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METHOD OF PRODUCING A SOLDERABLE METALLIC COATING ON A CERAMIC BODY AND OF SOLDERING TO THE COATING

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The present invention refers to a method for producing heat resistant soldered seams between metals and fire-resistant, non-metallic materials (e. g. ceramics, quartz, graphites, carbides, etc.), or between two fire resistant, non-metallic materials. Such seams may be used in the production of diverse apparatuses and devices, where strong and heat-resistant connections between parts of the afore-mentioned materials must be obtained. Since furthermore such seams must be made vacuum tight and may not contain any glassy components, they are especially fit for use as connections for metal and ceramic details in electron-discharge and vacuum devices, which are to work at very high frequencies and/or high temperatures, and other electric devices.

In order that such a seam may be made by means of a hard solder, the non-metallic body must be provided with a particularly well adherent, solderable metallic coating. It is known that a well adherent metal coating on a non-metallic body can be obtained by sintering onto the non-metallic seam surface a thin layer of molybdenum, tungsten or rhenium, possibly with addition of iron or manganese. The sintering operation is effected in an atmosphere of protective gas. In order that a strong connection be obtained between the sintered metal layer and the non-metallic surface, especially ceramics, the furnace atmosphere must however absolutely comprise a determined, though very small quantity of oxygen. Owing thereto, there arises on the sintered surface of the metal coating an oxide film, which, however invisible, cannot, due to the great affinity of the said transition metals with oxygen, be removed even by a possible subsequent treatment with hydrogen gas at a temperature lower than the deformation temperature of most of the non-metallic materials in question, for example ceramics. Said oxide layer seams prevent the usual hard solders from flowing evenly over the sintered surface of the metal coating, said surface having therefore to be coated with a thin layer of some other easily deoxidizable and easily solderable metal, as nickel or copper. In order to obtain with certainty a strong and vacuum tight seam, said metal coating must before assembly be sintered onto the foundation coating in a reducing atmosphere.

The afordescribed method for producing well solderable metallic coatings on non-metallic materials is thus characterized by the following two difficult moments: (1) the double metallizing of the non-metallic material, and (2) the necessity to regulate rather accurately the oxygen percentage of the protective gas.

The chief object of the present invention is to eliminate the over-metallizing of the metallic foundation coating without jeopardizing either its power of adhesion or its solderability.

A further object of the invention is to introduce the quantity of oxygen necessary for the fastening of the metal coating to the non-metallic material in such a manner, that the protective gas is kept free from oxygen.

Another object of the invention is to achieve, simul-

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taneously with the metallizing of the non-metallic body, a hard solder seam between said body and the other pertaining metallic or non-metallic body.

It is a further and more special object of the invention to achieve a simplified method for vacuum tight hard soldering of metals and metallized ceramics, or of two metallized ceramic bodies, a method, which can advantageously be applied in the production of electron-discharge devices or other electric devices, where strong and heat-resistant, vacuum tight seams are to be achieved.

The principle of the invention for eliminating the double metallizing of the non-metallic material derives from the discovery that, if to molybdenum, tungsten, rhenium or some other refractory transition metal from the groups 4 to 6 of the periodical system, the characteristic property of which is, that under suitable sintering conditions they form a very strongly adherent but difficultly solderable metal layer on non-metallic materials, is added a suitable quantity of some easily deoxidizable and well solderable metal, as nickel or cobalt, a well adherent sinter layer is obtained, having such good soldering properties, that an over-metallizing of said layer is not necessary.

Another principle of the invention relating to the possibility of obtaining a well adherent metal coating by sintering also in an atmosphere of protective gas free from oxygen is based on the fact, that the small quantity of oxygen, which is required in order to produce a strong connection between the sintered metal layer and the ceramic, is added in the shape of a metal oxide, which is mingled with the metal powder to be sintered onto the ceramic. Said oxygen carrier suitably consists of an oxide of any of the metals constituting the foundation component of the sintered layer. In order not to consume unnecessarily the added oxygen, the sintering should suitably take place in a neutral atmosphere, and the subsequent cooling take place in a reducing atmosphere.

