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D. M. YENNI ET AL

3,075,066

ARTICLE OF MANUFACTURE AND METHOD OF MAKING SAME

Filed Dec. 3, 1957

2 Sheets-Sheet 1

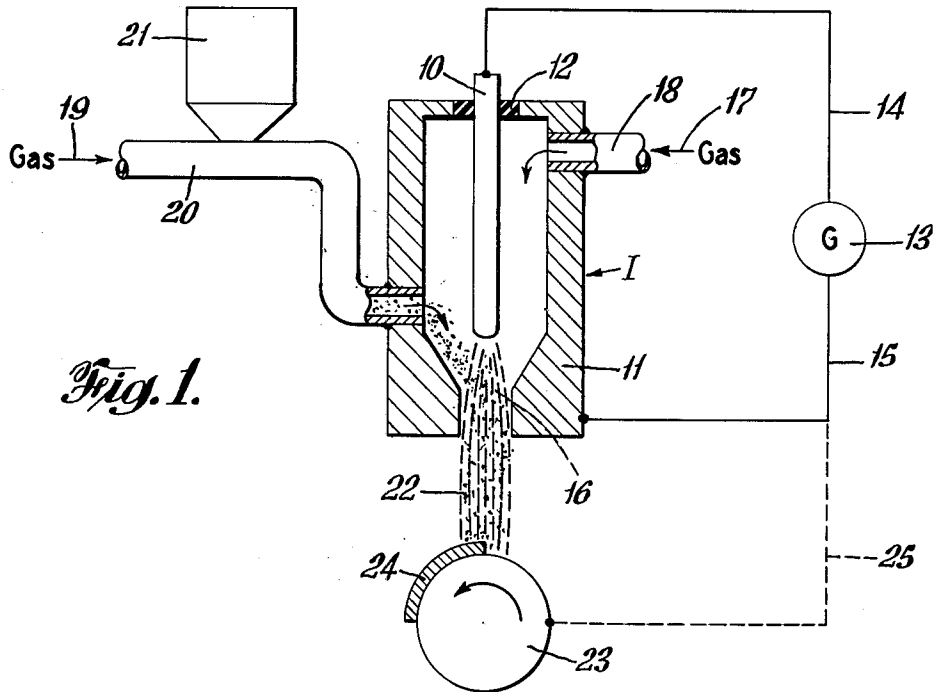


Fig. 1.

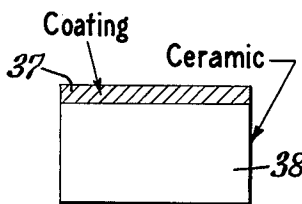


Fig. 2.

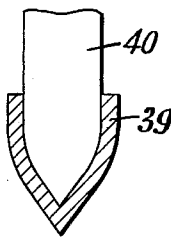


Fig. 3.

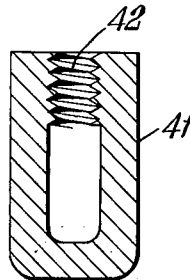


Fig. 4.

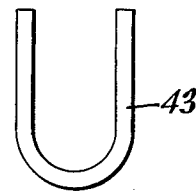


Fig. 5.

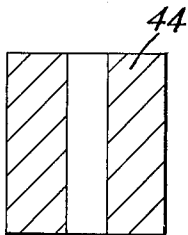


Fig. 6.

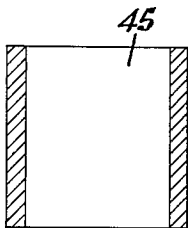


Fig. 7.

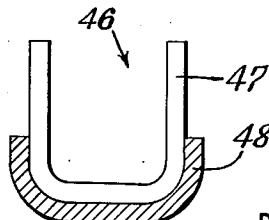


Fig. 8.

