ADVANCED THERMIONIC TECHNOLOGY PROGRAM
Summary Report

October 1984

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For
U. S. Department of Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

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Summary Report

**ADVANCED THERMIONIC
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Volume 2

October 1984

Prepared for:

**U.S. Department of Energy
Contract DOE-AC02-76ET11292**

Prepared by:

**Thermo Electron Corporation
Waltham, Massachusetts**

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PREFACE

This report summarizes the progress made by the Advanced Thermionic Technology Program during the past several years. This Program, sponsored by the U.S. Department of Energy, has had as its goal adapting thermionic devices to generate electricity in a terrestrial (i.e., combustion) environment. The technology has previously been developed for astronautical applications.

The report is organized in four volumes, each focused as much as possible on the needs of a particular audience. Volume 1 contains Part A, the Executive Summary. This Executive Summary describes the accomplishments of the Program in brief, but assumes the reader's familiarity with the thermionic process and the technical issues associated with the Program. For this reason, Volume 1 also contains Part B, a minimally technical overview of the Advanced Thermionic Technology Program. It is suggested that readers just being introduced to the Program review both portions of Volume 1 before consulting the more technical volumes which follow.

Volume 2 (Part C) concentrates on the progress made in developing and fabricating the "current generation" of chemical vapor deposited hot shell thermionic converters and is addressed to those primarily concerned with today's capabilities in terrestrial thermionic technology. Volume 3 (Part D) contains the results of systems studies of primary interest to those involved in identifying and evaluating applications for thermionics. Volume 4 (Part E) is a highly technical discussion of the attempts made by the Program to push

the state-of-the-art beyond the current generation of converters and is directed toward potential researchers engaged in this same task. These technical discussions are complemented with Appendices where appropriate.

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PART C

CHEMICAL VAPOR DEPOSITION (CVD)

HOT SHELL CONVERTER DEVELOPMENT

1. DESIGN EVOLUTION

1.1 Introduction

Although two major design approaches to integrating thermionic converters into fossil fuel power generation were developed during the Advanced Thermionic Technology Program, as described in Part B, Section 2, far more development work was done on the thermionic array module (TAM) design concept. This design consists of arrays of relatively small converters. Typically, a single TAM would have a total electrical output of about one-half megawatt. Individual converters in the array would more nearly approximate the size of diodes developed previously for astronautical applications [1, 2]. TAM systems for particular applications are discussed in Part D.

This development work resulted in continual and extensive design evolution. Central to each of the designs, however, was the concept that in terrestrial applications using fossil fuel, it was necessary to protect the converter from the flame environment by a "hot shell." Currently available converter performance necessitates emitter temperatures above 1700 K, and at these temperatures, the adequacy of hot shell lifetimes was unknown. Thus, a major objective of hot shell converter development during this Program was to construct and test diodes with hot shell materials which might achieve suitable lifetimes at high temperatures. Both ceramic and metal alloy materials were evaluated as potential hot shells in combustion atmospheres.

Preliminary screening studies for alloy materials in a simulated combustion atmosphere were conducted under subcontract to Thermo Electron by TRW, Inc. The most satisfactory alloy evaluated in the screening tests was Inconel 671, a super-alloy with a nominal composition of 52% nickel and 48% chromium. The most promising ceramic material was silicon carbide (SiC). Thermo Electron designed composite hot shell/emitters by chemical vapor deposition (CVD) of tungsten inside a graphite sleeve and CVD of silicon carbide outside. Fabrication methods for such a composite structure were extensively tested, and were eventually standardized as described in Part C, Section 2. However, at least in part because of the necessity of determining appropriate fabrication methods for the ceramic material, the initial designs within the Program focused on the super-alloy.

Several different configurations of combustion thermionic converters were designed and tested. Exhibit C-1.1 is a chart showing the converter genealogy. The configurations are discussed in greater detail in the remainder of this section.

1.2 Super-Alloy Hot Shells

The first configurations in Exhibit C-1.1 are super-alloy converters. The chief difference between the configurations is found in size and geometry, with later configurations being larger in diameter and having a non-planer, domed shell/emitter shape referred to as torispherical.

The planer configurations were intended for use in exploratory combustion tests with the understanding that they would not be prototype designs. Hot

EXHIBIT C-1.1
COMBUSTION CONVERTER GENEALOGY

<u>Hot Shell</u>	<u>Size</u>	<u>Geometry</u>	<u>Purpose of Modifications</u>	<u>Comments</u>
Inconel 671	1 inch dia.	Planar	N/A	Developed for exploratory combustion tests.
Inconel 671	2 inch dia.	Planar	Increased power	Operating life limited to about 2,000 hours at temperatures about 1400 K.
Inconel 671	2 inch dia.	Torispherical	Increased power; reduced thermal stress	Persistent metallization and seal cracking.
Inconel 671	2 inch dia.	Torispherical, modified seal	Improved operating life	Little prospect for operation at 1700 K.
CVD SiC	1 inch dia.	Hemispherical	Economical high temperature operation	Stable operation at 1730 K for 12,500 hours.
CVD SiC	2 inch dia.	Hemispherical, inboard seal	Increased packing density; increased power	Seal creep changed electrode spacing; emitter temperature inhomogeneous.
CVD SiC	2 inch dia., 2 inch sleeve	Torispherical	Reduced thermal stress; stabilize interelectrode spacing; improve temperature uniformity.	Temperature made uniform only when converters mounted well extended into furnace; stable interelectrode spacing.
CVD SiC	2 inch dia., 2 inch sleeve	Torispherical	Operation in industrial cogeneration application	Heat exchanger redesigned; oxide collector; heavy current leads.
CVD SiC	2 inch dia., 3 inch sleeve	Torispherical	Improve temperature uniformity	Temperature uniformity achieved; would probably be mounted extending further into furnace than most previous designs.

shell dimensions were determined by readily available Inconel 671 tubing and the shells were thus built in one-inch and two-inch inner diameter (2.54 and 5.08 cm) sizes. The effective areas of the converters were determined by the maximum size of the collector that could be inserted into the hot shell without short circuiting. Effective areas were 2.0 cm^2 for the one-inch size and up to 18 cm^2 for the two-inch size.

For converters utilizing alloy hot shells, it is advantageous to use the same material for the emitter as is used for the shell. At a minimum, if suitable converter performance is to be achieved, the thermal expansion of the emitter must match that of the hot shell. Potential emitter materials had been evaluated in electron bombardment-heated variable-spaced diodes [3] several years earlier, and Inconel 671 and L605 -- an alloy of 51% cobalt, 20% chromium, 15% tungsten, 10% nickel, 3% iron, and 1% manganese -- were found to be the preferred choices for use with an Inconel 671 hot shell. Since L605 produced a slightly higher output voltage, i.e., .1 Volts, at a given current than did the Inconel, and its thermal expansion coefficient was suitable, L605 was chosen for the emitter material. The collectors were made of nickel.

In order for the temperature drop through the collector structure to be minimized, a potassium-filled heat pipe was used in the collector stem of the one-inch converters. A cooling fin and/or an auxiliary heater could be clamped to the outboard end of the collector for diagnostic testing. Exhibit C-1.2 shows the one-inch design.

The general design of the two-inch planar devices is shown in Exhibit C-1.3. These converters were water-cooled, and the flexible ceramic-to-metal

Exhibit C-1.2

One-Inch Planar Design, Super-Alloy Hot Shell

Exhibit C-1.3
Two-Inch Planar Design, Super-Alloy Hot Shell

seal permitted incremental changes in emitter-collector separation by means of ceramic spacer blocks. The collector was readily accessible for instrumentation and for evaluating cooling options, although these latter features would prohibit packing of the converters as densely as would be necessary for a practical TAM. In one two-inch converter, an unbonded alumina tube was used to provide mechanical support to the hot shell/emitter assembly. The reduced mechanical stresses permitted this device to be tested at a 50 K higher temperature than would otherwise have been the case.

Successful operation with these planar devices was demonstrated. One converter was operated for ten hours at an emitter temperature of 1500 K and then 1200 hours before failure at 1400 K. As expected, deformation of the hot shell was evident after ten hours at 1500 K. However, there were no apparent dimensional changes during exposure to 1400 K. The test was terminated by a failure on the cold side of the ceramic seal.

The converter with the alumina support was tested at temperatures up to 1450 K for 2000 hours. Performance degraded after fifty hours of operation due to a fabrication flaw (i.e., a leaky pinchoff) but remained stable at the degraded level of performance after repairs were completed. Intermittent shorts, apparently because of metallization of the sides of the alumina support, were observed after 1475 hours.

Thus, in general, the planar super-alloy designs showed themselves to be capable of reliable operation for around 2000 hours at emitter temperatures around 1450 K. Power densities achieved were about one Watt per square centimeter. The tests, furthermore, did establish that the performance of

combustion-heated thermionic diodes correlated well with that of electron bombardment-heated diodes at the same operating parameters.

In particular, the absence of any apparent problem due to hydrogen diffusion was extremely encouraging. It had been feared that hydrogen from the combustion environment would diffuse through the hot shell structure and destroy the electrode properties required for efficient thermionic energy conversion. Since Inconel 671 is quite permeable to hydrogen at the emitter temperatures at which the diodes operated, the tests established that the effect of hydrogen on converter performance was benign.

In order to moderate thermally induced stresses -- permitting operation at higher temperatures for increased efficiency -- and in order to increase the effective surface area of a TAM of given size, the planar design was replaced by a torispherical design, as shown in Exhibit C-1.4. The hot shell/emitter assembly was hydroformed from Inconel 671. The interelectrode spacing was fixed at .7 mm, based on a design temperature of 1450 K. A potassium heat pipe would transport heat from the collector to an air-cooled heat exchanger. The diode was two inches in diameter.

This design was flame tested for 432 hours. The output of the converter was low, i.e., .25 Watts/cm², because of metallization of the sides of the emitter-collector insulator, which constituted a parasitic load. Testing was concluded when the converter developed a leak because of a cracked ceramic in the seal.

Exhibit C-1.4
Initial Torispherical Design, Super-Alloy Hot Shell

Because of the persistent problems with metallization and seal cracking the torispherical design was further modified as shown in Exhibit C-1.5. The primary modification was in the ceramic-to-metal seal geometry. The metal flanges mating to the ceramic were made thinner to minimize the stress from differential thermal expansion. A radiation shield was added to protect the ceramic-to-metal seal from excessive temperature and deposition of metal vapor.

Despite these modifications there appeared to be little immediate prospect for super-alloy hot shells which could operate with acceptable lifetimes at the 1700 K temperatures believed necessary for economical deployment. There existed the long term hope for devising converter designs operating more efficiently at lower temperatures, as discussed in Part E; however, adequate progress in this direction was not close at hand. Consequently, since fabrication problems for silicon carbide hot shells were being successfully addressed, as described in Part C, Section 2, Program emphasis switched to ceramic designs.

1.3 CVD Hot Shells

The initial efforts to build converters with composite hot-shell emitters focused on a one-inch diameter hemispherical design. A cut-away sketch of a one-inch SiC hot shell converter is shown in Exhibit C-1.6. The shell was one inch (25 mm) in diameter by four inches (102 mm) long. The shell was brazed to a molybdenum flange which was in turn brazed to a ceramic and metal seal. The size and shape of the hot shell was selected to make construction and operation of the early converters as easy as possible. The small active emitter

Exhibit C-1.5

Modified Torispherical Design, Super-Alloy Hot Shell

Exhibit C-1.6
One-Inch Hemispherical Design, CVD Hot Shell

area, 6 cm^2 , kept the total current low. The long emitter sleeve (76 mm) kept the flange and flange-to-hot-shell braze well away from the combustion temperatures. The collector was made from nickel and was cooled by passing air over a finned heat exchanger. The final vacuum seal was made by welding the metal-ceramic seal to the collector body. The cold spacing was adjusted to give an interelectrode gap of .25 mm at an emitter temperature of 1650 K and a collector temperature of 900 K.

Fifteen one-inch converters were built and tested during the Program, and more than 30,000 hours of operating time were accumulated. The converters were tested at emitter temperatures between 1400 and 1850 K, and a typical operating temperature was 1700 K. This represented an obvious and major advance in flame-fired thermionic converter capabilities, given that output power is so strongly dependent on emitter temperature. A typical diode had a power density of 4 Watts/cm^2 when measured at 1800 K.

As described in Part B, Section 1, the "barrier index" is a convenient parameter for characterizing thermionic converter performance at any given temperature. Operationally, it is defined as the minimum difference between the Boltzmann line (which gives ideal converter performance) and the measured current-voltage characteristic. Reductions in the barrier index can be translated into either higher efficiency at a given emitter temperature or the same efficiency at a lower temperature. Typically, state-of-the-art thermionic converters had barrier indices ranging around 2.1 eV.

The typical barrier index for the one-inch hemispherical CVD hot shell converter was 2.1 to 2.2 eV, i.e., close to that state-of-the-art. Exhibits

C-1.7 and C-1.8 show current density-voltage curves for an early one-inch converter at emitter temperatures of 1625 K and 1800 K, respectively.

An additional significant advance was achieved in terms of converter life-time during these tests; a converter was operated successfully at 1730 K for 12,500 hours, an increase of more than six-fold over what had been previously demonstrated with super-alloy hot shells. The testing of this converter, which was completed in fiscal year 1982, is discussed in greater detail in Part C, Section 4, since this converter represents the current operating state-of-the-art in several respects.

In order to increase converter power output and packing density relative to the one-inch design, a two-inch hemispherical design was next adopted, as shown in Exhibit C-1.9. The emitter area was 25 cm^2 and the ceramic insulator and the emitter flange were contained almost entirely within the emitter diameter, permitting the increased packing density sought.

Several oxidation problems encountered initially with the one-inch diameter converters were also rectified by this design. The copper pinch-off tube was replaced with a nickel tube that was sealed off by an electron beam welder. In addition, the copper braze bonding the hot shell/emitter structure to the molybdenum flange was protected from oxidation by a thin nickel plating and then by coating of the region with a suspension of silicon carbide.

Two problems with this converter design became apparent during performance evaluation. First, the temperature over the active area of the emitter varied by as much as 70 K from the tip of the hemisphere to the outer edge. Secondly,

Exhibit C-1.7

Current Density-Voltage Characteristic for an
Emitter Temperature of 1625 K in a One-Inch
Hemispherical Hot Shell Converter

Exhibit C-1.8

Current Density-Voltage Characteristic for an
Emitter Temperature of 1800 K in a One-Inch
Hemispherical Hot Shell Converter

Exhibit C-1.9

Two-Inch Hemispherical Design, CVD Hot Shell

the spacing between emitter and collector was not stable because of creep in the thin wall nickel section of the ceramic-to-metal seal. Since converter performance optimization depends on electrode temperature and spacing, the design was changed to torispherical in an attempt to rectify these difficulties.

The domed shape of a torispherical hot shell is intermediate between a planar geometry and a full hemispherical dome. Thus, this shape had a better "view factor" to the combustion gases (i.e., the gases impinged upon it more uniformly) and was expected to provide a more uniform emitter temperature than the hemispherical design. The torispherical shape would also result in a somewhat lower thermal stress level. A ceramic spacer was incorporated into the design to provide positive control of the interelectrode spacing. In addition, the length of the hot shell/emitter structure was decreased to two inches in order to minimize material costs and allow the converters to be more compactly arrayed. The active emitter area was 20 cm^2 . The collector was made from nickel and cooled by air flowing across a finned nickel heat exchanger. The cesium vapor could be supplied either by a conventional liquid cesium reservoir or a cesium-graphite reservoir. Exhibit C-1.10 is a cutaway sketch of the two-inch torispherical converter.

A variation of this basic design was also developed for use in an industrial cogeneration application [4], in which the device would be used in an array of six to eight converters connected in series. The variation's modifications included a heavy collector current lead, a combination emitter lead and air plenum, and a more efficient and simpler collector heat exchanger. A cutaway sketch of the cogeneration converter is shown in Exhibit C-1.11.

Exhibit C-1.10

Two-Inch Torispherical Design, CVD Hot Shell

Two-Inch Torispherical Design, CVD Hot Shell

Heavy interconnecting leads were also developed for this converter but were not an integral part of the device.

Although this basic design did solve the problem of controlling inter-electrode spacing, the expected improvement in emitter temperature uniformity was not realized. Performance appeared to reflect a temperature variation from 1700 K at the tip of the dome to 1600 K at the edge of the dome. Subsequent consideration suggested that the inhomogeneity could be due to conductivity losses down the emitter lead and down the hot shell to the collector flange rather than due to non-uniform exposure to the combustion gases.

When the converter was mounted extending further into the furnace so that the region of greatest thermal gradient was shifted farther from the dome (i.e., down the sleeve), emitter temperature uniformity improved. Although this solution was viable for a single converter, it would not be suitable for densely packed arrays.

Consequently, an attempt was made to achieve greater temperature uniformity by reducing heat conduction through decreasing the emitter and hot shell substrate (i.e., graphite) thickness. However, these hot shell structures often developed leaks during fabrication due to the thinner graphite, and this approach was abandoned.

In view of this, it appeared that the most practical design revisions were to retain the previous thickness of graphite, restore the hot shell length to three inches -- accepting the extra material requirements -- and reduce the thickness of the emitter lead as much as practical. It would be expected that

the longer hot shell would also be used in future cogeneration designs analogous to Exhibit C-1.11.

A converter built with these modifications was successfully tested at emitter temperatures up to 1700 K. The emitter temperature was uniform to within 5 degrees. The performance of the converter was excellent with a barrier index of 2.1 eV. The power output at 1650 K was 2.5 Watts/cm² at .4 Volts. A typical current density versus voltage (i.e., J-V) curve for this converter is shown in Exhibit C-1.12.

Exhibit C-1.12

Current Density-Voltage Characteristic for an
Optimized Two-Inch Torispherical Converter Design
Modified for Emitter Temperature Uniformity

SECTION 1 - REFERENCES

1. Huffman, F.N., Gunther, B., and Miskolczy, G., "Characteristics of Combustion-Heated Thermionic Diode," Proceedings 13th Intersociety Energy Conversion Engineering Conference (1978).
2. Huffman, F.N., Gunther, B., and Miskolczy, G., "Flame-Fired Thermionic Diode Development," Proceedings 14th Intersociety Energy Conversion Engineering Conference (1979).
3. Rufeh, F., Sommer, A.H., and Huffman, F.N., "Electrodes for Thermionic Energy Conversion," Proceedings 10th Intersociety Energy Conversion Engineering Conference (1975).
4. Thermo Electron, "Thermionic Cogeneration Burner Module," 4th Quarterly Technical Report, TE4317-215-83 (1983).

2. CONVERTER FABRICATION

2.1 Chemical Vapor Deposition

Three chemical vapor deposition (CVD) reactors were designed and constructed during the Program in order to fabricate composite ceramic hot shells. Tungsten or molybdenum could each be deposited in two of the reactors, while silicon carbide and carbon were deposited in the third.

