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MASTER

I. SURFACE STUDIES

A. SURFACE THEORY

A study was conducted of published data on the thermochemistry of the oxides of cesium. Nine oxides of cesium are known¹ - Cs_7O , Cs_4O , Cs_7O_2 , Cs_3O , Cs_2O , Cs_2O_2 , C_2O_3 , CsO_2 and CsO_3 . The properties of dicesium monoxide (Cs_2O) and cesium peroxide (Cs_2O_2) are the best known. The latter² exists in an oxygen rich atmosphere and can be expected to be more stable in a cesium rich atmosphere. Thermochemical data, based on third law theoretical calculations as well as second law theoretical calculations and experimental data, are given for vapor phase dicesium oxide in the JANAF Thermochemical Tables.³ The work of Gusarov, Goro chov and Efimova⁴ provides the most recent empirical information on the heat of formation of dicesium monoxide. Recent measurements of the specific heat⁵ and enthalpy of formation⁶ of solid phase dicesium monoxide, conducted at the Argonne National Laboratory, provide the corresponding thermochemical data. Enthalpy and free energy of formation data, based largely on theoretical calculations, are given for condensed phase Cs_2O , Cs_2O_2 , Cs_2O_3 and CsO_2 in U. S. Bureau of Mines Bulletin No. S84.

The data surveyed were correlated and used as a basis for calculating thermochemical equilibria among the following species:

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<u>Gas Phase</u>	<u>Liquid Phase</u>	<u>Solid Phase</u>
Cs ₂ O	W	W
O	WO ₃	Cs ₂ O
O ₂	Cs	WO ₂
O ₃		Cs
WO		
WO ₂		
WO ₃		
W		
Cs		
CsO		
Cs ₂		

These are the species which can be expected to be present in a tungsten emitter-tungsten oxide collector-converter. Solid phase oxides of cesium, other than Cs₂O, were not obtained from the calculations. The JANAF data³ on vapor phase dicesium monoxide, modified by the Gusarov et al. enthalpy of formation data,⁴ were used as a basis for the equilibrium values of Cs₂O gas. The Argonne data^{4, 5} were used as a basis for solid phase equilibrium values. Concentrations (pressures) for equilibrium among the foregoing tabulated species were determined on a computer by means of a convex programming algorithm.⁸ Pressures and concentrations of species are computed as a function of temperature for given total pressures and given concentrations of elemental species. Some results of these calculations are given in Figures I-1 through I-5. The molar amounts of condensed phase species existing at each temperature are noted along the temperature axis. Figures I-1 through

Figure I-1A. Equilibrium Pressures Among 1000 Moles Cs, 300 Moles O, 100 Moles W, Total Pressure = 3×10^{-3} Atm

Figure I-1B. Equilibrium Pressure Among 1000 Moles Cs, 300 Moles O, 100 Moles W, Total Pressure = 3×10^{-3} Atm

Figure I-2A. Equilibrium Pressures Among 1000 Moles Cs, 300 Moles O, 100 Moles W, Total Pressure 3×10^{-4} Atm

Figure I-2B. Equilibrium Pressures Among 1000 Moles Cs, 300 Moles O, 100 Moles W, Total Pressure 3×10^{-4} Atm

Figure I-3A. Equilibrium Pressures Among 1000 Moles Cs, 100 Moles O, 1000 Moles W, Total Pressure 3×10^{-3} Atm

Figure I-3B. Equilibrium Pressures Among 1000 Moles Cs, 100 Moles O, 1000 Moles W, Total Pressure 3×10^{-3} Atm

Figure I-4A. Equilibrium Pressures Among 1000 Moles Cs, 100 Moles O, 1000 Moles W, Total Pressure 1×10^{-3} Atm

Figure I-4B. Equilibrium Pressures Among 1000 Moles Cs, 100 Moles O 1000 Moles W, Total Pressure 1×10^{-3} Atm

Figure I-5A. Equilibrium Pressures Among 1000 Moles Cs, 100 Moles O, 1000 Moles W, Total Pressure 3×10^{-4} Atm

Figure I-5B. Equilibrium Pressures Among 1000 Moles Cs, 100 Moles O, 1000 Moles W, Total Pressure 3×10^{-4} Atm

I-3 relate to the tungsten oxide collector-vapor interface while Figures I-4 and I-5 are more relevant to the tungsten emitter-vapor interface. These calculations indicate that the major vapor specie carrier of oxygen is dicesium monoxide. In all cases, there is a low temperature tendency for the formation of dicesium monoxide. At high temperature, dicesium monoxide tends to decompose and condensed phases of tungsten oxides to form. These calculations provide insight into the mechanism of collector dispensation of oxygen to the emitter.

