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(Received 10 August 1987, accepted for publication 18 March 1988)

A research diode with polycrystalline molybdenum electrodes is described. Voltage-current characteristics are presented as a function of the cesium reservoir temperature. A power density of 4 W/cm^2 is obtained at an emitter temperature of 1400 °C. The influence of the temperatures of the emitter, collector, and cesium reservoir and of the interelectrode distance is experimentally investigated. Physical explanations for the various effects are given. The work function of the polycrystalline molybdenum emitter in a cesium atmosphere is evaluated as 2.5–2.7 eV depending on the reduced emitter temperature (i.e., the emitter temperature divided by the cesium reservoir temperature). A barrier index $V_b = 2.0$ eV and a cesium plasma drop $V_d = 0.4$ eV are found.

I. INTRODUCTION

A thermionic energy converter (TEC) is a device which directly converts heat into electricity. It consists of two electrodes, one of which (the emitter) is heated to a temperature at which it will thermally emit electrons.[1–3] The other electrode (the collector) is kept at a lower temperature and collects the electrons. Part of the heat removed from the emitter by evaporating electrons (S_{eva}) is transported to the collector by condensing electrons. The remaining part is converted into electric power in the load as the electrons return to emitter potential.

It is the aim of our research to develop a combustion-heated thermionic energy converter for industrial application.[4] To speed up the commercial application of TECs, higher efficiencies are needed. To improve the efficiency and the power density of a TEC, the cesium plasma drop and/or the collector work function should be reduced. We proposed[5,6] to use directionally solidified cermets as electrode materials to obtain these effects. To evaluate these directionally solidified cermets as electrodes we built the research diode described in this paper. To compare the cermet electrodes with the more frequently used refractory metal electrodes, we first set up the diode with molybdenum electrodes. Experimental work on converters with molybdenum electrodes is described in the literature.[7–16] Hirsch[7] has measured the effect of spacing on the power output. Houston and Webster[11] write that Hirsch's data are taken under slightly gassy conditions. Houston and Webster[11] report values for the power output under cleaner conditions; these values are lower. In the article by Kitulakis and Hatsopoulos[12] one voltage-current characteristic for molybdenum electrodes is shown, and the power density is 7.6 W/cm^2 at 1860 K. Weeks, Dahlem, and Gingrich[10] and Langpape and Minor[13] give optimized power densities that are still lower than the power densities given by Houston and Webster[11] and Kitulakis and Hatsopoulos.[12] As shown in Fig. 1 various values for the power density of a converter with polycrystalline molybdenum are given in the literature. The partial gas pressure in the converter is of importance for the resultant power density. However, exclusion of emission-active gases does not result in the lowest power densities reported in literature.[16] Critical assessment of the reported results is needed.

To have clean conditions we carefuly outgassed the diode and made use of an ion-getter pump. Many of the previous published results are less reliable because they are affected by the resistance of the leads. To eliminate the effect of the leads we use a four-point measuring method.

II. DESCRIPTION OF THE DIODE

A sketch of our diode is shown in Fig. 2. The various parts of the diode are interconnected using stainless-steel flanges joined by copper gaskets. The diode is situated in an evacuated bell jar to protect it against corrosion by air. The emitting and collecting surfaces are arc-cast polycrystalline molybdenum surfaces with an active area of 2 cm^2. The molybdenum (low carbon ABL2 quality) purchased from

