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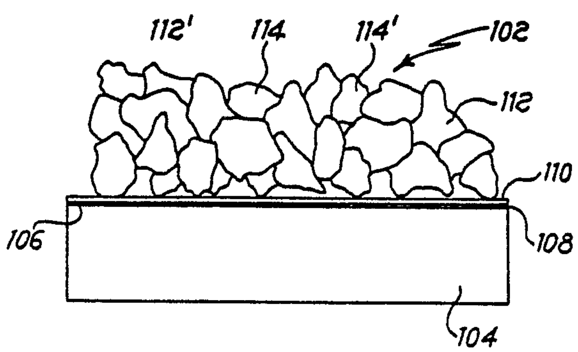
(54) **Non evaporable getter device incorporating a ceramic support and method for the manufacture thereof.**

(57) A porous non-evaporable getter device is described which comprises a ceramic support, a layer of sintered non-evaporable getter material and an intermediate electrically conducting layer at least partially diffused into the ceramic support and into the porous sintered getter layer. There also is described a method for the manufacture of such a getter device in which the ceramic support is coated with a thin conducting film on which is electrically deposited a thicker metallic layer which in turn is covered, by electrophoresis, a mixture of a non-evaporable getter material and an antisintering agent. The support is finally sintered to obtain the desired porous getter device and it is then cooled.

Fig. 1



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"NON EVAPORABLE GETTER DEVICE INCORPORATING A CERAMIC SUPPORT AND METHOD FOR THE MANUFACTURE THEREOF"

The present invention relates to a non-evaporable getter device comprising a ceramic support, as well as a method for the manufacture of such a device.

Non-evaporable getter devices are well-known in the art. They usually consist of a powdered metal or alloy which when heated to an elevated temperature, diffuse into the bulk a protective layer such that the surface of the particles become reactive towards a large number of gases.

In this active conditions they are capable of producing or maintaining a high vacuum.

Usually the non-evaporable getter material is held in a support such as, for instance, by pressing the powder into a U-shaped metal ring channel.

Another type of support has been described in US Patent 3,620,645 in which the getter material is pressure bonded onto the surface of a continuous metal strip. UK Patent Application GB 2,157,486 A describes the electrophoretic deposition of getter material onto a wide variety of supports.

One particular embodiment briefly described is a wire which has previously been coated with a ceramic insulating material such as alumina. The wire coated with alumina is used as one electrode in an electrophoretic coating bath in which there are suspended particles of the getter material. The getter material is electrophoretically deposited onto the ceramic coated wire. Unfortunately the use of such a support has several disadvantages. Firstly the alumina layer on the wire must be very thin otherwise it is very difficult to cause sufficient electric current to flow to effect the deposition. Due to the high electrical resistance of the alumina coating it is also very difficult to control the parameters of deposition, resulting in an uneven deposition. An additional difficulty is that during a subsequent sintering process the electrophoretically deposited getter material detaches from the ceramic support producing flakes and undesirable loose particles.

It is therefore an object of the present invention to provide an improved porous non-evaporable getter device free from one or more defects of prior art devices.

It is another object of the present invention to provide a porous non-evaporable getter device having a ceramic support in which the support may have any shape or thickness.

It is yet another object of the present invention to provide a porous non-evaporable getter device having a ceramic support in which during and after a sintering process the getter material remains firmly attached to the support.

It is a further object of the present invention to provide a method for the manufacture of a porous non-evaporable getter device having a ceramic support in which it is possible to accurately control the electrophoretic deposition characteristics.

These and other objects, advantages and characteristics of the present invention and its method of manufacture will become evident to those skilled in the art by reference to a preferred embodiment described as a non-limiting example with reference to the attached drawings in which:

FIGURE 1 is a diagramatic representation of a getter device of the present invention before being subjected to a sintering process;

FIGURE 2 is a diagramatic representation of a porous non-evaporable getter device of the present invention after being subjected to a sintering process;

FIGURE 3 is a cross-section of a prior art getter device showing detachment of porous non-evaporable getter material from a ceramic support; and

FIGURE 4 is a cross-section of a porous non-evaporable getter device of the present invention showing good adhesion of the non-evaporable getter material to the ceramic support.

