NOTICE

The invention disclosed in this document resulted from research in aeronautical and space activities performed under programs of the National Aeronautics and Space Administration. The invention is owned by NASA and is therefore available for licensing in accordance with the NASA Patent Licensing Regulation (14 Code of Federal Regulations 1245.200).

To encourage commercial utilization of NASA-owned inventions, it is NASA policy to grant nonexclusive, royalty-free, revocable licenses to any company or individual desiring to use the invention while the patent application is pending in the U.S. Patent Office and within a specified period, presently two years, after issuance of the patent to NASA. If commercial use of the invention does not occur during this period, NASA may grant a limited exclusive, royalty-free license thereby adding an incentive to further encourage commercial development. Any company desiring to make, use, or sell this invention is encouraged to obtain a royalty-free license from NASA.

Address inquiries and all requests for licenses to Assistant General Counsel for Patent Matters, Code GP-1, National Aeronautics and Space Administration, Washington DC 20546.

Application S/N 9251
Filed: 10/21/69
Contractor: Caltech/JPL
Contract NAS7-100

AWARDS ABSTRACT

Inventor: Scott S. Luebbers
John G. DeSteese
Contractor: Jet Propulsion Laboratory

~~JPL IR No. 30-11138~~
NASA Case ~~No~~. NPO-11138
October 1, 1969

THERMIONIC TANTALUM EMITTER DOPED WITH OXYGEN

An object of the invention is to improve the thermionic emission characteristics of tantalum thermionic emitters. Emission is enhanced by doping tantalum with at least 0.1 atomic percent oxygen.

Referring now to Figure 1, a planar-type thermionic converter includes an oxygen-doped tantalum emitter electrode 10 spaced an interelectrode gap "d" from a collector electrode 12. The ends of the electrode 10 are connected to a thin sleeve 16 which terminates in a flange 18. The collector electrode 12 is supported on a body of metal forming a heat sink 14, the heat sink having a shoulder portion 22 at its upper extremity. The electrodes 10, 12 are electrically insulated from each other and a hermetically sealed envelope is formed by means of an insulator 20 brazed to the flange 18 and shoulder 22. Electrical output connections 40 and 42 are provided on the heat sink 14 and the flange 18, respectively. A plurality of radial passages 24 extend through the collector electrode 12 and communicate with the envelope space 26. An axial tube 28 extends through the heat sink body 14 and through the center of the collector electrode 12 into the juncture of the radial passages 24. A cesium containing reservoir 30 is connected to the outer end of the tube 28. A portion of the tube immediately above the reservoir 30 is surrounded with a heating coil 32 connected to a temperature controller and power source 34. On activation of the controller 34 the reservoir 30 is heated and the cesium liquid vaporizes and fills the envelope space 26. The cesium vapor within the gap serves to modify the work-function of the electrodes 10, 12. The cesium vapor, when ionized, reduces the negative space charge within the interelectrode gap. The emitter electrode 10 is heated by a thermal source, not shown, to thermionic emission temperatures. The temperature difference between the emitter electrode 10 and the cooler collector electrode 12 provides a contact potential between the electrodes 10, 12. An output of about 15 to 25 watts cm^{-2} add an efficiency of about 10% is obtained through the connection 40, 42.

Figure 3 indicates that for a cesiated thermionic emitter operating at a temperature ratio T_p/T_{Cs} of about 3.0, the work-function of the oxygen-doped electrode is 0.54 eV lower than the theoretical value for pure tantalum (Φ_0-4.1 eV). At thermionic temperatures an emission enhancement much greater than an order of magnitude is realized. The enhanced effect is believed attributable to the presence of bulk absorbed oxygen in the emitter material which acts as an emission enhancing additive when the additive diffuses to the surface of the electrode and co-absorbs with cesium.

