TE-4203/4217-11-77

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Report No. TE4203/4217-11-77

MASTER

ERDA/NASA
ADVANCED THERMIONIC TECHNOLOGY PROGRAM
PROGRESS REPORT NO. 13

July 1976

ERDA Contract E(11-1)-3056
NASA Contract NAS3-20302

Prepared By

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I. SURFACE STUDIES

A. SURFACE THEORY

No work was performed on this task during this reporting period.

B. BASIC SURFACE EXPERIMENTS

1. Borides

Auger analyses were made of the surface chemical compositions of samples which have been studied in the Surface Activation Chamber. The results, shown in Table I, indicate the presence of a number of impurities on the surfaces. Carbon, oxygen, and nitrogen are atmospheric contaminants. Sodium can be introduced during handling. The presence of sulfur is attributed to contamination from the nickel support material. In the case of the cerium hexaboride sample, which had relatively large bare areas, sulfur concentrations were observed to be higher wherever the nickel concentration increased. The barium is a consequence of the support having previously had a (Ba, Ca, Sr) O spray coating. A similar explanation could be made for the presence of calcium on the tantalum and titanum diboride samples. However, the amount of calcium on the latter is substantially larger suggesting another source of calcium. Magnesium and silicon are most likely inherent impurities of the titanium diboride sample. There is a great disparity in boron concentrations among the four samples. The dominance of overlapping tantalum Auger peaks made detection of boron on the tantalum diboride sample questionable. There appears to be an inverse relationship between boron and cesium concentrations.

Titanium diboride was found to have thermionic emission characteristics similar to those of tantalum diboride; i.e., the work function

TABLE I

AUGER ANALYSES OF MATERIALS PREVIOUSLY STUDIED IN SURFACE ACTIVATION CHAMBER

Chemical Specie	Sample			
	CeB_6 %	TaB_2 %	TiB_2 %	ZrB_2 %
B	33	?	0.6	10
C	21	29	25	21
N	3	0.6		0.7
O	12	25	16	40
Na			0.2	
Mg			2.3	
Si			14	
S	1.3	1.0	0.5	
Ca		0.3	4.2	
Ti			0.9	
Ni	25	18	21	
Zr				26
Cs		13	13	1.0
Ba	2			
Ce	4			
Ta		13		

after activation with cesium was > 1.6 eV which was reduced with cesium-oxygen alternation to 1.10 eV. By contrast, the lowest work function obtained for zirconium diboride after cesium-oxygen alternation was only 1.25 eV. There is no obvious reason for this discrepancy and auger analyses detected no significant difference between the three diborides. In general, the results are not sufficiently promising to justify continued work on diborides at this time.

2. Evaporated Oxides

The results with BaO and ZnO collectors in experimental diodes suggest that the high resistance of these materials may limit their performance. It is not known whether the limiting resistance is bulk or interface resistance. To check the first possibility, experiments are in progress to replace the sprayed materials with evaporated thin films. In this way it should be possible to reduce the sprayed thickness of the material of about 25 μm to an evaporated thickness of around 250 Å. Accordingly, the bulk resistance should be reduced by a factor of 1000. In a preliminary experiment, standard (Ba, Sr, Ca) CO_3 material was spray-deposited on a platinum strip and the oxides thus formed were evaporated to a second platinum strip. The oxides were then evaporated in the Activation Chamber onto the usual nickel substrate. With this material a work function of 1.67 eV was obtained, which increased upon exposure to cesium. A similar effect had been observed previously with evaporated oxide films. Cesium-oxygen alternation produced a work function in the 1.2 eV region.

3. Zinc Oxide

Three sprayed ZnO substrates were activated, primarily to check out a new source (SAES) of cesium channels. The results confirmed earlier findings, viz., that a work function of 1.28 eV is obtained at 500 K with remarkable reproducibility and that cesium-oxygen alternation produces only a very small reduction of the work function (less than 0.1 eV).

