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ART OF PRODUCING EMITTER-TYPE ELECTRODE STRUCTURES

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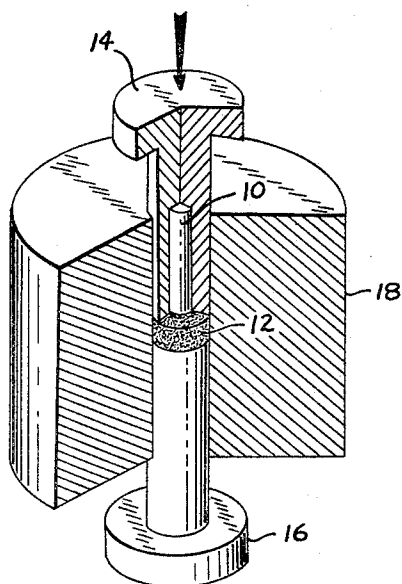


FIG. 1

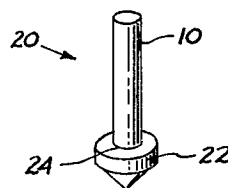


FIG. 2

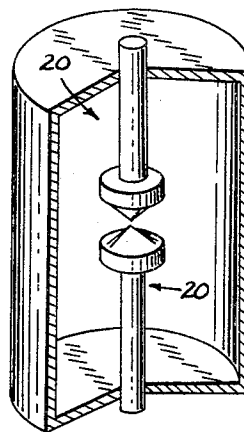


FIG. 3

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ART OF PRODUCING EMITTER-TYPE ELECTRODE STRUCTURES

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Electric Products, Inc., a corporation of Delaware
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7 Claims

ABSTRACT OF THE DISCLOSURE

Emitter-type electrode structures are made with an emissive head of shaped, sintered material that is capable, during use, of emitting electrons under high voltage from the upper surface thereof. On the opposite side of the head a lead (i.e., lead-in conductor), formed of an electrically conducting metal, has one end embedded in and integral with the said head. This lead or stem, which has a diameter less than that of the head, can be a refractory metal, e.g., tungsten, molybdenum or an alloy of two or more refractory metals; or it can be an expansion-type alloy. Use of the latter eliminates the need to employ a plurality of glasses at the point of seal in making graded glass-to-metal seals when the electrode structure is fixedly positioned within a sealed glass or ceramic envelope.

CROSS REFERENCE TO RELATED APPLICATION

This application is a division of S.N. 657,974, filed Aug. 2, 1967, assigned to the assignee of the present invention, now abandoned.

BACKGROUND OF THE INVENTION

The invention obviates prior brazing difficulties in fabrication since the need for brazing at or close to the emissive surface is eliminated. It also avoids failures or improper operation of devices (wherein the electrode structures are employed) as a result of bleeding, during operation, of the braze material onto the emissive surface.

Details are given of materials used and manufacturing technique including pressing and sintering conditions.

The electrodes are useful, for example, in forming spark-gap assemblies; in safety devices employed in aircraft-engine ignition systems; in runway flash-approach systems; and in low- or high-pressure gas tubes.

This invention relates broadly to the art of producing emitter-type electrode structures, which also may be designated as emissive (i.e., electron-emissive) electrode structures. More particularly it is concerned with the fabrication of an electrode that is especially adapted for use as a high-voltage cold electrode (anode or cathode) element in such devices as, for example, spark-gap assemblies, flash lamps, flash tubes and the like. The scope of the invention includes both article and method features.

Emitter-type electrodes are commonly made from powdered materials by techniques that involve pressing and sintering. Typically they consist of an emissive (including potentially emissive) material that is dispersed in a porous refractory metal matrix, e.g., tungsten, molybdenum, or mixtures of either or both with other refractory metals; or, alternatively, such electrodes can be described as consisting essentially of a porous refractory metal matrix impregnated with the emissive material. The emissive material can be, for instance, a compound of an alkaline-earth metal, e.g., an oxide, carbonate,

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aluminate or orthosilicate either singly or in certain combinations.

