Cesium Neutral and Ion Emission from Carburized and Oxygenated Porous Tungsten

A. Y. Cho* and H. Shelton†
TRW Space Technology Laboratoreis, Redondo Beach, Calif.

Experimental data on the temperature dependence of the ion, electron, and neutral emitting properties of clean, carbided, and oxygenated porous tungsten indicate that 1) W_2C has a higher work function (~4.85 v) than does clean tungsten, it adsorbs cesium less tightly at ion operating temperature than does clean tungsten, and therefore it emits fewer neutral cesium atoms and possesses a lower critical temperature than does clean tungsten; 2) oxygenated tungsten has a higher work function (~5.0 v) than does clean tungsten, it adsorbs cesium more tightly than does clean tungsten, and therefore it emits fewer neutrals and possesses a higher critical temperature than does clean tungsten. The clean tungsten is produced by exposure to oxygen to remove carbon, long-time high-temperature cesium ion operation, and sputtering in high vacuum free of oxygen and hydrocarbons. The carbided surface is produced by cracking hydrocarbon vapors (C_2H_2, CH_4, C_2H_4, etc.) and stabilizing by high-temperature operation. X rays show the surface to be W_2C, and an increase in thermal emissivity is noted. Oxygenated tungsten is produced by exposing to oxygen partial pressures of from 1×10^{-8} to 1×10^{-5} torr. The experimentally observed effects of other impurities (calcium, silicon, and boron) are also discussed.

Introduction

In the use of hot porous tungsten to produce cesium ions for electrical propulsion, the degree of tungsten purity is of extreme importance. Materials affect the tungsten performance mainly altering the work-function, the cesium binding energy, and the emissivity. The materials that raise the work-function lower the ratio of neutral emission to ion emission. Materials that lower the work function increase the neutral emission, often above the ion emission. If the binding energy is increased, the critical temperature necessary to evaporate a given current density of ions will increase. If the binding energy is decreased, the critical temperature will be lower.

Tungsten can be brought to a very high degree of purity simply by raising its temperature, causing foreign materials to diffuse to the surface and evaporate. In the case of practical ion emitters, however, the practical difficulties of heating large areas, the temperature limitations imposed by the brazes, and deleterious effects of further sintering interfere with the use of this method. The experimenter may, therefore, often be working with other than clean tungsten.

This paper describes experiments on porous tungsten emitters in which special measures were taken to control surface conditions. Ultrahigh vacuum was maintained, emitters were designed to allow prolonged heating to 2000°K, capability for surface sputtering was provided, and controlled amounts of impurities could be introduced.

Results are presented showing that oxygen decreases neutrals but increases critical temperature. Carbon decreases neutrals and decreases the critical temperature, but raises emissivity. Calcium increases neutrals and increases critical temperature. These observations result from careful repeated study of each of these materials deposited on tungsten that had first been cleaned by high-temperature operation in high vacuum followed by sputtering.

Experimental Procedures

The measurements were made on 1-in.-diam porous tungsten disks manufactured by Semicon of California. The ions are focused and accelerated by two fine grids of tungsten wires. These grids can be heated to 2600°K so as to keep the surface clean. Electron currents from the accelerating grid to the source during ion emission and from the focusing grid during electron emission are thus eliminated. When maintained hot and at a positive potential, the grids also can be used to sputter the tungsten source, since a fraction of the cesium from the source will be intercepted, surface-ionized, and accelerated back to the source.

A hot-ribbon neutral sensor off to one side of the ion beam "sees" the surface of the porous tungsten through the fine set of grid wires. Although the neutral detector measures propellant utilization as modified by the accelerating structure rather than the desired true neutral fraction, in this case, because of the small amount of neutral scattering by the fine grids, the two are essentially the same.

The vacuum obtained by a Welch "turbomolecular" pump is oxygen-free and hydrocarbon-free, as monitored by a mass spectrometer mounted in the system. A large copper surface at liquid nitrogen temperature surrounds the ion source, cools the neutral detector, and condenses cesium and water vapor. The total pressure when operating is a few times 10^{-8} torr and is mostly untrapped cesium.

