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ERDA/NASA
ADVANCED THERMIONIC TECHNOLOGY PROGRAM

PROGRESS REPORT NO. 3

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I. SURFACE STUDIES

A. SURFACE THEORY

No surface theory work was done during September. Computer programs, for FERP data analysis by deconvolution are under study.

B. BASIC SURFACE EXPERIMENTS

The BaO collector of converter No. 116 was subjected to Auger and scanning electron microprobe (SEM) analyses. The collector surface had a white-to-gray appearance, which was grayer near the edge closest to the cesium reservoir. A few (about 3) small (about 1 mm diameter) black spots appeared to be under the surface of the coating. Auger analysis indicated that the surface was clean except for traces of nickel and copper. Carbon was found to be present (7 - 8 %) only at the black spots. The grayer area was found to be higher in its trace concentrations of nickel and copper.

The SEM analysis found nickel, but no copper. The nickel concentration was also higher in the sample's grayer area. Nickel concentration between the grains of the coating was found to be higher than on the grains.

It appears that evaporation of material from the BaO coating occurred during testing. The surface copper most likely originated from the copper tube cesium reservoir.

A study of the effect of processing upon the surface chemistry of converter tungsten is being conducted. Slices of arc cast tungsten were cut to 0.015" thickness by electron discharge machining (EDM). Each sample was subjected to a different preparation treatment, as

summarized in Table I. Carbon, oxygen, and nitrogen can be expected to be present on specimens exposed to air. Carbon, sodium, and silicon are bulk impurities naturally occurring in silicone, iron, calcium, magnesium, aluminum, nickel, and copper could have been picked up during the machining process. Chemical removal of surface material produced the cleanest surfaces. The iron and potassium on sample W10 most likely were incurred during the etching process. If calcium was removed by etching, it may have been reintroduced by the subsequent washing of the etched sample with tap water. Lapping of the sample removed several impurities but, as revealed by subsequent Auger analyses (see Table V) of the heat treated sample, silicon was apparently added to the sample from the silicon carbide abrasive.

The effects of heat treatment upon samples W1, W5, W8, and W10 are outlined in Tables II thru V. The heat treatment activated diffusion to the surface of impurities which had been superficially removed by etching or abrasion. The pronounced rise in silicon on the surface of W10 was most likely caused by imbedding of the silicon carbide abrasive during lapping. Titanium could have been introduced by the EDM slicing. Sulfur and phosphorous are most likely bulk impurities which segregate at the surface at the medium range temperatures ($600\text{ C} < T < 1200\text{ C}$) Practically all impurities, except for oxygen and carbon, are removed by heat treatment to 1600 C . Above 1000 C the surface carbon changes from graphite to tungsten carbide, as evidenced by the characteristic change in the shape of carbon Auger spectrum. Carbide surface concentration increases up to

TABLE I

Effects of Surface Preparation upon Tungsten Surface Chemistry

Sample	W1	W2	W3	W4	W5	W8	W10
Preparation Treatment		Vacuum Fired at 1130° C for 2 minutes	Vacuum Fired, in machine oil and degreased	Sandblasted & degreased	Vacuum Fired, and Electro-polished	Etched for 30 sec. in 10% KOH	Lapped on wet SiC paper
Element							
W	15.0 %	3.4 %	2.9 %	9.7 %	8.4 %	27.8 %	34.8 %
C	60.1	60.5	59.8	67.1	79.5	50.9	58.6
O	7.7	9.1	8.8	4.2	9.4	8.2	9.2
Na	3.1	1.0	1.5	10.8		6.3	
K						1.4	
Si	3.3	14.8	13.7	4.3		1.1	
Ca	1.6	4.0	4.3	1.1	1.0	0.7	1.1
Mg	1.1	2.3	2.8	0.7			1.2
Al	2.0	3.6	5.1				
Fe	2.9			1.5	0.4	0.7	
Ni	1.1					0.2	1.5
Cu	0.8					0.4	
N	1.6	1.3	0.9	0.4	2.5	2.2	2.1

NOTE: All samples were initially vapor degreased in trichloroethylene, ultrasonically agitated in acetone, rinsed in methanol, and hydrogen fired for thirty minutes at 1030° C.