It will be understood, of course, by those skilled in the art that by "emitter-type" electrode or electrode structure is meant an electrode that functions during use, more particularly under high-voltage application, to emit electrons. By "cold" electrode or electrode structure is meant an emitter-type electrode device having an emissive surface that, in use, emits electrons only under high voltage as contrasted with an electrode or electrode structure that, in use, is continuously heated by a filamentary conductor. An example of the latter is, for example, a dispenser cathode.

Sintered electrodes, specifically sintered cathodes, usually have the general form of a disc. The emitting surface may be, for example, flat, concave, convex or conical. The opposite side is usually flat. One end of a lead (i.e., lead-in conductor) consisting of an electrically conducting rod or wire, having a diameter less than that of the electrode, heretofore has been attached to the flat surface of the electrode by brazing.

Because of the close physical relationship between the lead and the electron-emissive surface, this brazing step has been a very troublesome operation. Furthermore, the brazing problems increase as the percentage of alkaline-earth emissive material in the electrode composition, which may be from about 5% to about 20% by weight thereof, is increased to a percentage near to and above the usual amount of about 10 weight percent of the aforesaid composition. An even more serious problem is often encountered during operation of the article or device, containing the electrode element, as a result of bleeding of the braze material onto the emissive surface. Such bleeding can cause the device to operate improperly.

OBJECTS AND SUMMARY OF THE INVENTION

It is a primary object of the present invention to provide an emitter-type electrode structure, more particularly a cold-electrode composite structure, whereby the above described brazing difficulties are obviated by eliminating the need for brazing at or close to the emissive surface.

Another object of the invention is to provide a method of fabricating an emitter-type electrode structure of the kind with which this invention is concerned.

Other objects of the invention will be apparent to those skilled in the art from the following more detailed description and from the appended claims.

The objects of the invention are attained by constructing an emissive-electrode (specifically a cold-electrode) composite body in the form of an integral structure wherein the head or electrode, more particularly cathode, is comprised of the emissive material, and an electrically conducting stem or stud is formed integral with said head or electrode.

Briefly described, the article is constructed by pressing powdered, moldable, emissive, electrode material about the end of an electrically conducting lead. Molding pressures may range from about 10,000 to about 80,000 p.s.i.g. or more as may be required with the particular materials being pressed and structure being fabricated. During subsequent sintering of the pressed assembly, the electrode or head and the lead or stud become fixedly attached or united to each other thereby forming an integral structure.

The electrically conducting lead (or stem or stud as it also may be designated) comprises or consists essentially of, for instance, refractory electrically conducting metal, e.g., tungsten, molybdenum, alloys or composites thereof, or alloys or composites of tungsten and/or molybdenum with other refractory metals; or, for many applications, the stem or stud comprises or consists essentially

of an expansion-type alloy. Examples of such alloys, which are well known to those skilled in the art, are alloys containing iron and nickel such as, for example, Kovar (Ni 23-30%, Co 30-17%, Mn 0.6-0.8%, and the balance Fe); Fernico (an iron-nickel-cobalt alloy, nominally Fe 54%, Ni 28% and Co 18%); and Invar, which is a ferro-magnetic nickel-iron alloy containing 36% Ni together with minor amounts of carbon, manganese and silicon (maximum amount 1%), and the remainder being iron.

In some cases the lead may be a composite lead consisting of a combination of a refractory metal and an expansion-type alloy; or the lead may be a clad refractory metal such as nickel-clad tungsten or molybdenum.

The novel features that are characteristic of the invention are set forth in the appended claims. The invention will be best understood from the following more detailed description, especially when considered in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view, partly in section, of a double-acting die in the step or act of pressing an emitter-type electrode assembly which is then sintered to produce a structure embodying the invention;

FIG. 2 is a similar view illustrating one form of an emitter-type electrode structure, more particularly a cold electrode, embodying the invention; and

FIG. 3 is a perspective view, partly broken away, that illustrates an electrical device wherein a pair of cold electrodes (such as is illustrated in FIG. 2), with the electrodes facing each other, is functioning as a spark gap.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In producing the composite structures of this invention, (a) powdered emissive material (examples of which have been given hereinbefore) and (b) tungsten and/or molybdenum and/or other refractory metal powder are employed in the approximate weight percentages of from 5-20% of the former to from 95-80% of the latter. These ingredients, together with a small amount (e.g., from about 0.5 to about 3% of the weight of the primary components) of a temporary organic binder, for instance from 1 to 2 weight percent (on this same basis) of a wax or wax-like substance of natural or synthetic origin, are first thoroughly mixed together. When the organic binder is, for example, paraffin wax (in slivered or other suitable form) sufficient heat is generated during mixing to melt the paraffin thereby facilitating its more uniform dispersion throughout the mix. With higher melting waxes or wax-like substances it may be necessary to heat the mixture while admixing in order to effectively disperse the binder.