INVENTORS
DONALD M. YENNI
ROBERT G. RUDNESS
BY *Barnell R. King*
ATTORNEY

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2 Sheets-Sheet 2

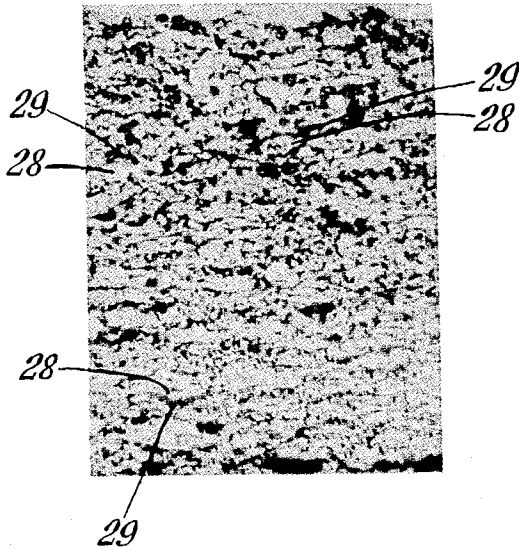


Fig. 9.

Fig. 10.

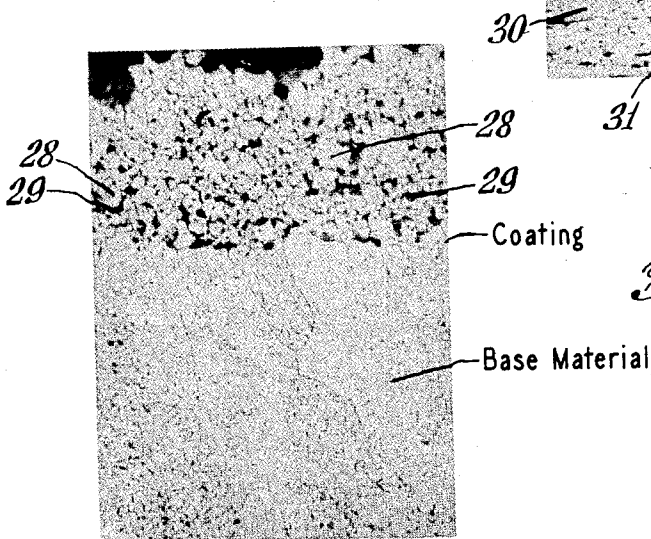
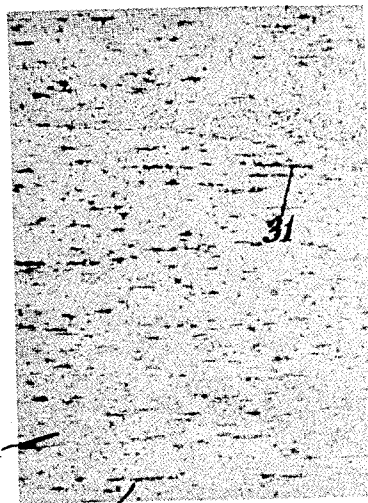


Fig. 11.

INVENTORS
DONALD M. YENNI
ROBERT G. RUDNESS

BY
Barnwell P. King
ATTORNEY

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3,075,066

ARTICLE OF MANUFACTURE AND METHOD OF MAKING SAME

Donald M. Yenni and Robert G. Rudness, Indianapolis, Ind., assignors to Union Carbide Corporation, a corporation of New York

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8 Claims. (Cl. 219-76)

This invention relates to novel articles of manufacture containing electron emissive materials and methods of making them.

Briefly, according to the present invention, there is provided an entirely novel article of manufacture comprising the combination of an electrically conductive material and at least one electron emissive material, said emissive material enabling the article to emit more electrons at a given temperature than does the pure electrically conductive material. Such novel combination is fabricated by accelerating and heating particles of the electrically conductive material and electron emissive material in a selected gas which is passed through a high pressure electric arc and applied to a suitable supporting member.