It has surprisingly been found that if a metallic layer is provided between the ceramic support and the electrophoretically deposited non-evaporable getter material not only is it possible to accurately control the deposition characteristics of the getter material, but also after the sintering process the porous non-evaporable getter material is firmly held in contact with the ceramic support without any detachment.

In order to manufacture a porous non-evaporable getter device of the present invention, a ceramic support is coated with a thin electrically conductive film. The ceramic support may be of any ceramic material which is compatible with use in high vacuum, preferably alumina. It may be of any shape size or thickness. The thin conductive film may be of any conductive material such as tin oxide or other conductive oxides. It is preferable however to use a thin metal layer such as aluminium or copper. The ceramic may be coated with this thin metallic film by any known method such as electroplating or by deposition in vacuum. The thin metal film can be Ni, Cu, Ag, Mo or Fe but is preferably aluminium. Its thickness is preferably between 0.1 μm and 5 μm. The thin conductive film is then made to be one electrode of an electroplating bath. Upon this thin (preferably aluminium) film there is electroplated a thicker metallic film having a thickness of several micrometers and preferably between 5 µm and 50 µm. The electroplated metal film may be of any metal which is compatible with use in high vacuum such as Ti, Zr, Mo, Fe, Cu, Ag, Pt, Au but it is preferably nickel.

The thin conductive film and the thicker metal layer constitute an intermediate electrically conductive layer which could however be a single metallic layer.

The electroplated support is electrophoretically coated with a mixture of a particulate non-evaporable getter material and an antisintering material. The electrophoretic coating takes place according to a process as described in UK Patent application publication GB 2,157,486 A.

The particular non-evaporable getter material is any getter material suitable for the sorption of active gases in vacuum. It is preferably chosen from the group consisting of titanium, zirconium and their hydrides. Its particle size should be between 20-60 µm and preferably with an average size of 40 µm.

The antisintering material is in particulate form and is any material which is capable of hindering the sintering of the non-evaporable getter material. It is preferably chosen from the group consisting of graphite, refractory metals and zirconium based alloys. If a zirconium based alloy is used as an antisintering material, then it is preferably chosen from the group consisting of:

A. an alloy of zirconium with aluminium in which the weight percent of aluminium is from 5-30%;

B. an alloy of zirconium with M_1 and M_2 where M_1 is chosen from the group consisting of vanadium or niobium and M_2 is chosen from the group consisting of iron or nickel;

C. an alloy of Zr-V-Fe whose composition in weight percent, when plotted on a ternary composition diagram in weight percent Zr, weight percent V and weight percent Fe, lies within a polygon having as its corners the points defined by:

i) 75% Zr - 20% V - 5% Fe

ii) 45% Zr - 20% V - 35% Fe

iii) 45% Zr - 50% V - 5% Fe

The antisintering material preferably has a particle size of between 20-60 µm with an average particle size of 40 µ. The weight ratio of the particulate non-evaporable getter material to the particulate antisintering material is from 1 : 4 to 4 : 1. After the electroplated ceramic support has been electrophoretically coated to the desired thickness of porous non-evaporable getter material is then removed from the coating bath and rinsed with a suitable liquid such as acetone and then it is dried. It is then heated in vacuum oven at a pressure preferably less than 10^{5} Torr (10^{3} Pa) at a temperature of between about 350°C and 450°C. If a hydrided material is used as the getter material then this temperature should be maintained for a sufficient time as to release all hydrogen. The getter device is then heated at a higher temperature such as between 900°C and 1000°C to produce a porous non-evaporable getter device in which the thicker metal layer diffuses into the ceramic support and the electrophoretically coated getter mixture. The getter device is then allowed to cool to room teperature whereupon it is removed from the vacuum oven and is ready for use.

