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NON-EMISSIVE ELECTRODE

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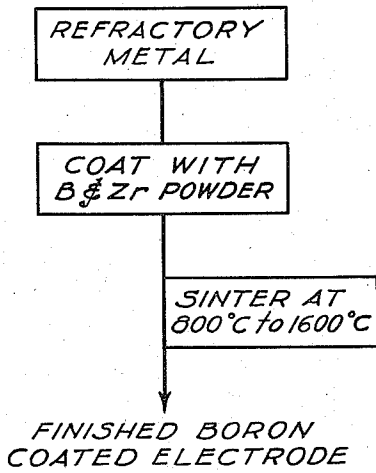


Fig. 1.

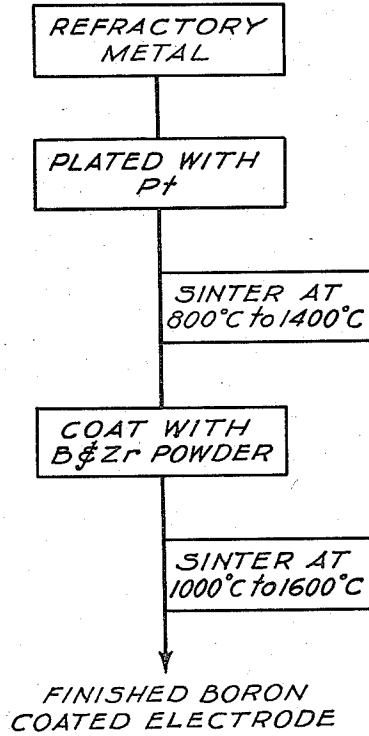


Fig. 2.

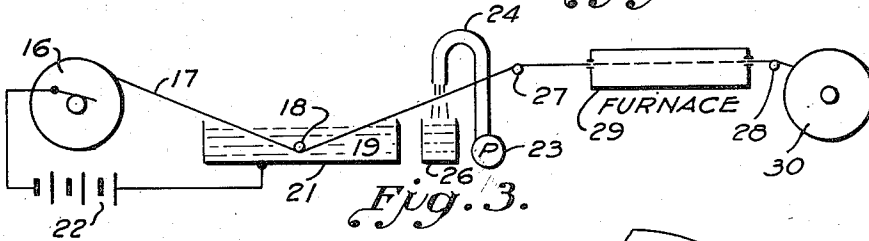


Fig. 3.

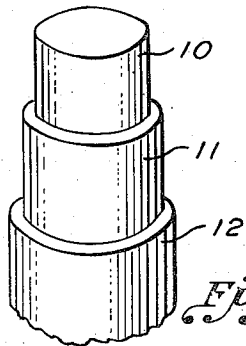


Fig. 4.

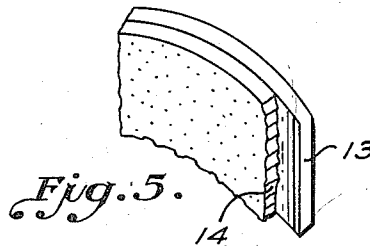


Fig. 5.

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2,822,302

NON-EMISSIVE ELECTRODE

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1 Claim. (Cl. 117—221)

This invention relates to the metallurgical structure of non-emissive electrodes in electron valve structures and has particular reference to boron coated electrodes.

The electrodes of electron valves (except for the cathode) must be low in emission in order to function properly. Thus the anode and various grids must have negligible primary and secondary emission regardless of their operating temperatures. This problem is particularly acute with control grids because they are disposed immediately adjacent to the cathode which is usually heated to a very high temperature to maximize emission. The control grid becomes heated from radiation as well as electron bombardment, and unless carefully constructed the control grid may become emissive, primarily or secondarily. Such emission by a control grid destroys the utility of the electron valve for most applications.

While some researchers have utilized boron or its compounds to assist in the emission of a cathode, I have discovered that it may be processed to achieve exactly the opposite result. Boron applied in accordance with the present invention will inhibit both primary and secondary emission.

It is therefore a general object of this invention to provide non-emissive electrodes coated with boron or its compounds.

Another object is to provide non-emissive electrode materials or stock having a coating of boron or boron compounds and from which electrodes may be formed or fabricated.

An additional object is to provide a method of applying boron to refractory metals from which non-emissive electrodes may be formed.

Other objects and advantages of this invention will be apparent in the following description and claim considered together with the accompanying drawings in which:

Fig. 1 is a flow diagram of the process of the application,

Fig. 2 is a flow diagram of a modified form of the invention,

Fig. 3 is a diagrammatic illustration of plating, coating, and sintering apparatus for use with a modified form of the invention,

Fig. 4 is a perspective view of a terminal portion of a grid wire made in accordance with the invention and showing different layers stripped off, and

Fig. 5 is a perspective view of a portion of a sheet electrode formed in accordance with the invention.

I have found that the boron is most effective when combined with zirconium. This is apparently due to the formation of zirconium boride since mixtures of molecular weights in accordance with the boride formula are most effective. Microscopic examination does reveal, however, uncombined boron and some uncombined zirconium. Preferably these elements are separately applied in elemental form and the boride is formed during a sintering step.

Referring now to the drawings, Fig. 1 is a flow diagram of the basic practice of the invention in forming an electrode. The refractory metals tungsten, molybdenum,

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or tantalum are the most commonly used for electrode materials and my invention is preferably employed on these and other refractory metals. One of these refractory metals is coated with a film of non-metallic vehicle such as lacquer, varnish or shellac in which is suspended boron together with zirconium. This coated metal is then sintered at temperature of 1000° C. to 1600° C. This sintering preferably takes place in a non-reactive atmosphere, or a hydrogen atmosphere, or a vacuum to avoid contamination. The sintered material is then ready for use as a non-emissive electrode.