More particularly, according to the invention, there is provided a novel article of manufacture composed of a body containing or coated with a mixture of refractory metal, such as chromium, niobium, molybdenum, nickel, tantalum, titanium, or tungsten, plus highly emissive material, such as the emissive oxides calcia, ceria, baria, strontia, thoria, or yttria; fabricated by such arc accelerated coating process. In particular, novel bodies containing major amounts of emissive metal oxide can be fabricated according to the present invention which could not be formed by any prior art methods known to us.

A specific novel modification of the present invention is an electrode composed of material such as tungsten which has a thin, dense, lamellar adherent coating of refractory metal plus emissive metal oxide.

Novel bodies of the invention are useful as welding electrodes, hot cathode emitters for electronic equipment, and arc or spark erosion-resistant electrodes.

The electron emissivity of welding electrodes and cathode emitters can be increased by the incorporation therein of minor amounts of emissive materials, such as metals, metal compounds and metal oxides, such as thoria, calcia, baria, yttria, strontia, ceria, and mixtures thereof. Bodies containing such emissive materials can be formed by slip-casting, sintering, and other powder metallurgy techniques. Sintered bodies are often formed into finished shapes by swaging. As a general rule the higher the emissive material content, the more difficult the swaging operation. In commercial practice the upper limit for emissive oxide in swaged materials has been about 10% by weight.

Novel bodies containing emissive materials, such as emissive metals, metal alloys and metal compounds such as metal oxides, having a broad composition range can be fabricated directly according to our invention by the arc accelerated plating process.

In the drawings:

FIG. 1 is a diagrammatic view of equipment illustrating the invention;

FIG. 2 is a view in side elevation of a ceramic base provided with a tungsten-yttria coating that is shown in cross section;

FIG. 3 is a similar view of a stick electrode, the end portion of which is provided with a tungsten-yttria coating;

FIGS. 4-7 are views in cross section and elevation of variously shaped bodies of the invention;

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FIG. 8 is a view similar to FIG. 2 of an electronic member illustrating the invention;

FIG. 9 is a photomicrograph of a cross section of body of the invention in the as-formed condition;

FIG. 10 is a similar view of the prior art; and

FIG. 11 is a similar view of a body like that of FIG. 9 after heat treatment.

As shown in FIG. 1, the heat source comprises an arc torch 1 consisting of a central electrode 10 and a nozzle electrode 11 separated from each other by an electrical insulator 12. Electrical supply 13, which can be direct current-straight polarity, direct current-reverse polarity, or alternating current, is connected between electrodes 10 and 11 by lines 14 and 15. Upon completion of such connection an arc 16 is initiated. Selected torch gas stream 17 enters through inlet tube 18 and passes out through nozzle 11. An additional selected gas stream 19 enters the arc torch through tube 20. Coating material in the form of particles in hopper 21 drops in controlled amounts into gas stream 19 and the gas stream plus coating particles pass out through the nozzle electrode 11 where they are heated by arc 16. The gas stream is accelerated as it passes out through the nozzle and thus accelerates the coating material. The accelerated and heated gas plus coating material form effluent 22 which impinges onto the workpiece 23 to deposit a coating 24. The equipment shown is used to deposit a coating on a rotating support. A flat surface or surface of other contour can also be coated by traversing through the torch effluent.

The electrical connection 25 from power supply 13 to workpiece 23 is alternatively used when a transferred (work-in-circuit) arc is desired. An electrically conductive workpiece is necessary for this latter process.

The gas streams 17 and 19 are selected so as to be inert both to the workpiece and the coating material. In such way bodies of controlled composition can be formed. In particular, gases such as argon, helium, hydrogen and nitrogen are desirable. A reactive gas, however, might be used, if desired, provided that the arc torch equipment is properly protected.

A suitable base material can thus be coated with a mixture of refractory metal plus emissive oxide or a refractory metal can receive a coating of pure emissive oxide. The base material can be either an electrical conductor or non-conductor as desired.

The following examples describe the application of emissive coatings and operational results of the coated product.