The term "sintering" as used herein refers to the process of heating powdered material at a temperature and for a time sufficient to give some mass transfer between adjacent particles without appreciably reducing the surface area of the powdered material. The mass transfer serves to bind the particles together thereby increasing strength and reducing the number of loose particles. Lower temperatures require longer times. The sintering temperature of a material is that temperature at which the above-described sintering takes place in about one hour. In a preferred embodiment of the present invention a temperature is chosen which is at or slightly above the sintering temperature of the non-evaporable getter material and below the sintering temperature of the antisintering material.

As it is used herein the term "ceramic" means any material that is not electrically conductive at the temperature of use including glass-ceramics, quartz-glass, SiO_2, refractory metal oxides in general and Al_2O_3 in particular.

Figure 1 shows a porous non-evaporable getter device 102 comprising a ceramic substrate 104. Ceramic support 104 has one of its surfaces 106 coated with a thin film 108 of conductive material. On the thin film 108 of conductive material is an electrodeposited thicker layer 110 of metal. Onto thicker film 110 has been electrophoretically deposited particles 112, 112′ of particulate non-evaporable getter material and particles 114, 114′ of antisintering material.

Figure 2 shows a porous non-evaporable getter device 202 similar to that shown in Fig. 1 except that it has now been subject to a sintering process. Getter device 202 comprises a ceramic support 204 that supports particles of non-evaporable getter material 206, 206′ and particles 208, 208′ of antisintering material. As a result of the sintering process the thin and thick conductive layers have diffused into the ceramic to produce a diffusion layer 210 and they have diffused into the getter and/or antisintering material particles to produce diffusion zones 212, 212′. As mentioned above these diffusion zones may result from a single metallic layer.

EXAMPLE 1

This comparative example was designed to show the behaviour of a prior art porous non-evaporable getter device comprising a ceramic support and a porous sintered getter material layer. A metallic wire was coated with a thin layer of alumina thereby forming a tube which was coated electrophoretically following the process as described in the above mentioned UK Patent Application Publication GB 2,157,486 A using getter material particles of titanium hydride and antisintering particles of a Zr-V-Fe alloy both having a particle size of approximately 40 µm. After the sintering process and cooling down to room temperature a metallurgical cross-section was made and is shown in Fig. 3.

In order to start the electrophoretic process it was necessary to apply a voltage of 50 V. To maintain a current flow of 800 milliamps it was necessary to rapidly increase the voltage over a period of about 5 seconds. At this time the formation of H_2 gas had commenced making the deposited getter layer have a very rough irregular appearance with spots having no getter metal at all. The deposition of getter material is insufficient. The getter material exhibits undesirable flaking, and produces a large quantity of undesirable loose particles.

Figure 3 shows the cross-section 302 where can be seen the ceramic support 304 of alumina. The sintered non-evaporable getter material 306 comprising titanium and Zr-V-Fe is found to be separated from the ceramic support 304 by a space 308 showing a detachment of the getter material 306 from the ceramic support 304.

EXAMPLE 2

This example is designed to show the behaviour of a porous non-evaporable getter device of the present invention. An alumina tube was taken and its external surface was coated with aluminium in a vacuum deposition apparatus. Using the aluminium film as an electrode a thicker layer of Ni was electroplated upon it. The Ni layer was then used as an electrode in an electrophoretic deposition bath exactly as for Example 1. The porous non-evaporable getter material again comprised Ti hydride and a Zr-V-Fe alloy as an antisintering agent. The particle size of both components was approximately 40 µm. After the sintering operation and cooling to room temperature a cross-section 402 of the getter device was made and reported in Fig. 4. The alumina support 404 and the getter material 406 are shown to be clearly adhering to each other along line 408. The aluminium and nickel layers can no longer be seen as they have diffused into the alumina and the getter material.

In this case the deposition took place in a few seconds at an applied voltage of 15 V with the passage of 1 ampere. No H_2 formation was observed and the deposition was able to take place for 20 seconds thus providing a sufficient quantity of getter material with a smooth uniform surface appearance.