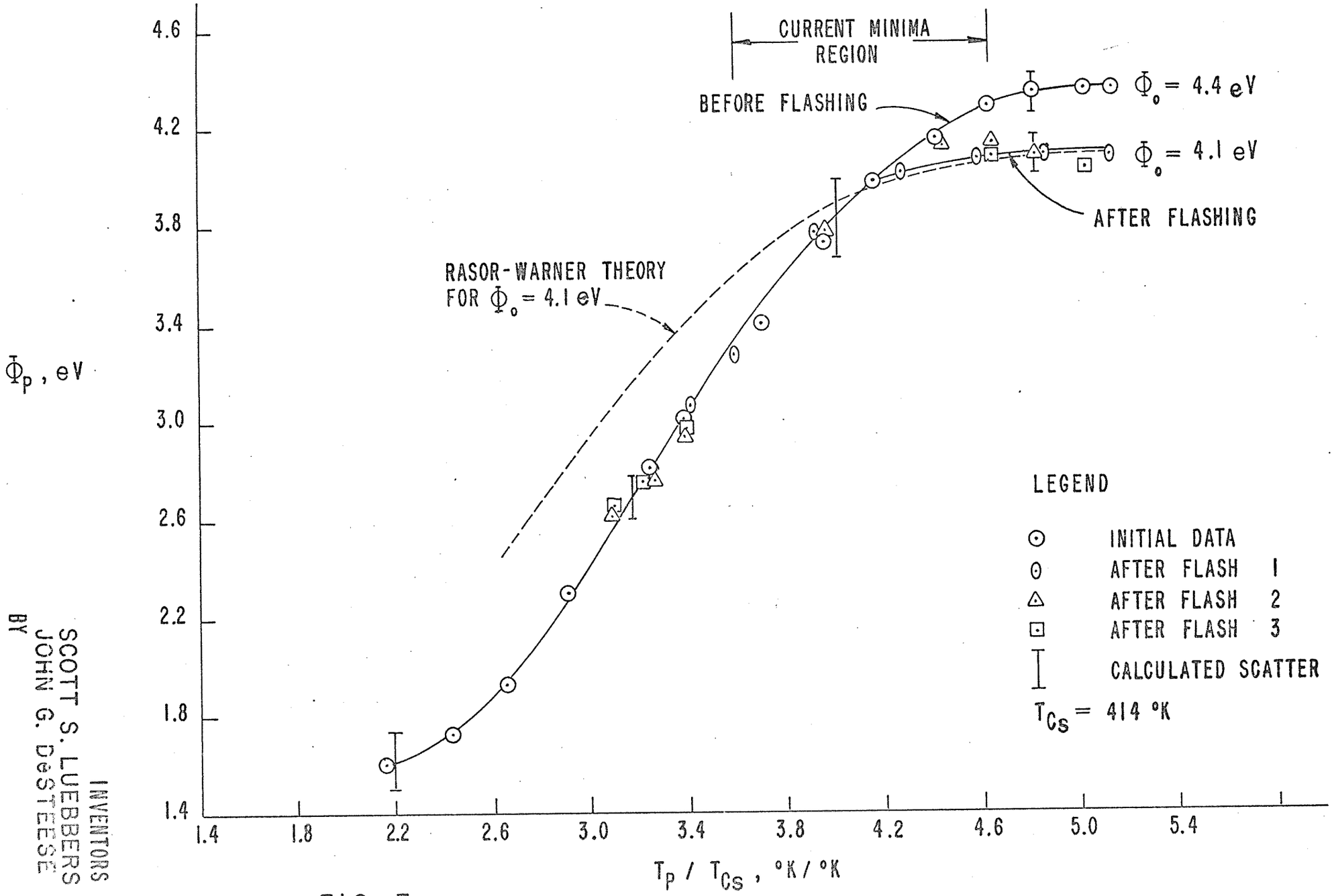


FIG. 3

INVENTORS
SCOTT S. LUEBBERS
JOHN G. DeSTEESE
BY

ATTORNEYS

NASA CASE NPO-11138

~~69/388~~
~~JPL IP No. 30-11138~~
~~Case No. 1832~~

Application S/N 9251
Filed: 10/21/69
Contractor: Caltech/JPL
Contract NAS7-100

S P E C I F I C A T I O N

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT SCOTT S. LUEBBERS and JOHN G. DeSTEESE each a citizen of the United States of America, residing respectively at Tujunga, in the County of Los Angeles, State of California and Richland in the County of Benton, State of Washington, have invented a new and useful

THERMIONIC TANTALUM EMITTER DOPED WITH OXYGEN

of which the following is a specification:

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

1. Field of the Invention:

The present invention relates to a thermionic emitter and, more particularly, this invention relates to a novel thermionic emitting material useful in vapor-type thermionic devices.

