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ELECTRON-EMITTING MATERIAL AND METHOD OF MAKING THE SAME

No Drawing. Application filed June 29, 1926. Serial No. 119,476.

This invention relates to an electron-emitting body and to a method of producing the same and more particularly to the manufacture of an alloy of tungsten and molybdenum containing either admixed or alloyed therewith a small proportion of thorium or other metal having good electron emissivity, such as uranium, vanadium or zirconium.

Heretofore numerous attempts have been made to prepare alloys of thorium with refractory metals such as tungsten and molybdenum in order to alter their physical properties, such as ductility and resistance to off-setting when employed as an incandescent lamp filament. The processes suggested for producing such alloys involves a reduction treatment of compounds, such as nitrates, oxides, etc., of the constituent metals, by hydrogen or other reducing agents. I have found, however, in attempting to carry out the processes heretofore suggested, that it is not possible to obtain the pure metal thorium alloyed or mixed with the tungsten or molybdenum because hydrogen will not reduce the oxide of thorium which forms at some stage in the process while reducing agents, such as carbon, frequently exert deleterious effects on the metals and limit their uses to filaments of large sizes. The carbon, moreover, forms carbides with the constituent metals which persist, to some extent, throughout the wire drawing operations.

In a copending application Serial No. 618,396, filed Feb. 10, 1923, entitled Manufacture of alloys or mixtures of metals, I have disclosed a successful method of producing an alloy or mixture of tungsten or molybdenum and thorium for electron emission purposes and in a division of such application Serial No. 114,859, filed June 9, 1926, and entitled Molybdenum-thorium alloy, I have claimed specifically the molybdenum-thorium alloy or mixture:

While the methods set forth in each of these applications produces an electron-emitting body of great utility, the tungsten-thorium alloy must be produced with extreme care and the heating conditions carefully regulated and controlled since the volatilization temperature of thorium is far below the temperature to which it is necessary to heat the tungsten during fabrication. The tungsten-thorium alloy at the completion of the wire drawing operation, moreover, requires a high temperature seasoning schedule to develop the thorium emission, due possibly to a thorium poor area near the surface, resulting from volatilization of the surface thorium during the high heating to which the material is subjected during manufacture.

The molybdenum-thorium alloy is much more readily manufactured due to the lower treating temperature thereof and more thorium, as metal, appears to be retained in the molybdenum, as manifest by the ease with which thorium emission is obtained. However, molybdenum vaporizes more rapidly than tungsten at the normal operating temperature of the electron-emitting filament so that after a period of use the filament must be operated at other than its rated voltage. Another disadvantage with activated molybdenum is its inability to withstand over voltage without destruction, due to its low melting point.

One of the objects of the present invention is to provide an electron-emitting body of the thoriated type which combines the advantages of the tungsten-thorium alloy or mixture with the advantages of the molybdenum-thorium alloy or mixture.

Another object is to provide an electron-emitting body which may be readily manufactured without substantial loss of the active electron-emitting constituent and which is sufficiently refractory to withstand rough usage.

Other objects and advantages will hereinafter appear.

In accordance with my invention I produce an electron-emitting body composed of an alloy or mixture of thorium or other highly thermionically active metal with an alloy of tungsten and molybdenum. The presence of molybdenum in the tungsten renders it possible to lower the treating temperature of the mixture below that of tungsten without impairing its working qualities, this lowering of the treating temperature being sufficient to prevent, to a large extent, the volatilization

of the thorium which normally occurs in working a thorium-tungsten mixture alone. Tungsten and molybdenum appear to form a continuous series of solid solutions the fusion point of which is intermediate that of tungsten and molybdenum and which appears to vary directly with the proportion of molybdenum present. It is possible, therefore, by choosing the proper proportion of tungsten and molybdenum to obtain a refractory carrier for the thorium metal which is sufficiently refractory to resist rough usage, such as over voltages but which has a sufficiently low working temperature to prevent substantial vaporization of the thorium constituent.

There appear to be other reasons, besides the lowering of the treating temperature which accounts for the retention of the thorium metal in the body. Molybdenum is in many respects a more susceptible metal than tungsten, responding more readily to treatment and alloying more easily with other metals. It is possible that the molybdenum imparts this characteristic to some degree to the tungsten-molybdenum alloy so that this alloy has a stronger alloying action with the thorium than does tungsten alone.

In order to retain the thorium in the tungsten-molybdenum alloy, however, during fabrication of the body and to present suitable conditions for the formation of the alloy, it is necessary to observe certain precautions as will more fully appear hereinafter.

