Electron emission microscope measurements on cermet electrodes for thermionic converters

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ELECTRON EMISSION MICROSCOPE MEASUREMENTS ON CERMET ELECTRODES FOR THERMIonic CONVERTERS

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The electron emission is studied of a polycrystalline Mo-Al₂O₃ cermet. Measurements with an electron emission microscope show that, both in vacuum or with Cs coverage, the Mo matrix contributes most to the emission. Work functions are measured at Cs effusion cell temperatures between 90°C and 130°C; the lowest work function measured is 1.2 eV. The enhanced emission of the cermet as compared to pure Mo is attributed to Cs-O interaction at the Mo surface.

1. INTRODUCTION

A thermionic energy converter (TEC) is a device which directly converts heat into electricity (Fig. 1). It consists of two electrodes, one of which (the emitter) is heated to a temperature at which it will thermally emit electrons. At the other electrode (the collector) the Fermi level is more negative than that of the emitter. The collector is kept at a lower temperature and collects the electrons. Part of the heat removed from the emitter by evaporating electrons is rejected to the collector by condensing electrons, and the remaining part is converted into electric power in the load as the electrons return to emitter potential. A TEC can operate in vacuum and a plot of its potentials is shown in Fig. 2. The output potential of the TEC is limited to the difference in work functions of emitter and collector. As the electrons need a finite time to reach the collector there is a density of electrons in front of the emitter. Raising the temperature of the emitter will increase the electron current, so the electron density will increase as well. A high density of electrons in the interelectrode space will push the emitted electrons back to the emitter surface. This effect is called the space charge effect. As a result the vacuum TEC will not produce any electricity whatsoever unless the interelectrode gap is smaller than 5 μm.

As the emitter temperature of a TEC will in most cases exceed 1200°C and may even be as high as 2000°C the electrode will be susceptible to recrystallization and creep which can easily cause a short-circuit between emitter and collector.

To avoid these problems, cesium is introduced into the interelectrode gap. Cesium is
a metal with a low melting point (270°C), reasonably high vapour pressure and what is more important it possesses the lowest ionization potential of all the elements. Therefore the cesium vapour will ionize partly at the hot emitter surface, forming a cesium plasma, the positive ions of the cesium plasma neutralizing the space charge effect. Positive cesium ions will also be created in the interelectrode space by collisions (see Fig. 3).

A TEC is a low-voltage (0.5 V), high-current density (10A/cm²), DC power source. At the present stage of development it will operate at an emitter temperature of 1200°C and a collector temperature of 500°C with an efficiency of 15%. Our aim is to raise the efficiency of the TEC by development of better electrode materials.

The reduction of the collector work function $\phi_c$ could contribute substantially to the efficiency of the TEC. It has been demonstrated that oxygenated refractory metals may show very low work functions upon cesiation\textsuperscript{1}. This is thought to be due to the Cs-O-metal complex which is formed at the collector surface. These low work function collectors, however, are not stable; at least they are not, above 500°C. So under TEC operating conditions the collector work function will show a marked increase after half an hour of operation of the TEC. This is probably due to the decomposition of the Cs-O-metal complex with the formation of a stable cesium oxide with a much higher work function. It is one of the objectives of our materials development programme to overcome this problem by using a cermet electrode\textsuperscript{2}.

A cermet consists of a metal and a ceramic part. We investigated Mo/Al$_2$O$_3$, Cr$_2$O$_3$ systems.

An emitter consisting of a cermet will evaporate a little at very high temperatures. The vapour will condense on the collector producing a Mo/Al$_2$O$_3$, Cr$_2$O$_3$ surface. We measured work functions of Mo/Al$_2$O$_3$, Cr$_2$O$_3$ surfaces in a thermionic emission microscope.

2. THERMIONIC EMISSION MICROSCOPE

Measurements were performed using an emission microscope facility at the Deutsche Forschungs- und Versuchsanstalt für Luft- und Raumfahrt.
In Stuttgart. At the DFVLR in Stuttgart an emission microscope has been developed which is suitable for the study of electrode surfaces with cesium adsorption layers\(^3\). This instrument is particularly useful for the investigation of cermet electrodes with their heterogeneous morphology, because it allows the qualitative observation of emission distribution on the surface in a magnified display and simultaneously the quantitative measurement of emission current density. In Fig. 4 the emission microscope is shown schematically. It is designed as a vertical construction with the emitting electrode at the lower end and the fluorescent screen at the top of the apparatus. The emitting electrode is mounted in a much larger molybdenum cup for better temperature uniformity. It can be heated by radiation and by electron bombardment using a spiral tungsten filament inside the cup. With this heater construction temperatures up to 1800°C can be attained and be maintained for long operation times if the electrode material itself has a sufficient thermal stability. The entire heater unit, including the emitting electrode, can be shifted in two horizontal directions in order to bring any interesting area of the electrode under the objective of the microscope. The projecting objective of the microscope is an electrostatic immersion lens. It is adjustable in vertical direction for focusing the screen picture.

