March 3, 1959 J. K. FLOWERS 2,876,139

METHOD OF BONDING COATING ON A REFRACTORY BASE MEMBER AND COATED BASE

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FIG.1.

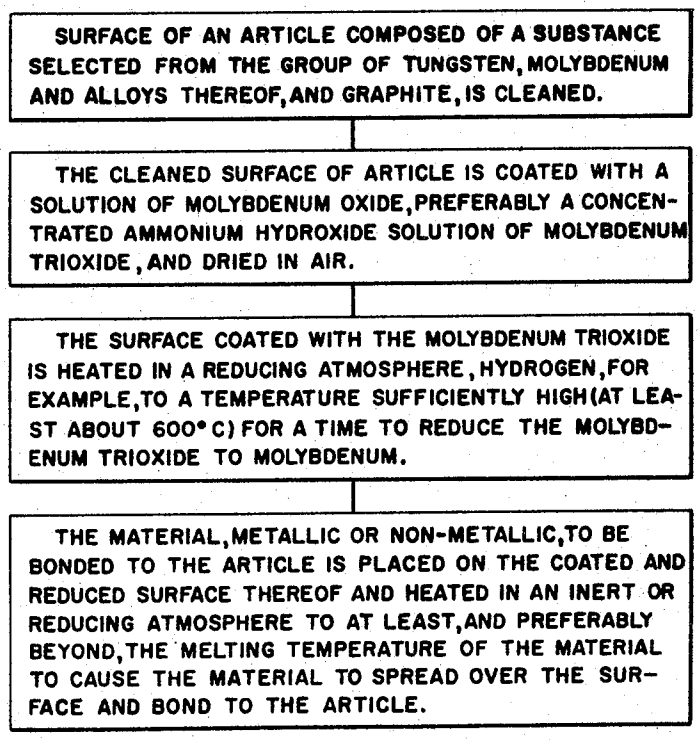
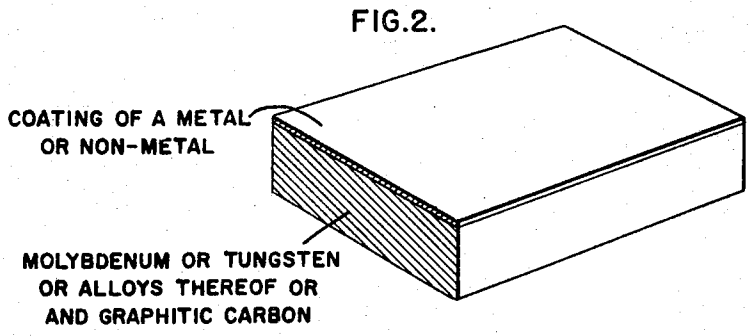


FIG.2.



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METHOD OF BONDING COATING ON A REFRACTORY BASE MEMBER AND COATED BASE

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11 Claims. (Cl. 117—131)

The present invention relates to the bonding of an adherent metallic or non-metallic coating on to refractory base members. More particularly, it relates to the formation of an adherent stable continuous coating of an element or alloy, such as copper, gold, tin, indium, germanium, solders comprising copper and silver and known as silver solders, silver, iron and nickel, upon an article or object made of a refractory metal such as molybdenum and tungsten and alloys thereof, and of a material such as graphitic carbon.

As is well known, molybdenum and tungsten and alloys thereof have coefficients of expansion comparable to the coefficients of expansion of silicon, germanium, glass, ceramics and the like. Consequently, where it is desired to make a metallic bond to such substances as those in the latter category, either directly or indirectly, it should be desirable to use molybdenum, tungsten and alloys thereof. However, in the past difficulty has been experienced in suitably coating molybdenum, tungsten and alloys thereof with the materials mentioned in the first paragraph above in order that good bonding could be achieved. Difficulty has also been experienced in making conventional lead or silver solder connections to molybdenum, tungsten and alloys thereof.

The present invention is directed to the solution of such problems as those requiring the formation of a tightly adhering bond of a metal or non-metal to objects consisting of molybdenum, tungsten and alloys thereof, and also carbon.

Accordingly, an object of the present invention is to provide an improved conductive object consisting of molybdenum, tungsten and alloys thereof having other metals or non-metals bonded to the surfaces thereof.

Another object of the present invention is to provide a method of applying an adherent metallic or non-metallic coating on an article composed of a metal selected from the group consisting of tungsten and molybdenum and alloys thereof.

A further object of the present invention is to provide an improved method of applying an adherent metallic or non-metallic coating on a body of graphite.

Referring to the drawing:

Figure 1 is a flow diagram illustrating how the present invention may be practiced; and

Figure 2 is a perspective view of a product in accordance with the present invention.