TABLE II

Effects of Heat Treatment Upon Surface Chemistry of Sample W-1

Treatment	W	C	O	Na	Si	Ca	Mg	Al	Fe	Ni	Cu	Ti	P	S
As admitted	8.6	69.6	7.4	2.4	3.0	1.1	0.7	1.7	1.8	0.6	1.2			
400° C	20.7	56.9	6.6	2.6	2.3	1.6	1.1	1.3	2.4	0.3	0.5		2.2	0.4
600° C	26.6	43.7	3.5	1.4	2.5	3.4		1.1	3.8	0.8	1.0		9.6	1.1
700° C	41.4	17.4	1.6		3.5	1.9		2.0	3.1	1.1			25.1	2.3
750° C	38.4	18.8	2.2		2.9	2.9		1.4	3.5	0.8			25.9	2.1
800° C	38.8	21.0	1.8			2.9		1.7	1.1	0.4		2.8	23.6	1.8
900° C	48.1	8.4	3.8		1.7	5.1		2.8	0.3			5.5	19.8	1.4
1000° C	51.2	2.6	11.5		2.8	20.2		4.8				3.0		
1100° C	51.5	?	12.5		1.8	14.2		5.3				3.0	0.2	0.2
1200° C	75.6	8.8	6.9		1.3			1.0				1.5	2.7	0.5
1300° C	75.8	14.7	3.4					1.8					0.9	0.5
1400° C	73.3	21.7	2.8											
1700° C	87.2	9.7	3.1											

TABLE III

Effects of Heat Treatment Upon Surface Chemistry of Sample W-5

Treatment	W	C	O	Na	Si	Ca	N	Al	Fe	Cu	P	S
As admitted	30.4	58.2	5.7	1.6	1.3	0.7	1.5		0.3	0.2		
200°C	28.3	58.1	6.5	3.0	1.4	0.7	1.4		0.2	0.2		
400°C	30.4	55.5	5.6	4.8	1.0	0.8	1.2		0.4	0.4		
600°C	22.0	55.4	4.8	8.8	1.1	0.3	0.9	1.0	0.4			0.3
800°C	70.5	21.8	1.5		2.8	2.5			1.0			
900°C	65.7	14.4	0.4		7.2				7.4		2.8	2.2
1000°C	73.0	11.5	0.4		9.0						5.0	1.1
1100°C	73.5	10.3	0.5		6.1						8.3	1.3
1200°C	77.2	4.7	0.3		2.2						11.6	4.0
1300°C	79.9	8.7	0.7		1.5						9.2	
1400°C	76.3	12.2	1.0		4.9						5.1	0.5
1500°C	81.0	12.7	1.0		1.0						4.3	
1600°C	87.8	3.8	1.1		0.5						6.7	
2000°C	89.4	9.3	1.2									

TABLE IV

Effects of Heat Treatment Upon Surface Chemistry of Sample W-8

Treatment	W	C	O	Na	Si	Ca	N	K	Fe	Ni	Cu	Ti	P	S
As Admitted	27.8	50.9	8.2	6.3	1.1	0.7	2.2	1.4	0.7	0.2	0.4			
400°C	32.9	43.7	7.7	7.3	1.8	0.7	1.3	3.1	1.7	0.3				
600°C	66.6	8.2	8.0		2.5	3.2	1.9	0.2	7.0				2.1	0.3
700°C	66.8	2.7	2.0		1.9	1.6	3.2		8.7			1.8	6.5	4.6
800°C	70.1	2.5	5.9		1.8	5.5	4.1					2.7	4.6	2.8
900°C	71.1	4.2	3.6			1.7	4.5					4.1	8.6	2.2
1000°C	70.3	4.7	1.2		1.3		2.8					1.8	16.3	1.5
1100°C	77.4	12.2	1.5		1.8								7.1	
1200°C	75.9	18.3	5.7											
1300°C	76.5	22.8	0.7											

TABLE V

Effects of Heat Treatment Upon Surface Chemistry of Sample W-10

Treatment	W	C	O	Na	Si	Ca	N	Cu	S	P
As admitted	30.7	53.6	7.2	0.9	1.1	0.5	4.2	1.6	0.3	1.1
400° C	35.2	52.3	7.2	1.7	1.4	0.6	0.7	0.6	0.2	
600° C	45.6	39.5	5.1	2.6	1.2	1.1	0.6	3.9	0.5	
700° C	71.7	4.3	0.8		5.0	2.8	0.6	8.6	6.2	
800° C	71.6	6.7	0.4		15.3	0.6			5.4	
900° C	59.3	1.7	0.1		37.4	0.2			0.1	
1000° C	57.2	1.7	0.1		40.6	0.3			0.1	
1100° C	89.2		0.5		10.3					
1200° C	86.8	6.4	0.5		6.1	0.2				
1300° C	82.9	11.3	0.6		5.2					
1400° C	78.7	19.2	1.1		1.0					
1500° C	77.6	21.5	0.9							
>1700° C	77.4	21.9	0.8							