At the end of the mixing period the admixture is allowed or caused to become harder, for instance by permitting it to stand undisturbed until it reaches room (ambient) temperature. Or, hardening can be accelerated by placing the mixture immediately after the mixing step has been completed in a cold room or box thereby to bring it more quickly to ambient temperature. The resulting material is then comminuted to form a powder that flows freely, after which it is pressed (as is illustrated in FIG. 1) onto one end of an electrically conducting metal lead or stud 10 to form the head 12.

Illustrative examples of other organic binders in addition to paraffin wax that may be employed in producing the moldable composition containing the primary components, viz., (a) and (b), supra, are the waxy, high-molecular-weight polyethylene glycol monoesters of long-chain fatty acids such as oleic, palmitic and stearic acids; and solid polyvinyl alcohol. Carbowax 6000 (Union Carbide Chemical Company, New York, N.Y.) is typical of the various synthetic waxes that can be employed as

the temporary organic binder. Mold lubricants in the usual small amounts, and additives that lower the sintering temperature of the pressed assembly also can be incorporated into the moldable composition as desired or as conditions may require.

The pressing unit shown in FIG. 1 consists of an upper plunger 14, a lower plunger 16 and a body portion or die 18. As is indicated in FIG. 1, with one end of the lead or stud embedded in the mass of moldable electrode composition to a desired depth, pressure is applied to the said composition through plungers 14 and 16. The depth to which the lead or stud is embedded in the moldable electrode material is at least sufficient to cause it to be firmly and rigidly united to the head, as an integral part thereof, at the end of the pressing and sintering operations.

The double-acting die shown in FIG. 1 is made of hardened steel such as "Stentor" steel or a metal carbide composition. For simplicity of illustration only a single, simple die arrangement has been shown. However, it will be readily understood by those skilled in the art that the process can be either semi- or fully-automated on either a single or a multi-cavity press. The stems or studs can be fed to the pressing unit by hand or automatically; or wire can be cut and fed during the cycle of operations on an automatic press in order to form the stem or stud, one end of which (i.e., the end nearest to the moldable electrode composition) is then firmly embedded in the said composition.

Any desired configuration of the head can be pressed, e.g., flat, concave, convex, pointed or conical, etc. Likewise the diameters and lengths of the studs can be varied as desired or as conditions may require.

After pressing the moldable electrode material onto one end of the stud, the resulting composite is fired (i.e., sintered) in a reducing atmosphere, usually hydrogen. The temperatures employed during the sintering step depend upon the particular constitution of the metal stud and of the pressed electrode composition of which the head is formed.

When refractory metals and alkaline-earth materials only are involved, sintering temperatures are usually within the range of from about 1100° C. to about 1800° or 1900° C. Sintering temperatures above 1300° C. but nearer to 1800° C. are most often used. The sintering time within the afore-mentioned temperature ranges, which are ranges of furnace temperatures, may vary from 1 to 2 hours to about 20 hours. The longer sintering times are needed at the lower temperatures in the afore-mentioned ranges.

In some cases it may be desirable to lower the sintering temperature below that which is normally used, for instance when the stud is formed of or comprises an expansion-type alloy. This can be done, for example, by incorporating a small amount (usually less than 1%, e.g., from 0.2 to less than 0.5% by weight) of an activated sintering compound into the electrode composition of which a head thereof is to be pressed onto such a stud. Any of such materials, which also may be designated as "sintering activators," that are capable of lowering the sintering temperature of the moldable electrode composition previously described can be employed for this purpose. Examples of such activators are powdered alloys or admixtures containing iron and nickel in varying proportions (often also certain other metals), and more particularly powdered materials having the compositions (or the approximate compositions) of expansion-type alloys including those specifically identified hereinbefore.