2. Description of the Prior Art:

A continuing effort is in progress to develop efficient and practical thermionic devices for use in direct conversion of heat to electricity. In vapor-type thermionic devices, a metallic vapor, suitably the Group I metal, cesium, is employed within the device. The cesium vapor is believed to form an adsorbed alkali metal film on the exposed surfaces of the electrodes which results in a reduction of the work function of the emitter and collector electrodes, depending on the surface temperature and cesium reservoir temperature. The positive cesium ions existing within the interelectrode region tend

to neutralize the space charge effects of the electrons in the space. Rhenium has been most prominently utilized for emitter construction in cesium vapor-type thermionic power converters. However, rhenium is a fairly scarce and costly material. Tantalum is not currently being used in such devices since the current expected from pure tantalum emitters is below the level considered practical, and certain undesirable chemical reactions are more likely to occur.

OBJECTS AND SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide an improved thermionic emitting material.

A further object of the present invention is to provide enhanced emission properties from thermionic tantalum emitters.

Another object of the invention is to increase by an order of magnitude the level of current obtainable from tantalum thermionic emitters.

Yet another object of this invention is the provision of a solid state reservoir of emission enhancing additive within an emitter material.

These and other objects and many attendant

advantages of the invention will become apparent as the description proceeds.

The improved thermionic emitting material, in accordance with the invention comprises a body of tantalum doped with oxygen. The doping level is at least 0.1 atomic percent of oxygen to obtain the desired enhanced emission effect. Thermionic devices, according to the invention, include the novel emitter electrode spaced a selected distance from a collector electrode. The electrodes are hermetically sealed within an envelope provided with a supply of ionizable vapor such as cesium.

The invention will now become better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a front view in section of a planar configuration of a thermionic converter as a representative device including the novel oxygen containing tantalum electrode according to the invention.

Figure 2 is a schematic view of an apparatus for determining the work function of the novel oxygen containing tantalum electrodes according to the invention; and

Figure 3 is a graph of the work function of the electrodes versus the ratio of the metal surface temperature, T_p, to the liquid cesium reservoir temperature, T_{Cs}.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now to Figure 1, a planar thermionic converter contains an emitter electrode 10 formed of oxygen-doped tantalum according to the invention. The emitter electrode 10 is spaced an interelectrode gap D from a collector electrode 12. The collector electrode 12 is supported on a body of metal 14 forming a heat sink for rejecting excess heat so that the device operates at its most effective temperature for thermionic energy conversion.

The ends of the planar emitter electrode 10 are connected to a thin sleeve 16 which terminates in a flange 18. The electrodes 10 and 12 are electrically insulated from each other and a hermetically sealed envelope is formed by means of an insulator 20 suitably formed of a high temperature refractory such as alumina joining the flange 18 to a shoulder 22 provided on the heat sink body 14. The insulator 20 may be joined to the shoulder 22 and flange 28 by known brazing techniques. Output is obtained by means of an electrical connection 40 to the collector

heat sink 14 and to the emitter electrode 10 through a connection to the flange 18.

A plurality of radial passages 24, extend through the collector electrode 12 and communicate with the envelope space 26. An axial tube 28 extends through the heat sink body 14 and through the center of the collector electrode 12 into the juncture of the radial passages 24. A cesium containing reservoir 30 is connected to the outer end of the tube 28. A portion of the tube immediately above the reservoir is surrounded with a heating coil 32 suitably in the form of a sheath heater and the ends of the heating coil 32 are connected to a temperature controller and power source 34.

In a typical converter, the oxygen-containing planar emitter electrode 10 is spaced an interelectrode distance, d, of from about 2 to 10 mils from a lower work function collector electrode, suitably formed of molybdenum or tantalum. During operation, the cesium is independently heated by setting controller 34 to heat the coil heater 32 to a temperature of about 475°K to 675°K, suitably 575°K. The cesium liquid within reservoir 30 vaporizes and fills the envelope space 26. The cesium vapor within the gap serves to modify the work function of the electrodes 10, 12. The cesium vapor, when ionized, reduces the negative space charge within the inter-

electrode gap.

