Electron Field Emission Properties of Textured Platinum Surfaces

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ELECTRON FIELD EMISSION PROPERTIES OF TEXTURED PLATINUM SURFACES

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Abstract
During ground tests of electric microthrusters and space tests of electrodynamic tethers the electron emitters must successfully operate at environmental pressures possibly as high as 1 x 10^4 Pa. High partial pressures of oxygen, nitrogen, and water vapor are expected in such environments. A textured platinum surface was used in this work for field emission cathode assessments because platinum does not form oxide films at low temperatures. Although a reproducible cathode conditioning process did not evolve from this work, some short term tests for periods of 1 to 4 hours showed no degradation of emission current at an electric field of 8 V/μm and background pressures of about 1 x 10^-6 Pa. Increases of background pressure by air flow to about 3 x 10^-4 Pa yield a hostile environment for the textured platinum field emission cathode.

Introduction
Low-power electric thrusters, spacecraft plasma contactors, and electrodynamic tether systems need electron emitters that require very low gas flow rates or no gas flow to perform their functions [1-3]. In order to ensure that very low-power colloid thrusters, Field Emission Electric Propulsion (FEEP) devices, ion engines, Hall thrusters, and gridded vacuum arc thrusters are attractive systems, an expellantless neutralizer is certainly desirable [1]. Electron emission current requirements for colloid and FEEP thrusters may be as low as 20 to 400 μA [4,5]. The demand for very high current density microthruster neutralizers is not as important as developing a long-lived device for operation in a relevant environment. During ground tests of electric microthrusters and space tests of electrodynamic tethers the electron field emitters must successfully operate at environmental pressures possibly as high as 1 x 10^-4 Pa. High partial pressures of oxygen, nitrogen, and water vapor are expected in such environments. Much of the propulsion-related work to date has dealt with developing molybdenum or ZrC-coated molybdenum Spindt-type and carbon nanotube devices for field emission cathodes (FECs) [2,4]. Molybdenum and ZrC-coated molybdenum Spindt field emission cathodes were tested in an oxygen environment at about 1 x 10^4 Pa; the best results indicated that the emission current decayed to 30% of its initial value in 17 minutes as shown in Table 1 [2,6]. Tests of high current density carbon nanotube FECs at about 3 x 10^-4 Pa had emission current degradation to 15% of its initial value in 17 minutes [7]. When a carbon nanotube FEC was operated at derated current levels, very little current degradation was observed over the first 23 hours in a 1 x 10^-5 Pa gas background [8]. There still is a need to develop FECs that provide stable operation for thousands of hours at background pressures of 10^-5 to 10^-4 Pa of oxygen and nitrogen for electric microthruster or electrodynamic tether applications.

As indicated in environmental tests of Reference 2, the oxygen was adsorbed by the cathode surface, and the work function was increased and electron emission was decreased. Since platinum does not readily form oxide films in air at low temperatures (< 800 K) [9], it was thought that it might be a suitable candidate for a textured FEC, even though the work function of platinum is high (5.39 eV). For example, using Pt(111), it also has been found that adsorption of molecular oxygen predominates at temperatures below 120 K, adsorption of atomic oxygen predominates at temperatures between 170 K and 700 K, and oxide films can be produced in the temperature range of 800 K to 1100 K [10]. Molecular oxygen can adsorb on a clean platinum surface or on a surface with adsorbed oxygen atoms. Even though oxygen adsorption is expected on platinum in the environments of interest, the development of platinum oxide films is not expected at the normal temperatures of
FEC operation. Since this experiment was conducted in an air environment, it can be expected that molecular nitrogen was also readily adsorbed. For example, molecular nitrogen is adsorbed by Pt(111) when it is exposed to a local nitrogen pressure of $3 \times 10^6$ Pa for only 15 seconds [11].

It has been well documented that adsorbed gases on a solid surface will change the work function [12]. The change in work function is proportional to the density of adsorbed molecules. As the work function increases due to changes in surface chemistry, the emission current decreases. It is also likely that the oxygen and nitrogen molecules will encounter dissociation and ionization processes due to collisions with the field emitted electrons [2]. Ionized species, molecules, and atomic species all will react with the emitting surface to produce changes in the work function.

In previous work, an ion beam textured copper FEC was tested and found to suffer emission current degradation of 30% to 40% after only one hour of testing in an air background environment of $5 \times 10^6$ Pa [13]. The textured copper had a beginning-of-life current density of about 380 $\mu$A/cm$^2$. The objective of this work was to coat the textured copper surface with the more inert platinum material with a view of producing a more stable FEC performance in an oxygen/nitrogen environment.

This paper will report on work characterizing the FEC electrical performance of a platinum coated, ion beam textured surface. FEC emission current stability will be assessed using air background environments of $9 \times 10^7$ Pa to $3 \times 10^4$ Pa. Electrical characteristics, effects of adsorbed gas species, and performance stability of the textured platinum FEC in a simple diode arrangement are summarized.

