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EMISSION CHARACTERISTICS
OF TANTALUM, TUNGSTEN, RHENIUM
AND IRIDIUM IN PLASMA DIODES

Livermore, California

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ABSTRACT

Experimental determinations of the ionic and electronic emission characteristics of tantalum, tungsten, rhenium, and iridium cathodes in vapor thermionic converters are compared. It is shown that tantalum provides superior thermal ionization qualities at high pressure compared with tungsten, rhenium, and iridium. High electronic current densities may be obtained from cesium on rhenium and cesium on iridium at much lower cesium vapor pressures than from tantalum or tungsten.

An overall efficiency of 19% was achieved with a rhenium cathode at 2440°K.

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INTRODUCTION

Theory and experimental results of vapor thermionic converters have been widely discussed in recent literature.¹⁻⁵ The types of converters investigated recently at this laboratory, usually designated as high-temperature converters, have consisted of an incandescent refractory metal cathode, a metallic anode maintained at a temperature considerably lower than that of the cathode, and a quantity of cesium, all enclosed in an evacuated envelope.

The density of the cesium vapor is controlled by varying the ambient temperature of the reservoir portion of the envelope. The cesium vapor does at least three things:

(a) It adsorbs on the comparatively low-temperature anode, thereby establishing a low work function surface. If cesium pressure and anode temperature are properly optimized, a work function of about 1.6 volts may be achieved. If more than a monolayer is adsorbed, the work function approaches that of cesium metal: 1.81 volts.

(b) The cesium particles strike the incandescent cathode and, providing the work function of the cathode is comparable to or greater than the cesium ionization potential, they become thermally ionized in accord with the Saha-Langmuir equation and hence provide positive ions which neutralize, to some degree, the space charge in the interelectrode region.

(c) As the cesium pressure is increased, usually to a pressure corresponding to a few millimeters of mercury, the cesium adsorbs on the

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incandescent cathode to the extent of a fraction of a monolayer, thereby reducing the initial cathode work function to values of about 3 to 3.5 volts. Electron emission is then greatly increased.

Briefly then, converter operation consists of thermionic emission of electrons from a medium-value work function surface into a space-charge neutralized region through which they may drift to the low work function anode surface where they are collected. The inequality of the cathode-anode surface potentials provides a voltage difference so that electrical power may be extracted from a circuit that connects the two.

Overall efficiencies of about 15% have been reported for some material combinations;⁶ theoretical analyses have indicated that efficiencies of 40% or more should be possible.

Plots of self-developed output current vs output voltage with constant cathode temperature and variable pressure have exhibited the same general characteristics for most material combinations reported.

Figures 1a and 1b show typical examples of curves taken at high cathode temperature. At low cesium pressure the optimum power output voltage, located at the knee of the curve, is about equal to the difference between the work functions of the cathode and anode surfaces, i.e., $V_p = \phi_c - \phi_a$. As the cesium pressure is increased, the "break-off" voltage decreases and the profile becomes more rounded. At high pressure no sharp break-off voltage occurs.

The reason for the decrease in output voltage and the rounding off of the profile as cesium pressure is increased is usually attributed to one or more of the following:

- (a) A decrease in the difference between the work functions of the cathode and anode caused by cesium adsorption on the cathode.
- (b) A change in the work function of the anode caused by thermal conditions which are not optimized to provide a monolayer thereon at all pressures.
- (c) A loss of current caused by electron scattering in the high-density cesium vapor.
- (d) Loss of voltage and current by inadequate space charge neutralization at either the cathode or anode surface or both.
- (e) Changes in the ambient potential which exists in the interelectrode plasma.⁷

Recent work concerning cesium adsorption on metals⁷ has indicated that cathode materials which possess high work functions, for example rhenium and iridium, adsorb to such an extent that currents of the order of amperes/cm² may be obtained at relatively low cesium pressures. This phenomenon offers a method of studying high electron emission, with a constant cathode temperature, at various cesium pressures and consequently will give information on space-charge neutralization and electron scattering in the plasma diode. The intention of this report is to compare experimental results obtained from thermionic converters which had high bare surface work functions with the more commonly used materials, i. e., Re, Ir vs W, Ta.

