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ELECTRON EMISSION MATERIAL AND METHOD OF MANUFACTURE.

No Drawing.

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This invention relates to electron-emission material and more particularly to that composed of alkaline-earths made conductive by the admixture therewith of finely-divided metallic material.

An object of my invention is the manufacture of electron-emission material in which the active electron-emitter is a refractory oxide, substantially non-conductive and having conductivity imparted thereto by the incorporation therewith of conductive material, for example, metallic powder.

Another object of my invention is the production of electron-emitting material consisting of alkaline-earths impregnated with metallic material to make them conduct electric current, cohere firmly in the desired form and adhere more firmly to a metallic core, if such is used, with less cracking off in use, whereby the life of such material may be increased.

A further object of my invention is the formation of filamentary material provided with a thicker coating of electron-emitting oxides than heretofore, without impairing the electron-emissivity of the material.

A still further object of my invention is the manufacture of composite wire consisting of metal impregnated with alkaline earths to make it emit electrons efficiently when heated and which may, if desired, be provided with a metal core.

Other objects and advantages of the invention will be disclosed from the following detailed description.

The alkaline earths, that is, the oxides of barium, strontium and calcium have been found to be excellent material for electron-emission purposes when heated to proper temperatures. Barium oxide has been found to have the highest electron-emissivity of the three but is usually mixed with strontium oxide for mechanical reasons, that is, the mixture of the two oxides is found to adhere to filamentary material better than barium oxide alone. A common method of making use of the electron-emitting properties of said oxides is to coat platinum-iridium ribbon with a mixture of the oxides of barium and strontium and introduce the same into an electron device as the hot cathode thereof.

It has been found that only a very thin coating can be applied to a ribbon or filament for this purpose, because of the non-

conducting properties of such oxides. When used in such electron device, the small amount the oxide on the filament gradually vaporizes and the filament finally develops bare spots or portions from which the oxide has been completely vaporized, thus causing a diminution of the electron-emissivity of such coated filament as well as other undesirable consequences. If the oxide is applied thicker than usually, the electron-emissivity of the filament is reduced because of the insulating properties of the oxide.

According to my invention, I obviate the above noted difficulties by mixing a finely divided conductive material with the oxide material.

Another embodiment of my invention involves the making of the filament entirely of electron-emitting oxides impregnated or intimately mixed with conductive material. Such conductive material is preferably one of the refractory metals, such as platinum, tantalum or the like, but other metals are contemplated for use in this connection, for example, chromium, iron, nickel and the like.

Essentially, my invention comprises intimately mixing and incorporating together powdered alkaline earths, for example, a mixture of the oxides of barium and strontium or the carbonates thereof, which may readily be decomposed to form the oxides, with finely divided or powdered platinum, tantalum or the like. Instead of using platinum, a platinum compound, such as platonic chloride, mixed with reducing agent, such as paste, may be used.

The mixture may then be made into the form of a suspension and applied to any desired filamentary material by any suitable known method; for example, it may be mixed with a suitable binder, such as nitrocellulose dissolved in amyl-acetate, applied to filamentary material, such as tantalum or platinum-iridium ribbon, by passing the same through said suspension, and baking the same onto the filament in the same way, as is described, for example, in the copending application of Marden and Rentschler, Serial No. 489,108, filed August 1, 1921, composite bodies and method of producing the same and assigned to the Westinghouse Lamp Company.

The mixture of oxides and metal may be made up as an aqueous suspension, if desired, and the platinum-iridium or other

filament uniformly coated therewith and heated to cause it to bake firmly thereto. Such procedure is similar to the method described and claimed in the copending application of MacRae and Richardson, Serial No. 586,847, filed June 8, 1922, getters and the application thereof and assigned to the Westinghouse Lamp Company.

The method described and claimed in the copending application of Duncan MacRae, Serial No. 587,270, filed September 11, 1922, electron emitting devices and method of making and assigned to the Westinghouse Lamp Company, may be used for coating filamentary material with a mixture of alkaline-earth carbonates and powdered metal, such carbonate being eventually reduced to oxide according to the method disclosed in said application.

Instead of coating filamentary material with such mixture, the same may be formed into a thick paste and squirted into a filament in a manner similar to that in which squirted tungsten filaments were formerly made. Instead of squirting the filament, platinum or tantalum powder, for example, could be mixed with the desired amount of alkaline earths, pressed into a slug and treated in accordance with the method now commonly utilized for treating tungsten and molybdenum; that is, the slug could be swaged or rolled down by suitable known processes and finally drawn to wire of the desired size, by which method there would be obtained an oxide-impregnated filament having an electron-emissivity corresponding with that of the alkaline-earth employed.

The following description is given to illustrate more clearly how my invention may be practiced, but it is to be understood that the proportions given are merely suggestive and I do not intend to be bound thereby. Filamentary material, for example, platinum-iridium ribbon, may be thoroughly cleaned, as by passing it through an electric tube furnace, according to the method described in the aforementioned copending application of Duncan MacRae. A suspension of preferably about equal parts of the oxides of barium and strontium, with any desired proportion of metal powder, for example, platinum powder, tantalum powder or the like, may be prepared.

