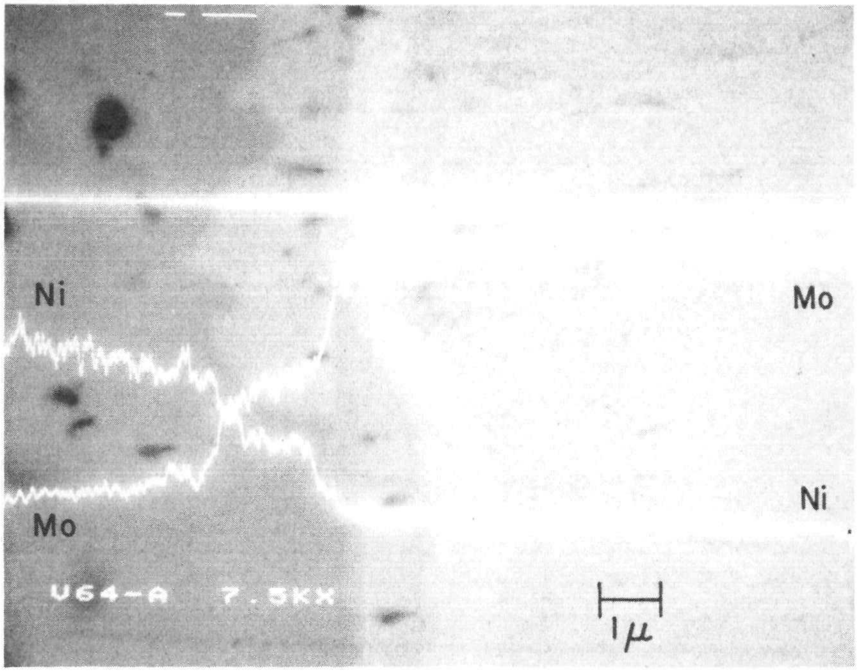


Figure 2. SEM and Microprobe Scans of Nickel-Moly Oxide Interface (As Deposited)