4. Tungsten Oxide

ESCA (Electron Spectroscopy for Chemical Analysis) studies were performed on the tungsten oxide collectors of Converters 114, 122, 124, and 137. Each converter represents a different stage of activation. After the cesium was distilled out of these diodes they were transported to Physical Electronics Industries, Inc. (where the ESCA analyses were performed) and placed under nitrogen atmosphere just prior to transfer to the ultrahigh vacuum of the analytical chamber. Although interpretation of the results has not yet been completed, preliminary indications are that the "active-state" surface is of the order of 100 Å thick and that the surface oxide layer is a mixture of WO_3 and WO_2.

II. PLASMA STUDIES

A. CONVERTER THEORY

One of the simple boundary conditions on the emitter side of the plasma is

$$\Gamma_e = \Gamma_E - \Gamma_{re}\, e^{-V_E/KT_e} \qquad (1)$$

where Γ_e is electron current, Γ_E is the Richardson saturation electron current, Γ_{re} is the random electron current, V_E is the emitter sheath height, and T_e is the plasma electron temperature. Equation (1) is valid if the sheath height V_E is relatively large as compared to KT_e. However, when a double sheath forms, this assumption of large sheath height becomes questionable. If the electron distribution in the plasma is considered to be a perturbed Maxwellian distribution function then to the first order approximation Equation (1) becomes[1]

$$\Gamma_e = \Gamma_E - (\Gamma_{re} - \frac{1}{2}\,\Gamma_e)\, e^{-V_E/KT_e} \qquad (2)$$

A more general form of Equation (2) is

$$\Gamma_e = \Gamma_E - (\Gamma_{re} - \alpha\Gamma)\, e^{-V_E/KT_e} \qquad (3)$$

Matching the density at the boundary between the sheath and the plasma allows the variable α to be solved in terms of current ratio, J/J_s, temperature ratio, T_e/T_E, and the emitter sheath height V_E/KT_e.

$$\alpha = \frac{1}{2}\left(\frac{J_s}{J}\right)\left(\frac{T_e}{T_E}\right)^{\frac{1}{2}}\left[H\left(\psi_p\right) - \left(\frac{T_E}{T_e}\right)^{\frac{1}{2}}\left(1 - \frac{J}{J_s}\right)H\left(C^{\psi}p\right)\right]$$

$$H(X) = e^{X}\left[1 - \frac{2}{\sqrt{\pi}}\int_{o}^{X^{1/2}} e^{-t^{2}}\,dt\right] \qquad (4)$$

With Equation (3) as one of the boundary conditions and Equation (4) defining the variable α, conditions between the sheath and the plasma can be fully matched at their boundary. The solution of a sample plasma problem with these equations is shown in Figure 1. A comparative solution using the original simple boundary conditions is also shown.

B. ENHANCED MODE CONVERSION EXPERIMENTS

Emitter-collector spacing measurements for the bell-jar, close-spaced diode ("Powder-Puff") simulation tests are complicated by the fact that, during testing of the emitter, electrical interference prevents using a Wheatstone bridge to measure the capacitance and thereby, the spacing of the diode. This problem was solved by incorporating the diode into a self-contained tank circuit whose resonant frequency was measured with a grid-dip meter. At an emitter temperature of 1400 K, the spacing between the electrodes was determined to be 0.6 mil, with a corresponding resistance of 200 kilohms.