An anode tube with a fluorescent screen at its upper end is arranged above the objective. The display can be observed and photographed through a vacuum window from the reverse side of the screen. The potential distribution in the microscope is the following: the emitter electrode is operated at ground potential, the filament at negative potential up to -1kV for electron bombardment, the two diaphragms of the electrostatic lens at intermediate positive potentials and the anode with the fluorescent screen at a positive potential of +5kV. The visible image on the screen results from variations of emission current density on the electrode surface. Since the temperature of this surface is uniform, variations of thermionic emission can only be caused by different work functions. Thus the electronic image is a magnified display of the work function distribution on the electrode. Bright areas correspond to low work function areas on the electrode. Adsorption layers are also clearly visible because most adsorbed substances change the work function of the underlying surface considerably.

The magnification of this simple electron optical system with only one lens is not very high. The linear scale factor can be adjusted by varying the potential of the first diaphragm of the lens within the range from \(V = 60\) up to \(V = 240\). Mostly a value of 100V is used. This magnification provides the possibility to investigate grain structures of electrode materials with dimensions ranging from 0.01 mm to some

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**FIGURE 4**
Schematic drawing of an emission microscope.
0.1 mm.

For calculating the emission current density the magnification has to be taken into account. The current density at the electrode \( J_e \) is higher than the measured current density at the screen \( J_s \) by the factor \( V^2 \):

\[
J_e = V^2 J_s
\]

By means of the measured current density \( J_e \) and the electrode temperature \( T \) the work function of the electrode \( \Phi \) can be calculated using the Richardson-equation:

\[
J_e = A T^2 \exp \left( \frac{-\Phi}{kT} \right)
\]

with \( k \) = Boltzmann constant, \( A = 120 \, \text{A/cm}^2 \).

The temperature of the electrode is measured by means of a thermocouple or an optical pyrometer.

Adsorption layers can be build up on the electrode surface by evaporation of cesium from a heated effusion cell through a tube heated as well and ending just above the electrode. From the end of the tube an atomic beam of the adsorbate strikes the surface at a slight angle, limited by the narrow slit between electrode and first diaphragm of the objective (see Fig. 4). Not only by cesium adsorption the work function can be altered; adsorption of components from the residual gas also have a severe effect. Generally the degree of coverage of an adsorption layer increases with increasing residual gas pressure and decreasing surface temperature. This effect has to be taken into account especially when studying electrodes with a cesium adsorption layer. These electrodes sometimes exhibit minimum work functions of 1.2 eV to 1.0 eV and the temperature range where considerable emission occurs, goes down to below 300°C. For that reason the instrument is constructed completely in ceramic-metal technique and it is operated in a ultra high vacuum system with a background pressure in the \( 10^{-9} \) mbar range at operating conditions.

3. OBSERVATIONS AND MEASUREMENTS WITH THE ELECTRON EMISSION MICROSCOPE

The electrode investigated has a composition of 70 v/o Mo and 30 v/o \( \text{Al}_2\text{O}_3 \). The alumina particles have a mean grain size of 90 \( \mu \text{m} \) (linear intercept). The alumina used for the cermet was "korund abramax F120" and is supplied by Lonza (Rotterdam). The chemical analyses is:

- \( >99.5\% \text{Al}_2\text{O}_3; \text{SiO}_2<0.06\%; \text{TiO}_2<0.02\% \),
- \( \text{Fe}_2\text{O}_3<0.04\%; \text{MgO}<0.007\%; \text{CaO}<0.05\%; \text{Na}_2\text{O}<0.2\% \).

The molybdenum used is supplied by H. Drijfhout & Zoon's Edelmetallbedrijven nv, purity 99.96%.

The electrode was sintered at 1600°C in vacuum \( (5\times10^{-6} \, \text{mbar}) \) for 9 hours. Fig. 5 shows the light microscopic image of the same before it was mounted in the electron emission microscope. The electrode was outgassed for three weeks in the electron microscope at 1450°C.

Fig. 6a shows an image of the electrode in the electron microscope (the temperature of the electrode is 1500°C). The heterogeneity of
FIGURE 6
Emission micrograph of a Mo-Al<sub>2</sub>O<sub>3</sub> cermet. a) in vacuum, the temperature of the electrode is 1500°C. b) covered with a Cs layer, the temperature of the electrode is 350°C. — 50 μm.

FIGURE 7
S-curves of the Mo-Al<sub>2</sub>O<sub>3</sub> cermet at different Cs effusion cell temperatures: top 130°C, middle 110°C, bottom 90°C. +: increasing temperature, O: decreasing temperature.