Illustrated in Fig. 2 is a more elaborate version of the process of Fig. 1 for use on grid wire. Fig. 2 illustrates the added step of applying a platinum coating which aids in maintaining the ductibility of the wire, probably because it acts as a barrier to boride penetration of the refractory metal. Borides are considered to cause embrittlement of the refractory metals. The platinum coating may be applied in any convenient manner and I have found that electroplating from an aqueous solution of platinum chloride and basic lead acetate is satisfactory. This plating step is well known in the art and produces a fluffy coating of metallic platinum and platinum compounds that is dark in appearance and consequently known as platinum black.

This platinum coating may be rendered dense by sintering. This sintering may be a separate sintering operation from the boron sintering or may be accomplished at the same time as the boride sintering. For large production the separate sintering is preferred and may be accomplished by a temperature in the range of 800° C. to 1400° C. in an oxygen-free atmosphere.

The sintered platinized wire may next be coated with the boron-zirconium powder and thereafter sintered in a temperature in the range from 1000° C. to 1600° C., also in an oxygen-free atmosphere. The finished wire is illustrated in Fig. 4 wherein a refractory wire 10 is coated with platinum 11 and then a zirconium boride layer 12 is applied to the surface. The layer thicknesses are exaggerated for purposes of illustration, as both layers are but thin films.

The invention also applies to sheet electrodes such as anodes, illustrated in Fig. 5, wherein a sheet 13 of refractory metal has a surface coat 14 of boron and zirconium mixture. This coat may be applied by the same method as for wire by covering with a liquid vehicle carrying boron and zirconium.

Illustrated in Fig. 3 is a schematic diagram of apparatus for producing the grid wire of Fig. 4. A reel 16 of refractory wire may act as a source of supply for a grid wire core 17 which passes under a pulley 18 submerged in a platinum plating liquid 19 in a conductor container 21. A source of D. C. current is represented by a battery 22 and the opposite terminals are connected to the reel 16 and the container 21 so that an ionic path is established between the liquid and the wire to cause platinum or one of its compounds to plate out on the wire 17. The plated wire may next be sintered but this step is omitted in Fig. 3 and the alternate procedure of coating the platinum plate with lacquer is illustrated by a pump 23 delivering liquid vehicle through a pipe 24 to drop upon the platinized wire 17 with the excess falling into a receptacle 26 from which the pump draws its supply.

The platinized and lacquered wire 17 is next guided by a pair of pulleys 27 and 28 through a sintering furnace 29 which causes adherence of the platinum, zirconium and boron to the core wire 17 and to each other. The cooled wire after sintering may be collected upon a reel 30 and is ready for immediate fabrication into vacuum tubes or other electron valves.

Grid wire so treated may be rewound on a spool and then subsequently used to fabricate grids. It is relatively easy to spot weld and is quite ductile and exhibits very

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excellent properties with respect to non-emission, both primary and secondary.

The precise action of the boron or borides in inhibiting emission is not known. The sintering step does not melt the boron or zirconium, but produces fusion, fritting and coalescence and adherence of these substances to the wire core or to the platinum. Sintering seems to cause boron and zirconium to imbed in platinum and thereby adhere. The amount of boride formation is difficult to determine and the action may be due to the elemental boron present as well as the zirconium boride. In any event, the emission inhibition is greater with my zirconium-boron coated wire than with zirconium coating alone and greater also than platinum plated wires.

The platinum plating is preferred for grid wires in that ductility is preserved and the wires may be bent, twisted, formed and welded without breaking. An illustration of quantitative data for such a wire is as follows. Molybdenum wire was plated in a bath of 3 grams of platinum chloride ($H_2PtCl_6 \cdot 6H_2O$) and 0.5 gram of basic lead acetate to one liter of distilled water. The resultant platinum black was sintered at a temperature between $800^\circ C.$ to $1400^\circ C.$ and thereafter nitrocellulose lacquer was applied having dispersed there fine powders of elemental boron and zirconium. This mixture was composed of 90 grams of zirconium powder to 18 grams of boron powder. The lacquered wire was then sintered at a temperature between $1000^\circ C.$ and $1600^\circ C.$ The lacquer was completely decomposed and vaporized permitting the zirconium and boron to fuse to the wire and to each other.

Various modifications will be obvious to those skilled in the art. The powdered materials can be brushed onto the wire or could be fused on by dipping the wire while hot into the powder or powders. Various liquid vehicles can be used and the mechanisms for sintering are numerous including conduction and induction heating. The molecular ratio to satisfy the formula for zirconium

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boride (ZrB_2) would indicate that there should be two moles of boron to one of zirconium. However, I have found that the ratio range of one to three moles of boron to one of zirconium is practical and that greater inhibition of emission occurs at the higher boron ratios. Theoretically, zirconium boride could be applied as a powder but practically, it is too hard to powder effectively. Boron could be applied to bare wire or platinumized wire to function as a boride of a refractory core metal or as elemental boron, or both.

In view of these and various other modifications and variations, I do not limit myself to the specific disclosure, but claim all modifications and variations that fall within the true spirit and scope of the invention.

I claim:

A non-emissive electrode for an electron valve comprising: a refractory metal; and a surface coating of a sintered mixture of finely divided boron and zirconium in the ratio range of one to three moles of boron to one of zirconium.

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