The underlying chemistry for deposition of such materials is straightforward. The surface to be coated is placed in an enclosed area and maintained at a high temperature. Suitable gases containing the elements to be deposited are then introduced into the chamber. These gases are chosen such that at high temperatures a chemical reaction will occur freeing the material to be deposited as a solid and leaving all other chemical species in gaseous form. For deposition of tungsten or molybdenum, a tungsten- or molybdenum-hexafluoride and hydrogen mixture provides suitable reactants, the chemical equations being, respectively:

For deposition of silicon carbide, a liquid, methyltrichlorosilane (MTS), is decomposed in a carrier stream of hydrogen, although smaller amounts of free carbon and silicon are also deposited from subsequent disassociation of the SiC:

However, while the chemistry may be straightforward, engineering considerations are not. Achievement of uniform deposits of suitable thickness for optimal converter performance and acceptable reliability was critically dependent upon the geometry of reactor design and the procedures for reactor operation. For example, the spacing between the gas injector and the substrate, as well as the design of the injector opening affected the structure and thickness profile of the tungsten deposits.

Similarly, for silicon carbide, the temperature of the substrate -- a graphite shell -- was the most critical and most difficult parameter to control. In early tests, the temperature profile of the graphite shell prior to the start of the deposition showed that the hemispherical nose was 60 to 80 K colder than the base, inhibiting deposition at the former location. Attempts to obtain a more even temperature profile from the dome to base by changing the coil configuration used for radio frequency (RF) heating were not successful.

Consequently, five silicon carbide chamber designs were built and compared in order to achieve a uniform temperature from the dome to the open end of the graphite shell. These five designs are illustrated in Exhibit C-2.1. Exhibit C-2.2 presents a comparative evaluation of these designs. Only two of these, the RF concentrator and venturi chamber, allowed the RF power to be adequately concentrated onto the dome of the graphite shell and resulted in a uniform temperature profile while also supplying adequate power. Silicon carbide deposits made with these two furnace designs produced leaktight silicon carbide hot shells.

A
STANDARD SIC CHAMBER

B
GRAPHITE RADIATOR

C
HOT WALL CHAMBER

D
VENTURI CHAMBER

E
R.F. CONCENTRATOR

Exhibit C-2.1
SiC Chamber Designs for Uniform Substrate Temperature

EXHIBIT C-2.2

UNIFORM SUBSTRATE TEMPERATURE CHAMBER DESIGN EVALUATION

<u>DESIGN</u>	<u>TEMPERATURE PROFILE</u>	<u>SILICON CARBIDE CVD RESULTS</u>
Standard Chamber	1250 $\pm$ 40 K Dome 60 - 80 K Colder Than Base of Graphite Shell	Black-Shiny Deposit on Hemispherical End
Graphite Radiator	1250 $\pm$ 30 K Dome 40 - 60 K Colder Than Base of Graphite Shell	Dome Deposit Very Thin Not Leaktight
Hot Wall Chamber	1100 $\pm$ 10 K Uniform Temperature	Inadequate RF Power Available for Deposition Temperatures of 1250 K
Venturi Chamber	1250 $\pm$ 10 K Uniform Temperature	Thick Deposition at Dome Leaktight Shell
RF Concentrator	1250 $\pm$ 10 K Uniform Temperature	Uniform Deposition Thickness Leaktight Shell

There was a significant difference between these two designs in terms of cost and reliability. Since the venturi chamber was fragile and expensive, the RF concentrator design was used to deposit silicon carbide. The concentrator design was also easy to scale up to larger diameter hot shells.

Exhibits C-2.3 and C-2.4 present simplified schematics of the tungsten reactors and silicon carbide reactor, respectively. All three reaction vessels were mounted horizontally and allowed rotation of the substrate to be coated. All were equipped with a hood for safety precautions in view of the gases used in the CVD processes; all exhaust gases were pumped through a scrubbing trap before venting to the atmosphere. All input valves were weldable stainless steel with bellows, and all input lines were made from quarter-inch stainless steel tubing. All reactors were designed to produce pressures below 100 millitorr.

The two tungsten or molybdenum reactors employed resistance-heated hot wall furnaces, utilizing a monel cylinder sealed with stainless steel end flanges as the deposition chamber. The smaller reactor could coat surfaces up to two inches in diameter by four inches long. The larger reactor allowed surfaces up to four inches in diameter by twenty inches long. The maximum deposition temperature in the smaller reactor was 1100 K, while the larger reactor had three independent temperature zones with a maximum temperature of 1300 K. The smaller reactor utilized rotometers to control the gas flow, while the longer reactor used more precise mass flow meters.

The substrate mounts were graphite, and shims of Grafoil -- a thin paper-like form of graphite manufactured by Union Carbide Corporation -- were used as necessary to mount the substrate snugly.

Exhibit C-2.3
Simplified Schematic of a CVD Reactor for Deposition of Tungsten or Molybdenum

Exhibit C-2.4
Schematic Diagram of CVD Silicon Carbide Reactor

The temperature of the substrate was monitored by a thermocouple located in a Monel shaft supporting the mount. In order to avoid premature reaction, the input lines and gas injector must be kept at a much lower temperature than the substrate. To properly control the reaction, the temperature in these areas must also be known and stable. Thus, these portions of the system were maintained between 310 and 330 K by heating tape applied to the input lines and a water jacket for the gas injector. The temperature of the hydrogen fluoride (HF) traps was maintained by a liquid nitrogen bath. A heating system was also available for the traps during system purging.

The pressure in the injector line and the furnace was monitored by Wallace Tiernan pressure gauges. The injector gauge range was 0-200 torr. The furnace gauge range was 0-800 torr. The pressure was controlled by the flow rate and by a throttling valve.

Flows were monitored and controlled by Tylan mass flow controllers. The WF_6 controller's range was .010 to .500 liters/minute and the H_2 controller's range was .010 to 5.0 liters/minute. The exhaust line was made from one-inch stainless steel tubing with one-inch ball valves packed with Teflon.

The Monel shaft rotated the substrate at approximately 20 rpm; the shaft could also be adjusted horizontally to position the substrate. The gas injector was normally positioned on the inside of the graphite substrate approximately one-half inch from the nose; the position of the injector could also be adjusted by moving it horizontally within a Cajon fitting on the end flange.

The silicon carbide reactor was a cold wall design, i.e., RF induction heated the substrate. Various diameter quartz cylinders from 30 mm to 110 mm

in diameter could be used in this furnace, and Vycor, a General Electric trade name for recrystallized quartz, was most commonly employed. The cylinders, which remained at a reduced temperature, contained the reaction gases and allowed temperature monitoring of the substrate with a Leeds and Northrup pyrometer. End flanges were made of stainless steel.

The amount of MTS carried into the furnace was originally controlled by monitoring the temperature of the MTS reservoir. This was accomplished by designing an MTS retort with a water jacket such that water could be circulated at a controlled temperature. Hydrogen flows to the MTS retort and chamber were originally controlled by rotometers. Later, Tylan mass flow controllers were installed to improve the repeatability of the deposition parameters from run to run. The H_2 controller's range (i.e., on the line used for system purges) was .010 to 5.0 liters/minute. The H_2 range on the line connecting the hydrogen carrier stream to the MTS chamber was .010 to 8.0 liters/minute. The MTS controller range was from .010 to 5.0 grams/minute.

The exhaust line was made of one-half-inch stainless steel tubing with ball valves packed with Teflon. Sodium hydroxide was used in a scrubbing trap for the hydrogen chloride exhaust gases.

The substrates, i.e., graphite shells already coated with emitter material on their interior surfaces, had their open ends covered with Grafoil washers to prevent any overcoating by silicion carbide and were tightly mounted on graphite holders such that no slippage could be observed with the shell held nose-down. The graphite holder was attached to a quarter-inch stainless steel rod held by the end exhaust flange. The position of the holder could be adjusted by the

Cajon fitting on the exhaust flange. The hold and shaft were rotated during the SiC deposition at approximately 20 rpm.

The graphite RF concentrator was positioned approximately one-half inch in front of the shell. It was attached and could be positioned by the Cajon fitting on the input flange.

2.2. Hot Shell/Emitter Fabrication Procedures

Procedures for the fabrication of the composite hot shell/emitter structures were standardized. These standardized procedures are described in the paragraphs which follow.

Shells were machined from blocks of graphite (i.e., either Stackpole 2128 or Poco PCL-1) on a tracer lathe without oil in order to maintain tolerances and reproducibility of the shells. A dial indicator was used to measure and record a profile of the machined thickness for both the nose and open end of the shells. The machined graphite had a wall thickness of 1 mm (.040 inches) over its entire length. The shells were cleaned by blowing with compressed air to remove loose graphite powder. A molybdenum shear plane was then attached to the base of the shell (see Part C, Section 2.3).

The shell was then mounted in the deposition reactor, as described in Part C, Section 2.1 above, for coating of the interior with tungsten, or, in some cases, molybdenum. During reactor operation, a number of operating parameters were recorded:

- o Temperature
 - furnace
 - inflowing injector cooling water
 - outflowing injector cooling water
 - WF_6 bottle
 - WF_6 line
 - WF_6 mass flow meter
- o Pressure
 - injector gas flow (i.e., at point immediately before injector head)
 - furnace
 - water cooling line
- o Gas Flow Rates
 - H_2
 - WF_6
 - N_2 (i.e., purge line)
- o Power
 - furnace power supply potential (volts)
 - furnace power supply current (amperes)
 - input gas line heating tape potential (volts)
 - WF_6 bottle heating tape potential (volts)
 - liquid N_2 trap heating tape potential (volts)

Unrecognized changes in any of these parameters could result in a loss of reactor performance.

The reactor pressure was first reduced to operating vacuum, i.e., below 100 millitorr. With the throttle valve wide open, hydrogen was allowed into

the chamber through the injector at a rate of three liters/minute. After the system pressure had stabilized for five minutes, and the pressure in the injector and the furnace had been recorded, the power to the heating tapes for the WF_6 bottle and the gas lines was turned on. As mentioned previously, these portions of the system were maintained between 310 and 330 K. Cooling water for the injector and flange was then turned on.

Power was next supplied to the furnace itself and adjusted as necessary to maintain the furnace temperature at a stable 1020 K. This normally required one to two hours. After furnace stability had been achieved for thirty minutes, the liquid nitrogen cold traps were filled. These traps were replenished as necessary throughout the coating process.

Such a thirty-minute period of stability was considered a minimum operating standard for the system before deposition could begin, and all parameters were required to remain stable throughout the deposition period. Upon first injection of the WF_6 into the furnace, system pressure and temperature, of course, changed to new equilibrium values. Changes in pressure in both the injector and furnace were recorded.

WF_6 was injected into the chamber at .300 liters/minute, resulting in a deposition rate for tungsten of about .010 inches/hour. Deposition time then depended on the desired coating thickness, but was typically two hours for production of a .020 inch shell.

After the deposition period ended, the WF_6 tank was isolated from the system. After an additional five minutes to clear any unreacted WF_6 from the

system, the mass flow controller indicator was recorded to document isolation of the WF_6 tank, and furnace and injector pressures were checked to insure that they had returned to their recorded values prior to introduction of the WF_6 into the chamber, i.e., that operation had remained stable. The WF_6 flow meter was then purged with H_2 for fifteen minutes by opening the purge valve between the tank of WF_6 and the mass flow controller.

Furnace power was turned off, the H_2 valves were closed, and the furnace and cold traps were isolated. The furnace remained under vacuum during the approximately two to three hours required to cool to ambient temperature. After cooling, the injector and flange were removed and cleaned with water and steel wool.

While the furnace cooled, liquid nitrogen was salvaged from the cold traps. These traps were kept isolated from the pump and the furnace and allowed to warm. After approximately fifteen minutes, the traps were purged with nitrogen for another fifteen minutes. The traps were heated during this time. Following the nitrogen purge, the traps were then purged with hot water. Water and hydrogen fluoride were collected in five gallon plastic beakers and neutralized with sodium hydroxide. After fifteen gallons of purge water had been collected, the nitrogen purge was resumed and continued overnight.

After the furnace cooled, the coated shell was removed for inspection. The inner surface of an acceptable shell would be smooth (e.g., free of any nodules), uniformly shiny, and free of any discoloration. Any bluish color could indicate that a water leak had been present.

The open end of the shell was polished with 120 or 240 grit SiC paper until a smooth, continuous surface appeared on the end as well. The polished end surface was necessary for making a vacuum tight seal for subsequent leak checking. Care was taken to avoid unnecessary polishing; if the tungsten surface was broken and the graphite substrate exposed; the shell would be worthless. It could never be completely sealed unless a second coating of tungsten was applied.

A soft rubber gasket, without vacuum grease, was placed on the open end of the shell, and the shell's seal was checked with a commercial helium leak detector. An acceptable shell would show no helium leaks at the most sensitive scale.

The thickness profile of the shells was again recorded with a dial indicator mounted on a pedestal for measurements of the inside nose. Using the earlier measurements of the uncoated shell, the thickness of the tungsten deposit could be determined and recorded. The tungsten thickness profile was typically $.5 \pm .1$ mm ($.020 \pm .004$ inches) over the inside of the shell. However, this degree of uniformity could only be measured to the accuracy with which the dial indicator could measure a cross section of the shell.

The shells were then ready for SiC deposition. The shell was mounted in the SiC reactor as described above in Part C, Section 2.1. During reactor operation, the following parameters were recorded:

- o Temperature
 - center of shell nose
 - side of shell nose

- open cylindrical end at two different locations
- o Position
 - RF coil
 - RF concentrator
 - shell
- o Pressure
 - input line
 - exhaust line
- o Gas Flow Rates
 - H_2 byflow (i.e., direct to chamber)
 - H_2 to MTS (i.e., carrier stream)
 - MTS
- o Power Supply
 - potential (volts), current (amperes), and power (watts)

To prepare for deposition, the furnace was first evacuated and then back-filled to atmospheric pressure with hydrogen. The valve to the pump was closed, and the valve to the sodium hydroxide scrubber was opened. Hydrogen was allowed to flow into the scrubber at a rate of three liters/minute for fifteen minutes. The MTS piping was also purged with hydrogen at a rate of one to two liters/minute for 15-30 minutes. During this time care was taken to maintain input pressure at one atmosphere; higher pressures were grounds for terminating the run by shutting off the hydrogen and isolating the furnace.

The RF generator was then turned on and used to heat the shell to 1490 ± 10 K. The temperature of the nose of the shell could be controlled relative to the rest of the shell by adjusting the distance between the concentrator and the shell, i.e., the smaller the distance, the hotter the nose. When the

temperature of the nose and shell had been stable for fifteen minutes, deposition could start.

To begin deposition, the valve connecting the MTS supply to the chamber was opened and the hydrogen carrier stream was permitted to bubble into the MTS. The MTS "pick-up" was controlled by a Tylan mass flow controller; the flow rate was allowed to stabilize at 2.0 grams/minute of MTS. Formation of a light coating of white powder near the exhaust was normal during the first few minutes of deposition.

Deposition typically continued for ninety minutes. The run was terminated by stopping the flow of hydrogen into the MTS and isolating the MTS from the furnace. The MTS lines were then purged with hydrogen for fifteen minutes. Next, with hydrogen still flowing into the furnace, RF power was turned off and the shell was allowed to cool. Only when the shell had reached room temperature was the hydrogen turned off and the shell removed from the furnace.

The final steps in hot shell fabrication involved leak testing and measuring the SiC thickness prior to assembly with the emitter flange. These steps are discussed in detail in Part C, Section 2.4. The silicon carbide deposit was usually $.5 \pm .1$ mm ($.020 \pm .004$ inches) thick at the domed end of the shell. The thinnest section, typically .15 mm (.006 inches), was at the open end. Deposit thickness depended somewhat on the geometry of the shell.

Exhibit C-2.5 summarizes the operating parameters of the various reactors.

Only eight runs were made using MoF_6 , compared to several hundred for tungsten deposition. The temperature of the graphite, pressure of the deposition

EXHIBIT C-2.5

CHEMICAL VAPOR DEPOSITION OPERATING PARAMETERS

	Flow Rate				Deposition Time min	Pressure Furnace Torr	Deposition Temp K
	H ₂ l/min	WF ₆ l/min	MoF ₆ l/min	MTS gram/min			
Tungsten	3.0	.3	-	-	120	5	1020
Sic	4.0	-	-	2.0	90	770	1490
Molybdenum	3.0	-	.2	-	90	5	1020

chamber, and molar ratio of H_2/MoF_6 were varied. Two runs resulted in thin molybdenum deposits (.0004 inch thick) completely covering the inside of the graphite shell. The molybdenum deposits were not leaktight. Silicon carbide coatings were nevertheless deposited on these shells. The silicon carbide deposits were leaktight and caused no cracking of the porous molybdenum deposit. These shells were also cycled from 1475 K to room temperature and remained intact.

As a final test, these shells were heated to 1700 K in vacuum for eight hours. They were cross-sectioned and sent to TRW to determine if there were any evidence of reaction between the molybdenum and graphite. None was found. Nevertheless, based on the difficulty in obtaining leaktight molybdenum deposits and the expense of the material, the Program concluded that the emitter material of choice was tungsten rather than molybdenum.

2.3 Hot Shell/Emitter Fabrication Development

The procedures outlined above were established following an extensive period of experimental development.

All hot shell/emitters that were successfully fabricated utilized a graphite mandrel. Two types of graphite were successfully used, i.e., PLC-1 from Poco Graphite and 2128 from Stackpole. Both graphites closely matched the thermal expansion characteristics of silicon carbide and tungsten.

Initially in the Program these graphite shells were outgassed to 1400 K in a vacuum of 10^{-6} torr for eight hours. This step was found to be unnecessary

and subsequently eliminated from the process. The only outgassing that takes place under current procedures is during the stabilization period before deposition starts.

Several surface preparation methods for the graphite were considered, including polishing and grit blasting. On the outside surface of the shell, the as-machined surface bonded well to the silicon carbide deposit, and there was no advantage to polishing the outside surface. In fact, tests indicated that it adversely affected the adhesion of the silicon carbide to the graphite. However, a small amount of polishing of the inside surface helped to eliminate any formation of nodules when the tungsten was deposited. It was very important to obtain a smooth and uniform thickness profile of tungsten for proper converter operation. Polishing the inside surface with 600 grit paper was sufficient surface preparation for good, uniform tungsten deposit. Subsequently, when the practice for the graphite shells to be machined via a tracer lathe to ± 0.02 mm (.001 inches) was adopted this step was also eliminated. These shells required no additional surface preparation.

