

UNITED STATES PATENT OFFICE

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METHOD OF FORMING OXIDE COATING ON
TANTALUM ELECTRODES

Earl K. Smith, West Orange, N. J., assignor to
Electrons, Incorporated, Newark, N. J., a cor-
poration of Delaware

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This invention relates to electron discharge tubes, and more particularly to a process for forming a surface coating for the electrodes of such tubes to facilitate heat radiation and reduce electron emission from the surface of such electrode at a relatively high operating temperature.

One problem in the construction of electron discharge tubes, more particularly for gas filled tubes of the higher continuous current rating, is that the anode, and also the control electrode when used, tends to become overheated and emit electrons to a degree to interfere with the proper performance of the tube. Among other things, excessive electron emission from the anode of a gas filled tube tends to reduce the negative or inverse voltage which the tube will stand without an arc-back or discharge through the tube in the wrong direction.

Such objectionable electron emission from electrodes depends of course upon the temperature the electrode assumes in operation of the tube, and also the nature of its surface as an electron emitter at such temperature level. The heat accumulated by electrodes during operation of the type of tube contemplated is dissipated largely by radiation, assisted by conduction of heat to the outside of the tube envelope through the supporting elements for the electrode; and from the standpoint of temperature rise of the electrode, it is desirable that it should have a surface with good heat radiating qualities. Also, in addition to facilitating heat radiation from the electrode to reduce its operating temperature, it is desirable that the electrode surface should be such as to have minimum electron emission at the temperature it assumes in operation.

In certain types of tubes, tantalum is preferably employed for electrode material, more particularly for the anode of gas filled tubes, primarily because tantalum has a marked affinity for various gases other than the insert or rare gases such as xenon, used as the final gas filling the tube. For example, tantalum readily absorbs small traces of gases such as carbon monoxide, hydrogen and oxygen that may be given off during operation of the tube and might otherwise have a deleterious or poisonous effect upon electron emission from the cathode. Hence tantalum is a desirable material for the anode of hot cathode gas filled tubes. Tantalum, however, is a grayish white metal, and in its usual commercial form, has a definite metallic luster causing its surface to have a low heat

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radiation coefficient, so that tantalum tends to assume a high temperature in the operation of the tube.

With these and other considerations in mind, the primary object of this invention is to provide a surface coating or treatment for tantalum electrodes to facilitate radiation of heat and reduce electron emission, as compared with plain metallic tantalum. More specifically, this invention relates to a process for treating tantalum electrodes to form a uniform and consistent oxidized surface, which has the desired qualities of low emissivity and superior heat radiating ability, without rendering the tantalum brittle or incapable of forming a strong weld.

This application is a division of my prior application Ser. No. 12,726, filed March 3, 1948, now U. S. Patent No. 2,538,053, and relates to the process of forming a coating of an oxide of tantalum on the surface of a tantalum electrode, as originally disclosed and claimed in said prior application.

The surface treatment for a tantalum electrode in accordance with this invention involves the application of heat to the electrode in such a way as to form on its exposed surface a film or coating of a dark color, which apparently is one of the lower oxides of tantalum presumably the tetroxide Ta_2O_4 . It is found that the oxide film or coating resulting from the oxidation process of this invention has the desired high heat radiation coefficient and low electron emissivity with the same operating temperature, as compared with a plain tantalum surface.

In forming this oxide coating for the plain tantalum surface of the anode, this surface is first thoroughly cleaned and degreased by any one of the well known procedures, and then is subjected to repeated cycles of alternately heating in a gas flame and cooling with a brief exposure to the atmosphere until the desired coating has been formed. The preferred method of treatment involves heating the tantalum to a moderate temperature generally approximately a dull red heat in the hot part of a gas flame, preferably adjusted to be slightly oxidizing, moving the heated part of the tantalum out of the hot part of the gas flame into exposure to an oxidizing atmosphere, until the temperature drops and the visible color disappears, and then repeating this cycle several times until a coating of the desired thickness and density is formed.

It is found that this method of forming the surface coating gives a more consistent and uni-

form surface film and adequate bonding to the metal surface, without the tantalum becoming too brittle, than a single heating in a flame and exposure to the atmosphere, or by continuous heating in air by induction heating or the like. The reasons for this are not fully understood. In this connection, one characteristic of tantalum when heated in air to a dull red heat is that it absorbs nitrogen greedily and tends to become brittle, presumably on account of formation of an excessive amount of a nitride or other nitrogen tantalum compound; yet temperatures of that order are needed to assure the formation of an oxide of tantalum. It may be that the brief exposures to the air in connection with moving the tantalum into and out of the hot part of a gas flame, in accordance with the preferred method of treatment, tends to limit the absorption of nitrogen and the formation of tantalum-nitrogen compounds tending to make the tantalum too brittle. There are indications that it may be desirable to form a nitride of tantalum to some extent for optimum heat radiation and minimum electron emission qualities of the surface coating, so that cyclic heating and brief exposures to the air in accordance with this invention is preferable to a process of oxidation in a nitrogen free environment. It may be added that the gas flame may contribute to the formation of the desired film in some manner not clearly disclosed or understood by my investigations to date, and also that it is likely that the repeated heating and exposure to the air tends to build up the desired thickness and density of the oxide film, including formation of crystals, with more cohesion and bonding to the body metal than a single heating.

It should be understood that the specific procedure herein described merely represents a typical embodiment of the process characteristic of this invention, and the various adaptations and additions may be made in this particular manipulation or apparatus used without departing from the invention.

What I claim is:

1. The method forming a uniform and consistent oxide coating on a tantalum electrode

closely bonded to a tough and non-brittle body which consists in moving said electrode a number of times into and out of a gas flame to cause intermittent exposure of the electrode to the atmosphere when heated to a dull red heat, whereby the desired oxide is formed without causing the tantalum to absorb nitrogen to a degree to become brittle.

2. The method of forming a uniform and consistent dense coating of a dark colored oxide on the surface of a tantalum electrode for electron discharge tubes, which consists in repeatedly heating in a gas flame a portion of a thin tantalum sheet to a dull red heat and briefly exposing such heated portion to the atmosphere after each heating until the visible color disappears, said cycle of heating and brief exposure to the atmosphere being repeated for the different portions of said tantalum sheet until an oxide coating of the desired density has been formed.

3. The method of forming on the surface of a tantalum electrode a uniform and closely bonded coating of a dark colored oxide of tantalum which consists in heating the various portions of the tantalum electrode to a dull red heat in the hot part of a gas flame adjusted to be slightly oxidizing, exposing said heated portions of the tantalum electrode to the oxidizing action of the atmosphere until the temperature has dropped to a level corresponding with disappearance of visible color of temperature, and repeating such alternate heating of the portions of the tantalum surface and exposure to the atmosphere until an oxide coating of the desired density has been formed over the entire surface.

EARL K. SMITH.

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