Testing is in progress on a ZnO collector guarded diode operated as a triode by using the central collector as the positively charged auxiliary electrode and the guard ring as the collector. At low currents

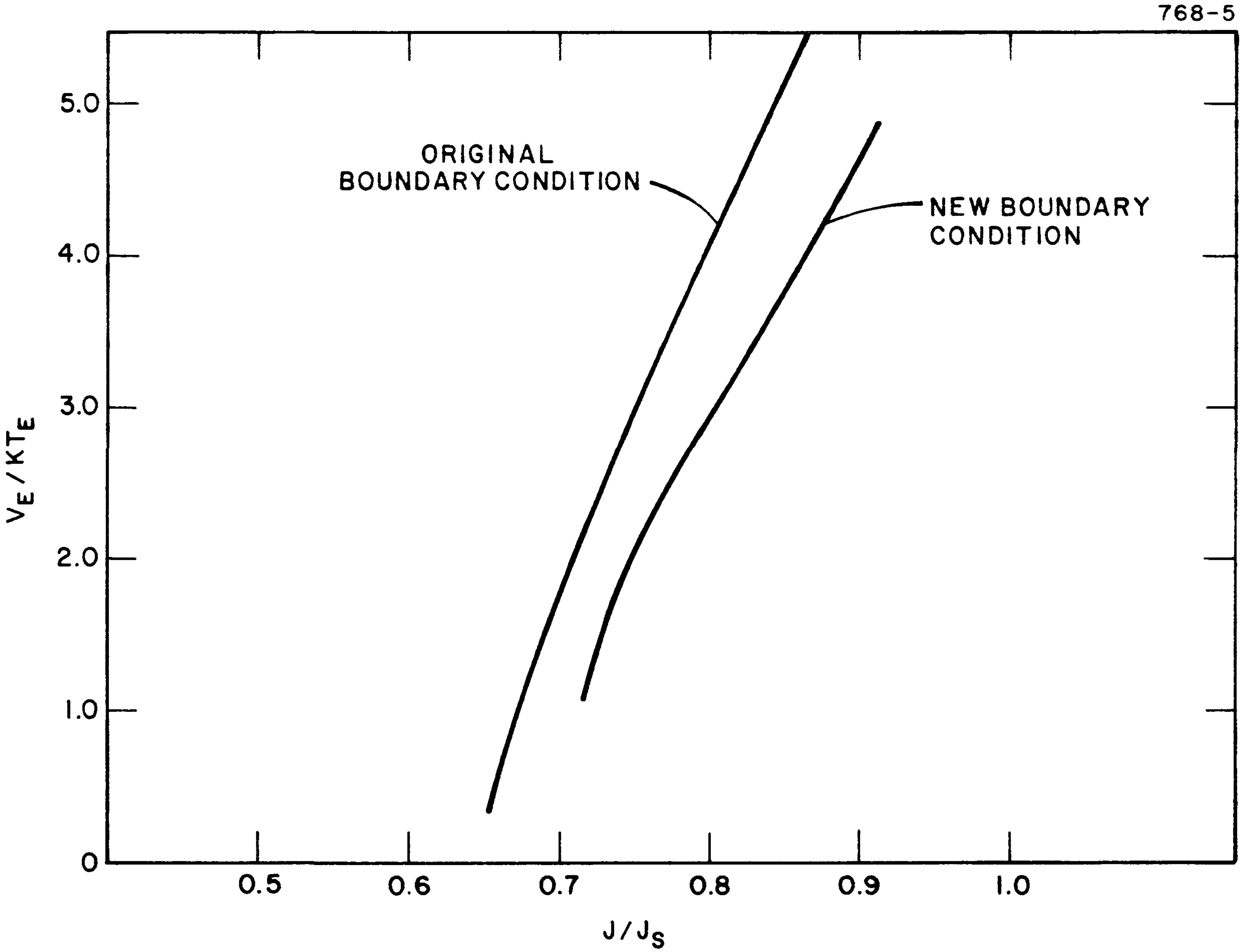

Figure 1. Solution of the Plasma, Sheath Height V_E/KT_E Versus J/J_S

(approximately 200 mA) and 3.2 torr of xenon, a positive voltage shift of 1 V was observed. However, anomalies noted in the output current versus applied auxiliary voltage suggested that unusual discharge patterns must exist in the diode which shift with voltage and, in some instances, with time.