Example 1

A coating 37, FIG. 2, of tungsten-yttria was applied to a ceramic base 38 by passing 6.2 grams per minute tungsten powder containing 3 weight percent yttria suspended in a 50 c.f.h. argon stream through a non-transferred arc torch operated with an arc of 100 amps. and 53 volts drawn between a central electrode and a nozzle electrode. An additional 50 c.f.h. argon gas passed down through the torch to shield the inner torch electrode. The 100 c.f.h. total gas stream plus coating particles passed out through the 1/8-inch diameter orifice in the torch nozzle electrode. The distance from torch nozzle to ceramic base was 3/8-inch.

The resulting coating was then connected as an electrode in a high-frequency spark circuit and was operated for one hour without failure.

Example 2

A thin coating 39, FIG. 3, of tungsten-yttria was applied to a 1/8-inch diameter pointed tungsten stick electrode 40 by passing 6.0 grams per minute tungsten powder containing 10 weight percent yttria in a 50 c.f.h. argon carrier

gas stream through a non-transferred arc torch operating at 100 amps. and 53 volts. This gas-powder stream plus 50 c.f.h. argon shielding gas passed out through the 3/16-inch diameter torch nozzle. Distance from torch nozzle to base material was 1/2 inch.

Such coated electrode was operated as an electric arc cathode up to 500 amps. (DCSP) without melting. Uncoated pointed tungsten electrodes failed under comparable conditions. Our procedure can also be used to coat worn electrodes to rejuvenate their useful life.

An alternate procedure is to apply a coating onto a pattern and then remove the pattern to form a shaped body having the desired composition. FIGS. 4-7 illustrate variously shaped bodies of the present invention containing emissive metal oxides.

The body 41 of FIG. 4 is hollow and is internally threaded at 42. FIG. 5 shows a body 43 of U-shape. The member 44 of FIG. 6 is tubular; as is member 45 of FIG. 7. FIG. 8 illustrates an electronic member 46 in which a coating 48 containing emissive metal oxide is applied to a support 47 which is also a component part of the electronic member.

One of the advantages of using an arc accelerated coating process for fabrication of such novel articles is the control obtained over the coating composition. The arc torch using an inert shielding gas is a chemically inert heat source. Therefore the coating composition is determined primarily by the coating feed material minus any vaporized material. A coating or body of controlled varying composition can thus be obtained. For example, pure tungsten can be applied as a coating. Gradually additional emissive oxide or oxides could be added to the feed material and the tungsten content decreased. The resulting body formed could thus have an increasing emissive oxide content along a radial direction if so desired. As another modification a coating containing emissive material might only be applied to selected areas on the surface of a support.

Laminated articles of the present invention can also be fabricated by forming a coating or body of refractory metal, then alternately applying coatings of emissive metal oxide and refractory metals or mixtures thereof.

The following table indicates the variety of materials which have been added to tungsten and applied as a coating according to the invention. In addition to tungsten, other refractory metals can be used, such as molybdenum, nickel, chromium, niobium, tantalum, and titanium.

TUNGSTEN COATINGS WITH VARIOUS ADDITIVES

Oxide	Additive Content Original Powder (Wt. Percent)	Additive Content Coating (Chemical Analysis, Wt. Percent)
Y ₂ O ₃	3	2.2
Y ₂ O ₃	10	6.6
Y ₂ O ₃	30	26.4
CeO ₂	3	1.7
ThO ₂	1	0.01
ThO ₂	3	0.09
Al ₂ O ₃ -BaO-CaO	10(3 1/4 each)	10.0

The refractory metal-emissive material, such as metal oxide, coatings and formed bodies of the present invention have a characteristic lamellar microstructure in their as-formed, unswaged and non-drawn state composed of irregularly shaped microscopic leaves overlapping and interlocking with each other. When a mixture of refractory metal and emissive material is used, the resulting coating or formed body of the present invention has a characteristic microstructure composed of irregularly shaped microscopic leaves of emissive material dispersed among and interlocking with similarly shaped microscopic leaves of refractory metal.