The emitter electrode 10 is heated by a thermal source, not shown, such as solar energy or nuclear fuel elements to thermionic emission temperatures of about 1270°K to 2100°K, suitably about 2000°K. The collector electrode 12 is maintained at a lower temperature of about 675°K to 1100°K by means of the radiator heat sink body 14. The temperature difference provides a contact potential between the electrodes 10, 12. An output of about 15 to 25 watts cm^{-2} at an efficiency of about 10 percent is obtained through the current leads 40 and 42 which are in electrical contact with the electrodes 10, 12. The vapor may be a Group I or Group II metal, preferably the Group I metals, cesium, rubidium or potassium. Cesium is preferred since it is the most readily ionizable Group I metal.

The interelectrode spacing may be increased to much larger values of the order of 2 to 50 mils for other configurations and uses such as the cupped emitter geometry having electron emission from the side walls of the emitter disclosed in SPS 37-44, Vol. IV, pp 59-66. Devices including the cupped emitter geometry are utilizable in applications disclosed in commonly assigned copending application Serial Number 728,234, filed May 10, 1968, for "Thermionic Diode Switch". The oxygen-doped

tantalum emitter electrode according to the invention will also find use in thyratron tubes.

The saturation emission characteristics of the oxygen-doped tantalum thermionic emitter were measured using the plasma-anode technique. A plasma immersion probe tube and associated circuitry as shown in Figure 2 were constructed. The experimental tube consists of an electrically heated tungsten filament 52 and a large anode disc 54 located at opposite ends of a cylindrical pyrex glass envelope tube 56. The tube 56 is filled with liquid cesium which, when heated in a thermostatically controlled oven 58 establishes an equilibrium vapor pressure of cesium in the tube.

The cesium vapor is ionized to produce a glow discharge by an applied potential between the filament 52 and anode 54 supplied by a constant current power supply 60. The filamentary cathode 52 is independently heated from heater power supply 62. The filament electrode was operated at 2000°K and the discharge current adjusted between 0.2 and 2.5 amperes.

Test probes 64 were inserted into the discharge from a side port and were heated by a halfwave rectified current heater supply 66. The probe bias potential was swept automatically with a motor driven power supply 68 and data was collected

in the current-voltage sampler 70 during the heating off-cycle to eliminate any problem associated with probe-voltage offset caused by the heating current.

The cesium vapor and accompanying discharge modify the probe work function and neutralizes space charge effects which results from electron emission from the hot test probe. The probe is sized to ensure that the emission current is only a small perturbation on the total discharge current of the tube. The thermionic electrons from the test probe are emitted into the plasma column of the discharge, which acts as the collecting anode. From the measured volt-ampere curves, the electron-saturated emission from the probe is established and related to the surface work function via the Richardson equation.

Prior to any emission measurements, a probe temperature versus heating-current calibration was made over the visible range of a pryrometer and then extrapolated to the low temperature region by resistance measurements. During actual emission measurements, probe temperature was determined by measuring the heating currents since cesium discharge and filament radiation within the tube would enter into any pyrometric temperature measurement. Saturation currents were determined from the intersection of the straight-line extensions of the saturation and Boltzman curves.

Saturation ion current collected by the probe was interpreted in a similar manner with the probe cold. The net difference between these saturation currents was taken as the saturated electron current from the probe. The probe area was taken as the simple arithmetical estimation based on nominal diameter and exposed length of the probe. The cesium-reservoir temperature was measured by a separate thermocouple attached to the pinch off region of the tube envelope. The entire tube was placed in a thermostatically controlled oven 58.

The work function of an uncontaminated metal in a cesium environment has been shown, both theoretically and experimentally, to be a unique function of the ratio of the metal surface temperature T_P to the liquid cesium reservoir temperature T_{Cs} for given metal having an uncesiated work function of Φ_0. The theoretical cesiated work function for a material such as pure tantalum with Φ=4.1 eV is shown as a dashed line in Figure 3. A plot of this type provides a convenient means to display the electron emission data from the probe formed of the oxygen-doped tantalum material according to the invention.