EXAMPLE 3

This example illustrates that embodiment of the present invention wherein the intermediate electrically conductive layer is a single metal.

The procedure of Example 2 is repeated except that the aluminium is replaced with nickel such that the intermediate electrically conductive layer is substantially all nickel.

Although the invention has been described in detail with reference to certain preferred embodiments and applications it is intended that variations and modifications can be made within the spirit and scope of the invention itself.

Claims

1. A porous non-evaporable getter device comprising:

I. a ceramic support;

II. a porous sintered getter material layer comprising:

A. a particulate non-evaporable getter material; and

B. a particulate antisintering material; and

III. an intermediate electrically conductive layer at least partially diffused into the ceramic support and the porous sintered getter material layer.

2. A getter device of claim 1 in which the ceramic support is alumina.

3. A getter device of claim 1 in which the particulate non-evaporable getter material is chosen from the group consisting of titanium, zirconium and their hydrides.

4. A getter device of claim 1 in which the particulate antisintering material is chosen from the group consisting of graphite, refractory metals and metallic getter alloys.

5. A getter device of claim 1 in which the antisintering material is an alloy of zirconium.

6. A porous non-evaporable getter device comprising:

I. an alumina support; and

II. a porous sintered getter material layer comprising:

A. a particulate non-evaporable getter material chosen from the group consisting of titanium, zirconium and their hydrides; and

B. a particulate antisintering material chosen from the group consisting of graphite, refractory metal and zirconium based alloys; and

III. an intermediate electrically conductive layer comprising:

A. a thin film of aluminium; and

B. A thicker layer of nickel at least partially diffused into the alumina support and the porous sintered getter material layer.

7. A getter device of claim 6 in which the zirconium based alloy is chosen from the group consisting of:

A. an alloy of zirconium with aluminium in which the weight percent of aluminium is from 5-30%;

B. an alloy of zirconium with M_1 and M_2 where M_1 is chosen from the group consisting of vanadium or niobium and M_2 is chosen from the group comprising iron or nickel;

C. an alloy of Zr-V-Fe whose composition in weight percent, when plotted on a ternary composition diagram in weight percent Zr, weight percent V and weight percent Fe, lies within a polygon having as its corners the points defined by:

i) 75% Zr - 20% V - 5% Fe

ii) 45% Zr - 20% V - 35% Fe

iii) 45% Zr - 50% V - 5% Fe

8. A method for manufacturing a porous non-evaporable getter device comprising the steps of:

I. coating a ceramic support with a thin conductive film;

II. electroplating the thin conductive film with a thicker metal layer to produce an electroplated support;

III. electrophoretically coating the electroplated support with a mixture of:

A. a particulate non-evaporable getter material; and

B. an antisintering material to produce a coated support;

IV. sintering the coated support at superambient teperatures to produce the porous, non-evaporable getter device; whereby the elctroplated thicker metal layer diffuses into the ceramic support and the electrophoretically coated mixture; and then

V. cooling said getter device to room temperature.

9. A method for manufacturing a porous non-evaporable getter device comprising the steps of:

I. coating a ceramic support with a thin conductive film;

II. electroplating the thin conductive film with a thicker metal layer to produce an electroplated support;

III. electrophoretically coating the electroplated support with a mixture of:

A. a particulate non-evaporable getter material chosen from the group consisting of titanium, zirconium and their hydrides; and

B. a particulate antisintering material chosen from the group consisting of:

a) an alloy of zirconium with aluminium in which the weight percent of aluminium is from 5-30%;

b) an alloy of zirconium with M_1 and M_2 where M_1 is chosen from the group consisting of vanadium or niobium and M_2 is chosen from the group consisting of iron and nickel; and

c) an alloy of Zr-V-Fe whose composition in weight percent, when plotted on a ternary composition diagram in weight percent Zr, weight percent V and weight percent Fe, lies within a polygon having as its corners the points defined by:

i) 75% Zr - 20% V - 5% Fe

ii) 45% Zr - 20% V - 35% Fe

iii) 45% Zr - 50% V - 5% Fe

IV. sintering the coated support at superambient temperatures to produce the porous, non-evaporable getter device; whereby the electroplated thicker metal layer diffuses into the ceramic support and the electrophoretically coated mixture; and then