The problem of sealing the graphite hot shells with the overlapping CVD deposits of tungsten and silicon carbide was also addressed during the Program. At the same time, more general questions as to the best geometry for the interface between the tungsten, graphite, and silicon carbide surfaces had to be considered. At first, the tungsten deposit was acid-etched along the outside of the graphite shell as shown in Exhibit C-2.6. This tended to cause undercutting of the tungsten deposit and acid absorption by the graphite. In order for the coating to fulfill its function, the graphite had to be reliably and completely sealed. Thus, the six different coating geometries shown in Exhibit C-2.7

Exhibit C-2.6
Acid Etching of Tungsten

Exhibit C-2.7
Six Coating Geometries of SiC and Tungsten

were tested using identical reactor conditions. These geometries were produced using one of three general methods.

Exhibit C-2.8 illustrates the principle of the first method (i.e., Method 1) as applied to geometry A of Exhibit C-2.7. A molybdenum shear plane, mounted in a specially constructed holder, was placed around the graphite substrate before deposition. After cooling, a break was made between the molybdenum shear plane and the graphite, resulting in a smooth and even cut around the edge of the tungsten. Exhibit C-2.9 shows the method in greater detail. The orientation of the shear plane, controlled by the design of the holder, determined the geometry of the tungsten deposit. Four different tungsten geometries were tested and each was found to be leaktight. On some shells, a lip of graphite was removed (i.e., geometries B and C) to expose a larger surface of the deposit. When silicon carbide was deposited over the graphite and tungsten, hot shell geometry D produced overlapping leaktight deposits around the graphite. Geometries A, B, and C had leaks at the open end of the shell where the silicon carbide and tungsten joined. An annealing step was later found to increase the percentage of leaktight hot shells produced in these last geometries: after the silicon carbide was deposited, the shell temperature was reduced to 975 K and maintained for two hours before further cooling.

Exhibit C-2.10 illustrates the second method. This method used molybdenum or tungsten sleeves which were machined to fit the graphite. The tungsten was deposited first and confirmed to be leaktight. However, the silicon carbide deposit reacted with the tungsten end cap and resulted in a silicon-rich deposit and tungsten carbide interface layer. Cracking of the silicon carbide

Exhibit C-2.8
Tungsten Deposition with Molybdenum Shear Plane

**STEP NO.1
TUNGSTEN
DEPOSITION**

**STEP NO.2
MACHINING**

**STEP NO.3
SILICON
CARBIDE
DEPOSITION**

Exhibit C-2.9
Method 1 Hot Shell/Emitter Structure Fabrication Steps

Exhibit C-2.10
Method 2 Hot Shell/Emitter Structure Fabrication Steps

occurred at the interface of the tungsten and graphite. Furthermore, leak testing of the hot shells showed that the graphite was not reliably sealed by the silicon carbide and tungsten deposit. A close fit between the graphite and metal sleeve was critical in determining whether a shell would be leaktight, and even when successful deposits of leaktight tungsten were made, the silicon carbide deposit always cracked at the metal sleeve interface.

The final method, i.e., Method 3, is illustrated in Exhibit C-2.11. This method reversed the order of the chemical vapor depositions (i.e., the silicon carbide deposition was followed by the tungsten deposition). The silicon carbide coating cracked when the graphite mandrel was made from Poco PLC-1. However, no cracks were observed after a change was made to Stackpole 2128. In the next step, graphite at the inside lip was removed, and tungsten was deposited on the inside of the shell. Although leak checks demonstrated that the silicon carbide coating was tight, the graphite was not completely sealed on the tungsten side.

Thus, the result of these investigations was a decision to incorporate the use of Method 1 and geometry D into the standard procedures for hot shell fabrication. Over 300 composite shells were made in this manner up to two inches in diameter and ten inches long.

A considerable amount of converter fabrication development was also conducted during the Program with the objective of developing a more cost-effective approach to the fabrication of thermionic converters. These results have not yet been made part of the standard procedures. For example, cost analyses have indicated that there would be a significant economic advantage

Exhibit C-2.11
Method 3 Hot Shell/Emitter Structure Fabrication Steps

in eliminating the graphite mandrel presently being used in the hot shell/emitter structure. A further advantage would be derived because such an approach would be more amenable to automation and large-scale production runs. Over the course of the Program, several different fabrication techniques of this type were conceived and tested.

In principle, the technique for fabricating production converter shells without consuming a mandrel was straightforward. First, the tungsten or silicon carbide would be deposited onto a mandrel with a coefficient of thermal expansion (CTE) that was different from the material to be deposited. Whether the material was deposited on the outside or inside diameter would be dependent on whether the mandrel CTE was higher or lower, respectively. After deposition, the deposit would be slipped off the mandrel to leave a free standing piece. Next, the other component would be deposited onto the free standing piece, and the hot shell/emitter structure would be complete.

Thus, such a design could be fabricated in two basic ways, the primary difference between the methods being the order of deposition of silicon carbide and tungsten. Both methods were evaluated during the course of the Program.

In the first evaluation, a silicon carbide layer was deposited onto the inside of a graphite mandrel. In this case, the CTE of the graphite was lower than that of silicon carbide and the silicon carbide would be expected to separate from the graphite upon cooling. The tungsten coating would then be deposited onto the inside of the free-standing SiC shell. No successful shells were made using this technique. The SiC layer was very sooty and nodular with an uneven thickness profile. In addition, the SiC could not be readily removed from the mandrel. It was decided at this time to abandon this method.

The second method involved depositing the tungsten onto the outside of a graphite mandrel. In this case, the CTE of the graphite is higher than that of tungsten. This procedure was attempted three times. Initially, the mandrel was coated with a carbon release agent prior to deposition in order to facilitate removal of the tungsten shell. However, this release agent left a carbon residue on the inside of the tungsten that was difficult to remove. Further experimentation showed that the release agent could be eliminated if the graphite mandrel were highly polished prior to deposition. Therefore, all of the remaining shells were fabricated without the use of a release agent.

The first reusable graphite mandrels were tapered from a one-inch diameter to a 3/4-inch diameter hemispherical dome in order to facilitate the removal of the tungsten deposit. If a ring shear plane was located about three inches from the dome of the mandrel, the tungsten would break cleanly at that point. A photograph of the graphite mandrel with a CVD tungsten layer is shown in Exhibit C-2.12.

A later design employed a graphite mandrel with a three-degree taper which ended with a torispherical dome. The tungsten shell could be removed with no damage to the graphite mandrel. An obvious benefit of this type of deposit was that all tungsten shells had identical inside geometries, facilitating the adjustment of emitter/collector spacing. However, on the outside of the deposit, it was difficult to maintain an even thickness profile of tungsten from the dome to the open end of the shell. There was a tendency for the tungsten deposit at the open end portion of the shell to be quite thin.

The silicon carbide coating was applied to the free-standing tungsten shell using the standard procedure outlined for the trilayer composite shell.

Exhibit C-2.12
Tungsten Deposition on Outside of Reusable Graphite Mandrel

Although these coatings appeared to bond well to the tungsten, they cracked when thermally cycled in a hydrogen atmosphere to 1400 K. This result was unexpected since there is a good thermal expansion match between silicon carbide and tungsten. Upon further investigation of the literature it was discovered that silicon carbide and tungsten interact during the deposition process to form an unstable tungsten silicide layer [1]. During the thermal cycling this layer could have expanded at a different rate, leading to the hot shell failure. Thus, in order for the silicon carbide protective coating to be applied there had to be a stable intermediate layer between the tungsten and silicon carbide. Carbon was the obvious choice, and four methods of applying the carbon coating were also assessed.

The first technique tried was to apply a CVD-carbon coating by cracking methane. Six attempts were made to coat tungsten with carbon from methane. Temperature of the substrate, pressure of the vacuum chamber and concentration of methane were varied. No successful deposit was made on the tungsten shells.

Applying a carbon suspension at room temperature from a conventional spray gun was more successful. The thickness and geometry of the carbon coating were easy to vary. A .12 mm (.005 inches) coating of carbon was deposited over most of the outside of a tungsten shell. The tungsten near the open end was not coated so that the carbon coating could be completely sealed with silicon carbide. The shell was baked in air for two hours to cure the carbon coating prior to silicon carbide deposition.

Two successful silicon carbide deposits were made on the carbon coating and the tungsten open end. One shell survived thermal cycling in hydrogen

to 1400 K. A photograph of prototype hot shell/emitter structures made with this CVD process is shown in Exhibit C-2.13.

The third method tested was a variation of the conventional hot shell/emitter structure. In this technique the body of the graphite shell was replaced with a thin sheath of Grafoil, cemented to a conventional graphite nose. This modification is shown in Exhibit C-2.14.

Since Grafoil is relatively inexpensive, significant production cost reductions could be achieved by this approach even though the Grafoil was being consumed. One hot shell was fabricated using this technique. The tungsten deposited evenly over all the surfaces and was vacuum tight. The silicon carbide was then deposited on the outside of the Grafoil. As with the tungsten, the silicon carbide evenly coated the entire surface and appeared to be well-bonded.

The fourth method evaluated was based on a patent by Clennedinning [1]. In this technique the carbon coating was formed by the pyrolysis of any of a variety of lacquer-type compounds. First, the tungsten was deposited onto a reuseable graphite mandrel to form a free standing tungsten shell. Next, the outside of the shell was coated with methyl cellulose lacquer and allowed to dry in air. If there were any bubbles or imperfections the shell was lightly sanded and the lacquer reapplied. The shell was then placed in the SiC CVD reactor and heated under a hydrogen atmosphere at 1400 K to pyrolyze the lacquer. After approximately one-half hour at 1400 K, the temperature of the shell was raised to 1550 K and SiC deposition began. The SiC coating was found to be of uniform thickness and adhered very well to the tungsten-carbon

8010-77

Exhibit C-2.13

Prototype Hot Shell/Emitter Structures Made with Alternative CVD Process

GRAFOIL
SHEET

GRAPHITE NOSE

Exhibit C-2.14
Fabrication of Grafoil/Graphite Nose Mandrel for Hot Shell

substrate. One of these shells was thermally cycled between 900 K and 1400 K in nitrogen fourteen times without any cracking or spalling of the SiC coating.

This technique had several advantages over the other methods discussed above. First, the technique was the simplest and most easily amenable to production runs. In production, the tungsten shells conceivably could be dipped into a bath of the lacquer and then placed in the SiC reactor without changing any of the jigging or removing any of the shells. Application of the lacquer was less messy than application of the carbon suspension. The pyrolysis took place in a hydrogen atmosphere and could be done in the SiC reactor without significant contamination of the reactor. The reactor would not even have to be brought back to room temperature between pyrolysis of the lacquer and deposition of the SiC. The lacquer was inexpensive and readily available. Finally, although only a .003 inch thick carbon layer was applied, this tri-layer structure was capable of handling the thermal cycling required of any thermionic device. Thus, it is anticipated that any further work in this aspect of hot shell fabrication development would be focused on this technique.

Another desirable step in the fabrication of the hot shell/emitter structure would be to locate a molybdenum flange in place of the shear plane. If this could be done, a copper braze step used in the standard assembly procedure (see Part C, Section 2.4) would be eliminated. Tungsten was successfully deposited onto such a 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 drawing A of Exhibit C-2.15. The tungsten shell and molybdenum flange remained leaktight after cycling in vacuum to 1200 K ten times.

A. First Flange Geometry

B. Second Flange Geometry

Exhibit C-2.15
Configuration for CVD Coating Tungsten onto Molybdenum Flange

A carbon coating was applied with a spray gun and then the SiC coating was deposited to complete the shell. The final coat of silicon carbide on the 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 nonuniform thickness which resulted in fracture.

Subsequently, graphite mandrels were machined with a closer fit to the molybdenum flange. The dimensions of the mandrel were also increased. The CVD tungsten shells produced were leaktight but were still extremely fragile at the flange interface. Also, one third 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 drawing B of Exhibit C-2.15. In this case, the fit between the flange and the graphite was made even tighter. However, with the exception of two deposits, all the CVD tungsten shells still cracked at the molybdenum interface.

2.4 Converter Assembly

Following fabrication of the hot shell/emitter structure, whether by the standard procedures outlined in Part C, Section 2.2 above, or by other procedures still to be fully developed for commercial-scale production runs, such as the lacquer pyrolysis approach discussed in Part C, Section 2.3, the structures still required assembly into finished converters.

All structures were thoroughly leak tested with a Veeco helium leak detector. An initial leak test to confirm the absence of any deposit of silicon carbide on the emitter surface was made. This step was followed by two, and sometimes three, additional leak tests. Each test was more sensitive than the preceding one.

In the first leak test, each composite shell was mounted in a bell jar under vacuum for 12 hours. It was then returned to atmospheric pressure in a helium atmosphere and soaked for one hour (see Exhibit C-2.16A). The composite shell was then leak tested with a "sniffer" that detected any helium that might have been sorbed by the graphite via cracks in either the graphite or silicon carbide coating (see Exhibit C-2.16B).

The second, and more sensitive, method was to mount the helium-soaked composite shell in a bell jar connected to the helium leak detector (see Exhibit C-2.16C). If any helium had been absorbed in the composite shell, it would be detected by this test. However, the significant limitation to this method was its inability to locate the origin of the helium leaking from the composite shell.

A third and destructive test required the removal of silicon carbide from the dome of the composite shell to expose the graphite layer. The exposed graphite was coupled to a helium leak detector (see Exhibit C-2.17) and helium was sprayed over the shell. If a leak existed in either the tungsten or silicon carbon layer, helium would pass through the opening in the graphite and register on the leak detector.

Exhibit C-2.16
Hot Shell Leak Testing

Exhibit C-2.17
Destructive Leak Test Method

This third test was used only to verify that the first and second tests were accurate in locating all leaks. The sniffer and bell jar leak tests proved to be extremely rigid tests to pass. In order for the shell to be accepted, no helium could be detected during either of the tests.

After a shell passed all leak tests, it would then be copper brazed at 1370 K to a molybdenum flange. To successfully make the braze joint, the tungsten deposit had to be free of surface impurities and provide a close fit to the molybdenum flange. Initially, to ensure that these conditions were met, the leaktight tungsten deposits were machined. However, because the interface between the tungsten and silicon carbide was brittle, many of the shells developed leaks at the open end during the machining step. Machining was avoided by sealing the open end of the shells with a Grafoil gasket prior to SiC deposition. The only precaution taken to clean the tungsten surface was to grit blast any residue of the graphite gaskets away. The flanges themselves were machined for a select fit to each emitter structure.

The emitter-to-flange braze was leak checked with the helium leak detector. Next the flange extension sleeve was copper brazed to the flange. This sleeve was made from nickel and provided a thin-sectioned transition piece between the emitter assembly and the rest of the converter.

Any excess copper on the inside of the hot shell was then etched from the tungsten surface with a 50% solution of HNO_3 . The shell was then rinsed with water and blown dry with nitrogen. A thin layer of nickel was plated at room temperature onto both the outside of the molybdenum flange and the braze area between the flange and the hot shell.

These elements, i.e., the hot shell/emitter structure, the molybdenum flange and the flange extension sleeve, constituted the emitter subassembly. A completed converter consisted of four subassemblies: the emitter, the collector and heat exchanger, the ceramic seal and spacing ring, and the air plenum and emitter lead. Exhibit C-2.18 shows these separate subassemblies for the prototype cogeneration converter previously sketched in Exhibit C-1.11. For those subassemblies other than the emitter, the ceramics used were made from aluminum oxide, Al_2O_3 , with a purity level of 97.6%, and all metal parts were made from either nickel or copper.

All materials were "class A" cleaned after machining. Class A cleaning procedures are listed in Exhibit C-2.19. Individual parts were either electron beam welded together or high temperature brazed to form the subassemblies, depending on the materials to be joined and the location in the converter. Copper was used for a braze when it would be exposed to high temperatures or cesium vapor. At several different stages of construction, parts and subassemblies were leak checked.

The collector subassembly included the collector electrode, the collector cooler, the collector sleeve, the collector current lead, and the cesium tube. The collector electrode, heat exchanger and current lead were copper brazed together in one step at a temperature of 1370 K. Then the collector sleeve was electron beam welded to the collector. Next the cesium tube was electron beam welded to the collector sleeve. The completed subassembly was leak checked using the helium leak detector.

The ceramic seal subassembly included three ceramic rings made of Al_2O_3 , two thin skirts made of nickel, and a spacing ring also made from nickel. The

Exhibit C-2.18
Subassemblies for Cogeneration Converter

EXHIBIT C-2.19

"CLASS A" CLEANING PROCEDURES

Tungsten and Molybdenum

- o Mechanically clean and rinse in tap water and alcohol
- o Vapor degrease 1/2 to 2 minutes
- o Clean ultrasonically in hot solution of .05% Igepal for 2 minutes
- o Rinse in hot water
- o Bright dip 1 to 2 minutes in a room temperature solution of:
 - 80% H_2O_2 (30% concentration)
 - 10% Formic acid
 - 10% H_2O
- o Rinse in cold water
- o Rinse in distilled water No. 1, No. 2, and No. 3
- o Rinse in ethyl alcohol No. 1
- o Rinse in ethyl alcohol No. 2

Nickel and OFHC Copper

- o Mechanically clean and rinse in tap water and alcohol
- o Vapor degrease
- o Bright dip 1 to 2 minutes at 330 K in a solution of:
 - 275 ml Phosphoric Acid
 - 175 ml Acetic Acid
 - 100 ml Nitric Acid
 - 2.5 ml Hydrochloric Acid
- o Dip directly into neutralizer (10% ammonia)
- o Rinse in tap water
- o Rinse in distilled water No. 1, No. 2, and No. 3
- o Rinse in ethyl alcohol No. 1, No. 2

tops and bottoms (only) of the ceramic rings were metallized with a mixture of tungsten and titanium and then plated with a thin coating of nickel. The metallized ceramics and the skirts were copper brazed together. After a helium leak check, the ceramic pieces were copper brazed to the spacer ring. A final leak check was performed on the completed subassembly.

The air plenum and emitter lead subassembly consisted of two nickel parts: the air plenum collar and the air sealing flange. These two pieces were joined together with a gold/nickel braze. This joint had to be mechanically and electrically perfect but not necessarily vacuum tight.

Prior to final assembly, the emitter, collector, and ceramic seal subassemblies were thoroughly cleaned; they were rinsed in both tap and distilled water, blown dry with nitrogen, vapor degreased, and ultrasonically cleaned in both acetone and ethyl alcohol. The emitter and collector subassemblies were also heated in a hydrogen atmosphere at 1120 K for fifteen minutes, and the emitter subassembly was again checked for leaks with the helium leak detector.

Final assembly began with setting of the converter's "cold spacing" between the emitter and collector surfaces. A set of plastic spacers was attached to the face and side of the collector subassembly. The spacers on the face directly determined the cold spacing and the side spacers helped to center the collector within the emitter subassembly. With the spacers in place the collector was placed inside the emitter and held vertically with the cesium tube on the top side. The spacing insulator and then the ceramic seal and spacing ring were installed. When all parts were firmly seated and centered properly, an electron beam weld was made between the collector sleeve and the

spacing ring. When this weld was made, the collector, and seal subassemblies were joined, and the cold spacing was set. The emitter subassembly was then separated and the plastic spacers removed from the collector.