A clean tungsten surface is obtained by first heating in oxygen to remove carbon, operating for hours at a relatively high (5–10 ma/cm^2) cesium ion current density at 2000°K, and then sputtering. Such a surface can then operate clean for many minutes. During this time a leak of oxygen producing a pressure of 1×10^{-8} torr will detectably alter the surface condition. Because the measurements were made on thoroughly cleaned porous tungsten at relatively low ion current density where the pore distribution has little effect, these data are believed to be valid for all clean porous tungsten regardless of manufacturer.

The carbided surface is produced by cracking hydrocarbon vapors (C_2H_2, CH_4, C_2F_4, etc.) and stabilizing by high-temperature operation. The short exposure time (minutes) and the low pressure (a few times 10^{-6} torr) results in a very thin

---

Presented as Preprint 64-11 at the AIAA Aerospace Sciences Meeting, New York, January 20–22, 1964; revision received August 6, 1964. This work was supported by Contract No. NAS3-2524 through the NASA Lewis Research Center.

* Member of Technical Staff. Associate Member AIAA.

† Member of Technical Staff. Member of AIAA.

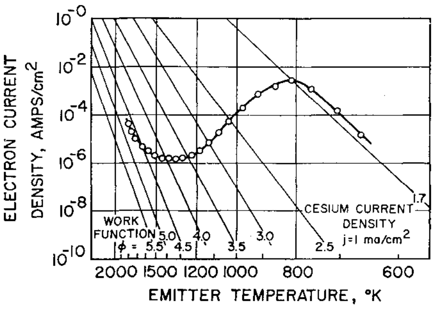

Fig. 1 Electron emission *S*-shaped curve for clean porous tungsten ionizer.

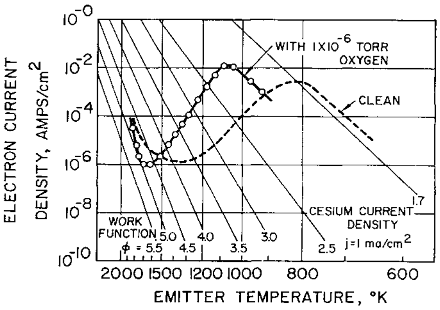

Fig. 3 Electron emission *S*-shaped curve for oxygenated porous tungsten ionizer.

coating of W_2C a few microns thick. It has been identified by x rays. This surface can be cleaned up by long (at high T) exposure to oxygen. It is noteworthy that oxygen at any pressure up to 10^{-5} torr or more has no effect on the electronic properties of this surface for considerable periods of exposure. This effect and the cleanup of carbon is attributed to the rapid formation and evaporation of CO.

The qualitative features of an oxygenated surface have been gathered over a long period of time on many different samples of porous tungsten. The quantitative effect depends on the degree of oxygenation, cesium ion current density, trace impurities, and the past history of the surface. The carbided surface, on the other hand, exhibits the same quantitative characteristics time and time again on different sources carbided in different manners. This surface is also much less sensitive to traces of poisoning contaminants. The truly clean tungsten surface is harder to achieve and maintain; after the tungsten is essentially clean, the remnant surface contaminants such as oxygen can be sputtered off.

Experimental Results

Clean Tungsten

In Fig. 1 is plotted the electron current density from clean porous tungsten fed with cesium. The feed rate was such as to produce 1 ma/cm^2 ion current density if the voltages were reversed. Plotted lightly in the background are constant work-function lines based on the Richardson equation $j = 120\, T^2 \exp(-e\Phi/kT)$ amp/cm^2. When the experimental points lie parallel to these lines, the surface is maintaining a constant work-function. The value of the work-function of any point can be interpolated from its position on the experimental curve relative to the lines of constant Φ. We can see in this instance that, at high temperature, cesium coverage is essentially zero, and we find the work-function of this clean porous tungsten to be 4.7 v. At lower temperatures, the cesium sticks; this lowers the work-function, and causes the electron emission to increase. The temperature at which the electron current crosses the 3.7 v line (1300°K in Fig. 1) is approximately the critical temperature for ion emission.