B. ACTIVATION CHAMBER EXPERIMENTS

It was previously reported that the thickness measurements of evaporated samples with the Sloan thickness monitor were qualitative because of the ill-defined geometry. The Sloan instrument has now been aligned in such a way that the measurements should be accurate within $\pm 30\%$.

1. Evaporated Barium Oxide

Earlier experiments with barium oxide were repeated with the improved Sloan geometry to obtain a more quantitative value for the minimum thickness required to achieve the minimum work function (in the 1.4 to 1.5 eV range). This thickness ranged between 40 and 60 Å, in good agreement with the results reported by the Naval Research Laboratories on single crystal substrates. A rapid rise of the thermionic emission (decrease of the work function) between 35 and 45 Å was observed. As in earlier experiments, exposure to cesium vapor increased the work function slightly. A diode with an evaporated barium oxide collector is being fabricated.

2. Experiments with Cesium Carbonate (Cs_2CO_3)

Experiment No. 187. This experiment was a repeat of No. 186, reported last month, with the aim of producing an Ag-O-Cs photocathode by adding evaporated silver to the deposit produced by evaporating Cs_2CO_3 . The result was more pronounced than in the earlier experiment. On adding silver the white light photoemission increased by a factor of 20 to a value typical for a good Ag-O-Cs photocathode. The infrared response through a Corning 7-56 filter (cut-off near $8000 \text{ \AA}$) was also typical for an Ag-O-Cs cathode. The addition of silver did not change the work function of 1.1 eV. This is not surprising because the value is also typical for Ag-O-Cs.

A direct identification of the specific cesium oxide contained in this deposit is difficult. Since the Ag-O-Cs cathode is believed to contain the oxide Cs_2O (as well as some excess elementary cesium) one might speculate that the Cs_2O_2 and cesium of the original deposit (see last month's report) may partially react according to $\text{Cs}_2\text{O}_2 + 2\text{Cs} \rightarrow 2\text{Cs}_2\text{O}$.

Experiment No. 188. An attempt was made to activate an evaporated antimony layer with the decomposition products of Cs_2CO_3 . The rationale was to compare the resulting photoemission characteristics with those of a conventional cesium-antimonide (Cs_3Sb) photocathode which is formed by exposing an antimony layer to elementary cesium. The result was a photocathode having a very low quantum efficiency combined with relatively high red response. This result is consistent with expectations from an over-oxidized Cs_3Sb cathode. In other words, this result is consistent with the assumption that a mixture of cesium and cesium oxide is released from the Cs_2CO_3 .

Experiment No. 190. This experiment had two purposes; namely, to obtain a more accurate thickness measurement with the Sloan instrument and to study the effect of additional cesium (released from a cesium channel) on the low work function surface. The minimum thickness required for a work function of about 1.1 eV was between 80 and 120 Å. The work function dropped sharply above about 60 Å, similar to the observation made on barium oxide. Additional cesium always increased the work function, but the low work function was easily restored by heating. A simple interpretation of these observations is as follows. Minimum work function requires a surface layer of adsorbed cesium. During decomposition of Cs_2CO_3 more than this minimum amount is deposited, but the excess is quickly evaporated during heating of the sample for thermionic emission measurements. If this interpretation is valid, additional cesium deposition will again produce an excess that can be removed by heating.

II. PLASMA STUDIES

A. CONVERTER THEORY

The ambi-polar diffusion equation with spatial dependent electron and ion temperatures is given by

$$\frac{d^2 \phi(x)}{dx^2} + f(x) \phi(x) \left[1 - \left(\frac{\phi(x)}{\phi_s(x)} \right)^2 \right] = 0 \quad (1)$$

where

$$\varphi_{\alpha} = n_{\alpha} k \left[T_e(x) + T_i(x) \right]$$

and

$$f(x) = \left[\frac{e}{M_i} + \frac{e}{M_e} \right] \frac{\beta_r n_s^2}{k (T_e + T_i)}$$

The charged particle density is given by n , M is the mobility, β_r is the ionization and recombination constant, T is the temperature and k is the Boltzmann constant. The subscripts e , i and s indicate electron, ion and Saha equilibrium densities, respectively. This equation has been solved numerically by a digital computer program.