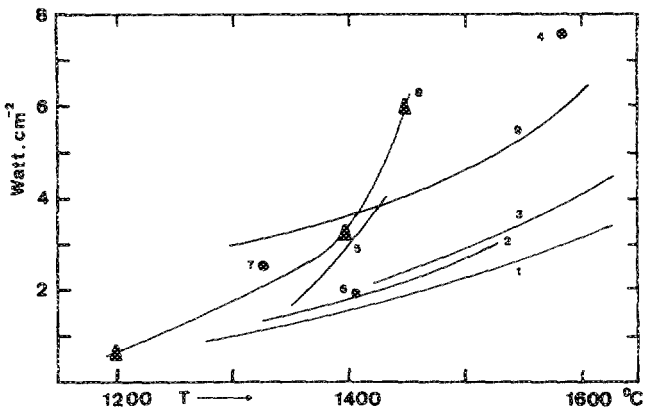

FIG. 1. Power density of a converter with molybdenum electrodes as a function of the emitter temperature. The interelectrode distance is 0.2 mm (except for nos. 2 and 9, respectively, 0.5 and 0.4 mm). Experiments are with a polycrystalline molybdenum emitter [except for nos. 6 and 9, Mo(110)] and a polycrystalline molybdenum collector. Curve 1: Weeks, Dahlem, and Gingrich, Ref. 10; 2: Fukuda *et al.*, Ref. 15; 3: Langpape and Minor, Ref. 13; 4: Kitulakis and Hatsopoulos, Ref. 12; 5: Houston and Webster, Ref. 11; 6: Hansen, Ref. 14; 7: Baum and Jensen, Ref. 8; 8: this work; 9: Gverdtsiteli and Korobova, Ref. 16.

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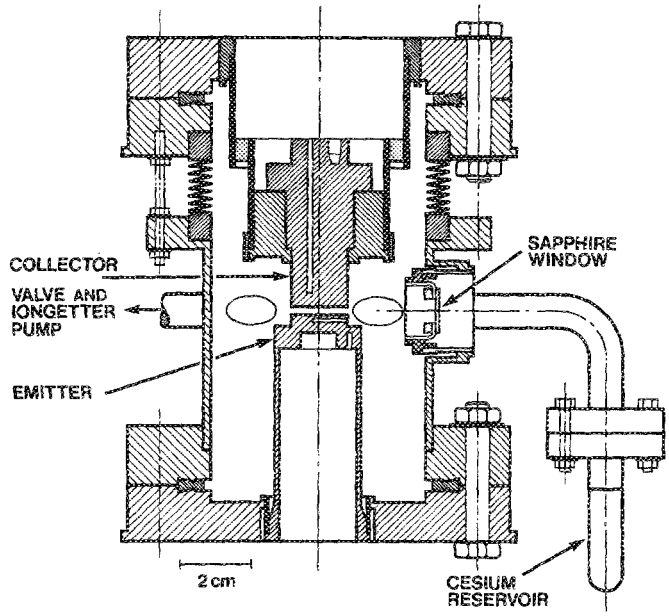

FIG. 2. Schematic drawing of the research diode.

Amax Inc. has a chemical composition of C, 0.003 wt. %; O_2, 0.0012 wt. %; H_2, <0.001 wt. %; N_2, 0.0002 wt. %; Fe, <0.0001 wt. %; Ni, <0.001 wt. %; Si, <0.001 wt. %; Mo, >99.97 wt. %.

After the experiments the molybdenum emitter was found to be recrystallized and showed an average grain size of 250 μm. Emitter, collector, and cesium reservoir temperatures were automatically controlled and measured with Pt–Pt-10 at. %-Rh thermoelements. The emitter temperature was constant within 5 °C, the collector temperature within 1 °C, and the cesium reservoir temperature also within 1 °C. The emitter thermoelement indication was compared with data from an optical pyrometer. After correction for absorption losses the pyrometer temperatures were 80 °C lower than the thermoelement values. Since the temperature never exceeded 1450 °C, where diffusion phenomena are relatively slow, the thermoelement readings are thought to be the most reliable. Calibration indicates that the absolute values are correct to within 20 °C.

In order to reach a sufficiently high emitter temperature (up to 1450 °C) a 0.5-mm-diam tungsten electron gun was used. The interelectrode distance is variable in the range 0.02–1 mm. The bell jar protecting the diode is evacuated by an oil diffusion pump. The diode is evacuated by a separate pumping system using a turbo molecular pump and for the final vacuum a Leybold IZ30 ion-getter pump. Before the diode is assembled, all parts are thoroughly cleaned with freon, alcohol, and distilled water. The diode was outgassed at temperatures as high as the highest temperatures to be used in the experiments. After outgassing, cesium (purity 99.98 wt. % Cs) was introduced into the diode. After the introduction of the cesium the last measured pressure in the diode was 2×10^{-8} mbar.

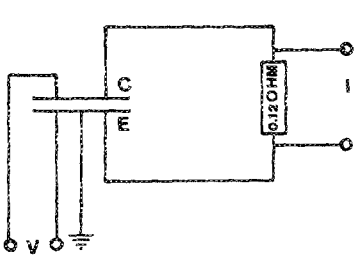

FIG. 3. Electrical circuit used for the measurement of the voltage-current characteristics.