1600 C and decreases thereafter.* The remaining samples listed in Table I are also to be subjected to heat treatment - Auger analysis. A goal of this study is to determine an optimum surface preparation procedure applicable to the fabrication of low work function tungsten converter electrodes. The effect of carbon upon the work functions of cesiated and cesiated-oxygenated tungsten surfaces will eventually be studied

II. PLASMA STUDIES

A. CONVERTER THEORY

During the past month attention was focussed on determining the existence of a double sheath at the emitter electrode. Such sheaths will allow solution of the diode equations at low ratios of directed to saturation currents, whereas, purely monotonic sheaths will not. By considering non-vanishing collisional effects in the sheath, specific forms of the ion distribution function at the sheath-plasma interface near the emitter can be chosen, so that both electron and ion distributions vary smoothly across this interface, with the formation of a double sheath at a specific ratio of the directed to saturation currents. The form of this distribution function, which satisfies the boundary conditions and which produces such double sheaths, does not seem to be unique, and studies are in progress to determine the sensitivity of converter performance to differing distribution functions.

A final revision of the topical report on the present state of the plasma analyses is being completed.

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* R. W. Joyner, J. Rickman, M. W. Roberts, Surface Sci.39, 44S (1973).

B. ENHANCED MODE CONVERSION EXPERIMENTS

A preliminary model of the ring ionizer Triode was constructed and tested in order to determine the pulse discharge characteristics of such a device. In approximately 2 Torr pressure of Argon, a uniform glow discharge was observed between the ring, charged as high as 100 volts positive with respect to the emitter, for pulse lengths down to 5 μ s, and repetition rates up to 30 kHz. These limiting conditions were dictated by the electronic components used rather than any physical constraint of the converter. Ion recombination emission was observed, from spectral measurements, to last over 100 μ sec after completion of a pulse.

III. CONVERTER DEVELOPMENT

A. LOW TEMPERATURE CONVERTER DEVELOPMENT

1. Electrode Screening
- a. Simulated Converter

Experiments measuring the work function of promising collector materials at high cesium impingement rates were continued. A sample was prepared by electroplating gold on a molybdenum substrate.

Bare work function measurements could not be obtained since the currents involved were very small. Cesium data showed a work function of 1.30 eV at a sample temperature of 550 K. The addition of oxygen, via a silver tube, improved the work function only slightly, and subsequent cesium-oxygen exposures did not significantly reduce the work function from 1.3 eV.

Oxygen addition was achieved via the silver tube, and this method of oxygen addition appears promising for converter application.

2. Converter Evaluation

a. Tungsten Oxide Converter No. 115

This converter is a standard variable spacing converter with an electropolished arc cast tungsten emitter and a deposited tungsten oxide collector. At the time of the last monthly report, this converter had been outgassed and cesiated and initial testing had been carried out following the history of Converter No. 111 (which had a barrier index of 1.92 eV at an emitter temperature of 1400 K and an inter-electrode spacing of 80 mils (2 mm)). Initial results were similar to those of Converter No. 111, with the barrier index approaching 2 eV as the converter aged. Manipulation of the collector temperature had reduced the barrier index to 1.95 eV at an emitter temperature of 1400 K and an interelectrode spacing of 80 mils (2 mm).

During this reporting period, additional manipulation of the collector temperature reduced the barrier index to 1.92 eV. ($V_B = 1.87$ eV at $T_E = 1600$ K and $d = 40$ mils (1 mm)), Reflux Converter No. 98 ($V_B = 1.92$ eV at $T_E = 1400$ K and $d = 80$ mils (2 mm)), and Tungsten Oxide Converter No. 111 ($V_B = 1.92$ eV at $T_E = 1400$ K and $d = 80$ mils (2 mm)). This converter (No. 115) was placed on life test to determine how long the performance (and the collector surface) would remain stable. The results of the life test were:

$V_B = 1.95$ eV	55 hours
$V_B = 1.92$ eV	55 hours
$V_B = 1.95$ eV	25 hours

The barrier index then deteriorated to 2.0 eV and further attempts to re-attain a barrier index of 1.92 eV were unsuccessful.

The converter will be cut open and analysis of the collector surface will be carried out during the next reporting period.

b. Barium Oxide Converter No. 116

A standard variable spacing converter, with a guarded lead-through and with a reflux reservoir system, was constructed with an electropolished arc cast tungsten emitter and a sprayed barium oxide on nickel collector. Prior to final assembly, the emitter and collector were degassed in the predegas flange, and the barium oxide collector was preconverted, giving a bare work function of 1.7 eV at a temperature of 800 K. The converter was partially outgassed, and subsequent reactivation of the barium oxide collector gave a bare work function of 1.8 eV at the same temperature.

