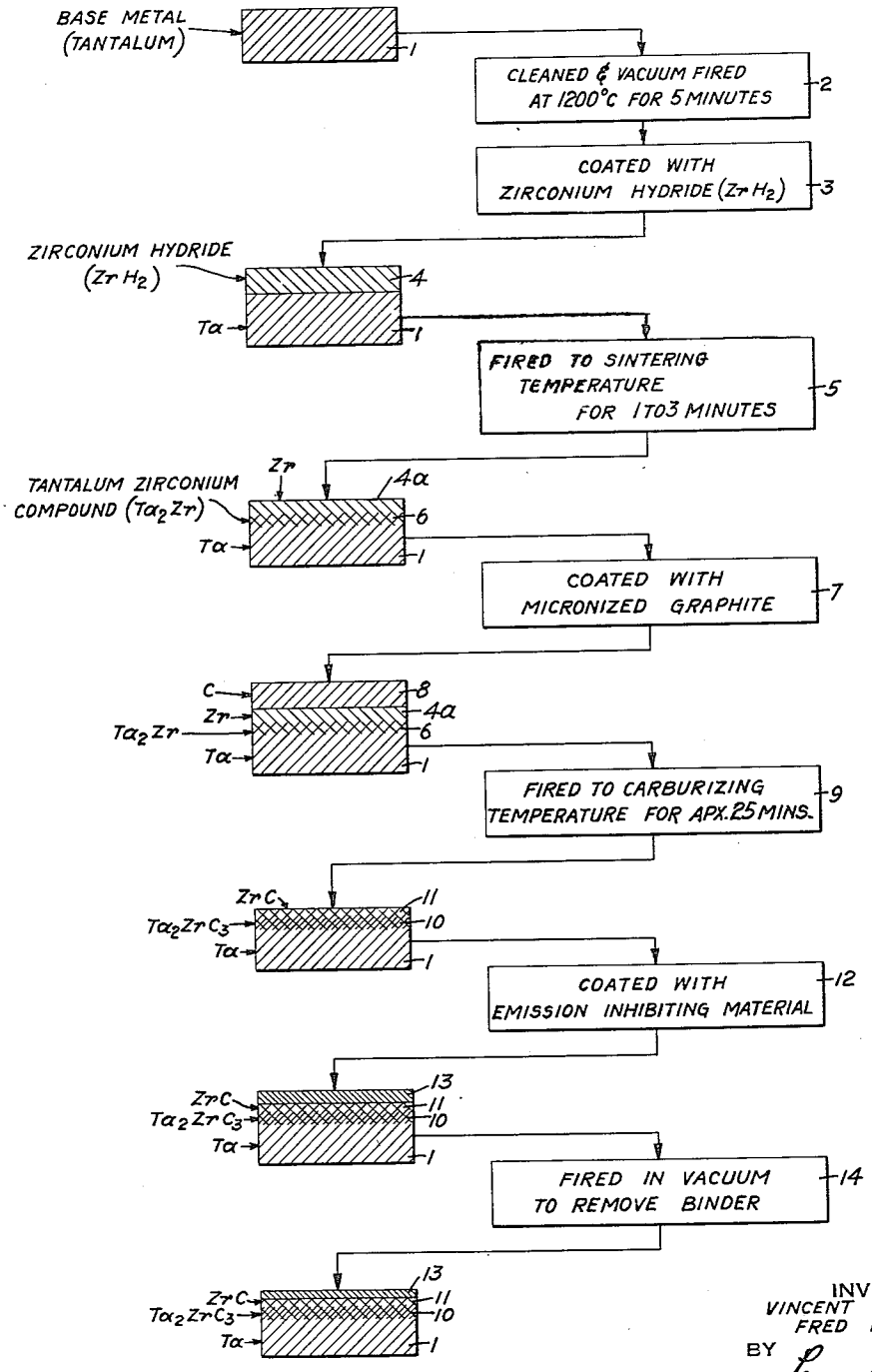
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METHOD OF FORMING PROTECTIVE COATINGS FOR METALLIC SURFACES

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METHOD OF FORMING PROTECTIVE COATINGS FOR METALLIC SURFACES

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This invention relates to methods of forming protective barrier layers or coatings for metallic surfaces whereby such barrier layers provide for the underlying metal a protection against chemical reactions with substances that may contact the surface thereof, and more particularly to methods of forming barrier layers for electrodes of electron discharge devices to prevent migration of substances therethrough to the base metal of the electrode.