III. CONVERTER DEVELOPMENT

A. LOW TEMPERATURE CONVERTER DEVELOPMENT

1. Zinc Oxide Collector with Platinum Emitter Converter No. 146

This variable spacing converter has a standard tungsten emitter structure with a 50 mil platinum insert brazed to it and a sprayed zinc oxide collector. Platinum was used for the emitter in order to obtain higher current densities at the lower cesium pressures required by zinc oxide collectors. Retarding collector work function measurements gave values of 1.5 eV at a T/T_R of 1.4. Low current dc testing using back emission gave collector work functions around 1.3 eV at T/T_R values of 1.5 to 1.7. A current density of better than 10 amperes per cm^2 at a T_E/T_R value of 2.88 was measured (T_E = 1300 K, TR = 452 K). This current is almost an order of magnitude better than the current polycrystalline tungsten. Power data have shown that at the low cesium pressures (2×10^{-2} torr) needed for the collector, exceedingly large spacings are required to attain the proper for efficient ignition. Further experiments will be performed to determine if this low pressure cesium vapor can be more effectively ionized by pulsing the converter.

2. Strontium Oxide Converter - No. 142

This standard variable-spacing converter had an electropolished tungsten emitter and a sprayed strontium oxide-on-nickel collector. The nickel collector structure was prepared by coating it with an approximately one-mil-thick film of strontium carbonate in an organic binder. The collector was then fired to 1000 C to release the binder and decompose the $SrCO_3$ to the oxide before final assembly into the converter.

Attempts to measure back-emission by dc methods were unsuccessful due to leakage current in the diode and a relatively poor bare collector work function. Several attempts to reactivate the collector, in order to lower the work function, by heating it to 1000 C failed; the emitter seemed to be slightly oxygenated after each attempt. The cesiated work function measured from retarding plots was greater than 2.0 eV. Current versus voltage curves indicated a series resistance limitation.

Despite the fact that no cesium was introduced into the diode during each bake, substantial emission from the tungsten emitter was observed. Measurement of the emitter work function gave values of approximately 3.0 eV, about 1.0 eV lower than that expected for a tungsten emitter at this cesium coverage. A possible explanation for this phenomenon is that strontium oxide or strontium from the decomposed oxide evaporated from the collector onto the emitter. Although strontium oxide does not decompose at these low collector temperatures, changes in chemical stability with cesium impingement might cause dissociation. Accordingly, to form a coating, the collector was heated to 1270 K while the emitter was flashed to 1800 K and then cooled to 570 K.

Upon opening the converter, the collector was observed to be blackened over most of its surface. Photomicrographs of the tungsten emitter showed pitting in areas corresponding to those blackened on the collector. These photographs also showed material transferred from the collector surface indicating that the electrodes had touched each other. Auger analyses of the emitter will follow.

B. HIGH-EFFICIENCY CONVERSION EXPERIMENTS

1. Lanthanum Hexaboride Collector Converter No. 144

This converter has an electropolished tungsten emitter and a LaB_6 collector. A silver tube is used for oxygen admission through the center of the collector. The converter has been fabricated and outgassing has begun.

IV. COMPONENT HARDWARE PROGRAM

A. HOT SHELL DEVELOPMENT

Two more hot shells fabricated for furnace testing were found to be leak-tight after air firing for over forty-eight hours at 1100 C. A sintered hot shell, fabricated by British Nuclear Fuels, Ltd., was also found to be leak-tight after being subjected to the same heat treatment.

A group of silicon carbide pieces were subjected to etching treatments in mixtures of hydrofluoric and nitric acids. The occasional evolution of bubbles during these treatments indicated the presence of silicon or silica. Such impurities would be responsible for the unreproducibility of braze joints to silicon carbide. Pre-braze etching treatments for silicon carbide are presently under study.

The third silicon carbide reactor was constructed. This system establishes the sample axis at 5 degrees above the horizontal plane, permits the sample to be rotated about its axis, and is provided with a nozzle for directing reaction gases at the graphite mandrel.