One of the precautions to which I refer is the careful heat treatment and temperature control of the material during manufacture and while the treating temperature of the tungsten-molybdenum alloy is several hundred degrees below that of tungsten alone, depending on the particular molybdenum content, nevertheless, such temperature is considerably in excess of the volatilization temperature of the thorium.

Another precaution which it is desirable to observe in order to insure the obtaining of full electron emission characteristics of the thorium is to prevent the contamination of thorium with oxygen, or other impurities with which the thorium readily forms compounds difficult to dissociate.

In preparing the alloy the following procedure is preferably followed, although it is to be understood that changes may be made therein without departing from the invention. Pure molybdenum and tungsten metals in the desired proportion may be mixed in powdered form, after they have been carefully reduced in order to free them as far as possible from oxygen and oxides, and the desired percentage of pure thorium metal added thereto. In oder to insure the purity of the metal powders employed I prefer to extend the usual reduction treatment of the materials by hydrogen for an additional period of several hours at the reduction temperature of the compound although any suitable method of obtaining substantial purity of the metals may be employed.

In order to obtain a more homogeneous mixture and more intimate contact of the tungsten and molybdenum, the oxides of these metals may be simultaneously precipitated from their salts in the manner set forth in copending application of John H. Ramage, Serial No. 646,266, filed June 18, 1923, and entitled Refractory metal alloy and method of making. Briefly, this method consists in dissolving suitable compounds of the constituent metals in miscible solvents, mixing the solutions in the proper proportion and simultaneously precipitating an intermingled compound of the metals. In carrying out the process solutions of ammonium tungstate and ammonium molybdenate may be prepared by dissolving purified tungstic oxide and molybdenum oxide in ammonium hydroxide. The tungsten solution and the molybdenum solutions may then be mixed in such proportions as to give the desired proportion of tungsten and molybdenum in the precipitated mixture. The dissolved tungsten and molybdenum oxides are then precipitated from the mixture of solutions with hot nitric acid as is well known in the art. The precipitate should then be washed, dried, ignited, powdered and sieved.

The oxide mixture may then be subjected to any of the usual tungsten oxide reducing processes and the thorium metal added to the tungsten-molybdenum mixture after reduction.

A very uniform and intimate mixture of the powders is prepared by placing small portions of each of them in an agate mortar and thoroughly mixing the same by means of a pestle. Another portion of each metal is then added and mixed in the same manner. This procedure is repeated until all of the metals have been added. The material is removed from the mortar and mixed on a paper, after which it is again mixed in the mortar in the same manner as first stated, except that small portions of the mixture are added each time instead of separate metals. This procedure insures the breaking up of such lumps as may be in the material. The latter operation is repeated three times to insure a uniform mixture. The material is then placed in a revolving mixer and mixed for one hour.

As a precautionary measure it may be found desirable, as the thorium powder is very active, to avoid the same becoming contaminated. Therefore, to obtain this object, the powder may be treated by coating the particles thereof with paraffin or a similar substance in the manner more fully described and claimed in my Patent No. 1,566,793, granted Dec. 22, 1925, method of alloying rare metals and articles made therefrom and

assigned to the Westinghouse Lamp Company.

The mixture then is pressed into bars about 9" long and 1/4" square, the pressure used being about 40 tons per square inch.

The bars so formed are then sintered under a vacuum by placing them between the contacts of the secondary of a transformer. Before the heat is applied by passing current through the bar, the secondary contacts and the bar are enclosed in a metal bottle, or other container which may be hermetically sealed. The air is evacuated from the bottle until the pressure is about 20 on a McLeod gauge, which reading corresponds to a pressure of about .06 mm. of mercury. Current is then permitted to pass through the bar. Frequent readings are taken on the gauge and the current is so regulated that the pressure in the bottle at no time exceeds 110 on the McLeod gauge, which corresponds to .3 mm. of mercury. In order to maintain the desired vacuum conditions, two mercury diffusion pumps connected in series and backed up by an oil pump are connected to the bottle and kept running continuously through the treating operation. The initial current is increased about 50 amperes with a corresponding increase in voltage of approximately .25 of a volt. The increase in current and, therefore, temperature is dependent upon the indications on the McLeod gauge. Should the gauge show a considerable increase of pressure upon increase of current and voltage, the current should be decreased which would be accompanied by a corresponding decrease in voltage.