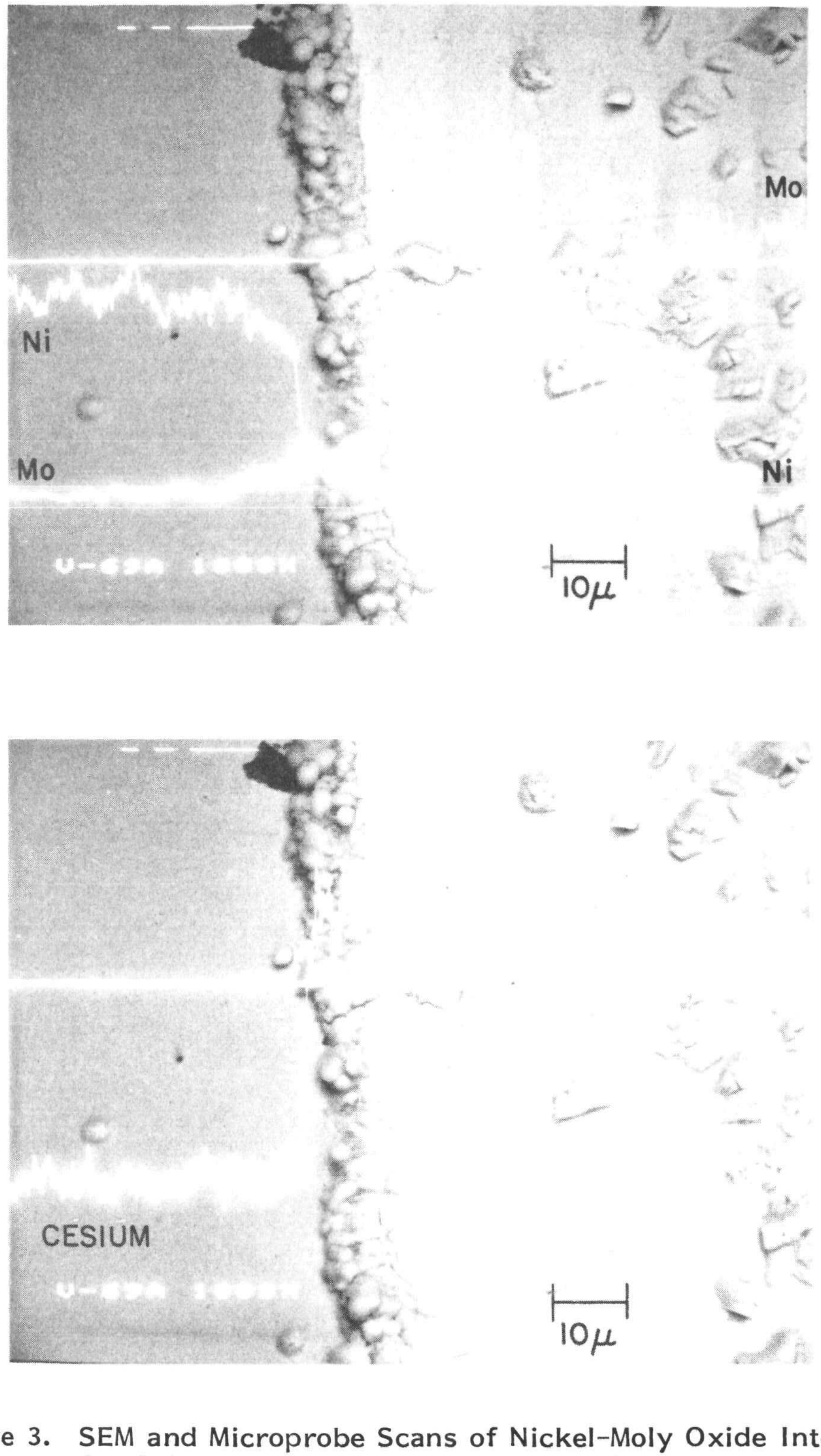


Figure 3. SEM and Microprobe Scans of Nickel-Moly Oxide Interface for Collector of Converter 262 After Operation

formed. The interfacial region contains only very small amounts of nickel and molybdenum and large amounts of cesium. This interaction region is 10μm wide, compared to 2 to 3 μm for the corresponding region for the as deposited molybdenum. Thus during converter operation, the cesium penetrates all the way to the nickel substrate, and this cesium interacts strongly with an unknown element (most likely oxygen) near and at the interface. This interfacial region is electrically conducting, since no voltage drop could be detected across it.

C. Converter No. 246: Tungsten Emitter, Nickel Collector, Heat Flux Diode

Initial current-voltage measurements showed a barrier index of 2.06 eV at T_E = 1700 K and J = 5 A/cm^2. The optimum collector temperature and cesium reservoir temperature at these conditions were 800 K and 577 K, respectively. The collector work function minimum was 1.54 eV at a T_C/T_R of 1.40 as measured by the retarding plot method. This output remained stable for the next 170 hours of operation. A subsequent retarding plot measurement gave a minimum collector work function of 1.74 eV. There was no corresponding increase in the barrier index at this time. The diode was subjected to an in situ leak check. No leak was found. After an additional 150 hours of stable operation, the barrier index increased to 2.30 eV. Again, the diode was leak checked, and a leak was identified. It is suspected that a small leak was initially present and perturbed the original work function measurement and that this condition deteriorated for the next 150 hours to the point where the effects were evident in the barrier index measurments.

The chronology of the measurements taken is given below.

Oct. 21, 1980	Retarding plot collector work function. Minimum $_c$ = 1.54 eV.
Feb. 19 & 20, 1981	Converter optimized at T_E = 1700 K. V_B = 2.06 eV at J = 5 A/cm^2.
Feb. 23 and March 13, 1981	Retarding plot collector work function. Minimum $_c$ = 1.74 eV. No increase in barrier index.
Feb. 23, 1981	In situ leak check - no leak identified.
April 1 - May 8, 1981	Heat flux measurements at T_E = 1700 K, T_R = 577 K, d = 0.25 mm and various T_C's.

June 24, 1981	Shift in barrier index to 2.30 eV.
June 26, 1981	In situ leak check - leak identified.