Preliminary reduced pressure experiments in System B resulted in substantial deposits of silica due to oxygen being introduced by a leaky flowmeter. All three silicon carbide synthesis systems have had their flowmeters rebuilt, using Teflon seals, to insure leak-tight operation.

POCO Graphite, Inc. is providing Thermo Electron with purified PLC-1 graphite mandrels for use as test growth substrates. POCO has taken five of the mandrels originally supplied by them to Thermo Electron and is subjecting them to a proprietary heat treatment in a special atmosphere in order to drive off residual gases.

Table II lists chemical species which play a role in the synthesis of silicon carbide from methyltrichlorosilane. Theoretical equilibrium concentrations of these species were determined by a computer program which uses free energy of formation data as a basis to compute the minimum free energy composition of the multicomponent system as a whole.[2]

Calculations were made for atomic concentrations of hydrogen, silicon, carbon, and chlorine consistent with an initial mixture of hydrogen and methyltrichlorosilane gases. Oxygen was added as a trace impurity. Figure 2 shows the yield of beta type silicon carbide as a function of reaction temperature and hydrogen concentration. The mixture also contained 10^{-3} moles of oxygen. Figure 3 shows the results of calculations made on the basis of reduced pressure – 9.22×10^{-3} atm, or 7 torr. At the lower pressure, reaction yield is much less sensitive to variations in hydrogen concentration. Based on equilibrium data, these plots, of course, do not provide a complete description of the pyrolysis reaction. As can be seen from comparison of Figures 2 and 3, however, they do establish a valuable guideline for selecting reaction gas concentrations and vessel pressure.

Testing of one General Electric silicon carbide and two Kanthal A-1 hot shells was continued at Thermo Electron. The General Electric silicon carbide hot shell has accumulated 7740 hours of test time; the Kanthal A-1 shells have accumulated 6152 and 6019 hours, respectively. (The Kanthal hours reported previously were low due to an earlier cycle reading error.) Additional samples of commercially available Inconel 601 and 617 were placed in the test furnace. During

TABLE II

SPECIES USED IN EQUILIBRIUM CALCULATION

Elements Entering Reactor

H

O

Si

Cl

Products		
Gaseous Species		Condensed Species
C	HCl	C
$CHCl_3$	$SiClH_3$	SiC-β
CH_2	SiCl	SiO_2
CH_2Cl_2	Cl_2	Si
CH_3	SiH_2Cl_2	
CH_3Cl	$SiCl_2$	
CH_3Cl_3Si	$SiHCl_3$	
CH_4	$SiCl_4$	
CO	H_2	
CO_2	H_2O	
C_2	SiH_4	
C_2H_2	SiO	
C_2H_4	O_2	
C_2H_6	O_2H	
H		