The sintering of firing step increases the strength and density of the electrode or head and decreases its dimensions. This step also fixedly attaches the electrode, as indicated at 24 in FIG. 2, to the stem so that an integral structure is produced, and removes the temporary organic binder, e.g., wax.

Upon completion of the sintering step, the resulting structure 20 (FIG. 2) comprised of the stem or stud (e.g., wire or rod) 10 having one end embedded in and integral with the sintered head or electrode 22 is solvent washed. Examples of solvents that can be used are the various low-boiling organic liquids, e.g., alcohols such as methyl or ethyl alcohol; the various halogenated hydrocarbons, e.g., trichloroethylene; and liquid petroleum hydrocarbons such as pentane, hexane and heptane. The solvent washing is followed by, or advantageously is carried out concurrently with, polishing. For example, the sintered parts can be cleansed and polished by tumbling in alcohol with polishing stones for from ½ to 2 hours or more as desired or as may be required.

After drying, the finished part is ready for use as a component in electrical devices where electrodes are commonly employed, for instance as one of a pair of electrodes to form a spark gap as illustrated in FIG. 3; in safety devices employed in aircraft-engine ignition systems; in runway flash approach systems; in low- or high-pressure gas tubes; and for innumerable other applications.

It has been indicated previously that the lead-in conductor or stud 10 can be made of an expansion-type alloy and that, when this is done, the electron-emissive (i.e., electrode) moldable composition is advantageously modified to include a sintering activator to lower the sintering temperature of the "green" molded part. Finished sintered articles that are thusly made are especially useful for making direct "ceramic" (including glass)-to-metal such as are necessary when the emitter-type electrode of this invention is sealed in a high temperature-resistant envelope of a ceramic material such as fused silica. The practical advantages of this will be apparent to those skilled in the art: it eliminates the necessity of using a plurality (e.g., two or three) different glasses of different expansion coefficients to make a so-called "graded" glass-to-metal seal; or, alternatively, the necessity of using a sleeve of an expansion type alloy in making a glass-to-metal seal.

The device illustrated in FIG. 3 shows a pair of electrodes 20 forming a spark-gap assembly (similar to that used in aircraft ignition systems) that is encased within a glass envelope 26 and sealed therein at 28 and 30, the joints or seals being formed between the lead-in conductors or studs 32 and 34, respectively, and the ends of the envelope 26.

Instead of the particular construction illustrated in FIG. 3, the free ends of the studs 32 and 34 may be brazed at a substantial distance from their emissive heads to leads formed of the same or a different electrically conducting metal, the latter then being passed through the ends of the glass envelope and sealed to its end walls.

In order that those skilled in the art may better understand how the present invention can be carried into effect, the following example is given by way of illustration and not by way of limitation. All parts and percentages are by weight unless otherwise stated.

This example illustrates the fabrication of a 0.375" D. x 0.125" conical-surfaced head of 90% W and 10% BaAl₂O₄ on a 0.188" D. x 1.00" tungsten lead (i.e., stem or stud). The dimension 0.125" is the total thickness of the head including the point.

(1) To a high intensity mixer are charged and therein thoroughly admixed: 450 g. tungsten powder having an average diameter of about 4 microns; 50 g. powdered barium aluminate (200-mesh particle size, U.S. Standard sieve series), and 7.5 g. slivered paraffin wax.

(2) The resulting substantially homogeneous admixture is removed from the mixer and allowed to become harder.

(3) The mixture from step (2) is forced through a 20-mesh screen (U.S. Standard sieve series) to provide a powder that flows freely.

(4) The powder is allowed to flow into the cavity of

a double-acting die mounted in a rotary mechanical press.

(5) Simultaneously with step (4) a tungsten lead in the form of a 1.050"-long rod is placed in the upper punch or plunger of the aforesaid press.

(6) The press is actuated such that the powder is pressed about the end of the lead at a pressure of about 40,000 p.s.i.g. This operation is illustrated in FIG. 1.

(7) After the part has been ejected from the press, it is subjected to a sintering operation. A satisfactory procedure consists of the following sintering and finishing steps:

(a) Embed the part in ZrO₂ sand contained in a molybdenum tray.