**Apparatus and Procedure**

**Preparation of Cathode Material**

The cathode material is ion beam textured copper [13,14] coated with 0.5 $\mu$m of platinum. The copper base was selected because copper is readily textured using an argon ion beam and a tantalum seed material. The deposition rate of the tantalum seed material was minimized in order to produce cone-like structures on the copper rather than a very dense spire-like structure.

Figure 1 shows the set-up used to texture the cathode copper base. A tantalum “seed” target was rotated 45 degrees with respect to the centerline of a 30 cm diameter ion source. The 15 cm by 15 cm tantalum target was translated so that the downstream edge was 20 cm below the centerline and 15 cm from the ion source. The copper substrate was located on centerline and 15 cm from the ion source. The argon ion energy was 1000 eV, and the average ion current density at the ion source was 2.1 mA/cm$^2$. The ion sputtering time in this case was 16 hours. Only wide-angle ions struck the tantalum seed target, so the tantalum arrival rate at the copper coupon was very low. As shown in Figure 2, the low seed arrival rate at the copper surface and the operating conditions produced cones with base diameters of 30 $\mu$m to 70 $\mu$m and cone-heights of about 30 $\mu$m to 100 $\mu$m. The color of the copper surface was dark orange.

The textured copper was then coated with platinum using a 500 W radio frequency sputtering system. The sputtering was performed in an argon environment at about 1 Pa. The sputter etch voltage was 1900 V and the platinum deposition rate was 270 angstroms per minute.

There were no special conditioning procedures for the platinum FECs prior to testing other than out-gassing at room temperature at about $1 \times 10^6$ Pa and “burning-in” by testing with an electric field of 8 V/$\mu$m. Other investigators have heated their emitters to 300 °C or higher to remove adsorbed molecules [15].

**Configuration of the Electrodes**

As shown in Figure 3, field emission measurements were made in a simple diode configuration consisting of a stack comprised of a steel cathode base, the textured material at cathode potential, polyimide spacers, and a steel anode. The stack was held in place using an insulated clamp. The steel anode was 2.54 cm x 3.81 cm x 0.32 cm, and the steel cathode base was made longer (2.54 cm x 6.35 cm x 0.32 cm) for handling purposes. Ground steel was selected for the electrode material because it had a smooth surface finish of about 0.5 $\mu$m rms. The area of the textured cathode material, exposed through an aperture in the polyimide, was 1.23 cm$^2$. Two polyimide spacers, approximately 125 $\mu$m thick, were used to insulate the anode from the material at cathode potential. The steel electrodes were drilled and
tapped for terminating wires for the electrical circuit.

**Test Facility and Instrumentation**

Cathode tests were performed in a cryogenically-pumped bell jar system containing gate valves to two test ports. The cathode/anode assembly was mounted in a 0.3 m diameter test port attached to the bell jar. A 0.3 m pneumatic gate valve provided isolation of the bell jar and the primary test port during equipment changes. With the gate valve open, the primary test port/bell jar system pressure was usually less than 1x10^-6 Pa. Power to the diode arrangement was provided by a 5 kV, 25 W power supply. A current limiting resistor of 100 kΩ was also in the electrical circuit. Current monitoring was made using an electrometer capable of measuring to tens of picoamperes.

When an air leak was required, a gate valve was opened to the secondary test port which had a gas feed system for air and xenon. An air flow rate of about 1.2 sccm produced a background pressure of 3 x 10^-4 Pa.

**Results and Discussion**

**Electrical Characteristics**

Electron field emission capability of ion textured copper and textured platinum cathode materials were compared by displaying current density versus the voltage applied to the electrodes as shown in Figure 4. The structure of the texture of both of the cathodes was identical. The main differences involve much less out-gas time for the copper cathode, and also the copper cathode was tested at a pressure 43X higher than the platinum cathode. Copper has a lower work function (4.6 eV) than platinum (5.39 eV), so one might expect greater electron emission from the copper FEC. At the higher voltages, the platinum current densities were about the same as those produced by the copper cathode. It is speculated that the copper FEC current density was lower than expected because the work function was degraded due to a higher density of adsorbed gas species, different initial surface chemistry than the platinum FEC, or performance variations with test history. The current density of the textured platinum cathode at the beginning-of-life was about 156 µA/cm², at 8 V/gm, which would probably yield acceptable emission current capability when configured into a practical cathode for micro-thrusters. The main questions are performance repeatability and the integrity of the emission current level over time in environments of interest, and this will be examined in a later section.