Prior to any emission measurements, the probes were outgased at 2100°K for periods up to 2.5 hours and flashed at 2270°K for 2 minutes. The plasma-immersion probe tube was baked and evacuated

to 10^{-8} torr and was subsequently charged with cesium.

Referring now to Figure 3, the results of the emission measurements at high temperature ratios indicate that the bare emitter work function of the probes is approximately 4.4 eV. The experimental data is not correlatable with a theoretical work function behavior of an uncontaminated material having a work function, Φ_0 of 4.4 eV. This non ideal behavior indicates the surface structure is not simply cesium adsorbed on tantalum.

Repeated flashing of the probe to temperatures as high as 2470°K results in a shift of the low, cesium-coverage region (high T_P/T_{Cs}) of the curve to that predicted for a surface with a bare work function, Φ_0, near 4.1 eV, while in the higher cesium-coverage region (low T_P/T_{Cs}) the affect of flashing was negligible. This shift occurred immediately after the first high temperature flash of 2470°K and further flashing caused no measurable change. The effect of the high temperature flashing was believed to reduce the original concentration of oxygen within the tantalum probe to a value at which the rate of diffusion through the lattice was insufficient to replenish oxygen desorbed from the high temperature surface. Therefore, the anticipated work function behavior for clean tantalum resulted.

The importance of the change in work function demonstrated for the oxygen-doped tantalum emitters, according to the invention, is evident for a cesiated thermionic emitter operating at a temperature ratio T_P/T_{Cs} of about 3.0 which is a typical ratio for thermionic power converters. The experimental curves indicate the work function is 0.54 eV lower than the theoretical value for pure tantalum (Φ_0 = 4.1 eV). At thermionic temperatures an emission enhancement much greater than an order of magnitude is realized. The enhanced effect is believed attributable to the presence of bulk absorbed oxygen in the emitter material which acts as an emission enhancing additive when the additive diffuses to the surface of the electrode and coabsorbs with cesium.

A quadruple residual gas analyzer was utilized to determine the presence of oxygen compounds evolving from the test probe. Before the probe was heated, a mass scan was performed to obtain the background amplitudes of the various elements present in this system. The probe was then heated to 2080°K and the scan was repeated. The increased signal amplitudes of corresponding elements were normalized by dividing by the background signal height. In practically all cases the heights of the observed signal peaks for mass numbers containing oxygen increased when the probe was brought to temperature.

X-ray diffraction shows the presence of tantalum suboxides (TaO and TaO_2) within the bulk lattice. These oxides were identified by the presence of a super-lattice structure in the diffraction pattern. The neutron activation studies indicated an absorbed oxygen content of 0.14 atomic percent in the probes, as received, which remained as high as 0.12 atomic percent even after the samples have been vigorously outgased at 2725°K.

The enhanced emission effect is thus provided at atomic percentages of oxygen above about 0.1 percent. Oxygen may be dissolved in tantalum up to several atomic percent. However, it is preferable to maintain the partial pressure of oxygen within the emitter envelope below about 10^{-6} torr to reduce erosion and corrosion effects from oxygen experienced at the operating temperature of the devices.

The enhanced emission effect is not of plasma or tube-wall origin. A tube-originated additive effect would return after the probe was cooled and allowed to reabsorb additive gases. However, the observed reduction in work function to that of clean tantalum remained even though the probe was cooled and reheated a number of times.

The comparison between the measured probe behavior and the theoretical behavior indicates a difference as large as 0.55 eV which is far greater than the effect which can be attributive to cumulative errors in measurement. The absence of significant hysteresis as observed in the emission characteristics further indicates the additive effect is not caused by residual gas in the plasma tube.

The presence of oxygen and the mechanism of its action in enhancing thermionic emission was further investigated. The test probes were sputtered with 50-volt cesium ions for 2 minutes at a probe temperature near 1000°K. The work function behavior that resulted, was typical of a clean tantalum surface with a bare work function near 4.1 eV and indicates the low voltage sputtering was effective in removing the additive oxygen from the surface of the probe. The level of oxygen-doping had been established by residual-gas analysis, X-ray diffraction and neutron-activation analysis, as was previously described.