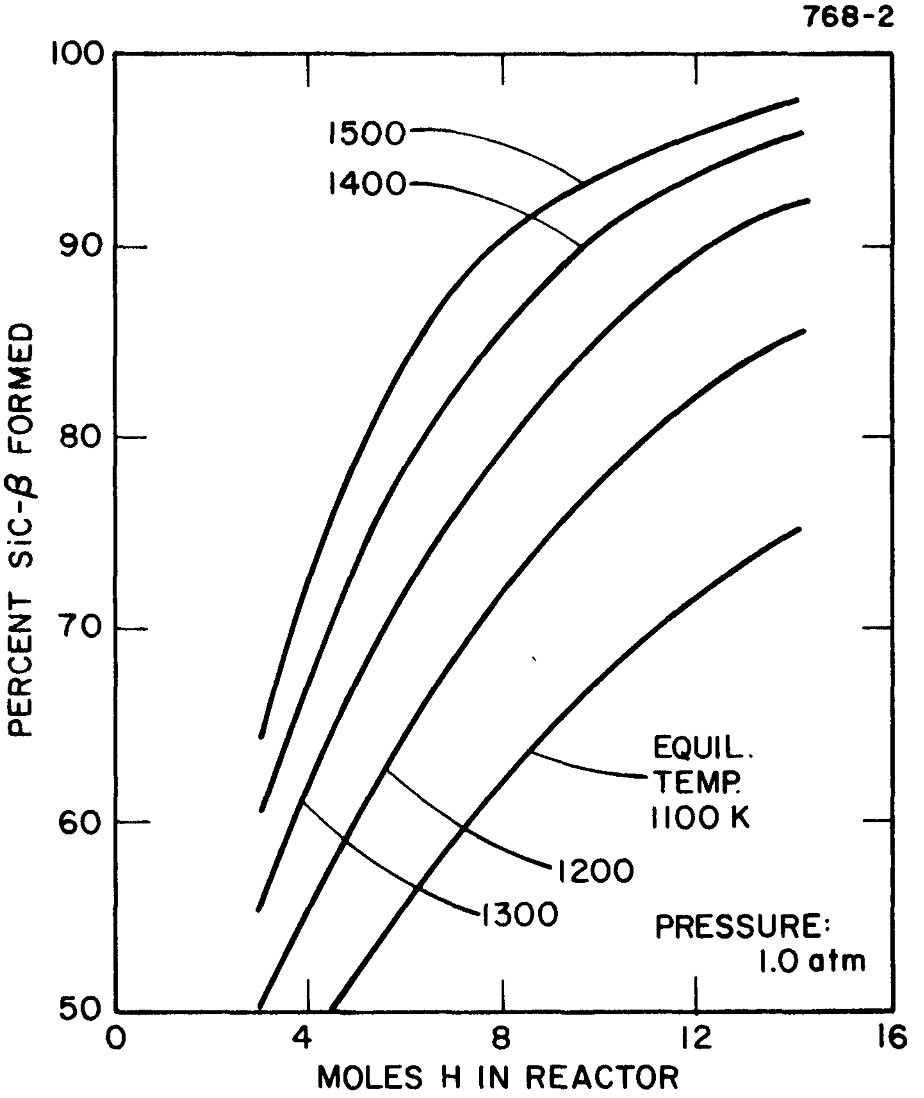

Figure 2. Equilibrium Calculations at 1 atm Pressure

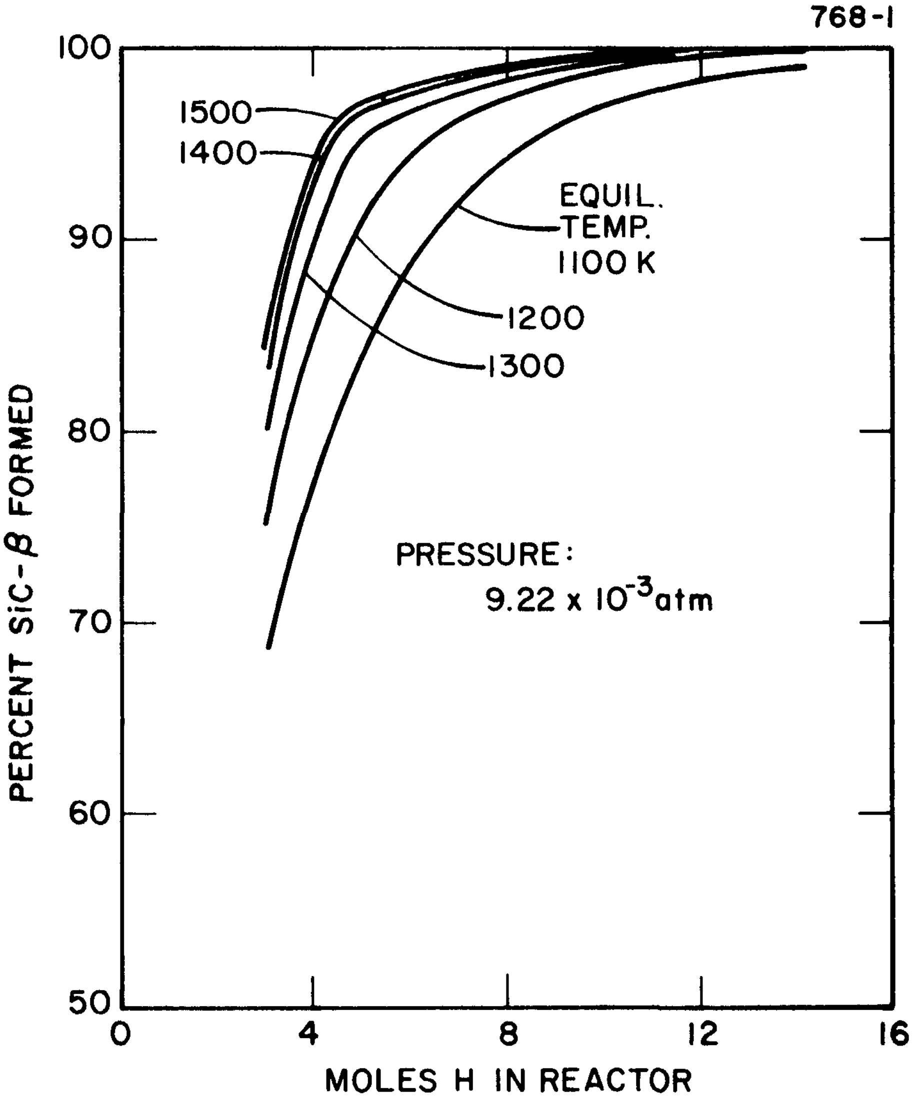

Figure 3. Equilibrium Calculations at 9.22 x 10^{-3} atm Pressure

these tests a vacuum of less than 10^{-7} torr was maintained in the interior of the test hot shells. Their exterior was exposed to the products of combustion of benzene heated to 2400 F (1589 K). The combustion products contain 6.7 percent oxygen and 13.7 percent carbon dioxide.

REFERENCES

1. McCandless, R. J., Wilkins, P. R., and Derby, S. L., "Theory of Thermionic Converter Volume Phenomena," IEEE Conference Record of 1961 Thermionic Conversion Specialist Conference.

2. Warga, J., J. Soc. Indust. Appl. Math., Vol. 11, p. 594 (1963).

DEVELOPMENT AND EVALUATION OF ALLOYS

FOR

ADVANCED ENERGY SYSTEMS

CONTRACT: 26784-4203-411 Mod #2
PROGRESS REPORT NO. 6
REPORTING PERIOD: 1 July through 31 July 1976

PREPARED FOR:

THERMO ELECTRON CORPORATION
101 First Avenue
Waltham, Massachusetts, 02154

Dated: 3 August 1976

1.0 INTRODUCTION

This report describes the program under contract 26784-4203-411 Mod. #2, during the period 1 July through 31 July 1976. It is submitted as a contract deliverable summarizing the monthly effort.

2.0 PROGRAM OBJECTIVES AND TASKS

The objective of this program is to develop, select and evaluate candidate alloys or alloy/coating combinations as protective cover materials for thermionic devices operating as energy converters (topping cycles) in the fossil fuel combustion product environment of steam power plants.

The program has the following tasks:

- Selection, preparation and evaluation of candidate materials in sulfidizing/oxidizing environments (simulated combustion products) at 2200-2400°F temperatures.
- Performance of long-term and thermal cyclic tests for chemical-metallurgical stability of promising materials.
- Fabrication of tube shape specimens as deliverables to Thermo Electron using fabrication methods which are considered technically and economically feasible.

3.0 TECHNICAL PROGRESS

During this reporting period test specimens from Run #5 (2200°F, 3% deficient air, 100 hours) were analyzed, and the first thermal cycle test was started. Also, a few specimens exposed to the coal combustion environment of TRW's Burner Test Facility were examined.