All parts were again thoroughly cleaned, i.e., rinsed in tap and distilled water, blown dry with nitrogen, vapor degreased, and ultrasonically cleaned in both acetone and ethyl alcohol. Thereafter, the subassemblies were handled with white gloves.

Next, the vacuum envelope of the converter was sealed. To do this, the collector was inserted into the emitter and seated on the ceramic spacer. The two subassemblies were realigned to the orientation they had when the spacing was set. The emitter extension sleeve was then beam welded to the sleeve of the ceramic seal. The vacuum envelope and hot shell were again both checked for leaks.

The air plenum/emitter lead subassembly was attached next using a silver-copper braze. After this braze the converter was ready for outgassing and cesium distillation.

First, a length of copper tubing was filament brazed to the cesium tube, which was made of nickel. A glass ampule containing one-half gram of cesium was placed in the tubing and then a high-vacuum pump was attached. The converter and the attached copper tubing were pumped to a pressure between 10^{-5} and 10^{-6} torr at room temperature.

The converter and tubing were then heated to temperatures just above typical operating conditions while they were pumped on by an ion pump. This

outgassing provided a final cleaning of both the surfaces and the bulk of the electrodes. The converter was mounted so that the emitter could be heated by an RF induction coil. The collector was heated by radiation from the emitter, and the tubing was heated by a resistance heater. All temperatures were slowly increased to the final values while maintaining the pressure at the pump below 5×10^{-5} torr.

The final pump pressure with the converter at operating conditions was typically 2×10^{-8} torr. When this pressure was reached, the converter was considered clean and the outgassing was complete. The converter was then isolated from the pump with a vacuum tight pinch-off on the copper tubing.

Next, the cesium was released from the glass ampule by squeezing the copper tube and cracking the glass. The tube was heated to 520 K for three hours. The cesium evaporated out of the tube and condensed inside the converter. After this distillation the copper tube was pinched-off.

Next, the nickel cesium tube was crimped at its end and then cut at this crimp using an electron beam welder. This cut formed a leaktight, high-temperature, oxidation-resistant seal. The cesium tube was wrapped with sheathed resistance heater and formed the cesium reservoir.

The molybdenum flange was designed to operate close to the collector temperature, i.e., about 1000 K. Exposure of the copper braze directly to air under this condition would result in oxidation and subsequent failure. Therefore, the braze region had to be protected.

The last step in the construction process was to spray Cermet 487, a suspension of silicon carbide powder in an inorganic binder, onto this emitter flange and braze area. In preparation for this coating, a thin layer of nickel had previously been plated at room temperature onto both the outside of the molybdenum flange and the braze area between the flange and the hot shell. The cured coating provided required oxidation protection at elevated temperatures. Long-term tests (up to 2500 hours) at flange temperatures of 850 and 950 K in air established that this procedure provided effective oxidation protection to the braze region. These tests are discussed in greater detail in Part C, Section 4.3.

Exhibit C-2.20 illustrates a completed converter.

Exhibit C-2.20
Completed Converter

SECTION 2 - REFERENCES

1. U.S. Patent Office, Award of Patent 3,317,356 to Clendinning, W.R., Assignor to Texas Instruments, Incorporated, May 2, 1967.

3. FABRICATION COSTS

The procedures developed by the Program and discussed in Part C, Section 2 above have successfully addressed the technical problems of fabricating hot shell thermionic converters. However, these fabrication methods can be considered successful in a practical sense only when their cost has also been determined.

Converter fabrication costs were assessed at several points in the Program as either major changes in converter capabilities, designs, or fabrication practices occurred, or in association with system economic studies discussed in Part D. Specifically, costs were assessed in 1975, 1979, and 1980. Although not as part of the Program covered by this report, Thermo Electron will be further updating fabrication costs later in 1984 as part of a follow-on effort for the Department of Energy [1].

These cost studies have generally assumed that then-current converter designs and fabrication practices could be scaled-up (i.e., either in size, operating capabilities, or production numbers) to practical system converters without adversely affecting either fabrication cost or reliability. They have been directed toward estimating a converter purchase price per kilowatt under that assumption. Thus, the cost estimates should be regarded as a projection of what a more mature technology should achieve rather than as a strict measure of present thermionic costs. Costs for complete thermionic energy systems (i.e., not just for the converters themselves) are discussed in Part D.

The 1975 study was performed in connection with an economic evaluation for a topping system [2]. The design of the converter was primitive (i.e.,

more complex than subsequent designs) and incorporated a potassium heat pipe. It was also based on metallic rather than ceramic hot shells. The estimated cost for such converters was \$250 per kilowatt.

By the 1979 study, the assumed design had been considerably simplified [3], and cost estimates had correspondingly declined to \$110 per kilowatt. The shell was made of Inconel 671, and was torispherical in shape. The collector was hollow to accommodate jet impingement gas/steam cooling. An alumina insulator was used between the electrodes; this insulator was recessed in the collector cavity so that the converters could be closely packed. A cesium-graphite reservoir was used, which operated at collector temperature so that no independent temperature control was needed. The emitter flange and the collector cooling tube were used as electrical output leads. The important parameters of the converter are shown in Exhibit C-3.1. As can be seen from the exhibit, the effective size of the emitter, and therefore the power output of the converter, was considerably larger than the hot shell devices which had or have since been actually constructed.

Numerous companies were contacted to obtain their estimates for the manufacturing cost of the converter components. A cost quotation for 200,000 parts per year was requested. It was assumed that a production line would be set up to assemble the components into a completed converter. A budgetary estimate of the required investment in capital equipment was also made. Costs were also allowed for material scrapping and labor inefficiencies. The costs are summarized in Exhibit 3-3.2.

Each such converter costs \$47; \$35 for purchased parts, \$3 for labor and \$9 for profit. With additional investment in machinery, the purchased parts

EXHIBIT C-3.1

SUMMARY OF CONVERTER PARAMETERS
FOR 1979 COST STUDY

EMITTER

Diameter	120 mm	(4.7 inches)
Length	76 mm	(3.0 inches)

COLLECTOR

Domed
CRES 304

INTERELECTRODE SPACE	1 mm	(.04 inches)
EFFECTIVE AREA	127 cm ²	(19.7 in ²)
POWER OUTPUT DENSITY	3.35 W/cm ²	(21.6 W/in ²)
POWER OUTPUT PER CONVERTER	425 W	

EXHIBIT C-3.2
1979 CONVERTER COST SUMMARY

<u>PURCHASED PARTS</u>	<u>LABOR (minutes)</u>	<u>COST (\$)</u>
Emitter		\$ 21.05*
Collector		2.71
End Ring		2.30
Air Tube		1.26
Seal Ring		3.51
Air Deflector		0.17
Seal Flange		1.12
Shield		<u>0.11</u>
Total Purchased Parts		32.23
Labor for Purchased Parts	2.67	
Inspection	1.60	
Sub Assembly 1	0.57	1.00
Sub Assembly 2	3.07	
Final Assembly	1.07	0.25
Final Inspection	0.50	
Subtotals	9.48	\$33.48
Scrap		1.67
Rework	0.95	
Totals	10.43	\$35.15
Labor @ \$15 per hour		\$ 2.61
Subtotal		\$37.76
Profit		<u>8.98</u>
Total		\$46.74

Converter area 127 cm²
Power density 3.35 W/cm²
Power per converter 425 W

Cost per kilowatt \$110

*Includes the Cost of INCONEL 671 Material at \$6.30 per lb.

could be manufactured in the same plant, reducing their cost and increasing the cost of labor.

The substitution of CVD technology for metallic hot shells has two important cost consequences, the assessment of which was the motivation of the study of 1980. As indicated by the discussion in Part C, Section 2.2, CVD fabrication is considerably more complicated than the analogous procedures for fabricating a metallic hot shell. More importantly, however, the use of a ceramic hot shell permits converter operation at significantly higher temperatures (i.e., by 300 - 400 K), which produces far greater power from an emitter of given size and, therefore, tends to lower the cost per kilowatt produced.

Thus, the 1980 study assumed a converter similar in design to the 1979 study, but produced with CVD technology, and capable of operating at 1800 K. This temperature is only slightly higher than temperatures which were demonstrated for extended periods of operation during the Program. Other key assumptions are listed in Exhibit C-3.3.

The results of the study indicated that the net effect of employing CVD technology would be to decrease the cost per kilowatt of thermionic converters to \$86. Exhibit C-3.4 shows a breakdown of that cost estimate.

The significance of such results can be appreciated more fully in the context of the system studies discussed in Part D, and the updated figures to be made available in the latter part of 1984 will provide a much better basis for evaluating the current economics of thermionic converter manufacture. Nevertheless, it is apparent at these values that converter cost is a less

EXHIBIT C-3.3

BASIS OF CONVERTER COSTS FOR 1980 STUDY

- REFERENCE CONVERTER DESIGN WITH CVD SILICON CARBIDE/CARBON/TUNGSTEN HOT SHELL-EMITTER
- CONVERTER DIAMETER AND EMITTER THICKNESS OPTIMIZED FOR EACH OPERATING POINT (I.E., EMITTER TEMPERATURE, HEAT FLUX AND BARRIER INDEX)
- DEPOSITION RATES BASED ON THERMO ELECTRON EXPERIENCE
- TUNGSTEN HEXAFLUORIDE COST* OF \$44/KG
- METHYLTRICHSILOXANE (MTS) COST** OF \$2/LITER
- COLLECTOR (INCLUDING CERAMIC SEAL, AIR TUBE, FLANGE, ETC.) COSTS KEYED TO VENDOR QUOTES IN THERMO ELECTRON TOPICAL REPORT NO. TE 4258-163-79***
- ASSEMBLY COSTS BASED ON ESTIMATES IN THERMO ELECTRON TOPICAL REPORT NO. TE 4258-163-79***
- CAPITAL EQUIPMENT, OVERHEAD, G&A AND PROFIT ADDED TO GIVE MANUFACTURED COST

* Air Products Quotation of 12 September 1979 (Lunt to Reagan)

** Dow Chemical Telephone Quotation of September 1979

*** George LaRue and Gabor Miskolczy, Manufacturing Cost of Flame Heated Thermionic Converters, Thermo Electron Report No. TE 4258-163-79 (April 1979)

Exhibit C-3.4
Converter Cost Breakdown for 1980 Study

critical issue for practical terrestrial application of thermionics than are questions such as converter scale-up.

SECTION 3 - REFERENCES

1. Study being performed by Thermo Electron under contract DE-AC02-83CE40635.
2. Thermo Electron Corporation, "Phase One Report, Conversion Topping System Study," Report No. TE4207-29-76, December 15, 1975.
3. Thermo Electron Corporation, "Manufacturing Cost of Flame Heated Thermionic Converters," Report No. TE4258-163-79, April, 1979.

4. CONVERTER CAPABILITIES

4.1 Introduction

The work on hot shell converters carried out during the Advanced Thermionic Technology Program has resulted in a well-defined prototype design, has demonstrated the fabrication of such a design, and, subject to updating late in 1984, has provided at least a rough estimate of the design's fabrication cost. This represents major progress in the development of terrestrial thermionic technology. Nevertheless, before the technology can be considered commercially viable in any power generation application, further progress will need to be made in at least some of the following technical areas: operational reliability (i.e., lifetime), operating temperatures (i.e., and tolerance of thermal stress), corrosion resistance, fabrication reliability, or power output (i.e., either efficiency or absolute magnitude).

These technical areas are, in practice, interrelated. For example, progress in corrosion resistance might permit either increased lifetimes for greater reliability, or operation at higher temperatures for greater power efficiency. Increased power density might permit economical operation at lower temperatures, reducing the need for corrosion resistance. On the other hand, increased corrosion resistance might be obtained at the expense of a less reliable or more costly fabrication process. Similarly, scaling-up the converter design to produce more power per converter could introduce new sources of thermal stress which might adversely affect operating temperatures, efficiencies, and/or lifetimes.

Consequently, as a basis for interpreting the power system evaluations of Part D, and for understanding the motivations for the research approaches discussed in Part E, the remainder of this section summarizes the capabilities and limiting conditions of the current prototype hot shell technology in these technical areas.

4.2 Operational Reliability

A base-line electrical generating station is typically expected to have an operating lifetime of some thirty years and routinely has a power output of 800 to 1200 MWe. A thermionic topping system (see Part D, Section 3.3) for an 800 MWe plant might produce 260 MWe of the total and could require some 86,000 converters each producing approximately three kilowatts. Inasmuch as the thermionic components might represent more than one-quarter of the direct capital investment in the station, and the process of physically replacing failed converters would not be trivial, there is an obvious incentive in seeing that the lifetime of the converters matches that of the station's non-thermionic components to the fullest extent possible.

One CVD hot shell converter has been demonstrated in 12,500 hours of operation over a period of two and one-half years. This test was performed in a high-temperature furnace that was fired with natural gas. The nominal emitter temperature during the test was 1730 K. The converter performance was measured at an emitter temperature of 1700 K and had a barrier index of 2.25 eV. The corresponding power output was 2 Watts/cm² at .25 volts, and the active emitter area was six square centimeters. The collector temperature was optimum at about 850 K. The converter performance remained stable for more

than 11,000 hours and then degraded slightly after the converter was thermally cycled to room temperature during the twelfth full thermal cycle of the test.

After 12,500 hours of testing, a complete loss of primary and back-up cooling air occurred due to freezing of an outdoor combustion line. This caused the collector to overheat and short to the emitter. The resulting mechanical stress on the emitter caused a crack in the dome of the SiC shell which led to a rapid failure of the diode. The middle graphite layer oxidized, and a white powder appeared between the tungsten and SiC layers. The converter was quickly removed from the furnace and cooled to room temperature.

Unfortunately, the mode of failure complicated the process of drawing inferences about the reliability of the converters. On the one hand, the degradation of performance observed after 11,000 hours could be used to infer that at 12,500 hours the converter was very near the end of its useful life in any event. More probably, the failure was a "fluke," and a repeat of the test would produce a longer lifetime. Consequently, the converter was subjected to extensive post-operational diagnostics after this life test. The converter was cut longitudinally and in cross section by a diamond saw to yield two semi-circular samples for analysis. Sample 1 had been exposed to an operating temperature of approximately 1585 K; sample 2 was held at approximately 850 K during the life test. Samples of the tungsten and the SiC at the hemispherical end of the shell were prepared and analyzed as samples 3 and 4, respectively. The locations from which the samples were taken are shown in Exhibit C-4.1.

The diagnostics for samples 1 and 2 included the following five categories:

- 1) trilayer structure examination by Scanning Electron Microscopy (SEM) and

Exhibit C-4.1
Sketch of Flame-Fired Converter Showing Areas Where Samples
were Taken for Postoperational Analyses

Energy Dispersive Analysis by X-rays (EDAX); 2) grain structure examination; 3) hardness measurements; 4) X-ray diffraction; and 5) chemical analysis.

SEM photomicrographs of the tungsten-graphite-silicon carbide trilayer for sample 1 are shown in Exhibit C-4.2. Exhibit C-4.2A shows a low magnification (i.e., x 50) view of the trilayer, and expanded views of the interfaces are shown in Exhibits C-4.2B and C-4.2C. A tungsten X-ray map corresponding to the tungsten-graphite interface in Exhibit C-4.2C is shown in Exhibit C-4.2D. The photomicrographs do not show any significant diffusion zone between the various elements when scaled in photographs showing a ten-micron white band for reference.

High magnification Robinson backscattered photomicrographs of sample 1 interfaces are shown in Exhibit C-4.3. The silicon and tungsten line scans show an interaction zone width of approximately three to four microns for both the SiC-graphite interface and the graphite-tungsten interface. The interaction zones are very narrow, considering the time-temperature history of this region. Thus, the lifetime of a flame-fired converter does not appear to be limited by interdiffusion of elements in the trilayer structure.

Similar SEM and EDAX analyses were performed for sample 2 taken from the low-temperature end of the converter. Photomicrographs of sample 2 are given in Exhibit C-4.4 and these photomicrographs, in general, are similar to the ones taken for the high-temperature end of the converter.

Enlarged Robinson backscattered photomicrographs of the interfaces of sample 2 are shown in Exhibit C-4.5. The silicon and tungsten line scans

(a.) SEM photograph showing cross-sectional view of all interfaces

(b.) Expanded view of graphite-SiC interface

(c.) Expanded view of W-graphite interface

(d.) X-Ray dot map showing tungsten distribution corresponding to Figure 2 (c.)

Exhibit C-4.2
Photomicrographs of Sample 1 from High-Temperature End of Hot Shell

(a.) SiC/Graphite Interface

(b.) Graphite/W Interface

Exhibit C-4.3
 Robinson Backscattered Images and EDAX Scans for
 Interfaces of Sample 1

(a.) SEM photograph showing cross-sectional view of all interfaces

(b.) Expanded view of graphite-SiC interface

(c.) Expanded view of W-graphite interface

(d.) X-ray dot map showing tungsten distribution corresponding to 4 (c.)

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(a.) SiC/Graphite Interface

(b.) Graphite/W Interface

Exhibit C-4.5
 Robinson Backscattered Images and EDAX Scans for
 Interfaces for Sample 2

are similar to those obtained for sample 1, and, again, interaction zones of approximately three microns are indicated. In general, the cross-sectional views of the SiC-graphite and graphite-W interfaces at the top of the converter are indistinguishable from those interfaces near the bottom of the converter.

Optical photographs of the etched trilayer cross sections for samples 1 and 2 are shown in Exhibits C-4.6 and C-4.7, respectively. These figures show typical grain size in the tungsten and the silicon carbide layers. The grain structure in sample 1 does seem to be somewhat finer and less columnar than in sample 2. In addition, there seems to be some grain refinement in the zone near the graphite surface.

Both sample 3 and sample 4 were taken from the topmost portion of the hot shell where the shell had cracked so that the graphite and tungsten layers were oxidized. Sample 3 was a piece of this oxidized tungsten, and sample 4 was a fragment of the SiC.

A section of sample 3 was mounted, metallurgically polished, and etched. An optical photograph from the etched surfaces, shown in Exhibit C-4.8, showed a columnar type grain structure with a slightly smaller grain-size material near the former graphite edge. SEM photographs of the two edges of the tungsten sample are shown in Exhibit C-4.9. On the former graphite edge, a very thin surface coating or reacted zone is evident. An EDAX X-ray mapping of that edge showed a slight difference in the level of the tungsten X-rays, apparently due to formation of an oxide or a carbide. The EDAX data were not able to

(a.) Outside edge W (exposed to cesium during operation)

(b.) W/Graphite Interface

(c.) Graphite/SiC Interface

(d.) Outside edge SiC (exposed to flame during operation)

Exhibit C-4.6
Grain Sizes in Trilayer Structure--Sample 1

(a.) Outside edge W (exposed to cesium during operation)

(b.) W/Graphite Interface

(c.) Graphite and SiC with band containing W and Si between them

Exhibit C-4.7
Grain Sizes in Trilayer Structure--Sample 2

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Exhibit C-4.8
Optical Photograph of Sample 3 Showing Various Layers

CESIUM
SIDE

(a.) SEM photograph of tungsten near edge which was exposed to cesium

TUNGSTEN

TUNGSTEN
OXIDE

FORMER
GRAPHITE
SIDE

(c.) SEM photograph of tungsten showing thin oxide layer

(b.) Tungsten distribution corresponding to (a.)