The oxygen-doped tantalum emitter, according to the invention, has a saturation-emission characteristic similar to that of rhenium in the region of work function having practical importance in a cesium-filled thermionic converter. The persistence of oxygen in the tantalum lattice after severe outgasing indicates that the tantalum-oxygen solid

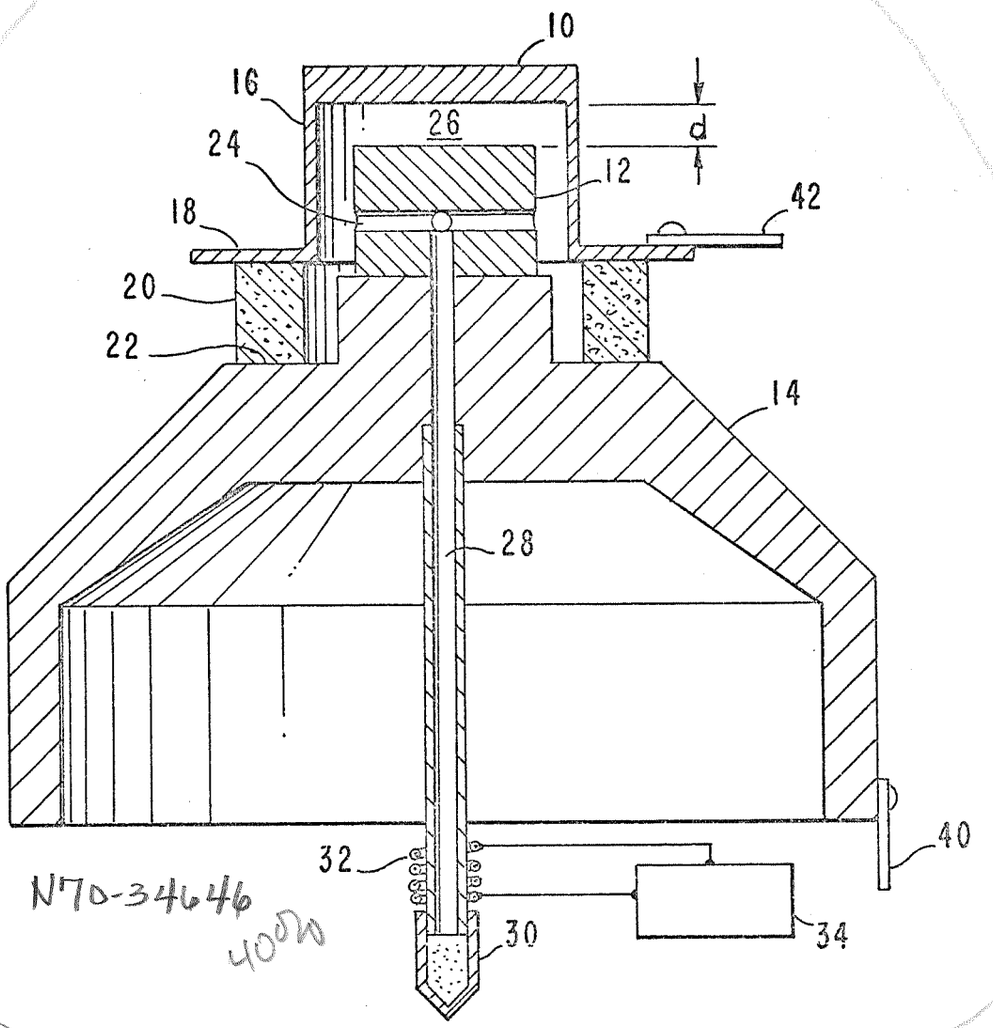
solution may be reliable means for storing and dispensing a surface-active additive from the bulk of the electrode. The coincidence of the anomalous tantalum work-function behavior with the rhenium curve suggests that at low values of T_P/T_{Cs} the oxygen-doped tantalum would also serve as a suitable collector allowing both the emitter and collector fabrication from the same material.