Under different surface conditions, the *S*-shaped curve may depart from the constant work-function line at higher temperatures, the minimum electron emission may occur at a higher temperature, and the rising portion of the curve on the low-temperature side of the minimum may have a greater slope. The critical temperature then will be higher. The portion of the curve to the right of the critical temperature relates to the adherence of large cesium coverages and has no bearing on ion production.

In Fig. 2 we see the percentage fraction of neutral cesium emitted from the same surface during ion operation at high voltages. At the right, the temperature is below critical, and the neutrals are nearly 100%. The critical temperature is indeed 1300°K. Constant work-function lines are shown, based on the Saha-Langmuir equation, which predicts that the fraction of the total cesium emitted as neutrals will be

$$\alpha = (1 + \tfrac{1}{2} \exp e(\Phi - V_i)/kT)^{-1}$$

where the cesium ionization potential V_i is 3.9 v. (A report[1] by Teem and co-workers shows that, when a patchy surface is involved, it is the electron work-function as we measure it with $A = 120$ which should be used in this equation to predict neutrals.) At high temperatures the cesium coverage is very low, and the work-function is that of clean tungsten. The resulting neutral fraction and its temperature dependence agree reasonably well with the work-function found from the *S* curve.

Oxygenated Tungsten

Figure 3 shows the *S*-shaped curve for oxygenated tungsten. The dotted curve for clean tungsten is included for comparison. For the higher temperatures to the left, we see a high work-function decreasing toward the value for clean tungsten. The abrupt steep rise as the temperature is decreased indicates that the cesium has a high binding energy and that a high critical temperature will result. Although oxygenated tungsten in vacuum results in a larger low-temperature maximum,[2] the continuous maintenance of an oxygen pressure pressure in this case suppresses the electron emission at low temperature. In Fig. 4 we see that the critical temperature is increased and that the neutrals are lower, relative to clean tungsten. The broad flat minimum region indicates the adherence of a sizable cesium coverage to quite high temperatures, again indicating a high binding energy.

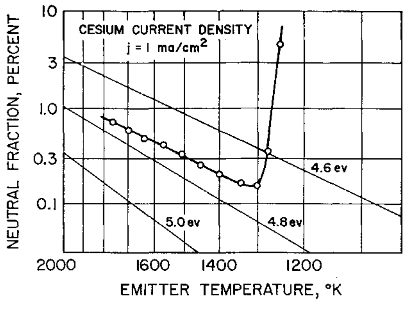

Fig. 2 Cessium neutral fraction vs temperature for clean porous tungsten ionizer.

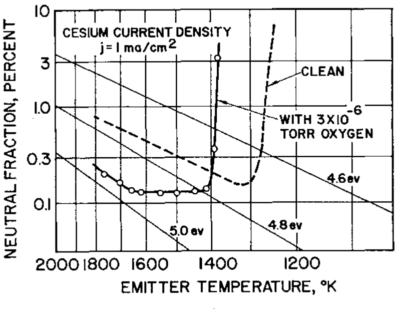

Fig 4 Cesium neutral fraction vs temperature for oxygenated porous tungsten ionizer.

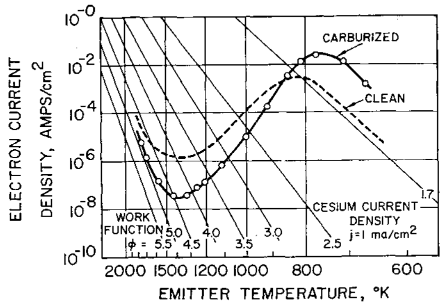

Fig. 5 Electron emission *S*-shaped curve for caburized porous tungsten ionizer.

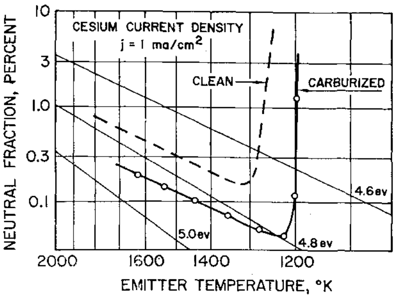

Fig. 6 Cesium neutral fraction vs temperature for carburized porous tungsten ionizer.