A collector heat flux measurement at T_E = 1700 K, T_C = 800 K, T_R = 577 K and d = 0.25 mm is shown in Figure 4. The slope of the straight line as determined by a least-squares linear regression fit is 2.07 eV. As can be seen from this figure, there is very little scatter in the data. This result is significant in that it is consistent with results obtained with a heat flux converter containing a nulling heater of a different design (for a discussion of the design changes, see Quarterly Report No. 42).

Heat flux measurements were taken over a range of collector temperatures from 700 to 900 K at T_E = 1700K, T_R = 577 K, and d = 0.25 mm. The results are shown in Figure 5. Also shown in this figure are the results obtained for the retarding plot collector work function.

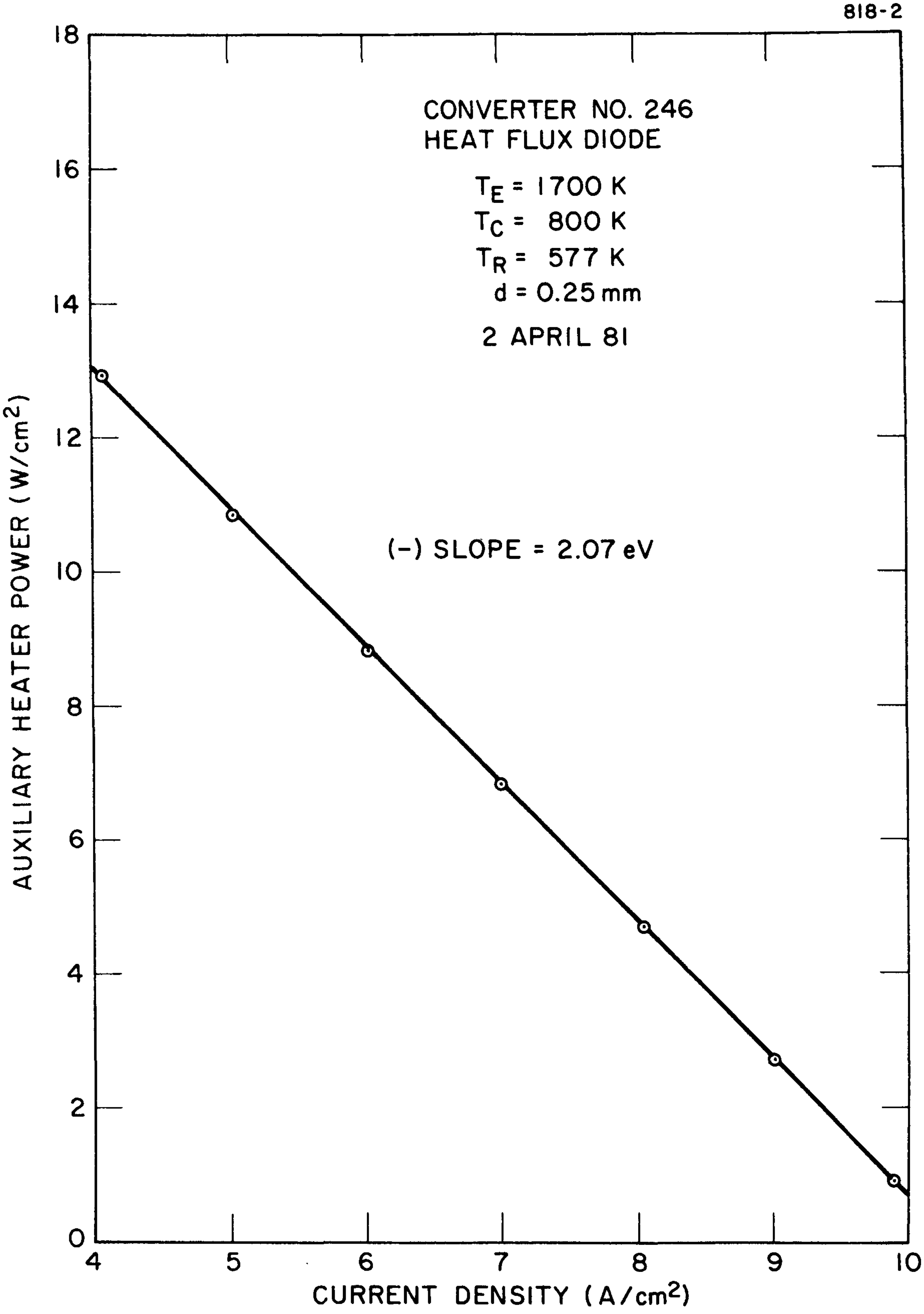


Figure 4. Collector Heat Flux Measurement of Converter No. 246 at $T_E = 1700$ K, $T_C = 800$ K, $T_R = 577$ K and d = 0.25 mm.

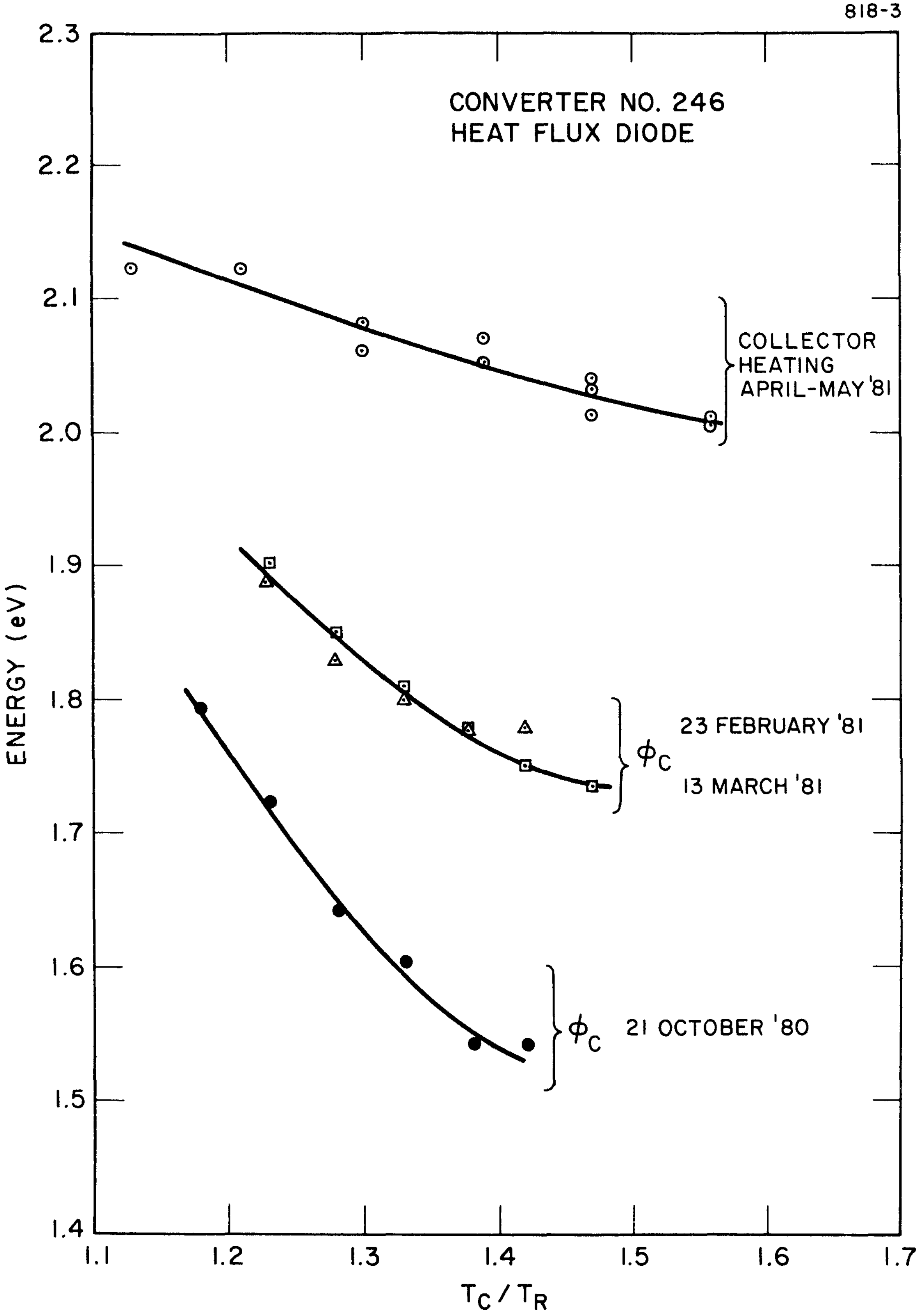


Figure 5. Collector Electron Heating and Collector Work Function Measurements Versus T_C/T_R for Converter No. 246.