EQUIPMENT

The thermionic converters tested consisted of a guard ring geometry, shown schematically in Fig. 2, which had a 20-mil-diameter cathode placed coaxially in a 40-mil-diameter bore. The small ratio of interelectrode spacing to cathode diameter, 0.5, produces an effective plane parallel interelectrode spacing of approximately 10 mils. All tubes were outgassed for several hours at 450°C, and the secondary electrodes were heated to a dull red by either electron bombardment or induction heating until the base pressure of the pumping system, 10⁻⁸ mm Hg, was reattained.

The cathodes were aged with occasional flashings until reproducible saturated emission curves were obtained in vacuum. Introduction of cesium into the system contaminates the insulators slightly, and even when the cesium is frozen with liquid nitrogen, currents may flow in a biased system which are about the same magnitude as the emission currents for the high work function materials. Hence the saturated emission curves were obtained prior to introduction of cesium.

Cesium pressure was controlled by operating the tube in an oven whose heating element was so wound that no magnetic field was contributed to the cathode-anode region. Ambient temperature of the cesium was determined from a thermocouple spotwelded to a tungsten pin which was imbedded in the bottom of the tube as shown in Fig. 2. Cesium pressures and neutral atom flux densities corresponding to the reservoir temperatures were obtained from reference 8. Cathode temperatures were determined by optical pyrometry; emissivity and glass wall corrections were added.

In operation, the cathode was heated directly with a regulated dc power supply which was pulsed off for about 8 milliseconds per second. Data were taken when the cathode power was off. The tubes were designed so that no positive applied voltage equal to or greater than the ionization potential of cesium was in the system at any time. Electrical circuitry used is shown in Fig. 3. All feed-through pins had pin guard rings at the header both inside and outside the tube. Pin guard rings and guard ring electrodes were maintained at anode potential. All guard ring potentials were controlled with a dc bias while anode potential was controlled by resistive loading only. Anode temperature was not controlled but was monitored with a platinum-platinum rhodium thermocouple spot welded to the anode.

Material combinations consisted of tantalum, tungsten, rhenium, and iridium cathodes with molybdenum anodes. Vacuum melted ultra-pure wire was used for all cathodes with the exception of tungsten. The highest purity tungsten wire available was used.

PROCEDURE

Ionic and electronic space-charge barriers and potential wells exist within the interelectrode region. However, the self-developed output current of the converter provides at least some measure of the properly neutralized electronic current emitted from the cathode. If the effects of the space-charge barriers and the potential well are neglected, it is possible to determine a lower limit on conditions at the cathode surface.

Langmuir has shown that under conditions of equilibrium, the Saha-Langmuir equation may be applied to a surface subject to cesium adsorption.⁹ This equation has been applied to plasma diode experimental results in order to get some notion of the thermal ionization characteristics even though complete equilibrium may not exist in these systems. Reflection coefficients are assumed equal to zero.

Then

$$\frac{\nu_i}{\nu_a} = \frac{\omega_i}{\omega_a} \exp \left[(\phi_b - I - \Delta\phi) \frac{e}{kT} \right], \quad (1)$$

where ν_i/ν_a is the ratio of emitted ion current density to emitted atom current density; ω_i/ω_a is the ratio of the statistical weights of the ions and

atoms, equal to 1/2 for alkali metals; ϕ_b is the bare surface work function of the cathode. $\Delta\phi$ is the contact potential of the adsorptively covered surface against that of the pure metal or the work function depression caused by adsorption, and I is the ionization potential of cesium. The remaining terms have their usual designations.