(d.) Tungsten distribution corresponding to (c.)

Exhibit C-4.9
SEM Photomicrograph of Sample 3

distinguish between an oxide and a carbide since the EDAX detector is insensitive to those light elements.

No SEM or EDAX analyses were conducted on sample 4.

Hardness data were also obtained from the tungsten and silicon carbide layers in the four samples. The data, obtained using a Leitz Microhardness Tester with Knoop Diamond and a 500 gram load, are given in Exhibit C-4.10. These hardness data are in agreement with values reported for these materials. The value for SiC is reported to be in the range of 2500-3000 KHN, while compacted tungsten powders have been measured in the 480-500 KHN range.

The material hardness values were nearly the same for the high- and low-temperature ends of the converter, also indicating structural stability of the trilayer even after extended operating times at high temperatures.

Microhardness data from various regions in the tungsten material (i.e., sample 3) did not show any significant variation across the samples. Knoop hardness values of about 490 to 500 are typical for tungsten metal. Impressions placed in the thin coating found on the specimen indicated that the material in the coating was much softer than the tungsten. In order to obtain reproducible data, the load on the diamond indenter had to be reduced to 100 grams. Data from the tungsten under the same load gave Knoop values in the 550 to 560 range. Slightly higher Knoop values are expected for lighter loads. A Knoop hardness number of 55 for the coating suggested that coating on the smooth edge of the tungsten was most likely an oxide, but definitely not a

EXHIBIT C-4.10

HARDNESS DATA FOR SAMPLES 1-4

<u>Sample</u>	<u>W (KHN)</u>	<u>SiC (KHN)</u>
Sample No. 1 (Average of 3 areas)	495	2565
Sample No. 2 (Average of 3 areas)	500	3273
Sample No. 3 (Average of 4 areas)	501	--
Sample No. 4 (Average of 4 areas)	--	2914 (smooth region) 2800 (polygrained region)

tungsten carbide formation. An oxide coating was expected since the tungsten was exposed to air after the SiC coating cracked open.

Sample 4, i.e., the sample of SiC, was ground into a fine powder and analyzed by both X-ray diffraction and microhardness measurements. The patterns indicated the bulk of the material to be the beta form of silicon carbide plus some silicon dioxide. There may have been a small amount, estimated to be less than three or four percent, of alpha silicon carbide (i.e., the low-temperature phase) in the sample. The material had Knoop hardness values of about 2800 - 2900.

Diffraction measurements were also made for two samples taken near the area of sample 1. The first sample was a piece of SiC, whereas the second was a glassy fragment covering the SiC. The latter fragment is discussed further in Section 4.4 below. The samples were crushed in a mortar and then affixed to a glass slide using a collodion solution. The diffraction lines on each of the patterns were then compared to known or expected standards.

The SiC sample was found to be the beta-cubic form of silicon carbide. Comparisons with patterns from the alpha-hexagonal form of silicon carbide did not show any significant amount of the hexagonal phase in the sample. There were, however, two relatively weak lines that could be matched to the strongest lines of some of the silicon dioxide phases reported in the literature.

A piece of SiC near the top of the shell was also chemically analyzed and compared to the composition of typical SiC as deposited by CVD, as shown in Exhibit C-4.11. The compositions of the SiC before and after operation were

EXHIBIT C-4.11
CHEMICAL ANALYSIS OF SiC

<u>Element</u>	SiC as Deposited (Average of 5 Samples)	SiC, 12,500 Hr. <u>Converter</u>
	Atomic (Percent)	Atomic (Percent)
Silicon	50.3	48.6
Carbon	49.6	45.0
Oxygen	0.02	5.2
Hydrogen		0.6
Aluminum		0.3
Calcium		0.2
Iron		0.1
Copper		0.007

very similar, except that after operation the SiC contained some oxygen. The oxygen undoubtedly came from the silicon dioxide glass layer which covered the SiC after operation, as discussed in Section 4.4 below. The small amount of hydrogen apparently originated from the gas flame, while the other impurities were most likely from the furnace environment.

Thus, the following conclusions can be drawn from the post-operational diagnostics of the 12,500-hour life-tested converter:

- o The silicon carbide-graphite-tungsten trilayer structure remained structurally stable during operation. The inter-action zones at the SiC-graphite interfaces and the graphite-tungsten interfaces were only 2-4 microns wide. These zones were most likely formed during CVD processing since they were no more pronounced at the hot end than the cold end. Thus, the lifetime of a flame-fired converter is not limited by interdiffusion of elements in the trilayer structure.
- o At the cold end of the converter, the junction of silicon carbide and tungsten resulted in a silicon-containing compound, probably WSi_2 . This compound is stable at the operating temperature of the collector side.
- o The hardness of both the tungsten and silicon carbide after operation were equal to accepted values for these materials. If there had been any significant interaction of the tungsten with the graphite to form tungsten carbide, the hardness of

the layers would have increased significantly. There was no evidence of such a change. Thus, the trilayer structure was not weakened by high-temperature operation for long periods of time.

- o Chemical analysis of the silicon carbide showed only small differences between composition before and after operation. For the most part, these differences related to the formation of a protective SiO_2 layer. The hydrogen content in the SiC after operation was only .6 atomic percent.

In confirmation and elaboration of these findings, TRW also analyzed a second converter after 5120 hours of operation at 1650 K. This converter developed a leak at its cold end and was removed from the furnace for examination before the electrodes became oxidized.

Metallographic, electron probe, microhardness and X-ray analyses did not identify any life-limiting degradation mechanisms. The silicon carbide surface was covered with a thin layer of glassy material. However, the X-ray diffraction data did not show any SiO_2 reflections, implying that any SiO_2 present was amorphous.

Electron microprobe analysis (EMA) profiles of silicon and tungsten were taken across the cross section of the hot shell to determine interaction of the trilayer components. EMA of the silicon carbide-graphite interface showed no evidence of interaction. Investigation of the tungsten-graphite interface by EMA did show an interaction zone.

4.3 Temperature and Thermal Cycling

The motivation for operating at the highest possible temperatures arises from the fact that, except for certain unusual situations described in Part C, Section 5, converter output increases with temperature. If converters are to have extended operating lives, they must also be able to tolerate repeated cycling between combustion and lower temperatures as the system of which they would be a part varies between operational and shut-down status.

In the 12,500-hour test described in Section 4.2 above, the converter operated at an emitter temperature of 1730 K and survived a minimum of 12 thermal cycles. This can be regarded as typical of today's converter capabilities. Nevertheless, higher temperatures have been achieved for shorter periods of time -- i.e., not for acceptable lifetimes for commercial use -- and converters have survived much more stringent thermal stresses.

These latter results were obtained during a series of environmental tests involving only the composite hot shell/emitter and flange configurations rather than fully operational converters. The primary goal of these tests was to further explore the causes of failure of the hot shell/emitter and flange structure during high-temperature operation and thermal cycling. Visual inspections and helium leak checks were made periodically to determine any degradation in the hot shell and flange.

A test stand was designed to allow the hot shell and flange to be inserted and removed quickly from a furnace. Both one- and two-inch structures were tested. One-inch shells were heated in air by RF induction, while two-inch

shells were flame-fired in a natural gas furnace. The hot shell/emitter structures were copper brazed to molybdenum flanges. A second flange made of nickel was brazed to the molybdenum flange, and a pumpout port was brazed to the nickel flange to maintain a pressure of 10^{-6} torr or better on the inside of the composite shell. All shells could be cooled to room temperature in less than five minutes.

Exhibit C-4.12 summarizes the results of the individual tests in the series, and Exhibit C-4.13 further highlights the results in terms of their implications for converter capabilities.

One one-inch shell, numbered 101, was temperature cycled from room temperature to an emitter temperature (i.e., dome temperature) of 1925 K in four minutes. This was repeated a total of nine times and produced no change in the shell. However, the molybdenum flange braze area expanded in volume and changed to a dark color. After 110 hours of testing, the shell was cross-sectioned to observe the braze area (see Exhibit C-4.14). X-ray analysis of the dark braze area showed both copper oxide and molybdenum oxide. No tungsten oxide or nickel oxide was found. The tungsten remained leaktight during the entire exposure, but helium soak tests indicated a possible leak to the graphite through the braze area. The flange temperature was 675 K.

A two-inch shell, numbered 102, was flame tested in a gas furnace with adverse results when the flange temperature was 675 K (see Exhibit C-4.15). Accelerated swelling of the braze area occurred at this temperature. Also, the swelling penetrated more deeply into the braze and probably caused the shell to crack at the braze end; the shell had many cracks at the silicon carbide and

EXHIBIT C-4.12

RESULTS OF INDIVIDUAL HOT SHELL-EMITTER-FLANGE COMBUSTION TESTS
TO INVESTIGATE EFFECTS OF HIGH TEMPERATURES AND
TEMPERATURE CYCLING

DESCRIPTION (NUMBER)	NUMBER OF HOURS	TEMPERATURE OF DOME OF SHELL (K)	TEMPERATURE OF FLANGE (K)	TEMPERATURE CYCLES	COMMENTS
1" DIAMETER 4" LONG HEMISPHERICAL HOT SHELL (101)	110	1925	675	9	Black residue on flange. No crack- ing of structure. Tungsten leaktight.
2" DIAMETER 4" LONG HEMISPHERICAL HOT SHELL (102)	70	1655	675	1	Black residue on flange. SiC cracked and braze swelled.
1" DIAMETER 4" LONG HEMISPHERICAL HOT SHELL (103)	80	1925	875	13	Flange coated with Cermetal 487. SiC cracked at dome. No black residue. Test followed opera- tion for 28 hours at lower temperatures.
2" DIAMETER 3" LONG HEMISPHERICAL HOT SHELL (104)	2480	1600	850	10	Flange coated with Cermetal 487. SiC leaked 1" from nose. Braze area remained leaktight.
1" DIAMETER 4" LONG HEMISPHERICAL HOT SHELL (105)	70 4 2	1875 1875 2025	675 675 700	20 150 102	Leaktight after 70 hours at 1875 K. Thermal cycles from 900 K to dome temp- erature shown. Heat- ing and cooling period each 30 seconds.

EXHIBIT C-4.12 (CONTINUED)

DESCRIPTION (NUMBER)	NUMBER OF HOURS	TEMPERATURE OF DOME OF SHELL (K)	TEMPERATURE OF FLANGE (K)	TEMPERATURE CYCLES	COMMENTS
2" DIAMETER 3" LONG HEMISPHERICAL HOT SHELL (107)	2600	1600	850	10	Test terminated due to furnace failure.
2" DIAMETER 3" LONG HEMISPHERICAL HOT SHELL (108)	230	1600	850	3	SiC cracked one inch from dome.
2" DIAMETER 2" LONG TORISPHERICAL HOT SHELL (109)	1100	1550	850	4	Leak at braze joint.
2" DIAMETER 3" LONG HEMISPHERICAL HOT SHELL (110)	1092	1600	850	4	SiC cracked. Shell destroyed.
2" DIAMETER 3" LONG HEMISPHERICAL HOT SHELL (111)	10	1500	800	1	Test terminated due to furnace failure.

EXHIBIT C-4.13

ENVIRONMENTAL TESTS OF THERMO ELECTRON
CVD TRILAYER STRUCTURE

Maximum Test Temperature	2025 K for 2 hr 1925 K for 110 hr
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Combustion Life Tests

(As Hot Shell/Emitter of an Operating Thermionic Converter)	12,500 hr at 1730 K
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Thermal Cycle Tests

	<u>Series 1</u>	<u>Series 2</u>
Number of Cycles	150	102
Temperature Range	900 K to 1875 K	900 K to 2025 K
Temperature Ramp	> 30 K/s	≈ 40 K/s

Thermal Shock Tests
(CVD Trilayer Structure Initially at 1875 K)

Doused in Liquid Nitrogen	10 Times
Sprayed with Water	10 Times

Pressure Test	500 psi for 3 hr
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Exhibit C-4.14
One-Inch Hot Shell-Emitter-Flange Structure #101

TUNGSTEN (CVD)

Exhibit C-4.15
Two-Inch Hot Shell-Emitter-Flange Structure #102

tungsten interface. This shell was also analyzed to determine the composition of the compounds in the braze area. Both optical and scanning electron microscopy photographs were taken within the flange area (see Exhibit C-4.16).

A series of spots located across the region containing a "black residue" similar to that which had formed on shell number 101 was further analyzed by obtaining X-ray intensity data using quantitative analytical programs in an EDAX system. These data indicated that the black residue was largely composed of molybdenum with some small percentages of tungsten, copper and silicon. The photographs showed the copper almost entirely confined to the area near the top ridge of the brazed joint between the molybdenum flange and the CVD layer of tungsten. The X-ray data showed that in the region enclosed within the molybdenum flange (see Exhibit C-4.16, spot 1) there was a slightly higher concentration of silicon and tungsten, while the outer areas (i.e., spots 2 and 3) had a slightly higher concentration of copper and were almost devoid of tungsten and silicon. The results of the analysis showed that the black residue was composed of 90% to 98% MoO, with the balance either silicon carbide or the oxides of tungsten and copper.

It was apparent from the results with these two shells that the flange area, if not somehow protected, represented a point of vulnerability for converter designs, despite the fact that the collector and flange temperatures might be 1000 K or more below that of the emitter dome. These findings were an important motivation for the research and development efforts which led to procedures, already described in Part C, Section 2, for protecting the flange

Exhibit C-4.16
Cross Section of Hot Shell-Emitter-Flange Structure #102

area with nickel covered by silicon carbide, and for attempts, so far unsuccessful, to CVD silicon carbide directly onto graphite mandrels and molybdenum flanges in a single operation.

Several protective coatings were deposited on hot shell/emitter structure number 103 around the molybdenum flange and the base of the silicon carbide hot shell. After evaluating several coating techniques, a deposit of Cermet 487 adhered to both the molybdenum flange and the CVD silicon carbide. This hot shell/emitter structure was heated in air by RF induction and showed no signs of black residue after 8 hours at a flange temperature of 800 K.

After this flange test logged 20 hours at 875 K, the emitter temperature was raised from 1575 to 1925 K. The test continued at a dome temperature of 1925 K. After a further 80 hours, the structure developed a leak at the dome. However, no black residue formed on the flange.

Structure number 104 was also coated with Cermet 487 on the flange area, and flame-fired in a natural gas furnace. It was cycled to room temperature ten times and remained leaktight. The flange was run at 850 K. Inspection at 1300 hours of testing showed no evidence of the black residue on the flange. However, a clear deposit coated one third of the dome of the shell facing the viewport.

Shell 104 remained leaktight for 2480 hours at an emitter temperature of 1600 K and a flange temperature of 850 K. A crack was then observed in the silicon carbide midway between the dome and the flange. The silicon carbide in the region of the crack operated at approximately 1300 K and appeared to

have reacted with the insulating material surrounding the hot shell. The shell was removed from the furnace after a small rise in pressure was observed. A leak check of the shell showed the dome and braze area to be leaktight. The shell was then cross-sectioned in order to inspect the braze area (see Exhibit C-4.17). A small amount of swelling (probably due to oxidized molybdenum) was evident on the outside of the braze area. However, this swelling was observed on the flange after 100 hours of operation and did not increase during the subsequent 2380 hours of operation. The copper braze was unaffected on the bottom and the inside of the shell.

The testing of hot shell 105 focused on the effects of thermally induced stresses. During this testing the CVD trilayer structure demonstrated outstanding resistance to thermal shock and thermal cycling.

The photographs shown in Exhibit C-4.18 give a dramatic demonstration of the resistance of the CVD trilayer structure to thermal shock. In this series of tests, the hemispherical end of the CVD structure was first heated to 1875 K in air by RF induction and then water-quenched in a small area to less than 800 K, producing more than a 1000 K temperature differential between the water-cooled spot and the remainder of the dome. This was repeated a total of ten times. A similar series of tests was performed with a quench of liquid nitrogen. The shell remained leaktight.

In addition, this trilayer structure was cycled from 800 to 1875 K in air by RF induction 150 times. The time for a complete temperature cycle of the hot shell was approximately one minute. The structure was leak checked by helium soaking after the test and remained leaktight. Next, the trilayer

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Exhibit C-4.17
Cross Section of Shell 104 After 2480 Hours of Test
in a Gas-Fired Furnace

WATER SPRAY HITTING
SHELL

HOT NOSE OF SHELL

R.F. INDUCTION COIL

SILICON CARBIDE GRAPHITE
TUNGSTEN HOT SHELL

a. Water Quench

SHELL QUENCHED WITH
LIQUID NITROGEN

b. Liquid Nitrogen Quench

Exhibit C-4.18
Thermal Shock Tests With CVD Trilayer Structure
Initially Heated to 1875 K in Air

structure was cycled from less than 900 K to 2025 K in air by RF induction 102 times. The inside (i.e., tungsten side) of the shell, which was always kept under vacuum during these high-temperature cycles, never exceeded 10^{-6} torr. However, during the last few temperature cycles, which remained less than a minute in duration per cycle, a crack was noticed on the dome of the silicon carbide. Testing was stopped to prevent oxidation of the inside tungsten layer.

Additional two-inch hemispherical shells were flame tested at temperatures of 1600 K at the emitter and 850 K at the flange. Shell 107 had silicon carbide nodules on the dome. Occasionally such nodules developed during the CVD of silicon carbide and had been a cause for rejection during converter construction. This structure provided an opportunity to test such a shell at operating temperature and observe the effect, if any, of the nodules on its integrity. This shell maintained its integrity for 2600 hours before a furnace failure ended the test with the shell still intact. A shell of similar design but without nodules (i.e., shell 110) failed due to SiC cracking after 1092 hours. Consequently, nodules did not appear to adversely affect shell lifetime.

Hot shell 108 failed after only 230 hours of testing. The nose of the silicon carbide cracked and completely oxidized the tungsten emitter. Like shell 107, this shell was tested at an emitter temperature of 1600 K and a flange temperature of 850 K.

Hot shell 109 was a torispherical design two inches in diameter and two inches long. It operated for 1100 hours at 1550 K on the emitter and 850 K at the flange. Then the vacuum in shell 109 rose to approximately 10^{-5} torr. As soon as this pressure was observed, the shell was removed from the furnace

in less than five minutes. Leak testing revealed the leak to be at the copper braze joint between the shell and flange. Since this leak was impossible to repair, no further flame testing was done on shell 109. An important result of this test, however, was that the emitter temperature varied only ± 15 K over the complete dome area.