Though the invention is not going to be limited by any theory concerning its manner of action, it should be stated as an explanation that the improved soldering properties of a metal coating achieved according to the invention seem to depend on the purposely added small quantity of oxygen, which has been evenly distributed in the powder layer, being unable to form any continuous oxide film on the surface of the coating, and this all the more as said coating, besides the difficultly oxidizable metal component, also comprises an easily deoxidizable component, which, even in case it were oxidized during the sintering process in neutral furnace atmosphere, is reduced again to metal at cooling in reducing furnace atmosphere. The condition that the atmosphere during sintering must be free from oxygen excludes the possibility of such considerable oxide films being formed, as can prevent a direct hard soldering on the coating.

The metallizing of non-metallic materials according to these principles is, in relation to the known methods, where owing to the difficulty of soldering the foundation coating said coating must be coated with a layer of another well solderable metal, both simpler and cheaper.

The procedure to produce the metal coating on a non-metallic body is the following: on the well cleaned non-metallic seam surface a thin layer of the component of the metal coating is applied in the shape of a fine-grain powder or a paste. According to the invention the powder mixture must have the following composition:

60-95 parts of a transition metal with high melting point from the groups 4 to 6 of the periodical system, for example molybdenum or tungsten, or rhenium,
0-5 parts iron,
5-40 parts, preferably about 15 parts, of easily deoxidizable heavy metal, as nickel or cobalt,

0.05-0.5% preferably about 0.2%, oxides of any of the aforesaid metals, preferably nickel or cobalt oxides.

When the layer is to be applied in the form of a paste (or paint) a suspension means as lacquer, a solution of a plastic, vegetable oil, alcohol, water, etc., is added. Said suspension is applied by means of painting or spraying.

The non-metallic body coated with powder or paste is heated with a suitable speed to a temperature of 1200 to 1350° C. in an atmosphere of protective gas free from oxygen or in a vacuum and is kept at maximum temperature during 30-60 minutes to sinter the metal powder. The whole is thereafter cooled, preferably in a reducing atmosphere.

Under certain circumstances it is also possible to achieve simultaneously both the metallizing of the non-metallic detail and the hard soldering thereof to the pertaining metallic or non-metallic detail. The condition is that a hard solder with a melting point above 1200° C. be used, for example an alloy of copper and nickel containing about 25% nickel. The solder may be fixed either in or above the seam in the shape of a metal sheet or wire or else be applied in the shape of a paste. The whole must thereafter be heated up to a temperature lying about 50° C. higher than the melting point of the solder. The heating must take place in an atmosphere free from oxygen or in a vacuum.

It is obvious that, besides the aforesaid modifications, different other changes and modifications may also be made without the principle of the invention being departed from.

I claim:

1. The method which comprises applying to the surface of a ceramic member a layer of a powdered mixture consisting essentially of 60-95 percent of a refractory metal selected from the class consisting of molybdenum, tungsten and rhenium, 5-40 percent of an easily deoxidizable metal selected from the class consisting of nickel and cobalt and 0.05-0.5 percent of an oxide of a metal of the aforesaid classes, heating said member and layer to a temperature of 1200-1350° C. for 30-60 minutes in an inert atmosphere to sinter said powders, and then cooling after sintering in a reducing atmosphere.

2. Process in accordance with claim 1 wherein the powdered mixture includes iron in an amount up to 5 percent.

3. A powdered mixture consisting essentially of 60-95 percent of a refractory metal selected from the class consisting of molybdenum, tungsten and rhenium, 5-40 percent of an easily deoxidizable metal selected from the class consisting of nickel and cobalt and 0.05-0.5 percent of an oxide of a metal of the aforesaid classes.

4. A powdered mixture in accordance with claim 3 which includes iron in an amount up to 5 percent.

5. Method of bonding a solderable element to a ceramic body which comprises metallizing the surface of the ceramic body by the method of claim 1, and soldering said element and said metallized surface.

6. Method of bonding a solderable element to a ceramic body which comprises metallizing the surface of the ceramic body by the method of claim 2, and soldering said element and said metallized surface.

7. Method of bonding ceramic bodies which comprises metallizing a surface of each of said ceramic bodies by the method of claim 1, and soldering said metallized surfaces.

8. Method of bonding ceramic bodies which comprises metallizing a surface of each of said ceramic bodies by the method of claim 2, and soldering said metallized surfaces.

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