Outgassing was completed, and cesiation was carried out. Collector work function measurements were obtained and the results showed a work function of 1.4 eV at a collector temperature of 600 K, and a work function of 1.45 eV at a collector temperature of 850 K (with a somewhat higher cesium pressure). Continually higher cesium pressures reduced the emission slightly, but it recovered with subsequent reduction in cesium pressure.

The current-voltage characteristics of this converter indicated a series resistance, possibly due to poor ohmic contact at the barium oxide - metal interface. The converter was cut open, and the analysis of the barium oxide collector appears in section IB of this report.

c. Guarded Converter Development

Several promising low collector work function surfaces have been generated in the surface studies part of the program. Evaluation and use of these surfaces in the present unguarded converter is difficult, as the typical operating conditions in the surface experiment chambers produce current levels that are not easily measured in the converter.

Currents in the surface studies experiments are low since high cesium pressures are not practical in a beam type chamber experiment. This low reservoir temperature dictates a low surface temperature, which in turn means low current densities, even from a low work function surface.

Low currents are difficult to measure in the present standard converters due to three effects:

- 1) Area definition
- 2) Leakage currents
- 3) Stray currents

Area definition in the present converter is achieved by a combination of electrode geometry and the limited high temperature area of the emitting surface. This is reasonably effective as long as current transport is confined to the interelectrode space only, by work function/temperature of the surface, or by attenuation of high currents by large spacings away from the interelectrode gap. Emission measurements from the collector of the present converter are usually not possible, as the entire collector structure emits similar to the electrode surface.

Likewise, at low emitter temperatures or low emitter cesium coverages, emission from the emitter structure may dominate compared to electrode surface emission.

Leakage currents arise from surface effects on the cesiated emitter to collector insulator. Cesium decreases the resistance of the insulators to about 10^3 , a value dependent on insulator temperature and cesium coverage. A guarded insulator can easily reduce this current by three or more orders of magnitude and extend the range over which data can be taken.

Other sources of leakage are the insulators associated with collector thermocouples, heaters and water lines. The above elements are also responsible for the bulk of noise pickup, bothersome at low current levels.

Stray currents collected by the collector are another source of interference very bothersome at low currents measurements. They originate at the EB gun used to heat the emitter, the ion guage or ion pump. These are difficult to reduce to small values by operating on the source, but can be reduced by careful shielding of all collector leads and structure.

A guarded converter was constructed which is designed to provide a well defined interelectrode area and reduce leakage and stray currents. Fig. 1 shows a cross section of the converter. Except for the mini-feed thru for the collector lead, the guarded converter envelope is identical to the standard converter. It fits the existing test stands, which can be used interchangeably for either type of converter.

Figure 1. Cross Section of the Guarded Variable Spacing Converter

The collector/guard subassembly is fabricated by placing 0.25 g of Lucalox chips in the cavity between the collector and the guard (see Figure 1). The assembly is then RF heated in hydrogen atmosphere until melting of the ceramics is observed. The collector is electrically insulated but thermally coupled to the guard by a 0.005 inch thick aluminum oxide layer. The collector output lead passes through a collector feedthru, attached to the guard structure. Guard and collector temperatures are measured by thermocouples.

The diameter of the emitter working area has been increased from 0.44 inches of the unguarded design to 0.649 inches. The 0.200 diameter collector is thus guarded by a 0.200 inch wide region. This is almost 4 times wider than previous guarded designs, and should insure a uniform discharge region at the central collector surface even at the large spacing of low temperature thermionics. Electrode areas are: Emitter 2 cm^2 , Collector 0.2 cm^2 , and Guard 1.8 cm^2 . Temperature and spacing operating range is the same as for the unguarded design, mainly limited by test stand heater power.

The electrical connections of the guarded design are such that only one lead is attached to the collector, and this is run inside 1/4" Cu tubing from guard heater to a baseplate guarded flange. Even with these precautions, stray currents from the EB gun were still present in the initial set-up. Magnitude however was only about 10^{-9} A, which is below the lower limit of the expected operating range of the converter. Testing will be carried out during the next reporting period.

FY 1976 THERMIONIC MILESTONES

<u>ITEM</u>	<u>TARGET DATE</u>	<u>ACTUAL DATE</u>
1. Construct guarded, variable spaced test converter	Sept. 1975	Sept. 1975
2. Parametric analysis of surface ionization triode	Nov. 1975	
3. Incorporate barium oxide collector into thermionic diode	Dec. 1975	
4. Screen rare earth oxides for low work function collector	Feb. 1976	
5. Compare effects of elementary and detailed boundary value assumptions on converter analysis	April 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	

Task Identification

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

NASA Tasks - IB, IIB, IIIB, & VI