III. EXPERIMENTS

A. Voltage-current characteristics

To avoid the effects of the electrical resistance of the leads the voltage-current characteristics are measured using a four-point method. The electrical circuit is shown in Fig. 3. The characteristics are obtained with a Tektronix 577D2 curve tracer with sense connection using alternating current (50 Hz). Various voltage-current characteristics were obtained by keeping the emitter temperature, the collector temperature, and the interelectrode distance constant and varying the cesium reservoir temperature; see Fig. 4. At higher cesium reservoir temperatures the current density is higher. Various voltage-current characteristics were obtained[17] at emitter temperatures ranging from 1200 to 1450 °C, the collector temperature ranging from 600 to 700 °C, and the cesium reservoir temperature ranging from 280 to 360 °C. The interelectrode distance was varied from 0.1 to 0.6 mm.

B. Power density

Electrical power densities (P) calculated from the voltage-current characteristics are shown as a function of the load voltage at various interelectrode distances in Fig. 5. The highest power density measured at 1400 °C emitter temperature was 4 W/cm^2 (collector temperature 680 °C, cesium reservoir temperature 340 °C, and interelectrode distance 0.1 mm). At 1450 °C and collector temperature 700 °C, cesium reservoir temperature 360 °C, and interelectrode distance 0.2 mm, we measured 6 W/cm^2. It was not possible to optimize the diode at 1400 and 1450 °C. As is seen in Fig. 4

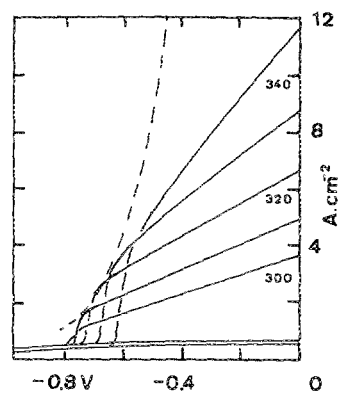

FIG. 4. Voltage-current characteristics at an emitter temperature of 1400 °C, a collector temperature of 680 °C, and an interelectrode distance of 0.3 mm. The various cesium reservoir temperatures are indicated in °C. The dashed line is the Boltzmann line ($V+2$) at 1400 °C.

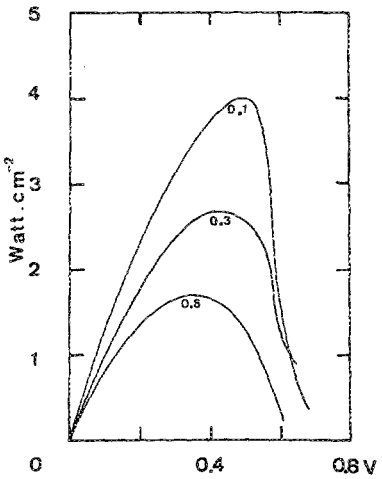

FIG. 5. Power density of the converter with polycrystalline molybdenum electrodes at an emitter temperature of 1400 °C. The collector temperature is 680 °C and the cesium reservoir temperature is 340 °C. The various interelectrode distances are indicated in mm.

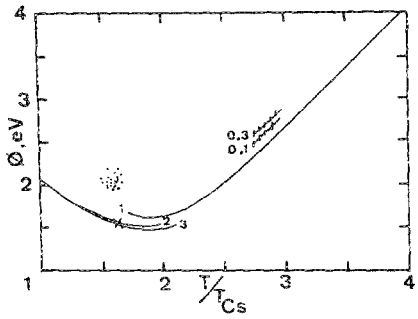

FIG. 6. Work function of polycrystalline molybdenum given as a function of the reduced electrode temperature (electrode temperature divided by the temperature of the cesium reservoir). Solid line 1 are values measured by Aamodt and Brown, Ref. 19. Solid line 2 is the work function of a metallic collector according to Rasor, Ref. 18. Solid line 3 are values measured by Gunther, cited in Ref. 1. The hatched lines are values measured by the authors; the collector temperature is 680 °C, the emitter temperature is 1400 °C, and the interelectrode distance is 0.1 and 0.3 mm. The dots indicate barrier indices measured by the authors at an emitter temperature of 1400 °C. One value of the collector work function evaluated from the back emission at a collector temperature of 680 °C, cesium reservoir temperature 310 °C, emitter temperature 1450 °C, and interelectrode distance 0.3 mm is shown (×).

higher cesium reservoir temperatures would result in higher power densities until an optimum cesium reservoir temperature is reached. The highest cesium reservoir temperature (still being the lowest temperature in the diode) we could reach depended on the emitter and collector temperatures.