In the DeSantis-Hunter-Majkrzak copending application, Serial No. 72,403, filed January 24, 1949, now U. S. 2,681,876, a barrier layer believed to be a carbide of an inter-metallic compound and methods of making same are disclosed. This intermetallic carbide barrier protects metallic surfaces against adverse effects such as might result from migration thereto of coating materials provided for resisting chemical reaction with oxidizing or other deleterious atmospheres at temperatures of 750° C. or above. In another DeSantisHunter-Majkrzak copending application, Serial No. 72,404, filed January 24, 1949, now U. S. 2,552,535, a similar barrier layer is formed on electrodes, such as the grid of a radio tube, to protect the base metal of the grid from an outer layer of electron emission-inhibiting material and also to avoid loss of such electron emission-inhibiting material by interaction with or absorption by the base metal, and which would also result in undesired embrittlement of the core material. This barrier layer when formed in accordance with the disclosures of said copending applications is found to be very stable and to prevent electron emission-inhibiting material, such as carbon, from migrating therethrough to the base metal at elevated temperatures, for example in the neighborhood of or above 1300° C.

The inter-metallic carbide layer formed in accordance with the disclosures of said issued patents are applicable to refractory metal as a base wherein such metal may be a selected one of the group of tantalum, molybdenum, columbium and tungsten or a mixture thereof. The inter-metallic carbide layer is formed by applying to the base metal a layer of oxide of a second metal such as zirconium, titanium or silicon. It is then dried and fired to partially decompose the oxide and cause the metal thereof to partially combine or alloy with the surface strata of the base metal. This sintered layer is then covered with a coating of carbon and fired in vacuum or inert atmosphere at a temperature of at least 1700° C., whereby the interface portions of the sintered layer and the base metal are converted into an inter-metallic carbide which is very stable even at temperatures above 2000° C. Where the barrier layer is applied to a grid, a further layer of high temperature resistant non-emissive material, such as carbon or platinum, is applied. The stable inter-metallic carbide effectively prevents migration therethrough of the the carbon, platinum or other substances forming or contacting the emission inhibiting carbide layer.

While the resulting inter-metallic carbide layer provides a very effective barrier for the purposes intended, some difficulties may be experienced in consistently, time after time, decomposing or converting all of the oxide coating

to an inter-metallic carbide. Any unconverted oxide, for example, which would tend during operation of a tube to produce gas must be completely converted by vacuum firing which requires prolonged heating. Furthermore, grids containing unconverted oxide tend to evolve oxygen and carbon monoxide gas during operation of the tube thereby poisoning the emissive quality of thoriated tungsten filaments and thereby slowly reduce filament activity.

One of the objects of this invention is to provide an improved method of forming inter-metallic carbide layers overcoming the aforementioned difficulties.

Another object of the invention is to provide an improved method of forming inter-metallic carbide layers for grid surfaces by utilizing components which liberate little or no gas during tube exhaust operation and which will not poison the emissive quality of thoriated tungsten filaments nor cause the emission thereof to slump off during life of the filament.

In accordance with this invention the desired protective intermetallic carbide layer is produced upon a refractory metal by applying a layer of a refractory hydride in the place of the oxide, which is converted during a heat treatment to the refractory metal by liberation of the hydrogen. This heat or firing treatment is believed to produce a compound of the surface strata of the base refractory metal and the metal of the hydride. By way of example, the base metal may be tantalum, molybdenum, columbium or tungsten or alloys in which one or more of the mentioned metals is present in a substantial predominant proportion, while the refractory hydride may be a hydride of one or more of the class consisting of zirconium, silicon and titanium. For example, where the base metal is tantalum and the hydride is zirconium hydride, the sintering operation is believed to result at least partially in a compound representable by the formula Ta_2Zr. The barrier layer is completed by a carburizing operation which includes the application of a coating of carbon in the form of micronized graphite sprayed or otherwise applied over the layer of the resulting zirconium-tantalum compound formed during the first firing operation and thereafter exhausting the grid in a vacuum at an elevated temperature above 1700° C., preferably at about 2000° C., at which it is held for about 25 minutes. This high temperature carburization converts the tantalum-zirconium compound and/or layers to an inter-metallic carbide which is believed to be a carbide of an inter-metallic compound representable by the formula Ta_2ZrC_3. This inter-metallic carbide compound is a very effective barrier to the migration therethrough of electron emission inhibiting material that may be coated on the outer surface of the barrier layer.