D. Converter No. 262: Tungsten Emitter, Molybdenum Oxide Collector

Converter No. 262 contains electrodes that will be prototypic of future combustion heated converters. Molybdenum was sublimed in an oxygen atmosphere onto a nickel substrate. Previously, niobium was used as a substrate material. This collector contained 6730 ppm oxygen by weight. The emitter was as deposited CVD tungsten.

The performance history of this diode was typical of molybdenum oxide diodes. Initial performance was poor, the barrier index for the first ten hours of operation was 2.14 eV at T_E = 1650 K. Within the next ten hours, output improved to a barrier index of 2.02 eV at T_E = 1650 K. A cesium reservoir temperature family at T_E = 1650 K, T_C = 750 K and d = 1.0 mm is given in Figure 6.

After approximately 20 hours of operation, output degraded precipitously. The converter was taken off test and the cesium reservoir was pinched off. The diode was leak checked through the cesium tubulation. No leak was found. Additional postoperative diagnoses, directed at the molybdenum-nickel interface, were performed. The results are given in Section IB of this report.

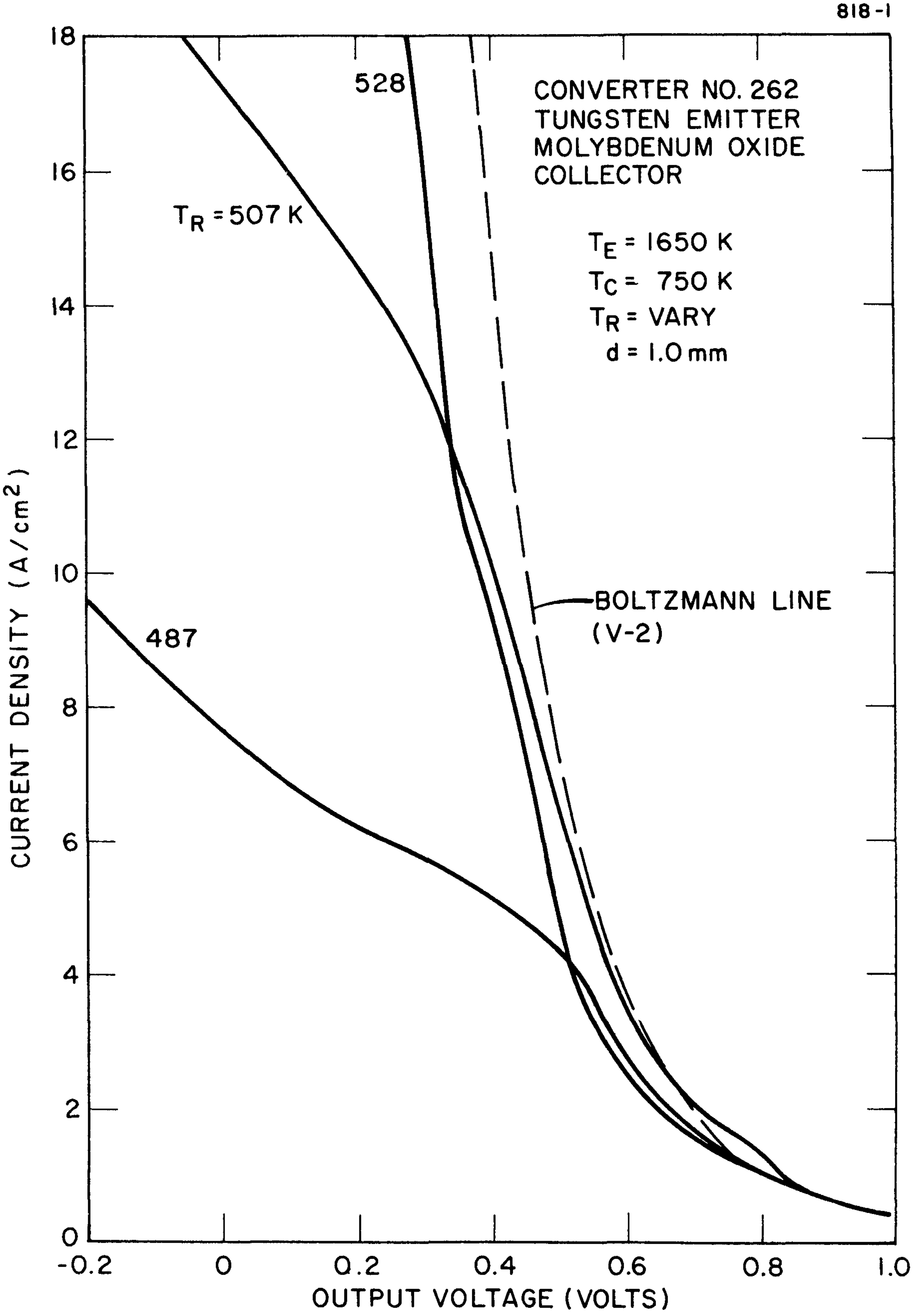


Figure 6. Cesium Reservoir Temperature Family of Converter No. 262 at T_E = 1650 K, T_C = 750 K and d = 1.00 mm.

II. COMBUSTION-HEATED CONVERTER DEVELOPMENT

The objective of this task is to develop flame-fired thermionic converters that are as prototypic of projected terrestrial applications as possible. These converters will be constructed with CVD hot shell-emitter structures and designed to minimize expensive materials and construction techniques.

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

This converter remained on life test during this reporting period and has accumulated 8580 hours. The performance has remained stable. At 1750 K the dc output is 6.6 A/cm^2 at 0.3 V. The test is continuing.

B. Converter No. 263: Two-Inch Diameter Torispherical Silicon Carbide Converter (CVD Tungsten as Deposited Emitter, Nickel Collector)

This converter was outgassed and cesiated prior to installation in the multi-converter furnace.