Testing on an additional shell, number 111, had barely begun when furnace failure required its cessation.

To further evaluate the mechanical integrity of the CVD hot shell/emitter structure, a two-inch diameter shell was pressurized in the apparatus sketched in Exhibit C-4.19. The open end of the shell was sealed so that the CVD composite shell sustained full applied pressure. After pressurization to 500 psi for three hours, the shell remained leaktight. This test demonstrated the high strength of CVD silicon carbide at room temperature, and although this test was performed at room temperature, it was relevant at higher temperatures because silicon carbide retains most of its strength at temperatures up to 1600 K.

In total, these environmental tests showed that the potential exists for converters to operate at significantly higher temperatures and through significantly more thermal cycles than the 1730 K emitter temperature and twelve cycles achieved in the 12,500-hour life test -- perhaps 200 K higher and upwards of 100 cycles. However, there was a wide disparity in the results of tests for individual converters, emphasizing the need to acquire still additional understanding of failure mechanisms, and the need for quality control during the fabrication process in order to ensure for nearly every converter long operational life at those high temperatures.

Exhibit C-4.19
Hot Shell Pressure Test Schematic

4.4 Resistance to Corrosion and Fuel Compatibility

Although the exact mechanisms by which converter failures can be prevented are not fully understood, it is clear that during normal operation a layer of silicon dioxide soon forms over the outside of a CVD trilayer hot shell, and that this layer very effectively delays further oxidation of the underlying SiC layer. The protective layer showed clearly in low magnification SEM photomicrographs during post-test analyses of the converter in the 12,500-hour life test. It appeared as a glass-white to light brown structure, thickest at the high-temperature end of the shell. Both wet chemical analysis and X-ray diffraction confirmed that the layer was, indeed, composed of SiO_2 .

A fragment of the glass taken from the immediate vicinity of sample 1 (see Exhibit C-4.1) near the dome of the converter was crushed in a mortar and then affixed to a glass slide using a collodion solution. X-ray diffraction lines were then compared to known or expected standards.

The fragment was found to have several weak lines that could be matched to some of the strong lines in various forms of silicon oxide. Since the sample was so minute, the possibility that the diffraction patterns might be produced by the glass support used for the sample was tested. However, patterns with and without the sample on the glass holder showed that all lines indexed on the pattern did, in fact, come from the fragment. The sample was found to contain two components, one phase being a light brown crust and the second phase being a granular white crust. The brown material was believed to be the beta-cubic form of silicon carbide, while all other lines were due to some form of silicon dioxide. The silicon dioxide was probably the beta-two-*Trydymite* form of SiO_2 , which is stable from about 1150 K to 1750 K.

The possible corrosive reaction modes of SiC are summarized in Exhibit C-4.20. Silicon carbide is stable under inert or nonoxidizing gaseous atmospheres. It is well known that SiC at moderate temperatures in an oxidizing atmosphere is passivated by the formation of the type of protective scale of SiO₂ seen in the 12,500-hour life test [1, 2].

At higher temperatures and lower oxygen partial pressures, "active" oxidation occurs with the evolution of SiO and CO. For example, at a temperature of 1770 K, an oxygen partial pressure of about 10⁻³ atmospheres must be maintained to prevent "active" oxidation [1]. Several studies have revealed the deleterious effect of basic melts on the corrosion performance of SiC. The protective scale is dissolved by basic melts, which leads to accelerated corrosion [2].

The oxidation kinetics of sintered alpha-SiC and hot-pressed SiC have recently been elucidated [3]; platinum markers revealed the formation of new oxide at the SiC/oxide interface. The good corrosion performance of passivated silicon carbide can be attributed to the slow diffusion of oxidant through the growing SiO₂ film to the SiC surface. Here, SiC is converted by the reaction:

This diffusion-limited reaction results in parabolic rate behavior in agreement with experimental observations. Corrosion behavior is sensitive to the presence of impurities because they increase the transport of oxidant through the film and, therefore, increase the corrosion rate.

Understanding of corrosive behavior is even more important in terms of predicting converter capabilities in thermal environments other than the flames

<p>A.</p>	<p>INERT</p>	<p>NO REACTION</p>
<p>B.</p>	<p>PASSIVATED</p>	<p>PROTECTIVE SILICA SCALE</p>
<p>C.</p>	<p>"ACTIVE" OXIDATION</p>	<p>EVOLUTION OF SiO AND CO GASES</p>
<p>D.</p>	<p>ACCELERATED CORROSION</p>	<p>FORMATION OF SOLUBLE IONIC SPECIES</p>

Exhibit C-4.20
Corrosion Modes for Silicon Carbide

derived from natural gas which have been used in most of the converter tests to date.

Recently, there has been an increasing interest in the direct firing of coal in all advanced energy conversion systems. The resulting elimination of extensive coal processing in advanced systems offers the promise of both economic and overall efficiency advantages. Since most U.S. coals contain about ten percent mineral matter, the high-temperature processes inherent to advanced conversion technologies such as thermionics or magnetohydrodynamics (MHD) would result in extensive slag deposits. These deposits may offer protection from erosion and oxidation at the expense of corrosion problems.

Most of the coal ash components condense out below a temperature of about 2100 K [4]; the volatile exception (aside from the alkali metals) is silica, which doesn't begin heavy condensation until 1900 K. Since commercial thermionic converters are likely to operate at temperatures between 1700 K and 1900 K, some fraction of the ash vapor and liquid droplets will condense out on the hot shell surfaces. The interaction of these molten slag deposits with hot shell materials will be a major issue for the reliable, long-duration operation of thermionic converters in coal-fired environments.

The behavior of materials in contact with molten slag has been investigated for other technologies, most notably for MHD and to a lesser degree for "high-temperature heat exchangers." During this Program, the extensive literature on slagging, high-temperature materials was reviewed with the goal of extending previous experience to thermionic hot shell development. The corrosion behavior of silicon carbide in both "clean" and "dirty" environments was

reviewed. An effective corrosion rate was determined at ten hours so that widely varying data could be compared over the temperature range 1200-1950 K. The results ranged over six orders of magnitude from clean, oxidizing environments to the high velocity, slagging MHD environment. The development of advanced modeling techniques was also pursued to provide a quantitative, analytical tool for the interpretation and extrapolation of corrosion test results to slag layers of various compositions and in various oxidation environments.

The literature contains several studies in which slag interaction with silicon carbide was investigated as part of a search for compatible ceramic materials for air preheater or electrode applications. Tests conducted with a rotating rod sample of high density SiC in a crucible of molten iron-rich slag resulted in a high corrosion rate [5]. Flow tests carried out with no ash, but with one percent potassium seed added to the gas also resulted in high corrosion rates [6]. Under these conditions, droplets of potassium silicate glass were found on the SiC surface [6, 7]. Other flow tests conducted with ash or coal and one percent potassium seed also resulted in very large (1-10 mm/hr) corrosion rates for SiC [8, 9].

Tests conducted on SiC heat exchanger tubes under boiler conditions resulted in virtually no attack due to slag deposits [10]. These seemingly contradictory results are elucidated by comparing corrosion rate data as a function of temperature. By defining an effective rate based on ten hours of testing, both the parabolic behavior of "clean" environments and the linear rates of "dirty" environments could be compared. As shown in Exhibit C-4.21, the corrosion rates for SiC in air are excellent, less than 10^{-4} mm/hr up to 1800 K. The estimated rate (from photomicrographs) of the hot shell in the

Exhibit C-4.21
Comparison of Various SiC Corrosion Data

12,500-hour life test under natural gas-fired conditions is ten times higher than the pure air result, but still quite acceptable.

The rates under MHD conditions were unacceptably high, i.e., several mm/hr. These large rates were attributed to a fluxing of the protective silica layer. In the case of "clean" fuel, the potassium seed fluxed the silica barrier to form potassium silicate. This reaction compound was rapidly scoured off by the high velocity flow (i.e., about 500 m/sec) of the MHD process. For tests with ash or coal, the protective silica film was dissolved by molten slag deposits. Accelerated corrosion along with scouring led to large corrosion rates.

The more optimistic heat exchanger tests [10] are made difficult to compare due to their relatively short duration (a few hours) and the absence of precise surface measurements. However, if we assume a limit of $\frac{1}{2}$ mil (.013 mm) for the visual observation of surface "damage," we arrive at the limiting values shown in Exhibit C-4.21. These values are consistent with the MHD data at high temperatures, since the MHD data was taken for samples at temperatures above the effective "freezing" point (T_{cv}) of most slags, while the heat exchanger tests were conducted below the freezing point. The reduced fluxing action and oxidant transport rate in frozen slag layers should lead to greatly reduced corrosion rates, although SiC under a molten sodium salt layer has a high corrosion rate even at low temperatures.

Thus, the interaction of molten slag with SiC is characterized by the formation of soluble ionic species in which the corrosion is governed by the diffusion of species through the slag layer. The behavior of this reacting slag layer is illustrated by Exhibit C-4.22. Here a steady-state, molten-slag

Exhibit C-4.22
Schematic of Molten Slag Layer Reacting with SiC.

deposit is shown over a portion of heat exchanger surface such as a thermionic converter hot shell. The slag layer builds up unless its surface temperature is high enough that the slag becomes sufficiently fluid to flow off due to gravitational or to gas shear forces. Oxidant from the gas slowly diffuses through the slag layer to a reaction zone at the SiC surface. Here, SiC is oxidized to form SiO_3 ions which dissolve readily into the silicate slag. The excess silicon is convected away by the flowing slag and the SiC surface recedes. The rate of this "accelerated" corrosion mode is dominated by the convection-diffusion behavior near the SiC interface.

In order to extend this semi-qualitative understanding into a predictive corrosion model, four essential elements are required: 1) a model of slag layer hydrodynamics; 2) a knowledge of slag-gas interface conditions; 3) a knowledge of slag-SiC interface conditions; and 4) a model of multi-component diffusion. Progress was made toward the development of a corrosion model during the Program. Although the model has not been fully implemented, guidelines on the use of SiC hot shells in slagging environments were formulated based on preliminary results.

Techniques for describing the slag layer fluid mechanics already existed [11]. The layer thickness, temperature and velocity distributions were predicted from the gas-flow field, surface geometry, and slag viscosity. Because slag viscosity is a strong function of both temperature and composition, the slag layer behavior was coupled to the solution for composition gradients induced by the reaction zone.

The composition at the surface was set by requirements for chemical equilibrium with the gas phase. If large amounts of low vapor pressure components

(such as the alkalis) were present, the slag layer would contain extra amounts of their oxides. For Eastern coals with large amounts of iron oxide, the oxygen partial pressure would govern the ferric/ferrous ratio in the slag with important property changes. For Western coals, low in iron oxide, the slag composition at the gas interface would be close to that of the ash composition minus the volatile sulfur oxide component.

The reaction at the SiC surface would be very rapid compared to the material transport in the slag. The reaction zone can be considered as negligibly thin with the liquidus composition occurring at interface B in Exhibit C-4.22. This behavior has been observed experimentally for the reaction of silica samples with potassium silicates [12]. Liquidus compositions were available from multi-component phase diagrams [13]. An example for a calcium-aluminum-silicate slag which is a reasonable approximation for Western coals is shown on the ternary phase diagram of Exhibit C-4.23. For a SiC surface at 1800 K, the original slag composition would become saturated in silica at the intersection of the composition tie line and the 1800 K liquidus curve. For this example, the boundary condition for silica is 76%.

Knowledge of interdiffusion coefficients for oxygen and metal species as a function of composition and temperature is critical for accurate corrosion predictions. Recent experimental and analytical studies of diffusion in alkali silicates and in silicate ternaries provided the input for modeling Western coals [12, 14, 15]. Diffusion in Ca-Al-silicates has been described in terms of form-effective diffusion units: Ca^{++} , free O_2^- , AlO_n , Si_pO_q , where n, p, q are functions of temperature [15].

Exhibit C-4.23
Ternary Phase Diagram Used in Determining Interface Condition

The governing equations for the various diffusion "units" were formulated from conservation of species considerations. A set of coupled, time-dependent, convection-diffusion partial differential equations described the behavior.

Sufficient data existed for the complete determination of SiC corrosion behavior for Western coals. This required the simultaneous solution of species diffusion in a time-varying slag layer. The corrosion rate, along with details of the slag layer behavior, could be predicted, although this has not yet been done.

Preliminary model results indicated that large SiC corrosion rates could occur for several slagging operation regimes. Guidelines to avoid entering any of those regimes would include the following:

- 1) Maintain reasonable oxygen partial pressure (10^{-3} atm).
- 2) Reduce slag layer flow near SiC.
 - a) flow field design
 - b) operate SiC below slag "freezing" temperature
- 3) Operate with a slag low in basic oxide components.

The "freezing" temperature of slag can be estimated from a correlation of the temperature of critical viscosity based on the mineral analysis of coal ash [16]:

$$T_{cv} = 3263 - 1470A + 360A^2 - 14.7B + 0.15B^2 \quad (C-4.2)$$

$$\text{where } A = \text{SiO}_2/\text{Al}_2\text{O}_3,$$

$$B = \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO},$$

T_{cv} is in K and the oxides are given in weight percent.

The meaning of the third guideline cannot be determined quantitatively at this time. However, for the purpose of selecting suitable test coals, a preliminary corrosion index was postulated. Since the basic oxides and the alkalis severely degrade corrosion performance, the index, R_c , was defined as follows:

$$R_c = \frac{\text{Base}}{\text{Acid}} * (\text{Na}_2\text{O} + \text{K}_2\text{O}) \quad (\text{C-4.3})$$

where $\text{Base} = \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}$

and $\text{Acid} = \text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2$,

with the oxides calculated as weight percent of the coal ash. This index can range up to around seven for U.S. coals. The corrosion index for the slag used in the rotating rod test displayed on Exhibit C-4.21 was 2.4. For initial SiC hot-shell tests, coals with a corrosion index less than one are recommended. A series of tests which would allow a correlation between corrosion rate and the corrosion index is still needed.

Although investigations into the use of coal as a fuel were limited to theoretical analyses, natural gas was not the only heat source tested for actual converter use. A gas-fired furnace used in the Program was modified so that it could also operate on No. 2 distillate oil, and a torispherical converter, denoted number 280, was life-tested in that fuel environment. The typical constituents of this fuel are 87.3 weight percent carbon, 12.5 weight percent hydrogen and 0.2 weight percent sulfur. The furnace was operated slightly oxygen rich with between one and two percent excess air. The emitter temperature varied between 1650 and 1750 K; most of the test period was at

temperatures above 1700 K. Combustion conditions with the No. 2 oil were significantly less stable than with natural gas.

The life test was run for 1200 hours and the performance was stable throughout that period. The test was concluded, for programmatic reasons, without converter failure. Visual inspection of the hot shell at that time showed an appearance similar to those tested in gas furnaces. Performance measures (e.g., barrier index, current-voltage characteristic) were identical for both fuels.

A converter also proved to be easy to control during solar heating. The temperatures of the emitter, collector flange, and reservoir were stable. These temperatures were easily varied within their operating range while optimizing the converter performance. Rapid thermal cycling (e.g., by passing clouds) caused no problems. At an emitter temperature of 1400 K, the highest achievable at the test facility, converter performance was identical to that measured in a combustion furnace.

4.5 Other Measures of Capability

It is now routinely possible to build thermionic converters which operate with a barrier index of 2.10 eV, improved from 2.35 eV in just five years (see Exhibit C-4.24). Exhibit C-4.25 illustrates the significance of this progress for the economic competitiveness of thermionic technology. Although the system costs shown should be regarded as relative costs for purposes of this discussion -- system costs are estimated more precisely in Part D -- lowering of the barrier index and raising of the converter operating temperature by the development

Exhibit C-4.24
Barrier Index of Flame Heated Converters
as Function of Time

Exhibit C-4.25

1.8 eV Barrier Temperature and Barrier Index

efforts of the Program have lowered estimated system costs by roughly a factor of twenty. Barrier indices slightly below 2.00 eV have been observed during the Program under electron bombardment rather than combustion heating. Significant further reductions in barrier index values are considered plausible, and have actually been observed in the laboratory, but will require one or more of the advanced design techniques which are the subject of Part E.

Total power output of most of the devices tested during the Program was less than 100 Watts, i.e., the size of a typical household lightbulb. Any practical system for generating power in quantity will employ more powerful devices. Work in the development of such larger devices has barely begun (see Part E, Section 2.7). It has been demonstrated with metallic converters having an active emitter area of $.3 \text{ m}^2$ that large devices can be stably operated and controlled. No unexpected plasma, magnetic field or other effects producing instabilities were observed. However, the characterization of preferred designs for large converters -- and, consequently, the evaluation of performance -- remains to be accomplished.

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5. CONVERTER ARRAYS

5.1 Introduction

Practical terrestrial applications of thermionic energy converters will usually require that output power be delivered with a higher voltage and in larger amounts than can be supplied by a single converter. While some work in the Program has attempted to address the first of these problems through such techniques as the use of inductive output power coupling (see Part E, Section 2.9) or by employing DC/AC power inverters, the most promising solution lies in electrically connecting multiple converters together in a series-parallel array, i.e., as in the Thermionic Array Module (TAM) design concept. Such an array would also serve to insure a very high overall system reliability, despite possible failures of individual converters.

While the major focus of Program efforts has been on development of the individual converter, progress has also been made in the development of the arrays themselves, including construction and testing of small arrays, as discussed below in Section 5.2, and theoretical analysis of the behavior of larger arrays under non-uniform heat fluxes, as described in Section 5.3.

5.2 Small Array Testing

In order to address the problems of operating converters in small arrays, a module was constructed and tested using four one-inch hemispherical converters, i.e., of the kind illustrated in Exhibit C-1.6. The module itself is

illustrated in Exhibit C-5.1. For these tests the converters were connected in electrical series. However, parallel and series-parallel connections were also possible.

The performance of each converter was measured separately at an emitter temperature of 1600 K, and with collector and reservoir temperatures optimized. Three converters showed satisfactory performances with barrier indices of approximately 2.15 eV. The fourth converter leaked. The module was consequently tested with only three operating converters.

Exhibit C-5.2 shows plots of current versus voltage for each of the three converters separately, labeled 250, 252, and 253, and when connected in series. The latter plot is the curve denoted "all" in the exhibit and represents the output of the array with the effects of emitter sleeve, contact resistance, and interconnecting lead losses included. These losses were quite high in the array, as shown in Exhibit C-5.3, in which the net power plotted directly from the "all" curve of Exhibit C-5.2 is compared to the gross power obtained by summing the three individual converter curves without losses (i.e., when individually operated at the same current delivered by the module).

Although the effort is not part of this Program, additional research into converter array design, specifically directed toward applications of the co-generation prototype discussed in Part C, Section 1.3, has been conducted as part of another Department of Energy project [1].