The time required to complete the sintering operation varies slightly with the proportions of molybdenum and tungsten but preferably should extend over a period of an hour or more. The maximum temperature should be as low as possible in order to obtain proper consolidation of the metals and permit them to be swaged and drawn. In the case of the bars referred to, the maximum current has been found to vary from about 950 amperes for pure molybdenum to about 1500 amperes for pure tungsten. With equal proportions of molybdenum and tungsten a heating current of about 1250 amperes should be employed. In order to determine the maximum current to which the bar may be subjected, for any desired percentage of constituent metals, a test bar may be subjected to increasing current flow until it fuses and the subsequent bars treated to not more than 90% of the fusion temperature so determined.

I prefer to employ an alloy of molybdenum and tungsten in about equal proportions for the manufacture of a cathode for electron discharge devices, although other proportions may be employed depending on the particular service to which the material is to be used. The percentage of thorium may vary from .25% to 1.0% of the total mixture.

The success of the process is to be attributed to a large extent in carefully observing the temperature treatment conditions, because the thorium will volatilize if the treatment is conducted too rapidly and will become oxidized or otherwise contaminated if the vacuum conditions are not maintained.

After cooling, the bar is removed from the furnace and drawn into wire in accordance with any approved process ordinarily followed in drawing tungsten wire, such as described in Patent No. 1,082,933, issued December 30, 1913.

When the wire has reached a diameter of approximately 1.6 mils, it is cleaned by the usual oxy-hydrogen annealing method or the surface carbide, if any, may be removed mechanically by abrasives, such as emery. Thereafter it may be formed into filaments and inserted into the ordinary bulbs used for audions, etc.

Tests which have been conducted on the wire made in accordance with my process show that the emissivity therefrom is plainly that of thorium.

If desired, instead of introducing the thorium into the tungsten-molybdenum alloy in the form of pure thorium, it may be incorporated into the metal mixture as thorium oxide, and after completion of the swaging and drawing operation, the filament may be activated as is the present practice with thoriated-tungsten wire. In such case the thorium will not be alloyed with the tungsten and molybdenum but a mechanical mixture only will result. Such a filament, however, has advantages over the pure thoriated-tungsten filament in the added ease with which it may be fabricated and activated.

Modifications of the invention which fall within the scope of the appended claims are contemplated by me as part of my invention.

What is claimed is:

1. The method of making an electron-emitting body consisting in mixing pure tungsten, molybdenum and thorium metal powders in suitable proportions, bringing the same into intimate association by pressure, and slowly heat treating the same in a high continuously maintained vacuum until the particles coalesce.

2. The process of forming a ternary alloy of tungsten and molybdenum containing thorium, which comprises admixing the substantially pure metal powders in the desired proportion, compacting the mixed metal powders, and thereafter sintering the compacted article and alloying the constituents therein by slowly heating the compacted article in a continuously maintained high vacuo to a temperature approximating but below the fusing temperature of the alloy.

3. The process of forming a ternary alloy

of tungsten and molybdenum containing a relatively small percentage of thorium which comprises intimately admixing the metal powders of these metals in the desired proportion, compacting and sintering the compacted articles in a continuously high vacuo by slowly heating the same to the sintering temperature, maintaining at all times within the evacuated device a pressure not exceeding .3 mm. of mercury.

4. The process of forming a ternary alloy of tungsten and molybdenum containing thorium, which comprises intimately admixing substantially deoxidized tungsten and molybdenum metal powders in approximate equal amounts, adding thereto approximately 1.0% thorium metal powder, thoroughly admixing the constituents, thereafter compacting and sintering the compacted articles in a high vacuo by slowly heating to a temperature approximating but below the fusion temperature of the alloy, maintaining at each increased temperature stage in the heating process a pressure not in excess of .3 mm. of mercury within the evacuated device.

5. The method of forming filamentary bodies of a ternary alloy of tungsten, molybdenum and thorium, in which the molybdenum is present in amounts up to 50 per cent and the thorium in amounts up to 1.0 per cent, which comprises admixing the substantially pure deoxidized metal powders in the desired proportion, compacting the admixed metal powders into rods, slowly heating said rods in a high vacuo so that the occluded gases therein are substantially removed as expelled by heat prior to sintering thereof, sintering said degasified article by heating the article in the same continuous vacuo to a temperature approximating but below the fusion temperature thereof, observing during said sintering operation a slow temperature rise to the highest sintering temperature so as to facilitate alloying and diffusion of the constituents of the alloy, and thereafter reducing the sintered article to desired sizes by hot mechanical deformation procedure.

In testimony whereof, I have hereunto subscribed my name this 28th day of June, 1926.

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