FIG. 9 is a photomicrograph at 500 diameters magnification of a cross section of a body of the present invention in the as-formed condition. The irregular shaped microscopic leaves 28 are the electrically conductive material, such as tungsten. The irregular shaped microscopic leaves 29 interlocked therewith are the emissive metal oxide, such a yttria. Prior art bodies formed by slip-casting, sintering, powder metallurgy and swaging techniques did not have this lamellar microstructure

FIG. 10 shows a photomicrograph at 500 diameters magnification of a cross section of a prior art swaged tungsten electrode containing minor amounts of emissive metal oxide. The tungsten grains 30 and the fibers of emissive oxide 31 are seen to be neither like microscopic leaves nor interlocking. Even though the chemical composition may be similar, the articles of the present invention are therefore characteristically different in microstructure from known prior art materials.

In addition, finished bodies of the present invention can have emissive oxide content far above that of the prior art due to the arc accelerated fabrication technique which does not require swaging or drawing.

FIG. 11 shows a photomicrograph at 500 diameters magnification of a cross section of a body similar to that of FIG. 9 which has been heat treated to recrystallize the refractory metal and to change the dispersed emissive metal oxide into irregularly shaped nodules.

What is claimed is:

1. Process of making an electrode containing refractory metal and electron emissive material which comprises accelerating and heating particles of said metal and emissive material in a non-swirling stream of selected gas which is passed through a high pressure electric arc at a current of the order of 100 amperes and a potential of the order of 50 volts, said accelerated and heated particles being then applied to a supporting member in a coherent mass.
2. Process of fabricating an electrode composed of refractory metal and metal oxides, which comprises simultaneously discharging a stream of inert gas, a high pressure arc, and a mixture of refractory metal and substantially unvaporized but highly heated metal oxide particles as an extremely hot effluent from an electric arc torch, applying such effluent to a support until there is built up thereon a composite composed of microscopic lamellules of such particles that are welded one to another without any change in the original purity of the refractory metal and metal oxide constituting such particles by virtue of the inert value of such gas and the kinetic energy of such application.
3. Process of fabricating an electrode composed of refractory metal and metal oxide, which comprises simultaneously discharging a stream of inert gas and a mixture of substantially unvaporized but highly heated refractory metal and metal oxide particles as an extremely hot effluent from an electric arc torch in which a high pressure arc is drawn between the end of a central electrode and a nozzle electrode surrounding such central electrode, applying such effluent to a support until there is built up thereon a composite composed of microscopic lamellules of such particles that are welded one to another without any change in the original purity of the refractory metal and metal oxide constituting such particles by virtue of the inert value of such gas and the kinetic energy of such application.
4. Process as defined by claim 1, in which the ratio of refractory metal particles to metal oxide particles is changed during the application of the mixture to vary the emissive and conductive properties of the resulting composite.
5. Process of fabricating an electrode which comprises depositing a layer of emissive metal oxide on a support composed of refractory metal by applying to said support an extremely hot effluent comprising a stream of inert gas and particles of said metal oxide which had

been heated by a high pressure arc, said layer of metal oxide consisting of interlocking and overlapping lamellules of metal oxide welded one to another and to said support, which lamellules are of the same purity as the original particles.

6. Process of fabricating an electrode which comprises depositing alternate layers of refractory metal and emissive metal oxide to a suitable support by alternately applying thereto an extremely hot effluent comprising an inert gas stream and refractory metal particles and an extremely hot effluent comprising an inert gas stream and emissive metal oxide particles, said effluents each having been heated by a high pressure electric arc.

7. An electrode made according to the process of claim 5, in which the support is a ceramic base.

8. An electrode made according to claim 5, in which the support is composed of tungsten and the emissive oxide is selected from the class consisting of thoria and yttria.

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