The electrode is manifest. Comparison of the image on the screen of the emission microscope with the image in the light microscope clearly indicates that the alumina parts are the less emitting parts. With a cesium adsorption layer the alumina parts are also the less emitting parts (see Fig. 6b).

At normal operation temperatures of the converter the adsorption layers are not stable. There is a dynamic equilibrium between thermal desorption and adsorption from the converter atmosphere. Therefore the emission characteristics show two distinct ranges of high thermionic emission. In the high temperature range (see Fig. 7) the coverage with adsorbate is nearly zero and the emission current density corresponds to the bare work function of the electrode material. In the low temperature range coverage is increasing. Therefore the work function decreases when the temperature is lowered. The emission current density attains a maximum when nearly complete coverage is reached.
The plot of the emission current density versus the surface temperature is shaped like an S. For that reason these kind of characteristics, measured first by Langmuir, are mostly called Langmuir S-curves. The value of the emission current maximum of these curves depends on the adsorbate arrival rate which is controlled by the temperature of the effusion cell. This temperature is normally used as a parameter value for a complete set of Langmuir S-curves. They are mostly plotted in a diagram of lnI against 1/T the so called Richardson plot, because in such diagram the lines of constant work function are nearly straight. The bare work function of the cermet (see Fig. 7) is found to be 4.3 eV.

S-curves are given for three effusion cell temperatures: 90, 110 and 130°C. During the measurement the sample was always in focus; the objective was not moved. The sample surface is partly shielded from the atomic cesium beam. Measurements during which the electron optical system was moved vertically were not reproducible. The lower electrode temperature side of the S-curve however is not as sensitive to movements of the electron optical system as the high temperature side. For the 110°C curve, crosses indicate a set of measurements obtained by raising the electrode temperature, the circles are values obtained by lowering the electrode temperature. Each set of measurements at a given effusion cell temperature was obtained within 11 hours.

As an indication of the time effect when measuring without moving the electron objective, Fig. 8 gives the current density variation with time after lowering the heating current.

4. COMPARISON WITH OTHER ELECTRON EMISSION MEASUREMENTS

In the apparatus under consideration two other kinds of cermets have been investigated: The Mo/UO₂ and the Mo/ZrO₂ system. We also published measurements on a 51 v/o Mo/Al₂O₃/Cr₂O₃ (1:1) cermet. (See Fig. 9) The S-curves of the Mo/Al₂O₃ cermet closely resemble the S-curve of the Mo/ZrO₂ cermet. The emission current of the Mo/Al₂O₃ cermet is a little higher. The minimum work function of the

FIGURE 8
Time dependence of the current density after lowering the heating current. The effusion cell temperature is 130°C.

FIGURE 9
Langmuir S-curves for various cermets: 1 = Mo-UO₂; 2 = Mo/Al₂O₃; 3 = Mo-ZrO₂; 30% ceramic. Effusion cell temperature: 130°C.
Mo/ZrO\textsubscript{2} cermet is the same as the minimum of the Mo/Al\textsubscript{2}O\textsubscript{3} cermet: $\phi_{\text{min}} = 1.2$ eV.

5. DISCUSSION

Measuring the work function in a cesium atmosphere at operating conditions of a thermionic converter ($T_{\text{Cs}} = 250^\circ\text{C}-300^\circ\text{C}$, $T_{\text{emitter}} = 1200^\circ\text{C}-1500^\circ\text{C}$) is a difficult task. Using the Rasor-theory\textsuperscript{9}, extrapolation to other temperatures is possible, although only in a narrow range.

In Fig. 10 our measurements are shown in a Rasor-plot together with equilibrium measurements for Mo/Cs\textsuperscript{10} and Mo/O/Cs\textsuperscript{11}.

In Table I some work function values for Mo and Mo/O/Cs are given. The low work function of cermet may be explained by the fact that the metal part of the cermet should have a minimum work function corresponding to that of Mo/O/Cs: 1.2 eV. Why Mo-UO\textsubscript{2} shows a slightly higher minimum work function is not yet well understood.

As the Mo-Al\textsubscript{2}O\textsubscript{3} cermet was sintered in a vacuum of $5 \times 10^{-6}$ mbar, it is obvious that the Mo in this case will be covered with an oxygen layer. The Mo-ZrO\textsubscript{2} cermet was produced by low pressure plasma spraying so it should also be covered by an oxygen layer right from the start.

In the case of the Mo-UO\textsubscript{2} cermet, the UO\textsubscript{2} used for the cermet production was oxygen deficient\textsuperscript{16}. So in this particular case, it is possible that prolonged high temperature equilibration in a
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