The above-mentioned and other features and objects of this invention and the manner of attaining them will become more apparent and the invention itself will be best understood by reference to the following description of an embodiment of the invention taken in conjunction with the accompanying drawing, where the sole figure is a diagrammatical illustration of a flow chart showing specimens, in exaggerated proportions for illustration purposes, at different stages in the process of forming the barrier layer.

In the drawing a base metal 1 is indicated as being of tantalum. The base metal, however, may comprise any one of the group of tantalum, molybdenum, columbium and tungsten or a mixture thereof. By way of example, the process will be described in detail using tantalum as the preferred base metal. As indicated in the drawing at 2, the base metal, tantalum, is first cleaned and fired to remove surface contamination, such as copper which may be on welds. The firing is performed in vacuum or inert atmosphere at an elevated temperature in the neighborhood of 1200° C. for a short period, such

as five minutes. The tantalum article is then coated with zirconium hydride (ZrH_2) as indicated at **3** and **4**. This coating is applied by any desired process such as cataphoresis to those surfaces to be protected or, in the case of a grid electrode, those surfaces to be rendered non-emissive.

The cataphoresis bath for the coating operation is prepared by first making up a magnesium nitrate solution wherein 7.5 grams of magnesium nitrate crystals are dissolved in 1 liter of distilled water. To 40 grams of zirconium hydride 20 ml. of the magnesium nitrate solution is added to make a thin paste. This paste is then poured into 840 ml. of pure methyl alcohol. The vacuum-fired tantalum article, or so much of it as is to be coated, is immersed in the bath thus prepared and connected in circuit as the cathode. One or more aluminum electrodes connected as anodes are arranged with respect to the tantalum article so that a potential gradient is obtained during the electrophoresis. With the voltage, current and area to be coated held constant the amount of zirconium hydride deposited is directly proportional to time and hence can be controlled and duplicated accurately. By using a current density of about 5 milliamperes per square centimeter at approximately 40 volts for a period depending upon the desired thickness of the coating, usually less than 60 seconds, a satisfactory uniform coating can be obtained. The article is then removed from the bath and the methyl alcohol allowed to evaporate.

The zirconium hydride is converted to zirconium metal **4***a* and caused to combine with the surface strata of the tantalum to form at least in part a thin skin of zirconium-tantalum compound Ta_2Zr. This conversion is brought about by the heating step indicated at **5** in the graph. The article coated with zirconium hydride is fired in vacuum or an inert atmosphere at a temperature, about 1400° C., sufficient to drive off the hydrogen and cause a chemical reaction between the interfaces of the tantalum and the zirconium layer. If desired, firing temperature may be increased to about 2000° C. to insure formation of a skin **6** of tantalum-zirconium compound Ta_2Zr. Decomposition of the zirconium hydride and evolution of the hydrogen occurs at a dull red heat at approximately 700° C. The inter-metallic compound of tantalum and zirconium, however, is believed not to form until the temperature exceeds 1400° C. The zirconium appears to form a skin without dissolving or penetrating into the base metal while the inter-metallic compound forms in the interface portions of the zirconium and the base metal. The article is allowed to cool to about 120° F. before it is removed from the vacuum for subsequent treatment.

The next step as indicated at 7 in the chart is the application of a layer of carbon **8** in the form of finely divided graphite in a suitable binder. The purpose of this coating is to carburize the zirconium and/or tantalum-zirconium compound now present on the surface of the tantalum article. This carburization is believed to produce a carbide of the inter-metallic compound **10** according to the formula Ta_2ZrC_3. Some zirconium carbide may also be formed.