Carburized Tungsten

In Fig. 5 the *S*-shaped curve for carbided tungsten is shown. The work-function is about 4.85 v. Also as evidenced by the low valley, the binding energy is lowered, predicting a lower critical temperature (1210°K). It is of interest to note that the binding energy for large cesium coverages is increased, giving a larger low-temperature peak emission. This characteristic is in close analogy to the effect of W_2C on electron emission from barium-impregnated porous tungsten. At high temperatures, W_2C is used to suppress electron emission by allowing the barium to evaporate. At low temperatures, electron emission is enhanced from W_2C areas.[3]

Figure 6 shows the neutral fraction vs temperature for carbided tungsten. We see that the critical temperature is lower, that the neutrals are lower, and that the strong temperature dependence as governed by the Saha-Langmuir equation is evidenced.

The improved ion emitter properties of carbided tungsten are offset by its higher thermal emissivity, which is approximately 0.4. Also a continuous high rate of carbon deposition will eventually form the nonequilibrium WC phase on the surface which has a lower work function[4] and will degrade the ion emitting properties.

Calcium, Flourine, and Other Contaminants

Calcium was studied and found to be a bad poison; it appeared both to lower the work-function, thereby producing high neutral emission, and to hold the cesium tightly, producing a high critical temperature. High-temperature operation was necessary in order to lower the calcium concentration on the surface by evaporation. A high pseudocritical temperature existed where the diffusion rate to the surface matched the evaporation. This temperature was often above 1700°K.

Fluorine acts like oxygen. It raises the critical temperature and lowers the neutrals. Silicon and boron were found to have little effect on ion and neutral emission, although they raised the tungsten work-function slightly.

The presented data have all been at the relatively low current density of 1 ma/cm² in order to illustrate graphically the basic effect of work-function and binding energy. The increase of neutrals with current density because of insufficiently fine pore distribution is barely seen here. As pointed out by the work of Hussman,[5] the neutrals increase at higher ion current densities, badly so with a coarse-grain porous tungsten and less so with a fine-grain porous tungsten. Also, the critical temperature is less well defined at high ion current densities with a large range of temperatures where an increase in temperature decreases the neutrals. High current densities up to 16 ma/cm² on many different porous tungsten samples have been studied by the authors, and the different characteristics of high-current-density ion emission and the data presented here are not contradictory and are due to the pore distribution.

Conclusion

An oxygenated tungsten surface is identifiable from its *S*-shaped curve by its high bare work-function and high cesium coverage at ion operating temperatures and from its ion emission by the high critical temperature and the small constant percentage value of neutrals at higher temperatures. A carbided surface is identifiable from its *S*-shaped curve by its stable 4.85 v work-function insensitive to oxygen and the deep minimum, and from its ion emission by the low critical temperature and the rapid rise of neutrals at higher temperatures. Clean tungsten is identifiable by its known work-function and its extreme sensitivity to small amounts of oxygen.

References

[1] Teem, J. M. and Taylor, L. H., "Ionizer development and surface physics studies," Electro-Optical Systems Rept. 1660/1-IR-1, p. 16 (December 1962).

[2] Langmuir, I. and Kingdon, K. H., "Thermionic effects caused by vapours of alkali metals," Proc. Roy. Soc. London **A107,** 75 (1925).

[3] Levi, R., private communication (1963); also Levi, R. and Rittner, E. S., "Role of carburization in the suppression of emission from barium-activated tungsten and molybdenum surfaces," J. Appl. Phys. **33,** 2336 (1962).

[4] Baker, J. B. and Gaines, G. B., "Evaluation of electron emission behavior for detecting carbon in tungsten and rhenium," Battelle Memorial Institute Rept. BMI-1649 (September 1963).

[5] Hussman, O., "A comparison of the contact ionization of cesium on tungsten with that of molybdenum, tantalum, and rhenium surfaces," AIAA J. **1,** 2607 (1963).