(b) Stoke the tray into the hot zone of a furnace operating at about 1800° C. under an atmosphere of flowing (ca. 30-40 c.f.h.) hydrogen. This requires about one hour.

(c) Hold the tray in the hot zone for 6 hours.

(d) Stoke the tray into the cool zone.

(e) Hold the tray in the cool zone for about one hour.

(f) Remove the tray from the cool zone and remove the finished part from the tray.

(g) The collected, sintered parts are tumbled in methanol while in contact with polishing stones for about 1 hour.

FIG. 2 illustrates, greatly enlarged, the finished part. The lead or stud is embedded 0.050" into the electrode or head.

I claim:

1. The method of making an emitter-type electrode structure which includes the steps of:

(A) molding under a pressure within the range of from about 10,000 to about 80,000 p.s.i.g., about one end of a lead formed of electrically conducting metal, a moldable composition comprising by weight, (a) from about 95 to 80% of powdered refractory metal, and (b) from about 5 to 20% of alkaline-earth emissive material, to form a head on the lead having a diameter larger than that of the lead and with the lead firmly embedded in the head; and

(B) sintering the resulting molded structure in a reducing atmosphere at a temperature within the range of from about 1100° C. to about 1900° C. for a period of time sufficient to form the structure.

2. The method as in claim 1 wherein the moldable composition contains from about 0.5 to 3%, based on the total weight of (a) and (b) of a temporary organic binder; the reducing atmosphere is hydrogen; and the sintering temperature is within the range of from about 1100° C. to about 1800° C. for a period of from 1 to about 20 hours.

3. The method as in claim 2 wherein the refractory metal powder is tungsten powder; the alkaline-earth emissive material includes a barium compound; the organic binder is a wax or wax-like material in an amount corresponding to from about 1 to 2% of the total weight of (a) and (b); and the lead about one end of which the moldable composition is molded is a tungsten wire or rod.

4. The method as in claim 2 wherein the moldable composition consists essentially of, by weight, (a) about 90% tungsten powder, (b) about 10% barium aluminate, and (c) paraffin wax in an amount corresponding to from about 1 to 2% of the total weight of (a) and (b); the lead about one end of which the moldable composition is molded is a tungsten wire or rod; and the sintering temperature is about 1800° C. for a period of about 6 hours.

5. The method as in claim 4 wherein the molding pressure is about 40,000 p.s.i.g.

6. The method of making an emitter-type electrode structure of the kind defined in claim 1 which includes the steps of:

(A) forming a substantially homogeneous admixture of the following ingredients in the following approximate weight ratios:

- 450 parts tungsten powder having an average diameter of about 4 microns,
 50 parts barium aluminate (200-mesh particle size)
 7.5 parts slivered paraffin wax;
- (B) removing the resulting admixture from the mixer in which mixing was effected and allowing or causing it to become harder;
- (C) comminuting the hardened composition from step (B), in order to provide a powder that flows freely, by forcing it through a 20-mesh screen;
- (D) allowing the powder from step (C) to flow into a cavity of a double-acting die mounted in a rotary mechanical press;
- (E) simultaneously with step (D) placing a tungsten lead in the form of a wire or rod in the upper plunger of the aforesaid press;
- (F) actuating the press so that the powder from step (D) is pressed, at a pressure of about 40,000 p.s.i.g., about the end of the aforesaid lead that is nearest to the powder;
- (G) ejecting the molded part from the press; and
- (H) subjecting the molded part from step (G) to a sintering operation which includes heating said part in a hydrogen atmosphere at a temperature of about 1800° C. for a period of about 6 hours.
7. The method as in claim 6 wherein the sintering operation consists of:
- (A) embedding the molded part in ZrO₂ sand contained in a molybdenum tray;
- (B) stoking the tray, over a period of about 1 hour, into a hot zone maintained at about 1800° C. under an atmosphere of hydrogen flowing at the rate of about 30-40 c.f.h.;

- (C) holding the tray in the hot zone for about 6 hours;
- (D) stoking the tray directly into a cool zone; and
- (E) holding the tray in the cool zone for about 1 hour; after which
- (F) the tray is removed from the cool zone and the sintered part is removed therefrom, and
- (G) the sintered part is cleaned and polished.

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