Field emission is described as electrons tunneling through a potential barrier at the surface of a solid when a large electric field is applied. Knowing some of the surface properties, one can calculate the probability of an energetic electron tunneling through the potential barrier [12]. The electron field emission can be expressed by the Fowler-Nordheim (F-N) equation. For a given electrode separation and material work function, the following equation results for the current density,

\[ J = aV^2 \exp\left(\frac{-b}{V}\right) \]  

where \( V \) is the applied voltage and \( a, b \) are constants. In Figure 5, the textured platinum data are plotted in the Fowler-Nordheim (F-N) coordinates. Except for one set of data, the data closely satisfy the F-N equation implying field emission is the mechanism for electron emission. All data shown in the figure were taken at the lowest base pressure attainable in the vacuum facility (~ 1 x 10^-6 Pa). For a given applied voltage, the highest current levels were obtained by out-gassing the cathode for a period of 140 hours and operating the cathode at 1800 V for a period of 4 hours. As shown in the figure there is a rather large variation in emission current capability for a given cathode and electrode geometry. Variations in cathode surface chemistry and small uncertainties in setting the electrode gap may account for these variations in performance. When using the textured platinum surfaces as FECs, it is clear that out-gassing, burn-in, or thermal conditioning of the cathode is required in order to obtain the maximum current capability at the beginning-of-life.

**Field emitter performance repeatability and stability test results**

Initial cathode tests were conducted with very little conditioning after exposure to atmospheric pressure. Since the test facility had no capability for thermal conditioning of the cathode surface, the textured platinum cathode was simply left to out-gas at 1 x 10^-5 Pa for periods ranging from 17 hours to 168 hours in an attempt to remove some of the adsorbed gases from the surface. As shown in Figure 6 there are considerable variations in FEC current density at the
beginning of six tests and also after a one-hour period. Emission currents after one-hour burn-in testing ranged from 9 μA/cm² to 119 μA/cm² at an electric field of 8 V/μm. The wide range of cathode performance at the beginning-of-life is attributed to different cathode surface chemistry, different out-gas times, history of electric breakdowns, and small uncertainties related to setting the gap of the electrodes. For example, Equation 1 can be used with experimental input to calculate the effects of gap on emission current. If the gap is increased by about 10%, from 230 μm to 250 μm, the emission current is reduced to 60% of its original value. Thus, the uncertainty in setting the gap could easily account for variation of emission current at the start of the tests.

Referring to Figure 6, Tests 1 through 3 have the lowest out-gassing times (17 h to 25 h) while tests 4 through 6 have out-gassing times of 142 h to 168 h. Tests 1 and 2 show some short-term degradation of the current density while tests 3 and 4 indicate improved performance or possible conditioning over the first hour of operation. All FECs that had extended out-gassing exhibited superior performance compared to FECs with less than 25 hours of out-gassing. Obviously there was poor control over the chemistry of the FEC surface since capability to remove carbon forms and adsorbed oxygen and nitrogen did not exist in the experimental set-up.

Other investigators [11] remove carbon by titration with oxygen and thermally desorb gases by heating to 1300 K. Surface cleanliness was then verified by using electron spectroscopy. Testing was performed at about 1 x 10⁻⁶ Pa which is an order of magnitude lower than the best background pressures obtained during this investigation. Conditioning FECs to temperatures as high as 1300 K on power-limited spacecraft might be impractical. Further, propulsion subsystem qualification testing is usually performed in large facilities with base pressures of about 1 x 10⁻¹³ Pa. Field emitters for electrodynamic tether applications might have to operate at oxygen pressures as high as 1 x 10⁻⁴ Pa [2], so it is very important to successfully operate FECs at these high ambient pressures.

Figure 7 provides data after an extended out-gas period of 140 hours including 3 hours of burn-in testing. With an electric field of 8 V/μm, the emission current density rose from 87 μA/cm² to over 150 μA/cm² in about 100 minutes. For the next 2 hours the current density, for the most part fell within a dead-band from 140 μA/cm² to 190 μA/cm². The beginning-of-life current density of this FEC did not exhibit a degradation over the first few hours of operation with a facility pressure of 1.2 x 10⁻⁶ Pa and extended cathode conditioning.

The effect of air background pressure is shown in Figure 8. The first 266 minutes show the current density values at a background pressure of 1.2 x 10⁻⁶ Pa after which the pressure if raised by a factor of 260 to 3.2 x 10⁻⁴ Pa by admitting air into the vacuum chamber. The emission current degraded to 33% of its initial value after only one hour. Apparently, the adsorbed gases on the platinum FEC significantly degrade performance over a very short period as was the case with molybdenum Spindt cathodes and textured copper FECs [2,6,13]. After the test at high pressure, the FEC was out-gassed for 140 hours at 1.2 x 10⁻⁶ Pa and burned-in for more than 80 minutes, but the platinum FEC could not be reconditioned to reach a current density approaching 150 μA/cm². The conditioning process by out-gassing at room temperature is not very effective since on can not expect to desorb oxygen atoms until surface temperatures of ~ 700 K are reached [16]. At temperatures above 170 K a surface coverage of one oxygen atom per four surface platinum atoms was determined in experiments with adsorbed oxygen on Pt(111) surfaces.