The saturated emission electronic current density in vacuum, given by the Richardson equation is

$$j_b = A_r \exp\left(\frac{a_r}{k}\right) T^2 \exp - \left(\frac{e\phi_b}{kT}\right), \quad (2)$$

where subscript b denotes bare surface, A_r is obtained from the intercept on a Richardson plot and is related to the universal

$$"A_0" \text{ by } A_0 = A_r \exp\left(\frac{a_r}{k}\right).$$

ϕ_b is obtained from $\phi_b = \phi_r + a_r T$ where ϕ_r is the slope of the Richardson plot.

Similarly, the emitted electronic current density at times when cesium has adsorbed on the cathode may be expressed by

$$j_p = A_p \exp\left(\frac{a_p}{k}\right) T^2 \exp - \left(\frac{e\phi_p}{kT}\right) \quad (3)$$

$$\text{Now } A_r \exp\left(\frac{a_r}{k}\right) = A_p \exp\left(\frac{a_p}{k}\right) = A_0.$$

Hence

$$\ln \frac{j_p}{j_b} = \frac{e(\phi_b - \phi_p)}{kT} = \frac{e\Delta\phi}{kT}, \quad (4)$$

where $\Delta\phi$ is the contact potential or work function depression caused by cesium adsorption.

Substitution of (4) in (1) gives

$$\frac{\nu_i}{\nu_a} = \frac{1}{2} \exp \left[\left(\phi_b - I \right) \frac{e}{kT} - \ln \frac{j_p}{j_b} \right]. \quad (5)$$

At steady state $\nu_i + \nu_a = \mu_a$, where μ_a is the number of atoms/cm²-sec incident on the cathode surface.

Solving for ν_i in terms of ν_i/ν_a and μ_a ,

$$\nu_i = \frac{\nu_i/\nu_a}{(\nu_i/\nu_a) + 1} \mu_a \quad (6)$$

Equations (5) and (6) may then be used to calculate the number of positive ions emitted from cathode surfaces as a function of cesium pressure, where ϕ_b , j_b , j_p , T , and μ_a are experimentally determined quantities, and I is the ionization potential of cesium equal to 3.89 volts.

Plots of self-developed output current vs cathode-anode terminal voltage for different cathode materials are shown in Figs. 1a-1d. The initial bare surface work functions, ϕ_b 's, and the corresponding " A_r " values as determined from Richardson plots are noted. Cathode temperatures for these data were about equal.

The plots of the tantalum and tungsten data duplicate what has been done before. However, the rhenium and iridium cathodes demonstrate qualities not previously reported.

Note the extremely rapid increase of current density of the rhenium and iridium cathodes as cesium pressure was increased. Indeed, the iridium cathode adsorbed cesium so strongly that it attained emitted current densities of the order of amperes per square centimeter at a cesium pressure of 160 μ Hg.

Further, at low pressure, the current density vs voltage profiles of the iridium tube certainly indicate the lack of proper space charge neutralization. This phenomenon has not been observed in well outgassed systems for the other materials at equivalent pressures and cathode temperatures. When the cesium pressure was increased to about 10 μ Hg, the system became reasonably well neutralized and the normal type of current density vs voltage profile was obtained. Further increase in pressure caused the profiles to become rounded in a manner typical of those of other materials at much higher pressures. Reduction of pressure to low levels again produced the distorted profiles.

Scattering cross sections for electrons with energies less than 0.5 volts are not well known. If a cross section of 25 angstroms squared is

assumed, the mean free path of an electron in cesium gas at $160 \mu \text{ Hg}$ is about 0.1 cm , while the average interelectrode distance was about $2.54 \times 10^{-2} \text{ cm}$.

Since the profiles exhibit the same rounded characteristics at pressures which differ by an order of magnitude, and the mean free path is about four times the interelectrode distance, it appears likely that scattering was not the primary inhibitor of further increased current under these conditions.

When the output voltage is at an optimum for power output, the surface potentials of the cathode and anode are about equal. This means that if the interelectrode plasma is properly neutralized, emission equivalent to zero field emission is obtained from the cathode. Profiles in which the output current density is not changed as output voltage is increased from about zero to the break-off voltage provide a good measure of the current density at the optimum power point. Data from rounded profiles are less accurate but have been included since they occur in a region of great interest.