Some preliminary results are shown in Figures II-1 through II-3. The family of solutions with constant electron and ion temperatures is shown in Figure II-1. For this case, the solution of Equation (1) can be expressed analytically in terms of Jacobian elliptic functions. The results show that (for boundary conditions $\phi = 0$ at $x = 0$ and $x = d$) the family of curves has the same electron temperature. Figure II-2 shows the family of solutions with constant electron temperature and the ion temperature distribution expressed by

Figure II-1. Family of Constant T_e and T_i

Figure II-2. Family of Constant T_e and Variable T_i

Figure II-3. The Effects of Temperature Distribution

$$T_i(x) = T_E \left[1 - \left(\frac{T_C}{T_E} \right)^{3/2} \right]^{2/3} \quad (2)$$

This solution assumes that the heat conduction of neutral atoms across the spacing is constant and the ion temperature equals the neutral temperature. The family also has the same electron temperature if the spacing d is the same. Figure II-3 shows the effects of temperature distribution. With constant electron and ion temperature, the maximum of four is located at $x = d/2$. The ion temperature tends to shift the peak toward the collector and the linear electron temperature distribution tends to shift the peak toward the emitter. The results shown in Figures II-1 through II-3 indicate that for fixed spacing all solutions have the same average electron and ion temperatures.

B. ENHANCED MODE CONVERSION EXPERIMENTS

A tantalum coil installed around the collector of the particulate spaced diode allows the temperature of the electrode to be independently controlled. Current enhancement was observed for a diode with a barium oxide sprayed molybdenum collector and magnesium oxide sprayed emitter when the emitter temperature was held constant and the collector temperature was raised. For example, when the emitter was fixed at 1070 K, a 40% increase in saturation current occurred when the collector was heated from 712 to 858 K. Such an effect would be expected if the hotter collector increased the transport of barium or barium oxide to the emitter. However, the accuracy with which the surface temperatures of the electrodes can be determined with thermocouples mounted in the bulk of the electrodes a short distance away from the surfaces is limited. Thus the possibility exists that increasing the collector temperature

will reduce heat transport from the emitter and produce a higher emitter surface temperature although the "bulk" temperature measured by the thermocouple remains constant. Such a higher emitter temperature would also enhance the output current.

Although the magnesium oxide particles are thought to play a vital role in maintaining electrode separation at high temperatures, they could be of little importance at lower temperatures. A series of experiments is in progress wherein only barium oxide is sprayed onto a molybdenum collector and a molybdenum emitter is contacted directly to this coating. Initial results indicate that the emitter can be increased to 1300 K with no electrical shorting between the electrodes. Comparison of the measured I-V characteristics with those generated from computer studies of close spaced "vacuum" converters suggests that the barium oxide coating provides 10 - 50 ohms resistance. Thinner coatings will be required to reduce these impedances to practical values.

For interelectrode spacing to be of the order of tenths of a mil, the particles providing this spacing must be smaller in characteristic diameter. In addition, the flatness and smoothness of the emitter and collector surfaces must be substantially finer than the specified interelectrode spacing. The surface topography of test electrodes was investigated by means of a Sloan Dektak Surface Profile Measuring System. This instrument consists of a 1.0 mil diameter diamond stylus which tracks (with a 10 to 50 mg loading) across a test surface while the corresponding stylus deviations from surface topography are recorded on a strip chart. Resolutions down to a few hundred angstroms are possible with the Dektak. Electropolished surfaces gave the smoothest surface on a microscopic scale, but also showed the greatest degree of

crowning (e.g., the center of a 0.440 mil diameter disk being about half a mil above the perimeter). "Laser polished" copper mirrors (obtained from PTR Optics) showed the highest degree of flatness and smoothness (± 0.05 mils).

The two copper laser mirrors obtained from PTR Optics were used as capacitor plates. With one surface electrostatically sprayed with zirconia, a spacing of as low as 0.33 mils was obtained. Below this spacing no grid dip signal could be obtained with further pressure. A continuity check with an ohm meter indicated that shorting had occurred. Visual inspection of the mirrors revealed minute scorch marks on each mirror. The grid dip meter was found to produce a 4 V peak-to-peak signal across the $1\text{ M}\Omega - 47\text{ pF}$ input impedance of an oscilloscope. Although it is doubtful that the grid dip meter could have supplied sufficient power for producing a scorch mark, the ohm meter may have produced such a mark from a breakdown initiated by the grid dip meter.

III. CONVERTER DEVELOPMENT

A. LOW TEMPERATURE CONVERSION EXPERIMENTS

1. Converter No. 163 Platinum Emitter-Titanium Oxide Collector

This converter is similar to the earlier tungsten emitter-titanium oxide converter, but uses a platinum emitter in an attempt to lower the operating cesium pressure and more nearly match the collector work function optimum.