Microscopic examination of Run #5 specimens under a stereo microscope up to 30X prior to sectioning and metallographic examination of polished cross-sections at magnifications up to 400X resulted in the following observations:

a) Inconel 671 (Ni-48 Cr plus 0.05 C and 0.35 Ti) and Inconel 690 (60 Ni-30 Cr-9.5 Fe plus 0.03 C) showed excellent corrosion resistance in this environment (H_2S-rich). Yttrium addition at the 1 wt. % level has no apparent effect on the corrosion resistance of Inconel 690.

b) Hastelloy C (nickel-based alloy with 14.5 wt. % Cr, plus Fe, Co, Mo, C, Mn, S, Si, P, V, and W) and the TRW nickel-based alloys VIA (Mod R), VIA (Mod S) also showed good corrosion resistance in this environment (H_2S-rich).

c) Haynes 188 (Co-Ni-Cr-W alloy with Fe, C, Mn, Si, and La) was severely corroded by this environment.

Electron beam microprobe analyses of the thin adherent scale on Inconel 690 showed a thick chromium-rich layer which is most likely the oxides of Chromium. This well-known mechanism of chromium enrichment on the surface of Cr - containing alloys in oxidation tests justifies the need of evaluating chromizing surface treatment.

Inconel 671, Inconel 690, and Hastelloy C were examined with the stereo microscope and metallograph after 5 minutes exposure to the coal combustion environments of TRW's Burner Test Facility. Test temperatures reached as high as 2600°F for a short time. The Inconel 690 alloy was again the best with a thin adherent scale. The Inconel 671 was also quite corrosion resistant but showed evidence of a grain boundary precipitation. Hastelloy C appeared to be partially melted and also showed a grain boundary precipitation.

A thermal cycle test of several alloys (Inconel 690, Inconel 671, TRW Co-25Cr-1-5Y, Haynes 188, Hastelloy C, Hastelloy C-276, and Supertemp) was initiated. Four thermal cycles in 3% excess air (heat up to 200°F in 2 hours, hold for 100 hours at 2200°F and furnace cool to RT in 24 hours) will be completed by 4 August 1976.

4.0 FUTURE ACTIVITIES

During the next reporting period, the thermal cycle test specimens will be examined and Run #6 initiated. Run #6 will consist of selected Stellite compositions (Stellite 21 and Stellite 31) as well as the chromized and aluminized alloys for exposure at 2200°F (3% excess air environment) for 100 hours.

A. TOY
PROGRAM MANAGER

FY 1976 THERMIONIC MILESTONES

	ITEM	TARGET DATE	ACTUAL DATE
1.	Construct guarded, variable spaced test converter	Sept. 1975	Sept. 1975
2.	Parametric analysis of surface ionization triode	Nov. 1975	Dec. 1975
3.	Incorporate barium oxide collector into thermionic diode	Dec. 1975	Nov. 1975
4.	Screen rare earth oxides for low work function collector	Feb. 1976	March 1976
5.	Compare effects of elementary and detailed boundary value assumptions on converter analysis	April 1976	Feb. 1976
6.	Test thermionic diode with cesium oxide reservoir	July 1976	
7.	Summary report on hot shell alloy development	Sept. 1976	
8.	Report on Thermionic topping of organic Rankine cycle	Oct. 1976	
9.	Evaluate components of existing vapor deposition apparatus	March 1976	March 1976
10.	Improve temperature and gas flow control	April 1976	April 1976
11.	Equipment update	May 1976	May 1976

12. Deposition Parameter Study	August 1976
13. Fabricate Hot Shells	Sept. 1976
14. Application Test	Sept. 1976
15. Evaluation of enriched commercial ceramics	Sept. 1976

Task Identification

ERDA Tasks - IA, IIA, IIIA, IV & V

NASA Tasks - IB, IIB & IIIB