Exhibit C-5.1
Four-Converter Array

Exhibit C-5.2
Output Current and Voltage for Three Converter Module

Exhibit C-5.3
Net and Gross Power of Three Converter Module vs. Voltage

5.3 Thermal Variation Effects Analysis

Significantly greater progress was made during the Program in terms of theoretical analysis of the behavior of thermionic arrays, particularly in regard to the effects of thermal variation on array performance.

Most heat sources will exhibit a non-uniform heat flux unless some smoothing mechanism such as heat pipes is employed to integrate the heat flux and provide a more uniform temperature. The performance of a converter array is very sensitive to any non-uniform distribution of input power.

Previous system studies [2-4] of non-uniform heat flux in a series-parallel array used a very elementary model of a thermionic converter. In this Program a phenomenological model formulated by N. S. Rasor [5] was used which took into account collector temperature, cesium pressure, interelectrode spacing, and electrode work functions in a realistic way. The model produced current density-voltage (J-V) curves for an ignited-mode cesium diode using a simplified treatment of plasma transport theory and sheath boundary conditions. The variation of emitter and collector work functions with surface temperature and cesium pressures was also included. A model-computed cesium pressure family is compared with experimental data in Exhibit C-5.4. The agreement between the two is quite close.

In the J-V curves produced by the phenomenological model, emitter temperature was held constant, and input heat flux Q_{in} varied with current density. To calculate a J-V curve where Q_{in} was constant and emitter temperature varied with current, the following correlation was used:

Exhibit C-5.4
 Comparison of Current-Voltage Curves Computed
 by Rasor Model with Experiment

$$Q_{in} = 1.636 \times 10^{-3} J T_E + 1.09 \times 10^{-12} (T_E^4 - T_C^4). \quad (C-5.1)$$

The first term in this expression represents the electron cooling of the emitter, and the second represents the radiation losses from the emitter. T_E and T_C are the emitter and collector temperatures, respectively. Q_{in} is expressed in Watts per square centimeter, J in Amperes per square centimeter, and T_E and T_C in Kelvins.

For specified values of Q_{in} , J , and T_C , Equation C-5.1 was solved for T_E . This result was used as an input to the cesium diode model to produce a J-V curve where Q_{in} was constant and emitter temperature varied with current.

The variation of emitter temperature with heat flux for fixed values of voltage is shown in Exhibit C-5.5. The variation is small until a certain critical value of Q_{in} is exceeded. The emitter temperature then rises abruptly. An increase in cesium pressure raises the critical value of Q_{in} . This latter behavior is illustrated in Exhibit C-5.5 using only the case where $V = .4$ Volts, although it is a general occurrence.

Exhibit C-5.6 illustrates a family of model-computed J-V curves for different values of constant heat flux. The collector and cesium reservoir temperatures of 1000 K and 591 K, respectively, were chosen to give optimum power and efficiency for the $Q_{in} = 30$ Watts/cm² curve. The curves for which the heat fluxes are 40 and 30 Watts/cm² both behave as having a "negative resistance" region. This feature was first analyzed by Schock [6], who showed that this effect can occur at high heat flux or low cesium pressure. The effect is due to the desorption of cesium from the emitter as the emitter temperature is

INPUT POWER Q_{in} (Watts/cm²)

Exhibit C-5.5

Razor Model Predictions of Emitter Temperature
vs. Input Power for Given Output Voltages

Exhibit C-5.6
Rasor Model Predictions of Current Density
vs. Output Voltage for Given Input Power

increased. This increases the emitter work function, causing the emitted current to fall, rather than rise, as emitter temperature increases. The phenomenon is also responsible for the reverse slopes seen in some of the curves in Exhibit C-5.5. Emitter surfaces which would not require cesium adsorption to produce a low work function would not produce negative resistance regions.

The same family of J-V curves which were presented in Exhibit C-5.6 are also shown in Exhibit C-5.7, but with the cesium reservoir temperature T_R adjusted to give optimum power for each value of heat flux. Optimizing T_R has eliminated the negative resistance regions.

The more realistic converter model thus emphasized the importance of avoiding the onset of cesium desorption as a practical operating constraint -- the resulting negative resistance could markedly cut converter performance, or in extreme cases, elevate emitter temperature enough to bring on early converter failure.

The model was incorporated in a computer program that simulated a series-parallel-connected converter array. The iterative program solved a set of simultaneous, nonlinear equations for the current and voltage of each converter in the array. The solution also yielded the emitter temperature of each converter, and the overall output current, voltage, power, and converter efficiency. An overall current-voltage characteristic for the entire array was drawn by varying the load resistance R_L . To date this program has only been used to compute operating conditions with non-uniform heat flux and cesium reservoir temperatures, but the effects of open or short-circuits in individual converters could be evaluated as well.

Exhibit C-5.7

Rasor Model Predictions of Current Density vs. Output Voltage
 for Given Input Power with Cesium Reservoir Temperature Optimized

The 5 x 5 array shown in Exhibit C-5.8 was used as the reference for this analysis. The mathematical model of the array and its computer program could handle any size of array, including non-square arrays, but the 5 x 5 array was chosen because it could be treated conveniently on a small desktop computer. The interconnecting resistors were chosen to have a resistance of 0.1 milliohms, a value similar to normal power connections.

Two cases of heat flux distribution were examined and compared to a baseline case with uniform, optimized operating conditions. For the baseline case, the heat flux to each converter was set at 30 Watts/cm². In the first example analyzed, heat flux was assumed to vary from 40 Watts/cm² to 20 Watts/cm² along the direction of the series connections ("series-variation"), and in the other case, heat flux was varied from 40 Watts/cm² to 20 Watts/cm² along the direction of parallel connections ("parallel-variation"). For the case of series-variation of Q_{in} , all the converters in the array operated at the same current, whereas for the case of parallel-variation, all converters operated at the same voltage.

In addition, these latter cases were themselves divided into two subcases; one in which all converters had the same reservoir temperature, and the other in which the reservoir temperature was set at the optimum value for each value of heat flux. Results are summarized in Exhibits C-5.9 through C-5.12.

Array output current-voltage characteristics for the case of a single value of reservoir temperature, $T_R = 591$ K, are shown in Exhibit C-5.9. The corresponding power/efficiency curves are shown in Exhibit C-5.10. The maximum output power of the series-variation case was 1.28 kW, approximately 61% of the maximum power of the baseline case with uniform heat flux.

Exhibit C-5.8
5 x 5 Series-Parallel Converter Array

Exhibit C-5.9
 Rasor Model Predictions for Current-Voltage Characteristics
 for 5x5 Converter Array (Non-Optimized)

Exhibit C-5.10
Rasor Model Predictions for Output Power and Efficiency

Exhibit C-5.11
 Rasor Model Predictions for Current-Voltage
 Characteristics for 5x5 Converter Array
 (Cesium Reservoir Temperature Optimized)

Exhibit C-5.12

Rasor Model Predictions for Output
 Power and Efficiency for 5x5 Converter Array
 (Cesium Reservoir Temperature Optimized)

The volt-ampere curve for the parallel-variation case consisted of three branches with areas of hysteresis existing. This hysteresis was caused by the negative resistance regions in the J-V curves for $Q_{in} = 40$ and 35 Watts/cm^2 . The high-current branch of the array volt-ampere curves was identical to the baseline case volt-ampere curve, whereas the low current branch approached the series-variation case volt-ampere curve. Maximum power output was 1.62 kWe, i.e., about 77% of the baseline.

In the calculations whose results are shown in Exhibits C-5.11 and C-5.12, the cesium reservoir temperature was adjusted for each converter in the array to provide optimum power output. The regions of hysteresis in the parallel-variation case disappeared. Exhibit C-5.12 shows that peak power for the series-variation case increased to 1.68 kWe, i.e., 80% of baseline. Peak power for the parallel-variation case was 1.87 kWe, i.e., 89% of baseline.

Exhibit C-5.13 summarizes predicted array operating conditions with an electrical load of 3.6 milliohms. Such a load yielded the maximum power and efficiency in the baseline case. The variation of emitter temperatures among the converters in the array for this load resistance is shown in Exhibits C-5.14 and C-5.15. Both the single cesium reservoir temperature and the cesium-optimized cases are illustrated.

For the series-variation cases, the emitter temperatures covered a wide range owing to the fact that all the converters were constrained to operate at the same current. For the non-optimized series-connected case, T_E varied from 2095 K to 1547 K. The maximum emitter temperature for the optimized series-connected case was 67 K lower, but it and the total temperature variation were still unacceptably high. Materials considerations might preclude

EXHIBIT C-5.13

PREDICTED 5 X 5 ARRAY OPERATING PARAMETERS
AT ELECTRICAL LOAD OF 3.6 MILLIOHMS

Non-Optimized

	<u>Baseline</u>	<u>Series-Variation</u>	<u>Parallel-Variation</u>
Current	762.8 A	587.7 A	600.7 A
Voltage	2.75 V	2.11 V	2.16 V
Output Power	2.10 kWe	1.24 kWe	1.30 kWe
Efficiency	13.95%	8.25%	8.65%
Emitter Temperature	1722 K	2095-1547 K	2230-1630 K

Cesium-Optimized

	<u>Baseline</u>	<u>Series-Variation</u>	<u>Parallel-Variation</u>
Current	762.8 A	682.4 A	715.0 A
Voltage	2.75 V	2.48 V	2.57 V
Output Power	2.10 kWe	1.69 kWe	1.84 kWe
Efficiency	13.95%	11.28%	12.25%
Emitter Temperature	1722 K	2028-1453 K	1826-1696 K

Exhibit C-5.14
Predicted Emitter Temperatures for Heat Flux Non-Uniformity
in the Series-Connected Direction

Exhibit C-5.15
Predicted Emitter Temperatures for Heat Flux Non-Uniformity
in the Parallel-Connected Direction

operating a converter array with any of the emitter temperatures above 1900 K. To correct this condition would necessitate operation at a lower overall input heat flux or a higher current. Both approaches would further reduce output power.

For the parallel-variation cases, non-optimized (i.e., single T_R) emitter temperatures of converters with $Q_{in} = 20, 25, \text{ and } 30 \text{ Watts/cm}^2$ were all approximately equal to 1640 K. However, the converters for which $Q_{in} = 35 \text{ and } 40 \text{ Watts/cm}^2$ had high emitter temperatures. In fact, these temperatures were higher than for the equivalent converters in the series-variation case. The cesium-optimized case for heat flux variation in the parallel direction is also shown in Exhibit C-5.15. Only a small variation in emitter temperature from 1696 K to 1826 K was produced in this case. These temperatures are well within the achievable region of operation.

In summary, these results showed that a factor of two non-uniformity in the input heat flux along the series-connected direction of a converter array would lead to a reduction in output power and a wide variation in emitter temperature even when the cesium pressure was optimized for each converter. Variations of this kind should therefore be avoided if possible in the design of a series-parallel array. The same heat flux variation in the parallel-connected direction, however, resulted in only a 12% drop in output power and only a 130 K variation in emitter temperature when the cesium pressure was properly controlled. It is important in this situation that the cesium pressure be maintained high enough so as to avoid negative resistance regions in the J-V characteristics of any of the converters in the array. If the non-uniformity in heat flux cannot be predicted in advance, a cesium reservoir could be coupled to the heat flux, so that pressure would increase with heat flux.

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APPENDICES TO VOLUME 2,
PART C

APPENDIX 2-A

THE CONVERTER TESTING PROGRAM

Except for a single converter tested with solar heating at Georgia Institute of Technology's Advanced Components Test Facility, and a few electron bombardment tests, all converter tests in the Program were performed in a high temperature furnace facility. The furnace was heated by a flat flame burner normally firing natural gas and later modified to accept light fuel oil and/or coal-oil mixtures. The burner was equipped with flue gas recuperation to pre-heat the combustion air. Temperatures in excess of 1850 K could be reached in this furnace, which was a firebrick-lined cubic cavity about .3 m along each edge.

The test furnace is shown in Exhibit 2-A.1. Converters were normally mounted flush with the furnace wall. A converter mounting fixture is shown in Exhibit 2-A.2. The furnace atmosphere was sampled by measuring the constituents of the flue gas. A typical sample is shown in Exhibit 2-A.3. The furnace was always operated with excess air when testing CVD hot shells because a silicon carbide coating is most protective in an oxidizing atmosphere.

Emitter temperatures were measured with an optical pyrometer. These measurements were corrected for the emissivity of the silicon carbide and the transmission losses in the site port glass. Furnace, collector, emitter flange, and cesium reservoir temperatures were measured with chromel alumel thermocouples. All converter and furnace temperature measurements were recorded on a strip chart recorder as a permanent test record.

Exhibit 2-A.1
Test Furnace

2-167

Exhibit 2-A.2
Test Furnace Mounting Assembly

EXHIBIT 2-A.3

SAMPLE TEST FURNACE ATMOSPHERE (VOLUME %)

OXYGEN (O_2)	2.5%
CARBON DIOXIDE (CO_2)	8%
NITROGEN (N_2)	69%
WATER (H_2O)	20%
NITROGEN MONOXIDE (NO)	100 ppm
CARBON MONOXIDE (CO)	100 ppm

Converters were initially tested by using an AC power supply to sweep the electrodes. A complete I-V curve was then displayed on an oscilloscope, and a curve sampler was used to drive an X-Y plotter to record the scope traces. The converter current was measured across a calibrated shunt, and the converter voltage was measured with voltage taps at the emitter flange, and on the collector. This voltage measurement included the emitter lead, or sleeve loss. After the converter performance had been mapped with AC sweep, direct current measurements were made. DC output was measured with appropriate meters. A schematic diagram of the converter test set up is shown in Exhibit 2-A.4. The curve sampler and the X-Y plotter are not shown.

Numerous converters, having a variety of designs and made from a variety of materials, were tested during the Program. A complete list of the converters tested, along with salient characteristics, is given in Exhibit 2-A.5.

Note: All TC's Type K

Exhibit 2-A.4
Schematic Diagram of Converter Test

EXHIBIT 2-A.5

CHARACTERISTICS OF CONVERTERS TESTED

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
126	1/76	R/V*	W**	W O***	Cs	
127	1/76	R/V	W	Zn O	Cs	
128	1/76	R/V	W	W O	Cs	
130	2/76	R/V	W	Sr O	Cs	
131	2/76	R/V	W	Au Foil	Cs	
132	1/76	R/V	W	ZnO on Ni	Cs	
133	3/76	R/V	Kanthal on W	Ni	Cs	Alloy Emitter Test
134	4/76	R/V	W	SrO on Ni	Cs	
135	4/76	R/V	Adquadag Graphite on W	Ni	Cs	Graphite work Function Measurement
136	4/76	R/V	W	ZnO on Ni	Cs	
137	5/76	R/V	W	W O	Cs	
138			Phillips Cathode	BaO on Ni	Cs	
139	5/76	R/V	W	BaO on Ni	Cs	
140	5/76	R/V	W	ZnO on Ni	Cs reflux	
142	6/76	R/V	W Sr	Sr O on Ni	Cs	
143	8/76	R/V	L605	Ni	Cs	

* Research-Variable Spacing Converter

** Sintered-Electropolished Tungsten

*** Mixed Oxides of Various Metal to Oxide Ratios; e.g., W_xO_y

EXHIBIT 2-A.5 (Page 2 of 12)

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
144	6/76	R/V	W	LaB	Cs	Au tube oxyger Barrier Index 2.0 source
145	6/76	R/V	Aquadag Graphite on W	ZnO on Ni	Cs	
146	7/76	R/V	Pt on W	ZnO on Ni	Cs	
147	6/76	Triode	Phillips Cathode	W	Cs reflux	
148	8/76	R/V	Pt	Ni Struc- tured	Cs	Barrier Index 2.04 eV
149	9/76	R/V	Pt	Ni	Cs	Control for No. 148
150	8/76	R/V	W	BaO on Ni	Cs reflux	Guarded collector
151	9/76	R/V	W-MgO	Ni	Cs reflux	
152	9/76	R/V	W	ZnO on Ni	Cs reflux	
153	9/76	R/V	W	W O 6n Nb 1% Zr	Cs	
154	9/76	R/V	Pt	ZnO on Ni	Cs reflux	Guarded collector
155		Triode	Phillips Cathode	Ni	Cs reflux	Window Triode
156	12/76	R/V	Pt	W O	Cs	
157	11/76	R/V	W	Al ₂ O ₃	Cs	Collector pla sprayed

EXHIBIT 2-A.5 (Page 3 of 12)

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
158	11/76	R/V	W	Ti ₂ O	Cs	
159	12/76	R/V	W	W O on Nb	Cs	Barrier Index = 2.0 eV
160	11/76	R/V	W	BaO on Ni	Cs reflux	
161	12/76	R/V	Pt	Ni struc- tured	Cs	
162	12/76	R/V	W	W O on Nb 1% Zr	Cs	Life tested for 2350 hours Barrier Index = 2.0 eV
163	1/77	R/V	Pt	Ti ₂ O	Cs	Barrier Index 1.96 at 1400 K
164	2/77	R/V	Pt	Ni	Cs	Guarded collector
165	4/77	R/V	W	Ni	Cs reflux	Collector heat flux experiment
166	2/77	R/V	W	LaB	Cs	Showerhead collector
167	3/77	R/V	W	MgO on Ni	Cs	
168	4/77	R/V	LaB	LaB	Cs reflux	Window Diode
169	4/77	R/F	W	Ta foil MgO parti- cles	Cs	Close-spaced compliant electrodes
170	4/77	R/V	Pt	BaO on Ni	Cs	
171	2/77	C/A*	L605	Ni	Cs	Potassium heat pipe collector

* Combustion Alloy Converter

EXHIBIT 2-A.5 (Page 4 of 12)

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
172	3/77	C/A	L605	Ni	Cs	Potassium heat pipe collector
173	4/77	R/V	W	Ni	Se	
174	6/77	R/V	W	Ni	Cs reflux Cs CO	
175	6/77	R/V	W	Ni	Cs	Heat flux measurement
176	6/77	R/V	Pt	BaO-B on Ni	Cs	
177	8/77	R/V	W,	Ni	Cs Cs CO	
178	7/77	R/V	W	W O	Cs	
179	12/77	C/A	L605	Ni	Cs	Potassium heat pipe collector
180	12/77	R/V	W	LaB on Mo	Cs reflux	Guarded collector
181		C/A	L605	Ni	Cs	Copper heat pipe collector
182	10/77	R/V	LaB Re	Ni	Cs Reflux	Guarded collec window
183	11/77	R/V	L605	Ni	Cs	
184	11/77	Heat pipe	W	W O on Nb 1% Zr	Cs	Lithium heat pipe emitter Potassium heat pipe collector
185	11/77	Heat pipe	W	W O on Nb 1% Zr	Cs	Lithium heat pipe emitter Potassium heat pipe collector