The performance history summarized in Table III-1 shows an initial performance ($V_B = 2.1$ eV) typical of refractory metal converters. After a bake at low collector temperature followed by excursions to higher collector temperatures, the performance improved to a $V_B = 1.96$ eV (see Figure III-1) in a similar manner to that observed with tungsten oxide collector devices. However, there was no observable oxygen effect on the platinum emitter from the titanium oxide collector. Although the optimum cesium pressure did match the collector work function for this platinum emitter converter, the minimum work function was 1.5 eV compared to 1.4 eV for the tungsten emitter diode (see Figure III-2). After about 50 hours, the performance decayed by 0.1 eV and there was a corresponding increase in the minimum collector work function to 1.6 eV.

Testing has been concluded and the collector will be examined for platinum deposits using Auger spectroscopy.

2. Converter No. 164 Platinum Emitter-Nickel Collector

In an effort to determine the work function and performance characteristics for platinum, a standard variable spacing converter was

TABLE III-1

TEST SUMMARY OF CONVERTER NO. 163

Performance					Collector Work Function		Remarks
T_E (K)	T_C (K)	T_R (K)	d (mil)	V_B (eV)	Min ϕ_C (eV)	T_C/T_R	
1300	800	528	20	2.1	1.68	1.4	Initial
1300	650	528	20	2.1			24 hour bake
1300	900	520	20				"Activation" 5 min.
1300	800	507	20	2.05			Test curve
1300	750	507	20				24 hour bake
1300	900	507	20				"Activation" 5 min.
1300	800	507	20	1.96	1.5	1.6	Test curves
1400	800	507	40	1.96			
1400	800	507	40	1.96			48 hour operation
1400	800	507	40	2.05	1.6	1.6	Performance decay

Figure III-1. Cesium Family of Titanium Oxide

Figure III-2. Data from Retarding Plots Made During Best Performance

fabricated with a guarded feedthrough collector and a platinum emitter cap. The guarded collector allows collection and emission only from a well defined area and extends the measurement to much lower currents.

The outgassing of this diode is in progress.

B. HIGH EFFICIENCY CONVERSION EXPERIMENTS

1. Converter No. 162 Tungsten Emitter-Columbium 1% Zirconium Tungsten Oxide Collector

This converter uses a standard electropolished tungsten emitter with a columbium 1% zirconium collector. Tungsten oxide was deposited on the collector in two steps separated by a high temperature bake. The converter was fabricated to study the life, performance and oxygen dispensing characteristics of tungsten oxide on columbium collectors.

After operating at the following conditions ($T_E = 1600$ K, $T_C = 800$ K, $T_R = 578$ K, and $d = 40$ mils) for 200 hours, the barrier index increased from 2.05 eV to 2.1 eV and the power output decreased from 2.7 W/cm^2 at 8 amp/cm^2 to less than 1.6 W/cm^2 at the same current density. The collector temperature was then raised 50 K to 850 K. Again, oxygen was dispensed to the emitter and the saturation current increased at a fixed cesium pressure. The converter performance became stable after approximately one day at the higher collector temperature. At this time, the barrier index was 2.05 eV and the power output was greater than 3 W/cm^2 at 10 amp/cm^2 (see Figure III-3). The converter has now operated over 750 hours and has a barrier index of 2.07 eV. The power output is better than 2.7 W/cm^2 at 8 amp/cm^2 with the converter operating at $T_E = 1600$ K, $T_C = 850$ K, $T_R = 578$ K and $d = 40$ mils. Further life testing will continue.

Figure III-3. Effect of Increased Collector Temperature on Performance

IV. COMPONENT HARDWARE

A. HOT SHELL DEVELOPMENT

Four preliminary test runs were conducted in the modified horizontal silicon carbide reactor (see Progress Report No. 18, December 1976). The reactor was modified to produce shells which are thickest at the closed end. As shown in Figure IV-1, the closed end was located upstream of the rest of the hot shell. The rotating paddle wheel evenly distributes the concentration of reactant gases throughout the cross section of the reactor vessel. Rotating the sample retards the formation of a reactant/product boundary layer at the growth interface and provides more uniform heating of the graphite mandrel on which the silicon carbide hot shell deposits.

The morphology, grain structure and chemical composition of the silicon carbide material deposited are sensitive to the paddle wheel parameters such as blade pitch and rotational speed. Stainless steel was found to be attacked by the reaction vessel atmosphere. Teflon is a suitable material for constructing a paddle wheel, provided that it is kept sufficiently cool that no thermal decomposition takes place.

The status of the simulated furnace tests is as follows: At the temperature of 2400 F in the presence of the products of benzene combustion, the General Electric silicon carbide shell has been successfully tested for 9937 hours and the Kanthal A-1 shells have survived periods of 8349 hours and 8216 hours. The INCONEL 671 and the chromized CRES 446 have each accumulated 1387 hours in the simulated furnace.

Figure IV-1. Principles of Operation of the Modified Horizontal Silicon Carbide Reactor

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