After all testing was completed, an Energy-Dispersive X-ray Analysis was performed on the cathode surface to verify the surface was completely covered with platinum. Local measurements of the tips of the cones verified the surface was completely covered with platinum, and there was no signature indicating the copper substrate was exposed.

Although a reproducible cathode conditioning process did not evolve from this work, some short term tests for periods of 1 to 4 hours showed no degradation of emission current at an electric field of 8 V/μm and background pressures of about 1 x 10⁻⁶ Pa. Increases of background pressure by air flow to about 3 x 10⁻⁴ Pa yield a hostile environment for the textured platinum FEC.

Concluding Remarks

A textured platinum surface was used in this work for the assessment of field emission cathodes that might find application for electric
microthrusters and electrodynamic tethers. Such cathodes must successfully operate at environmental pressures possibly as high as $1 \times 10^4$ Pa. High partial pressures of oxygen, nitrogen, and water vapor are expected in such environments. The platinum FEC was ion beam textured and then coated with platinum. The resulting texture was comprised of cones with base and height dimensions in the 30 $\mu$m to 100 $\mu$m range. The voltage-current data generally satisfy the Fowler-Nordheim equation thus confirming the electron emission mechanism is field emission. Emission currents after one-hour burn-in testing ranged from 9 $\mu$A/cm$^2$ to 119 $\mu$A/cm$^2$ at an electric field of 8 V/$\mu$m. The wide range in performance at the cathode’s beginning-of-life is attributed to different cathode surface chemistry, different out-gas times, and small uncertainties related to setting the gap of the electrodes. Although a reproducible cathode conditioning process did not evolve from this work, some short term tests for periods of 1 to 4 hours showed no degradation of emission current at an electric field of 8 V/$\mu$m and background pressures of about $1 \times 10^6$ Pa. Increases of background pressure by air flow to about $3 \times 10^4$ Pa yield a hostile environment for the textured platinum field emission cathode.

References


Table 1 – Decay of field emission current at relatively high environmental pressures

<table>
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<tr>
<th>Emitter type</th>
<th>Initial current density, mA/cm²</th>
<th>Electric field, V/µm</th>
<th>Initial pressure, Pa</th>
<th>Gas bleed</th>
<th>Final pressure, Pa</th>
<th>Fraction of initial current after 17 minutes</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>Spindt cathode, Mo</td>
<td>~ 8</td>
<td>--</td>
<td>3 x 10⁻⁴</td>
<td>O₂</td>
<td>1 x 10⁻⁴</td>
<td>0.1</td>
<td>6</td>
</tr>
<tr>
<td>Spindt cathode, ZrC coated Mo</td>
<td>20</td>
<td>--</td>
<td>5 x 10⁻⁷</td>
<td>O₂</td>
<td>1 x 10⁻⁴</td>
<td>0.3</td>
<td>2</td>
</tr>
<tr>
<td>Carbon nanotube</td>
<td>2600</td>
<td>16.7</td>
<td>3 x 10⁻⁵</td>
<td>--</td>
<td>3 x 10⁻⁵</td>
<td>0.15</td>
<td>7</td>
</tr>
<tr>
<td>Carbon nanotube</td>
<td>0.4</td>
<td>3</td>
<td>~ 1 x 10⁻⁵</td>
<td>--</td>
<td>~ 1 x 10⁻⁵</td>
<td>~ 0.98</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 1 – Illustration of texturing of the copper target surface using “tantalum seed texturing.” The seed target is tantalum, and the sputter target is copper.
Figure 2 – Surface structure of the ion beam textured copper coated with platinum.

Figure 3 – Schematic of the test setup (not to scale).
Figure 4 – Emission current density of ion beam textured surfaces. Electrode gap: 250 μm.

Figure 5 – Platinum coated, textured copper field emission data in Fowler-Nordheim coordinates. Background pressure: ~ 1 x 10^-6 Pa. Electrode gap: 250 μm.
Figure 6 – Emission current variations from test to test. Applied voltage: 1800 V. Electrode gap: 250 μm. Background pressure ~ 1.2 x 10^6 Pa.

Figure 7 – Variation of emission current density with time at low pressure. Applied voltage: 1800 V. Electrode gap: 250 μm. Out-gassed for 140 h. Background pressure ~ 1.2 x 10^6 Pa.
Figure 8 – Stability of emission current at different environmental pressures. Applied voltage: 1800 V. Electrode gap: 250 μm.
**Electron Field Emission Properties of Textured Platinum Surfaces**

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