V. cooling said getter device to room temperature.

10. A method for manufacturing a porous non-evaporable getter device comprising the steps of:

I. coating an alumina support with a continuous film of aluminium to a thickness of between 0.1 µm and 5 µm;

II. electroplating the aluminium film with a continuous nickel layer of thickness between 5 µm and 50 µm;

III. electrophoretically coating the electroplated support with a mixture of:

A. titanium hydride having a particle size of between 20-60 µm with an average size of 40 µm;

B. a Zr-V-Fe alloy having a weight percent composition of 70% Zr, 24.6% V, 5.4% Fe having a particle size of between 20-60 µm with an average particle size of 40 µm; wherein, the weight ratio A : B of the electrophoretically deposited layer is from 1 : 4 to 4 : 1; and then

IV. rinsing the coated support with acetone; and then

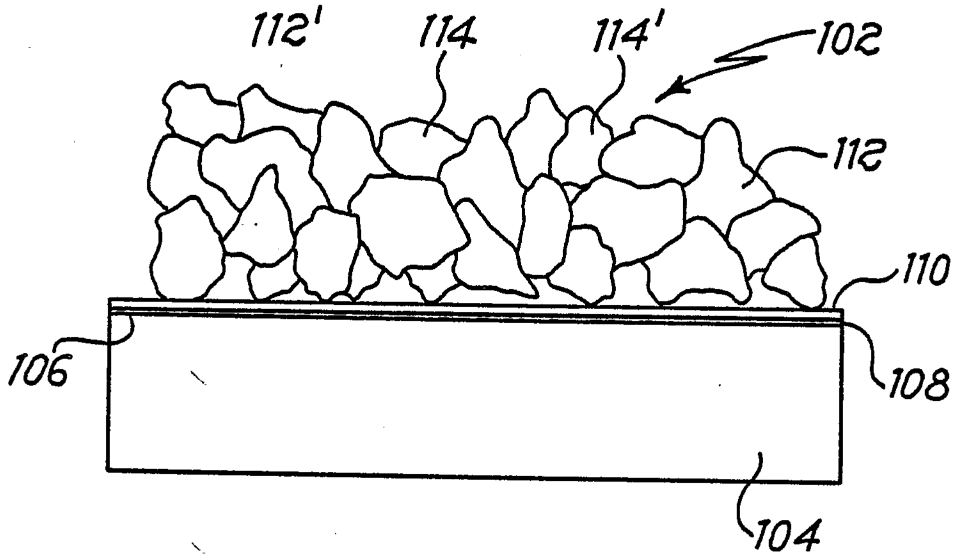
V. drying the coated support; and then

VI. maintaining the coated support at a pressure less than 10^{5} Torr (10^{3} Pa) at a temperature between 350°C and 450°C for a period of time sufficient to release substantially all hydrogen from the titanium hydride thereby yielding metallic titanium; and thereby producing a coated support; and then

VII. sintering the coated support at a temperature between 900°C and 1000°C to produce the porous, non-evaporable getter device; whereby the nickel diffuses into the alumina support and the electrophoretically coated mixtures; and then