The graphite is prepared by mixing 40 grams of the graphite with 100 cc. of a lacquer binder and milling same in a ball-mill with flint pebbles for 24 hours or more. The binder is prepared by dissolving 20 ml. of Du Pont pyroxylin in 180 ml. of amyl acetate. The carbon containing lacquer is then sprayed to coat all the surfaces to be carburized. Those surfaces which are not to be carbon coated are masked. The carbon coating should be fairly thin, preferably about 5 mg. per sq. cm.

The article thus coated with carbon is subjected to a second firing operation in vacuum as indicated at **9** in the graph. The furnace containing the article is first brought up to a temperature of 700° C. during an interval of 2 to 3 minutes permitting the gas from decomposing binder to be removed by the vacuum pump. The temperature is thereafter raised rapidly to above 1400° C. and preferably to about 2000° C. This heating operation continues for about 25 minutes to insure proper conversion of the tantalum-zirconium layers to the inter-metallic tantalum-zirconium carbide. The article is then allowed to cool to about 120° F. after which it may be removed from the furnace. Surplus carbon contained on the fired article may be brushed off, if desired.

The carburizing operation of the second firing operation **9** produces an interaction between the graphite which penetrates the tantalum-zirconium layers whereby an inter-metallic carbide **10** appears to crystalize into a stable compound. This carbide crystalization of the inter-metallic tantalum-zirconium compound prevents further migration of the carbon thus protecting the tantalum core underlying the carbide. This protective barrier formed during the second firing operation not only avoids carbon penetration into the core and therefore avoids undesired embrittlement of the core, but also prevents the core material from penetrating the non-emissive coating or other layer applied on the outer surface of the barrier layer. A cross-section of the article when polished shows up the barrier layer as a thin, hard bright protective skin over the core.

When the article is a grid for electron discharge devices, it is further treated by application at **12** of an electron emission inhibiting material **13** such as carbon, platinum or a refractory metal of the platinum group of elements. This particular coating may be applied by means of a suitable binder which is removed by firing as indicated at **14**. For further details of non-emissive coatings reference may be had to the aforesaid U. S. Patent 2,552,535.

For examples of other hydrides that may be used reference is made to silicon hydride and titanium hydride. The silicon hydride reacts similarly to zirconium hydride, the silicon forming a metallic-like skin coating on the base metal with shallow penetration into the base metals of the class consisting of tantalum, molybdenum, columbium and tungsten. The titanium hydride when sintered tends to penetrate deeper into the base metal than zirconium and silicon.

While we have described above the principles of our invention in connection with specific apparatus and method steps, it is to be clearly understood that this description is made only by way of example and not as a limitation to the scope of our invention, as set forth in the objects thereof and in the accompanying claims.

We claim:

1. A process for producing an oxygen-free non-emissive grid structure consisting in intimate combination of a refractory metal core, a non-emissive material and an inter-metallic carbide barrier layer disposed therebetween, the steps comprising applying to a core of a previously fired first refractory metal chosen from the class consisting of tantalum, columbium, molybdenum, tungsten and alloys in which at least one of said metals is the predominant component, a layer of a hydride of a second refractory metal chosen from the class consisting of the hydrides of zirconium, titanium, and silicon, elevating the temperature of the coated core to between about 1700° C. and about 2000° C. to decompose the hydride, convert it into a sintered refractory coating of said second metal and cause said sintered refractory coating to at least partially react with the surface strata of said base metal to form therewith an inter-metallic compound, applying a layer of carbon on said sintered coating, elevating the core temperature to between about 1700° C. and about 2000° C. to form an inter-metallic carbide with said inter-metallic compound thereby producing a barrier layer to prevent migration therethrough, applying a layer of a non-emissive material on said barrier layer and heating the resultant structure to obtain an intimate bond between the contacting surfaces of said non-emissive material and said barrier layer.

2. A process according to claim 1 wherein the first refractory metal is tantalum.

3. A process according to claim 1 wherein the first refractory metal is molybdenum.

4. A process according to claim 1 wherein the first refractory metal is tungsten.

5. A process according to claim 1 wherein the hydride is zirconium hydride.

6. A process according to claim 1 wherein the first refractory metal is tantalum and the second refractory metal is zirconium.

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