C. Work function

Work functions are calculated from the saturation current (J_s) using the Richardson equation:

$$J_s = AT_E^2 \exp(-\Phi_E/kT_E), \quad (1)$$

where A is a constant, 120 C s^{-1} cm^{-2} K^2, T_E the emitter temperature, Φ_E the emitter work function, and k the Boltzmann constant. The work function of the polycrystalline molybdenum emitter can be estimated from the voltage-current characteristic. The current density at the knee of the voltage-current characteristic is taken as the saturation current.[18] Work functions calculated in this way are shown as a function of the reduced electrode temperature (electrode temperature divided by the cesium reservoir temperature, both in K) in Fig. 6. In this so-called Rasor plot we also indicated some literature values for the work function of polycrystalline molybdenum surfaces. As we measured the voltage-current characteristics in the electron-rich region (the ion-richness ratio[1] $\beta = 0.03$) and at high values of pd (the cesium pressure times the interelectrode distance, $pd = 1.5$ mbar mm) the work functions calculated from these voltage-current characteristics are too high. It is seen in Fig. 6 that the agreement between the measured work function and literature value is better at lower interelectrode distances (smaller pd).

D. Influence of the interelectrode distance

The influence of the interelectrode distance on the voltage-current characteristics is shown in Fig. 7. At smaller distances the electrical current density is higher because the resistance of the plasma is lower.

E. Influence of the collector temperature

The voltage-current characteristics at various collector temperatures are shown in Fig. 8. At high electrical current density there is no influence of the collector temperature. At lower currents (and higher voltages across the electrodes) the voltages differ for various collector temperatures because at a constant cesium reservoir temperature the collector work function varies with the collector temperature. As shown in Fig. 6, increasing the collector temperature lowers the collector work function and as a consequence the barrier index. Clearly the load voltage in the retarding range is higher for higher collector temperatures.

F. Influence of the emitter temperature

The influence of the emitter temperature on the voltage-current characteristics is shown in Fig. 9. At constant cesium reservoir temperature and collector temperature there

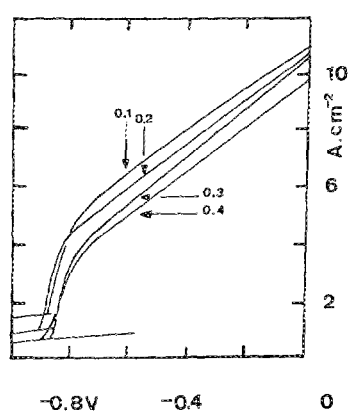

FIG. 7. Influence of the interelectrode distance (indicated in mm). The emitter temperature is 1450 °C, the collector temperature is 680 °C, and the cesium reservoir temperature is 340 °C.

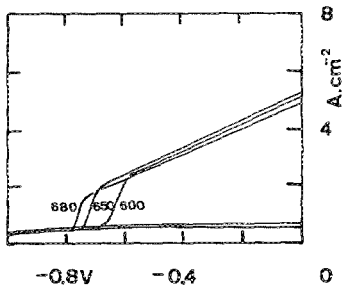

FIG. 8. Influence of the collector temperature (indicated in °C). The emitter temperature is 1400 °C, the cesium reservoir temperature is 310 °C, and the interelectrode distance is 0.3 mm.

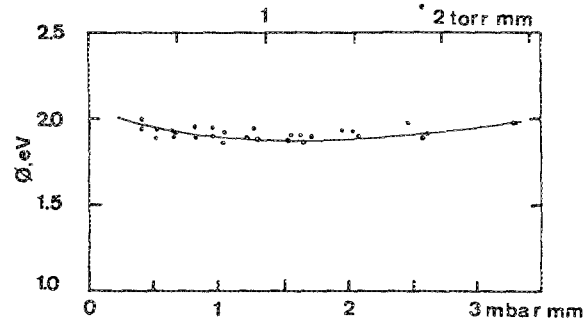

FIG. 10. Barrier index as a function of *pd* (pressure times interelectrode distance). The emitter temperature is 1450 °C.

are two effects: (1) at lower emitter temperature the current is higher at low voltage differences because the emitter work function is lower, and (2) at lower emitter temperature the current drops at smaller voltage differences because the kinetic energy of the electrons is lower. In general the emitter temperature is the most dominant factor. The higher the emitter temperature, the higher the power density of the optimized diode.