The converter was then tested at emitter temperatures of 1500, 1600, and 1650 K. The best barrier index (2.3 eV) was measured at current densities less than 2 A/cm^2. The slope of the I-V curve was such that the output power density was quite low. Several possible explanations for the poor performance are: 1) too great an interelectrode spacing, 2) uneven heating of the tungsten emitter, 3) delamination of the CVD trilayer structure, or 4) a series resistance in the output circuit (e.g., sleeve, contact resistance or flange-to-sleeve braze). Calculations and experiments indicate that the latter explanation is the most probable. X-rays of the assembled converter showed the cold electrode spacing to be as designed. The possiblity that the tungsten emitter was not as hot as expected was considered. A large temperature difference between the hot shell and emitter (100 K or more at T_E = 1650 K) would account for the poor performance. This possiblity was explored in a separate experiment in which a trilayer hot shell-emitter structure was heated in the gas furnace, and both the silicon carbide and tungsten temperatures were measured. The temperature difference between the two surfaces was never more than 30 K, which was not enough to explain the low output power. Experiments were also performed to test if only a portion of the emitter surface was active, by varying the direct current through the diode up to 300 amperes.

If only a small portion of the emitter were active, this area should be significantly cooler when the current is rapidly increased. However, no change in the temperature distribution was observed during several tests. Subsequently, the silicon carbide hot shell developed a crack which rapidly oxidized the graphite and tungsten layers.

C. Converter No. 266: Two-Inch Diameter Torisphericald Silicon Carbide Converter (CVD Tungsten as Deposite Emitter, Nickel Collector

The interelectrode spacing was measured by X-rays imediately after the last welding step. It was found to be as specified in the design and uniform over the entire dome. This converter has been outgassed using R-F induction heating, and the cesium has been distilled into the reservoir. During the next reporting period, the diode will be installed in the multi-converter furnace, and testing will begin.