An examination of the rate of thermal ionization at the cathode surfaces was made using Eqs. (5) and (6). The numerical values used in these determinations were: each ϕ_b obtained from a Richardson plot, $I = 3.89$ volts and a value of j_p taken at $V_p \approx 0.5$ volt as a function of pressure.

Figure 4 shows the ions/ $\text{cm}^2\text{-sec}$ emitted from each of the cathode surfaces as a function of cesium pressure. Two points to be noted on Fig. 4 are (a) the sharp decline of ionization efficiency of the adsorptively depressed iridium cathode, and (b) the fact that the tantalum surface continued to ionize efficiently at considerably higher pressures.

Assuming that the collected current for all pressures represents some lower limit on the emitted current, an apparent work function was calculated from the Richardson equation using the current values taken from the profiles. Figure 5 shows the apparent work functions of the cathodes as cesium pressure was varied.

These phenomena suggest that a cathode material composed of something like tantalum and rhenium might offer superior qualities. The high work function crystal faces of the rhenium would adsorb cesium readily to provide good electron emission, while the tantalum remained substantially bare and would provide positive ion emission. In other words, the high heat of adsorption of cesium on rhenium would cause the cesium to

condense, whereupon the mobility of the condensed cesium would allow migration to a tantalum crystal face where the heat of adsorption is less and the cesium could be emitted as an ion. Copious ion emission is then an inherent quality of the tantalum surface. Potential barriers that might prevent ion emission are, in principle, subject to elimination by other means.

It has been found that rhenium is a very tractable cathode material for thermionic converter investigations. Figures 6a-6d show the profiles obtained with a rhenium cathode for four temperatures as cesium pressure was varied. The rhenium plot in Fig. 1c may also be added to these data.

Output current density for tantalum and tungsten cathodes at low pressure is sometimes even less than the value obtained for saturated emission in vacuum. The rhenium cathode does not demonstrate this peculiarity but offers a steady increase in output current density for each pressure step. The work function depression of rhenium at five temperatures is plotted versus pressure in Fig. 7.

Efficiencies greater than 15% are easily attained with rhenium cathodes. Only a few high pressure points were measured for each of the curves shown in Fig. 6, and these are not necessarily the optimum obtainable. Nevertheless it is interesting to note that efficiencies greater than 15% were achieved with the four lower cathode temperatures and the best obtained was 19% at 2440°K.

SUMMARY

These experimental data have demonstrated the following:

- (a) That high work function materials adsorb cesium so readily that they offer superior qualities for high-temperature plasma diode cathodes compared with tungsten and tantalum.
- (b) For a single cathode surface, balanced positive ion emission for large electronic current densities may possibly be achieved by a material combination that has work function patches of about 4.0 to 4.2 volts combined with patches that have work functions 5 volts or greater.
- (c) Overall efficiencies greater than 15% are easily achieved with rhenium cathodes.

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Fig. 1a. Output current density j_p vs output voltage V_p for tantalum cathode at 2110°K .

Fig. 1b. Output current density j_p vs output voltage V_p for tungsten cathode at 2140°K .

Fig. 1c. Output current density j_p vs output voltage V_p for rhenium cathode at 2140°K .

Fig. 1d. Output current density j_p vs output voltage for iridium cathode at 2150°K .

Fig. 2. Schematic diagram of the experimental tubes used.

Fig. 3. Thermionic converter wiring diagram.

Fig. 4. Emitted cesium ion current density vs cesium pressure.

Fig. 5. Work function depression vs cesium pressure.

Fig. 6a. Output current density vs output voltage for rhenium cathode at 2250°K .

Fig. 6b. Output current density vs output voltage for rhenium cathode at 2350°K .

Fig. 6c. Output current density vs output voltage for rhenium cathode at 2440°K .

Fig. 6d. Output current vs output voltage for rhenium cathode at 2540°K .

Fig. 7. Work function depression vs cesium pressure, rhenium cathode.

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