The vehicle used for such a suspension is preferably water, but an organic binder such as nitro-cellulose dissolved in amyl-acetate may be used if desired. The proportion of the metal powder to the alkaline earths depends on the thickness of coating to be applied to the filamentary material and may vary from a small amount, for example, from 5 to 10% to a relatively large proportion, for example, from 80 to 90%. The thicker the coating to be applied to the fila-

mentary material, the larger the proportion of metal powder should be in the mixture.

The mixture may be ground up in a mortar with a pestle and enough water gradually added to form a homogeneous suspension having the consistency of a thin paste. Such a suspension may be poured into a gettering cup or the like and the filamentary material passed over or around the gettering wheel thereof to coat the same uniformly with the suspension, after which the filament may be passed through an electric furnace where the suspension is baked thereon, similar to the method described and claimed in the aforementioned application of Duncan MacRae for applying alkaline-earth carbonates to a filament.

One or more coatings of the suspension may be applied to the filamentary material, depending on the thickness of the coating desired thereon. Filamentary material, coated as aforescribed, permits the use of a thicker coating than if no metal were mixed with electron-emitting oxides, because the metal powder in the coating serves as a conducting medium to bring the electrons to the surface, the electron-emitting oxide serving merely as the final gate-way by means of which the electrons are discharged. Such coated material has a longer life than previously prepared oxide-coated filaments, because of the thicker coating of the oxide thereon, whereby the same may be heated for a longer time before all the oxide is completely vaporized from any portion of the surface of the original filament or metallic core of the coated filament. Such a part-metallic coating will adhere more firmly to a wire than one containing no free metal.

Another embodiment of my invention comprises utilizing such suspension as is heretofore described for making squirted filaments. Of course, in this case, it is necessary to use less of the vehicle, so that a suspension of a consistency of a very thick paste is formed. If water is used for the vehicle, it is preferable to use some binder, such as glue, but any suitable vehicle may be used so that a squirted filament of sufficient strength for the necessary handling is prepared.

Platinum or tantalum powder are preferably mixed with a relatively small proportion of the oxides of barium and strontium, or the oxide of barium only, so that the squirted filament, when sintered, will have substantially the physical characteristics of the metals themselves. Instead of squirting a filament from such a mixture, platinum or tantalum powder may be mixed with a small proportion of one or more of the alkaline earths, pressed into a slug and sintered, swaged or rolled and drawn to wire of the desired size, according to well known methods now employed in the manufacture

of metals of the tungsten class into filamentary form.

It will readily be appreciated that, according to my invention, I have devised a way for activating filamentary material with alkaline earths in a manner involving the use of said earths in greater thicknesses than have heretofore been feasible, whereby greater efficiency and longer life are obtained.

Although I have described what, at present, I consider to be the preferred embodiments of my inventive idea, it is to be understood that modifications will suggest themselves to those skilled in the art within the spirit and scope of the appended claims and that such modifications are to be considered as embodying my invention.

What is claimed is:

1. Electron-emission material comprising an alkaline earth uniformly distributed through tantalum.

2. Electron-emission material in coherent form comprising alkaline earths uniformly distributed through tantalum.

3. Filamentary material for electron-emission purposes comprising a mixture of the oxides of barium and strontium made conductive by having powdered tantalum metal uniformly distributed therethrough and incorporated therewith.

4. Electron-emission material comprising a conductive core, coated with a non-conductive oxide impregnated with tantalum.

5. Electron-emission material comprising a conductive filament having a coating thereon of alkaline earths mixed with tantalum.

6. Electron-emission material comprising a filamentary metal core coated with a mixture of alkaline earths incorporated with finely divided tantalum metal.

7. Filamentary material for electron-emission purposes comprising a refractory metal wire coated with the oxides of barium and strontium having finely-divided tantalum metal uniformly distributed therethrough.

8. The method of making electron-emission material comprising incorporating together alkaline earths and finely divided tantalum metal and working the same into the desired coherent form.

9. The method of making filamentary material for electron-emission purposes, comprising uniformly mixing together finely divided tantalum and a small proportion of at least one of the alkaline earths and working said material into coherent filamentary form.

10. The method of manufacturing filamentary material for electron-emission purposes comprising preparing a suspension of the oxides of barium and strontium and finely divided tantalum metal uniformly distributed therethrough, passing a refractory metal filament through said suspension to coat the same therewith and heating said filament to cause a firm adherence of the mixture thereto.

11. The method of manufacturing filamentary material for electron-emission purposes, comprising coating tantalum wire with a uniform mixture of metallic tantalum and alkaline earth material.

In testimony whereof, I have hereunto subscribed my name this 27th day of Sept., 1922.

JOHN WESLEY MARDEN.