III. SYSTEM STUDIES

The objective of this task is to identify and evaluate systems utilizing thermionic energy conversion to improve efficiency and reduce cost. Both powerplant and high-temperature cogeneration processes will be considered.

A draft report on thermionic topping of powerplants was prepared by Stone and Webster Engineering Corporation (SWEC). This draft was approved by Thermo Electron and returned to SWEC for printing.

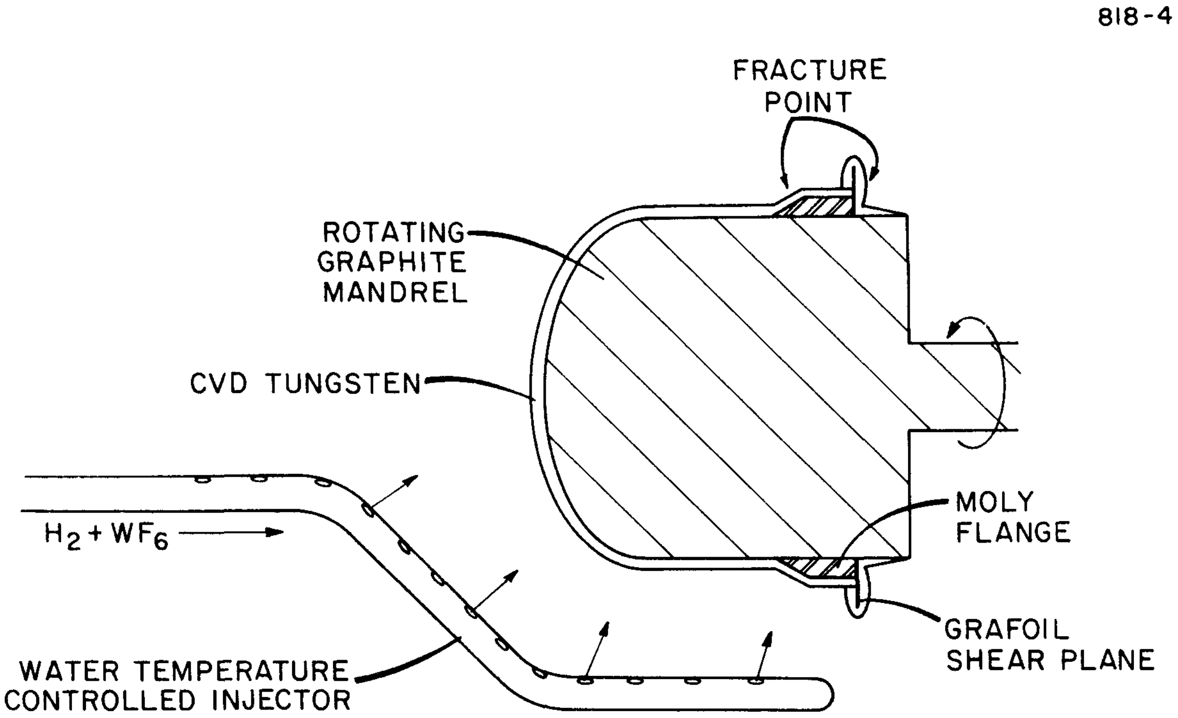
Stone and Webster Engineering Corporation (SWEC) has prepared a draft of a topical report on the application of thermionic topping to powerplants. This draft was reviewed and returned to SWEC.