VIII. cooling said getter device to room temperature.

Fig. 1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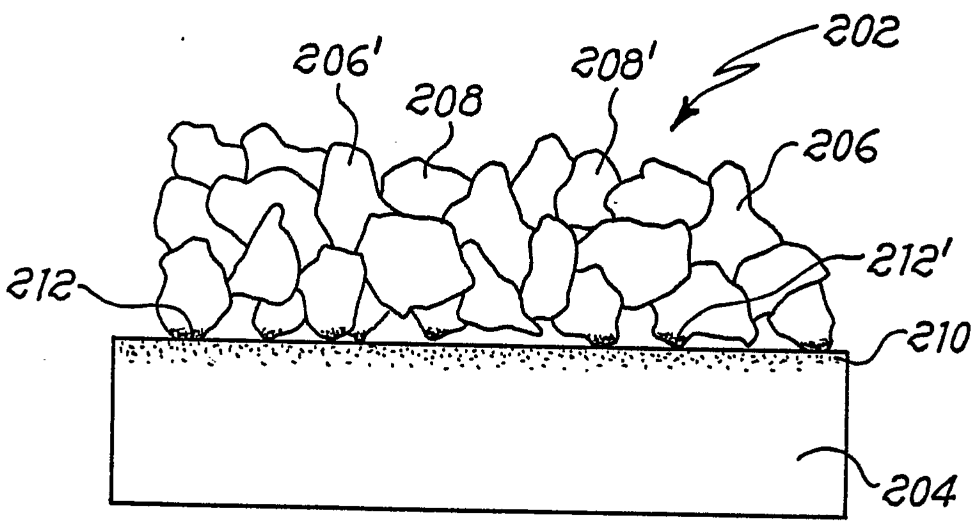
104

Fig. 2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204

Fig. 3

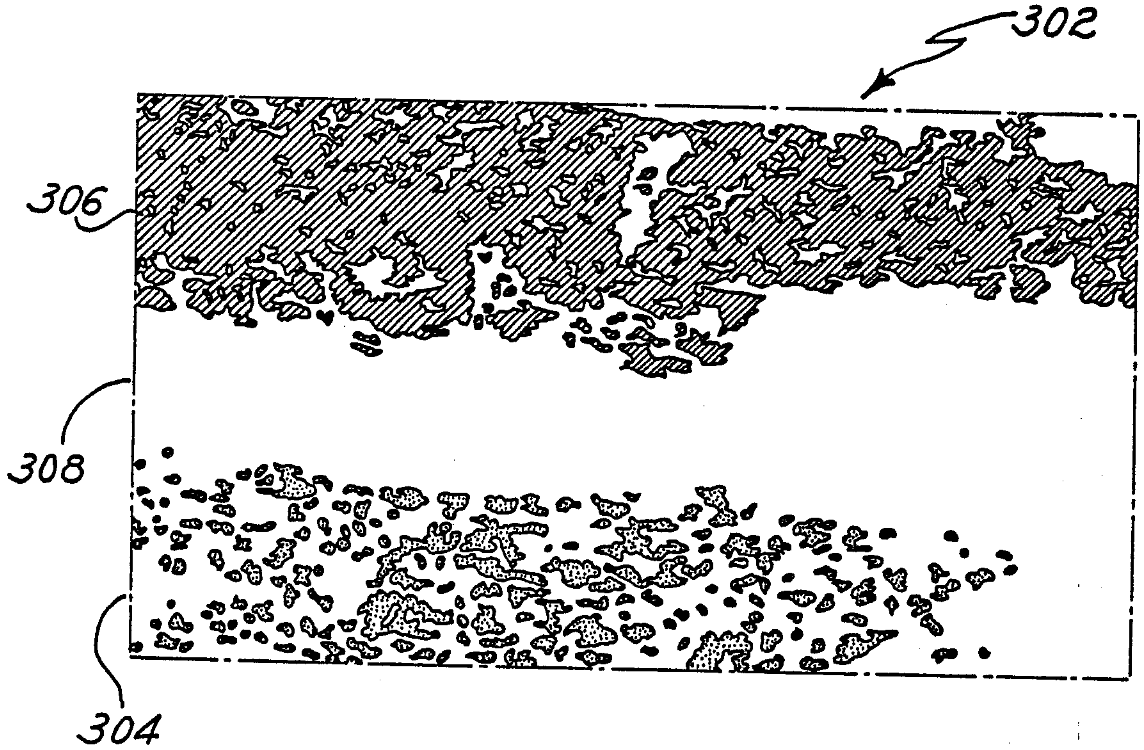

Fig. 4