EXHIBIT 2-A.5 (Page 5 of 12)

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
186	12/77	R/V	Inconel 671	Ni	Cs	
187	12/77	Heat pipe	W	W O on Nb 1% Zr	Cs	Lithium heat pipe emitter Potassium heat pipe collector
188	12/77	C/A	Inconel 671	Ni	Cs	18 cm ² Flat Emitter
189	1/77	Heat pipe	W	W O on Nb 1% Zr	Cs	Lithium heat pipe emitter Potassium heat pipe collector
190		C/A	L605	Ni	Cs	Barrier Index = 2.08 eV 18 cm ² emitter
191	2/78	R/V	W	Ni	Se	
192		Heat pipe	W	W O on Nb 1% Zr	Cs	Lithium heat pipe emitter Potassium heat pipe collector
193	3/78	R/ Tetrode	Phillips Cathode	Ni	Cs	Guarded collector window
194	3/78	Heat pipe	W	W O on Nb 1% Zr	Cs	Lithium heat pipe emitter Potassium heat pipe collector
195	3/78	Heat pipe	W	W O on Nb 1% Zr	Cs	Lithium heat pipe emitter Potassium heat pipe collector

EXHIBIT 2-A.5 (Page 6 of 12)

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
196		R/ Tetrode	Phillips Cathode	Ni	Cs reflux	Guarded collector
197	4/78	R/V	Mo/Re Hybrid Struc- tured	Ni	Cs	Barrier Index : 2.1 eV Window Diode
198	6/78	R/V	L605	Ni	Cs	Barrier Index : 2.05 eV
199		Heat pipe	W	W O on Nb 1% Zr	Cs	3 diode module
200	6/78	Heat pipe	W	W O on Nb 1% Zr	Cs	Lithium heat pipe emitter Potassium heat pipe collector
201	6/78	R/V	W	LaB shower- head	Cs	Window Diode
202	7/78	R/V	Mo/Re Hybrid struc- tured	Ni	Cs reflux	Window Diode
203	7/78	Heat pipe	W	W O on Nb 1% Zr	Cs	Lithium heat pipe emitter Potassium heat pipe collector
204	8/78	R/V	Ir on W	Ni	Cs	Barrier Index 2.09 eV
205		Heat pipe	W	W O on Nb 1% Zr	Cs	
206	9/78	R/V	W	W O	Cs	Barrier Index 2.02 eV

EXHIBIT 2-A.5 (Page 7 of 12)

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
207	10/78	R/V	W	W O	Cs reflux	Barrier Index = 2.04 eV
208		R/V	W	Ni	Graphite	
209	10/78	R/V	W	LaB shower- head	Cs	Window Diode
210	10/78	R/V	W	Mo O on Nb	Cs	Barrier Index = 2.08 eV
211	10/78	C/A	Inconel 671	Ni	Cs	
212		R/V	Mo/Re Hybrid Struc- tured	Ni	Cs reflux	Barrier Index = 2.1 eV Window Diode
213		C/A	Inconel 671	Ni	Cs	
214		R/V	LaB	Mo	Cs	Guarded collector
215		R/V	W	Ni	Cs	Heat flux
216		R/V	W	Mo O	Cs	
217		R/V	LaB on Re	Ni	Cs	
218	5/79	C/SiC*	W (CVD)**	Ni	Cs	One-inch hemispherical
219	5/79	R/V	LaB	LaB	Cs	
220	4/79	R/V	BaO on Mo	BaO on Ni (201)	Cs	Particle Diode
221	7/79	C/SiC	W (CVD)	Ni	Cs	One-inch hemispherical

* Combustion Silicon Carbide Hot Shell

** Sintered Tungsten Emitter, Chemically Vapor Deposited

EXHIBIT 2-A.5 (Page 8 of 12)

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
222	7/79	R/V	W	Ni	Cs Cs/ graphite	
223	8/79	R/V	Mo	W O	Cs	Window Diode
224	9/79	R/V	LaB	Mo	Cs	Window Diode Guarded collect
225	9/79	R/V	W (CVD)	Ni	Cs	
226	11/79	R/V	W (CVD)	Ni	Cs	
227	11/79	R/V	Mo	Nb	Cs	
228	11/79	C/SiC	W (CVD)	Ni	Cs	One-inch hemispherical
229	2/80	R/V	W	Ni	Cs/ graphite	One-inch hemispherical
230	2/80	C/SiC	W (CVD)	Ni	Cs	Two-inch hemispherical
231	11/79	R/V	Mo	Mo O	Cs	
232	2/80	R/V	Mo	Mo O	Cs	
233	3/80	R/V	Mo/Re Hybrid Struc- tured	Ni	Cs	Special pump- out tubing
234	4/80	R/V	W (CVD)	Nb	Cs	
235	4/80	R/V	MgO on W	Mo	Cs	Guarded collector
236	5/80	R/V	W	Mo O	Cs	
237	5/80	C/SiC	W (CVD)	Ni	Cs	
238		R/V	W	Mo	Cs reflux	Guarded collector

EXHIBIT 2-A.5 (Page 9 of 12)

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
239	6/80	C/SiC	W (CVD)	Ni	Cs	One-inch hemispherical
240	7/80	R/V	W (CVD)	Mo O	Cs	Barrier Index = 1.98 eV
241	7/80	R/V	W	Mo O	Cs	
242	7/80	R/V	W	Mo O	Cs	
243	8/80	R/V	Re	Mo O	Cs	
244	8/80	R/V	W	Ni	Cs	
245	8/80	R/V	W	Ni	Cs	
246		R/V	W	Ni	Cs	Heat flux measurement
247		C/SiC	W (CVD)	Ni		Two-inch hemispherical
249	11/80	R/V	W (CVD)	Mo O	Cs	
250	11/80	C/SiC	W (CVD)	Ni	Cs	One-inch hemispherical
251	11/80	C/SiC	W (CVD)	Ni	Cs	One-inch hemispherical
252	11/80	C/SiC	W (CVD)	Ni	Cs	One-inch hemispherical
253	11/80	C	W (CVD)	Ni	Cs	One-inch hemispherical Four-dial array
254	11/80	R/V	W (CVD)	Mo O	Cs	
255	12/80	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
256	12/80	R/V	W (CVD)	Mo O	Cs	

EXHIBIT 2-A.5 (Page 10 of 12)

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
257	12/80	R/V	Mo	Mo O	Cs	
258	1/81	R/V	W	Ni	Cs/ graphite	
259	1/81	R/V	W	Ni	Cs	
260	2/81	R/V	W	Ni	Cs	
261	4/81	R/V	Mo-O-Zr	Mo-O-Zr	Cs	
262	5/81	R/V	W	Mo O on Ni	Cs	
263	5/81	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
264	6/81	C/SiC	W (CVD)	Ni	Cs	One-inch hemispherical
265	6/81	C/SiC	W (CVD)	Ni	Cs	One-inch hemispherical
266	6/81	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
267	7/81	R/V	W (CVD) struc- tured	Ni	Cs	
268	8/81	R/V	Mo-O-Zr	Mo-O-Zr	Cs	
269	8/81	R/V	W	Mo O	Cs	
270	8/81	C/SiC	W (CVD)	Mo O on Ni	Cs	Two-inch torispherical
271	9/81	R/V	W	Ni	Cs/ graphite	
272	3/82	C/SiC	W (CVD)	Mo O on Ni	Cs	Two-inch torispherical
273	4/82	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical

EXHIBIT 2-A.5 (Page 11 of 12)

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
274	5/82	R/V	W	Ni	Cs/ graphite	
275	5/82	R/V	W	BaO 1% Ni on Ni	Cs	
276	6/82	R/V	W	Mo O on Ni	Cs	
277	7/82	R/V	Mo/Al ₂ O ₃ Cr ₂ O ₃	Mo	Cs	
278	8/82	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
279	10/82	R/V	W	Ni	Cs/ graphite	
280	11/82	C/SiC	W (CVD)	Ni		Two-inch torispherical
281	12/82	R/V	W	Mo O on Ni	Cs	
282	2/83	R/V	W	Mo O on Nb	Cs	
283	1/83	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
284	2/83	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
285	3/83	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
286	5/83	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
287	6/83	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
288	6/83	C/SiC	W (CVD)	Ni	Cs	One-inch torispherical

EXHIBIT 2-A.5 (Page 12 of 12)

<u>Converter Number</u>	<u>Date</u>	<u>Type</u>	<u>Electrode Materials</u>		<u>Reservoir</u>	<u>Comments</u>
			<u>Emitter</u>	<u>Collector</u>		
289	6/83	R/V	W	Zr O	Cs	
290	7/83	C/SiC	W (CVD)	Ni	Cs	One-inch torispherical
291	7/83	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
292	7/83	R/V	W (CVD)	Ni	Cs/ oxygen- ated	
293		C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
294	8/83	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
295	8/83	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
296	8/83	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical
297	10/83	R/V	W Struc- tured	Ni Struc- tured	Cs	
298	10/83	C/SiC	W (CVD)	W O on Ni	Cs	Two-inch torispherical
299	11/83	C/SiC	W (CVD)	Ni	Cs	Two-inch torispherical

APPENDIX 2-B

PUBLICATIONS RESULTING FROM CONTRACT

1976

1. Balestra, C., Miskolczy, G., and Wang, C., "Fabrication of Ceramic Hot Shells for Thermionic Converters," TE4203-20-77 (October 1976).
2. Huffman, F.N., "Thermionic Energy Conversion Progress Summary, "Proceedings of the 11th Intersociety Energy Conversion Engineering Conference, p. 1624 (1976).
3. Huffman, F.N., Lieb, D., Briere, T.R., Sommer, A.H., and Rufe, F., "Advanced Thermionic Converter Development," Proceedings of the 11th Intersociety Energy Conversion Engineering Conference, p. 1645 (1976).
4. Huffman, F.N., Lieb, D., Sommer, A.H., Briere, T.R., and Rufe, F., "Electrode Development for Thermionic Converters," Presented at the IEEE International Conference on Plasma Science, Austin, TX (1976).
5. Miskolczy, G. and Speidel, T.O.P., "Thermionic Topping of a Steam Powerplant," Proceedings 11th Intersociety Energy Conversion Engineering Conference, p. 1050 (1976).
6. Sommer, A.H. and Briere, T.R., "Thermionic Work Function of (Cs)ZnO," Applied Physics Letters, Vol. 29, No. 2, p. 89 (1976).

1977

7. Huffman, F.N., Lieb, D., and Rufe, F., "Thermionic Converter Studies at Thermo Electron," Proceedings of the 12th Intersociety Energy Conversion Engineering Conference, p. 1548 (1977).
8. Huffman, F.N. and Miskolczy, G., "Thermionic Energy Conversion Topping System," ASME paper, Winter Annual Meeting, Atlanta, GA, 77-WA/Ener-6 (December 1977).
9. Huffman, F.N. and Rufe, F., "Development of Advanced Thermionic Converters," presented at the World Electrotechnical Congress, Moscow, paper No. 5A.33 (1977).

10. Lieb, D., Goodale, D., Briere, T. and Balestra, C., "Thermionic Converter Performance with Oxide Collectors," Proceedings 12th Intersociety Energy Conversion Engineering Conference, (1977).
11. Miskolczy, G. and Huffman, F.N., "Study of a Thermionic Topped Steam Powerplant," presented at the World Electrotechnical Congress, Moscow (1977).
12. Miskolczy, G. and Huffman, F.N., "Study of a Thermionic Topped Steam Powerplant," presented at the World Electrotechnical Congress, Moscow, paper No. 5A.36 (1977).
13. Miskolczy, G. and Huffman, F.N., "Evaluation of MHD-Thermionic-Steam Cycles," Proceedings of the 12th Intersociety Energy Conversion Engineering Conference, p. 1610 (1977).
14. Miskolczy, G. and LaRue, G., "Preliminary Cost Estimate for Thermionic Converters for an Out-of-Core Space Reactor," TE4220-76-77 (Feb. 1977).

1978

15. Huffman, F.N., Gunther, B., and Margulies, A., "Conceptual Design of a Thermionic Topped Steam Plant Using an Advanced Boiler Concept," Proceedings 13th Intersociety Energy Conversion Engineering Conference, p. 1893 (1978).
16. Huffman, F.N., Gunther, B., and Miskolczy, G., "Characteristics of Combustion-Heated Thermionic Diode," Proceedings 13th Intersociety Energy Conversion Engineering Conference, p. 1898 (1978).
17. Oettinger, P.E. and Huffman, F.N., "Experiments with Enhanced Mode Thermionic Converters, IEEE Trans. on Electron Devices, pp. 5-6 (1978).

1979

18. Goodale, D.B., Lee, C., Lieb, D. and Oettinger, P.E., "Thermionic Energy Converter Investigations," Proceedings of the 14th Intersociety Energy Conversion Engineering Conference, p. 1862 (1979).
19. Huffman, F.N., Gunther, B., and Miskolczy, G., "Flame-Fired Thermionic Diode Development," Proceedings of the 14th Intersociety Energy Conversion Engineering Conference, p. 1899 (1979).

20. Miskolczy, G. and Margulies, A.E., "Design Study of a Coal-Fired Thermionic-Topped Powerplant Using an Advanced Boiler," Proceedings of the 14th Intersociety Energy Conversion Engineering Conference, p. 1875 (1979).

1980

21. Danielson, L.R., "Development of Low Work Function Zr/O/W(100) Emitter," Proceedings of the 15th Intersociety Energy Conversion Engineering Conference, p. 2338 (1980).
22. Goodale, D.B., Lieb, D., Reagan, Miskolczy, G. and Huffman, F.N., "Characteristics of Flame-Heated Chemical Vapor Deposited Thermionic converters," IEEE Plasma Science Conference, Madison, WI, (1980).
23. Goodale, D., Reagan, P., Miskolczy, G., Lieb, D. and Huffman, F.N., "Combustion Performance of CVD Silicon Carbide Thermionic Diodes," Proceedings of the 15th Intersociety Energy Conversion Engineering Conference, p. 2095 (1980).
24. Gunther, B. and Huffman, F.N., "Characteristics of a Cesium W(110) Electrode Annealed in Oxygen," Proceedings of the 15th Intersociety Energy Conversion Engineering Conference, p. 2103 (1980).
25. Miskolczy, G. and Huffman, F.N., "Terrestrial Applications Using a Thermionic Array Module (TAM) Combustor," IEEE Plasma Science Conf., Madison, WI (1980).
26. Miskolczy, G., Wang, C., Margulies, A.E. and Fusegni, L.J., "Thermionic Topping of Combined Cycle Powerplants and Cogeneration Applications," 15th Intersociety Energy Conversion Engineering Conference, (1980).

1981

27. Danielson, L.R., "Coadsorption of Cesium and Oxygen on Iridium and Lanthanum Hexaboride," Journal of Applied Physics, Vol. 52, No. 1, p. 300-304, January (1981)
28. Goodale, D., Reagan, P., Miskolczy, G., Lieb, D., and Huffman, F.N., "Characteristics of CVD Silicon Carbide Converters," Proceedings of the 16th Intersociety Energy Conversion Engineering Conference, p. 1974 (1981).

29. Miskolczy, G., Huffman, F.N., and Marguillies, A.E., "Application of Advanced Thermionic Combustor Concept to Combined Cycle Power Plants," Proceedings American Power Conference, Vol. 43, p. 466-472 (1981).
30. Miskolczy, G., Wang, C. and Lieb, D., "Thermionic Combustor Application to Combined Gas and Steam Turbine Power Plants," Proceedings of the 16th Intersociety Energy Conversion Engineering Conference, (1981).

1982

31. Goodale, D., Reagan, P., Lieb, D., and Huffman, F.N., "Thermionic Converters for Terrestrial Applications," Proceedings of the 17th Intersociety Energy Conversion Engineering Conference, (1982).
32. Huffman, F., Lieb, D., Reagan, P., and Miskolczy, G., "Thermionic Technology for Spacecraft Power: Progress and Problems," Proceedings of the AFOSR Special Conference on Prime-Power for High Energy Space Systems, P. IX-2 (1982).
33. Huffman, F.N., Reagan, P., Miskolczy, G., and Merrill, O., "Thermionic Technology Infrastructure for Space Power," Proceedings of the 17th Intersociety Energy Conversion Engineering Conference, p. 1913 (1982).
34. Miskolczy, G. and Lieb, D., "Cogeneration Using A Thermionic Combustor," Proceedings of the 17th Intersociety Energy Conversion Engineering Conference, p. 1918 (1982).

1983

35. Goodale, D., Lieb, D., Miskolczy, G., and Moffat, A., "Combustion Converter Development for Topping and Cogeneration Application", Proceedings of the 18th Intersociety Energy Conversion Engineering Conference, (In Press) 1983.
36. Huffman, F.N., "Overview of Terrestrial Thermionics", Proceedings of the 18th Intersociety Energy Conversion Engineering Conference, (In Press) 1983.
37. Miskolczy, G., Goodale, D., Moffat, A.L., and Morgan, D.T., "Thermionic Cogeneration Burner Design", Proceedings of the 18th Intersociety Energy Conversion Engineering Conference, (In Press) 1983.

APPENDIX 2-C
CHRONOLOGICAL SUMMARY OF REPORTS

<u>Date</u>	<u>Title</u>	<u>Report Number</u>
7/ /75	Advanced Thermionic Technology Program Progress Report 1	4202/4203-13-76
7/ /75	Development and Evaluation of Alloys for Advanced Energy Systems	4190-17-76
9/21/75	Advanced Thermionic Technology Program Progress Report 2	4202/4203-22-76
10/2/75	Advanced Thermionic Technology Program Progress Report 3	4202/4203-32-76
2-187 10/12/75	Advanced Thermionic Technology Program Progress Report 4	4202/4203-41-76
1/5/76	Advanced Thermionic Technology Program Progress Report 5	4202/4203-54-76
1/8/76	Advanced Thermionic Technology Program Progress Report 6	4202/4203-57-76
2/13/76	Advanced Thermionic Technology Program Progress Report 7	4202/4203-67-76
3/14/76	Topical Report Powder Puff Diode	4202/4203-83-76
4/20/76	Advanced Thermionic Technology Program Progress Report 8	4202/4203-90-76
5/ /76	Advanced Thermionic Technology Program Progress Report 9	4202/4203-91-76

5/24/76	Advanced Thermionic Technology Program Progress Report 10	4202/4203-98-76
6/16/76	Advanced Thermionic Technology Program Progress Report 11	4202/4203-106-76
7/9/76	Advanced Thermionic Technology Program Progress Report 12	4202/4203-4-77
8/5/76	Advanced Thermionic Technology Program Progress Report 13	4202/4203-11-77
8/5/76	High Efficiency Thermionic Converter Studies	4202-12-77
9/9/76	Topical Report: Fabrication of Ceramic Hot Shells for Thermionic Converters	4203-20-77
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