IV. CONVERTER PRODUCTION ENGINEERING

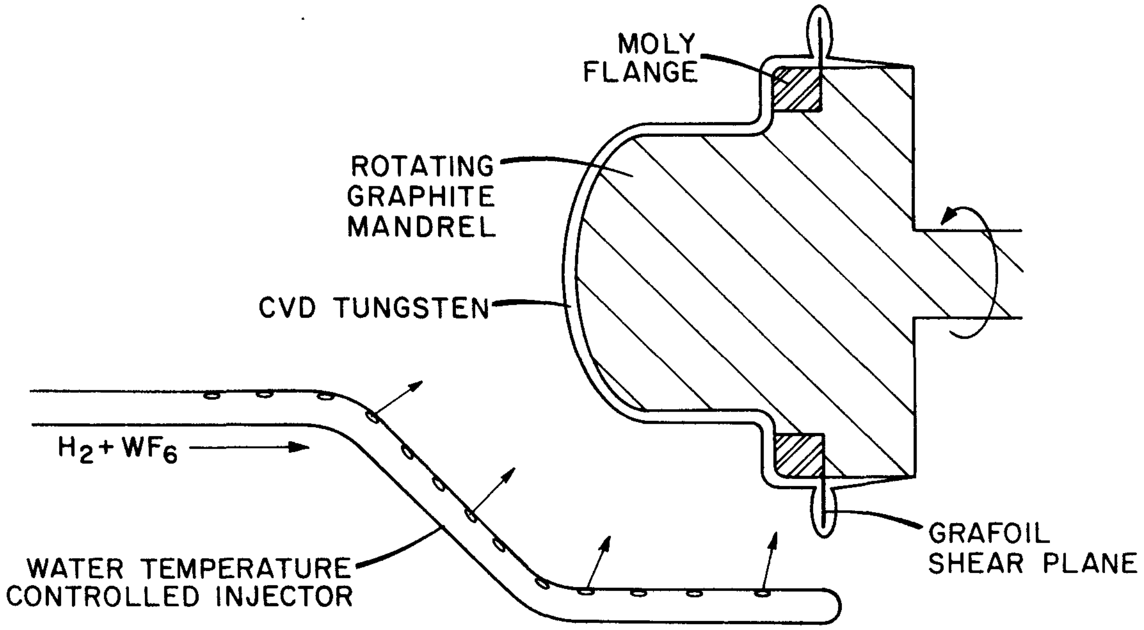
The objective of this task is to develop techniques suitable for high-volume production rates which will require automation of assembly and processing steps as well as a modified CVD fabrication method.

Tungsten has been successfully deposited onto a one-inch diameter molybdenum flange and removed from the graphite mandrel with the joint between the tungsten and molybdenum remaining leaktight. A cross section of the geometry of the CVD tungsten and molybdenum flange is shown in Figure 7A. The initial experiments had dimensions of one-inch in diameter by three-inches in length with a tungsten thickness of approximately 20 mils.

The second step was to apply a carbon coating over the CVD tungsten. A 5 mil thick coating of carbon was applied with a spray gun and baked in air for two hours. Without the carbon layer on the tungsten, the final deposit of silicon carbide did not adhere well to the tungsten-emitter structure. After thermal cycling in air or vacuum, the silicon carbide cracked and broke awav from the tungsten.



A. First Flange Geometry



B. Second Flange Geometry

Figure 7. Configuration for CVD Coating Tungsten onto Molybdenum Flange

The final coat of silicon carbide on the one-inch shell and flange was leaktight but the resulting structure was quite fragile. The entire trilayer structure would fracture at the area of the tungsten and molybdenum flange interface. Cross sections of the tungsten deposit showed a non-uniform thickness which resulted in fracture at an undersired position.

Subsequently, graphite mandrels were machined with a closer fit to the molybdenum flange. The dimensions of the mandrel were also increased to two inches in diameter and two inches long. The CVD tungsten shells produced were leaktight but extremely fragile at the flange interface. Also, 30 percent of the shells cracked during deposition along the flange interface.

In order to further reduce the gap between the flange and the graphite mandrel, the deposition geometry was redesigned as shown in Figure 7B. In this case, the step between the flange and the graphite was reduced even further. However, with the exception of two deposits, all the CVD tungsten shells cracked at the molybdenum interface. No further experiments are planned to CVD tungsten onto molybdenum flanges.

Scaled up CVD tungsten shells two-inches in diameter by two-inches long have been fabricated. The shells used shear planes made from either molybdenum or grafoil. Two of these shells were successfully coated with carbon and silicon carbide. They have been helium soaked leak tested successfully.

REFERENCES

1. L.R. Danielson, "The Zr-O-W(100) Emitter and Coadsorption of Zirconium and Carbon Monoxide on W(100)," J. Appl. Phys. Oct, 1981, accepted for publication.