Oxygen can be introduced into the tantalum lattice structure at a desired level to provide a reliable means of producing an oxygen dispensing electrode. A tantalum-oxygen solid solution can be produced by exposing heated tantalum to a known partial pressure of oxygen in a high vacuum environment for prescribed lengths of time. One such technique entitled "Precise Doping of Metals by Small Gas Flows" has been published as Tech Brief 68-10526 November, 1968 and the details of that technique are incorporated herein by reference.

It is to be understood that only preferred embodiments of the invention have been disclosed and that numerous substitutions, modifications and alterations are permissible without departing from the spirit and scope of the invention as defined in the following claims.

N70-34646

FIG. 1



N70-34646
40021

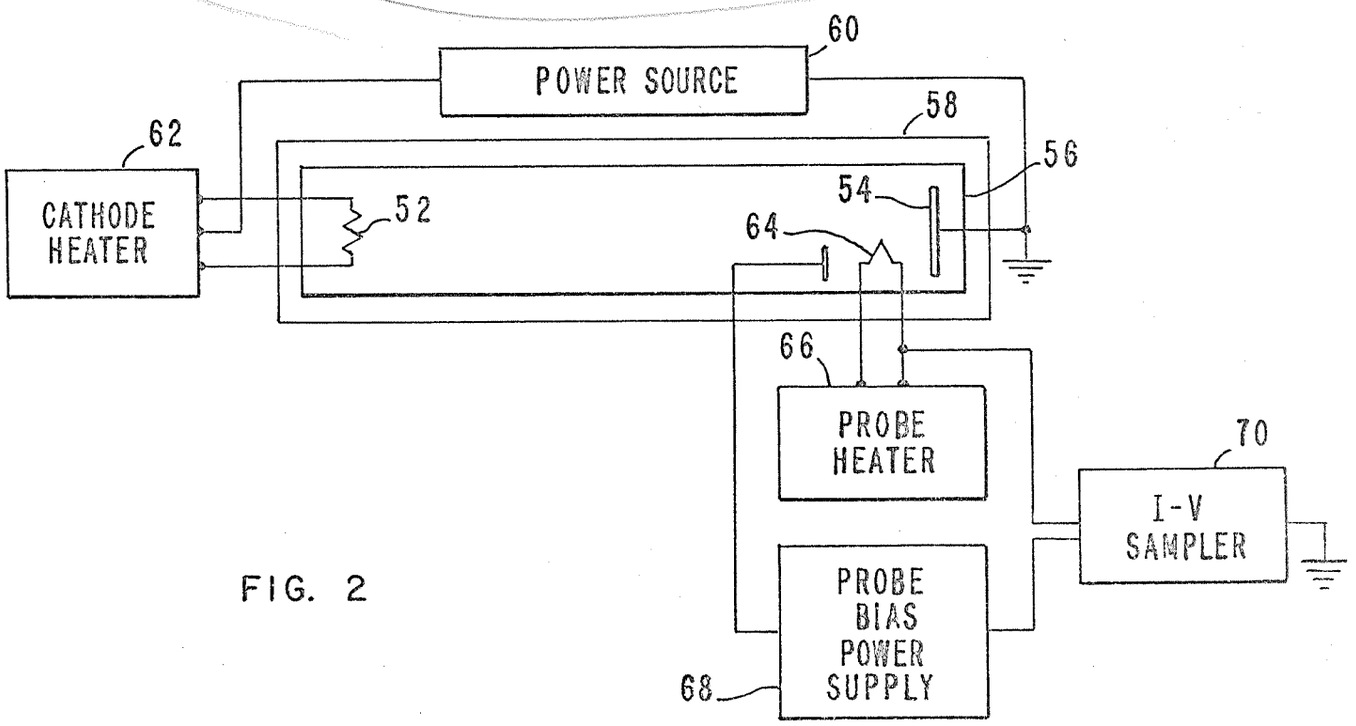


FIG. 2

INVENTORS
SCOTT S. LUEBBERS
JOHN G. DeSTEESE
BY

A134

ATTORNEYS