IV. DISCUSSION

The barrier index characterizes the performance of any real thermionic converter relative to the tabulated parametric performance for the ideal converter.[18] The barrier index V_b is the sum of two terms:

$$V_b = \Phi_C + V_d \,, \tag{2}$$

where Φ_C is the collector work function and V_d is the total plasma loss. The barrier index (taken at the knee of the voltage-current characteristic) as a function of the reduced collector temperature is shown in Fig. 6. The barrier index as a function of *pd* has a shallow minimum as shown in Fig. 10. If at an emitter temperature of 1200 and 1450 °C the work function of polycrystalline molybdenum is compared with the barrier index, a plasma voltage drop $V_d = 0.34 \pm 0.05$ eV is calculated. At 1400 °C a plasma voltage drop of 0.44 ± 0.05 eV is found.

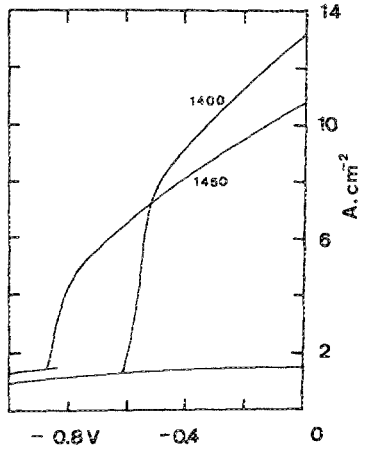

FIG. 9. Influence of the emitter temperature (indicated in °C). The collector temperature is 680 °C, the cesium reservoir temperature is 340 °C, and the interelectrode distance is 0.1 mm.

An estimate of the efficiency (η) of the energy conversion[2] can be made:

$$\eta = P/(S_{\text{eva}} + S_{\text{rad}}) \,. \tag{3}$$

S_{eva} is the power associated with the energy density transported by electrons from the emitter and S_{rad} is the power associated with the energy density transported by radiation from the emitter:

$$S_{\text{eva}} = (J/e)(\Phi_E + 2kT_E) \,, \tag{4}$$

$$S_{\text{rad}} = \sigma\epsilon(T_E^4 - T_C^4) \,, \tag{5}$$

where e is the charge of an electron, ϵ is the effective thermal emissivity, and σ is the Stefan–Boltzmann coefficient. The thermal emissivity of polycrystalline molybdenum[20] is 0.2; this value is not influenced by a cesium monolayer.[21] The effective thermal emissivity is calculated from the equation for two radiating parallel surfaces[2]:

$$1/\epsilon = 1/\epsilon_E + 1/\epsilon_C \,, \tag{6}$$

where ϵ_E and ϵ_C are the thermal emissivity of emitter and collector, respectively. The resulting value for the emissivity is $\epsilon = 0.11$. An efficiency of $\eta = 16\%$ at an emitter temperature of 1400 °C is calculated (the collector temperature is 680 °C, work function of the emitter 2.32 eV, and current density 8 A/cm^2 at a voltage of 0.5 V).

In Fig. 1 the highest power densities at each emitter temperature (and at an interelectrode distance of 0.2 mm) are indicated. The curve obtained in this study has a steep slope. Contrary to the situation at 1200 °C we could not fully optimize our diode at 1400 and 1450 °C. Because the diode at 1450 °C, where we could reach higher cesium reservoir temperatures, is better optimized than at 1400 °C, the point at 1400 °C lies too low. As a result the slope of the high-temperature part of the power density curve is too steep. At the highest emitter temperature (1450 °C) the work function of the collector was evaluated from the back emission and found to be $\Phi_C = 1.56$ eV at a collector temperature of 680 °C, a cesium reservoir temperature of 310 °C, and an interelectrode distance of 0.3 mm. As is seen in Fig. 6 this is the work function expected for polycrystalline molybdenum. Consequently it is not probable that there are foreign active gases present on the electrode surface.

As can be seen in Fig. 1 there is a great spread in the power densities obtained by various investigators with the same electrode material. Features of our diode measure-

ments are the four-point measuring method, the care with which the diode is outgassed, and the use of copper gaskets as a sealing. Particularly the four-point method will have resulted in better measurements at higher power densities.

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