The present invention will now be described with respect to a specific embodiment thereof, for example, the application of an adherent copper coating to the surface of a plate of molybdenum or molybdenum-based alloy. The molybdenum plate is first cleaned in any suitable manner, for example, by scouring with a soapy abrasive. The cleaned surface of the plate is then coated with molybdenum trioxide. The coating may be applied in one of several ways. For example, the cleaned article may be immersed in an oxidizing agent such as nitric acid, preferably a 40–60% solution by weight for about two seconds. If the molybdenum is immersed in the solution for a much longer period, the molybdenum rapidly etches away. After removal of the plate of molybdenum, the surface is blotted to remove the excess solution. The molybdenum coated with the molybdenum trioxide is then heated in a reducing atmosphere, preferably hydrogen. The temperature of the plate is raised to about at least 600° C. at which temperature the molybdenum trioxide begins to reduce. The higher the temperature, the more rapid is the reduction process. I have found that when the temperature is raised to about 800° C., substantially complete reduction of the molybdenum trioxide takes place is a few seconds. A fine deposit of particles of molybdenum is formed on the surface of the molybdenum plate as a result of the reduction process. These particles are apparently loosely attached since they can be wiped off.

In the next step of the process, a piece of copper is placed on the treated molybdenum surface and the temperature of the molybdenum is raised in a reducing or non-oxidizing atmosphere to beyond the melting temperature of the copper. At this temperature copper melts and simultaneously alloys and spreads over the entire surface of the molybdenum in the matter of a few seconds. At this time, the plate is allowed to cool. If desired, the entire operation of reduction of the molybdenum trioxide and the alloying of the copper into the molybdenum may be performed in a single operation by first placing the piece of copper on the surface coated with molybdenum trioxide and then raising the temperature of the place sufficiently to reduce the molybdenum trioxide and finally raising the temperature further to melt the copper and cause the alloying action described. The wetting action of copper on molydenum which takes place resembles very much the wetting action that takes place when water spreads in a blotter. The resulting copper-coated molybdenum plate has a strongly adherent smooth coating of copper on the surface thereof free from blisters to which solder and other contacts may be very readily made.

Excellent results have also been obtained by using molybdenum trioxide solutions to form a deposit of molybdenum trioxide on surfaces coated with metallic and non-metallic materials. A saturated water solution at room temperature is satisfactory (0.106 gram of MoO_3 in a liter of water). A hot water solution works better (2 grams of MoO_3 in one liter of solution). Preferably, a concentrated solution of molybdenum trioxide in ammonium hydroxide as the solvent is used. These molybdenum trioxide solutions are applied to wet the cleaned surface of the molybdenum plate and preferably allowed to dry in air. The dried plate is then heated in a reducing atmosphere as specified above to reduce the molybdenum trioxide. The remainder of the process is the same as described above.

An additional way in which the trioxide coating may be produced on the surface of an article of molybdenum is by simply heating the cleaned surface of the molybdenum in oxidizing atmosphere up to about 800° C., at which temperature the oxide forms quite readily. The plate is then subjected to the operations mentioned in the preceding examples.

In a similar manner, other metals and non-metals may be applied to the molybdenum plate, for example, indium, tin, gold, germanium, silver solders, copper, silver, gold-antimony alloys. Nickel and iron may be similarly applied to molydenum and alloys thereof to form an adherent coating. The steps for bonding such other materials is the same as specified above for copper except that in the case of the other materials specified in this parargraph in final step the temperature is raised sufficiently to cause the material which is to be bonded to melt, spread over and alloy into the molybdenum.

I have also discovered that the previously described coating techniques may be applied equally to tungsten and tungsten-based alloys and also to graphite bodies to produce a stable adherent coating thereon of a variety of materials including those mentioned above.

The theory of wetting of the surface of the refractory body and of obtaining good alloying action is not fully understood but it is believed that the reduced molydenum trioxide leaves irregularities on the surface of the body to be coated which is conducive to good wetting and alloying action with the result that good bonding over the entire surface of the body is obtained. Additionally, it is mentioned that the reduction of the oxide to elemental material leaves this material in fine particle form which facilitates alloying and wetting action.

While the process has been described in illustrative examples in which plates of refractory substances were used, it is to be understood that other forms such as cylinder wires, etc., may be used.

The invention has particular utility in the making of semiconductor devices constituted of germanium and silicon. In the making of such devices, it is necessary to make ohmic and other kinds of connections to the germanium or silicon body of the device. Molybdenum or tungsten are desirable for such use since they have coefficients of expansion comparable to the coefficients of expansion of germanium and silicon; and thus fracturing of connections is minimized in the fabricating operation, as well as when large currents are passed through the device. Additionally, modybdenum and tungsten are desirable for the reason that they have good thermal and electrical conductivities. While molybdenum and tungsten have been desirable for these reasons, it has been difficult to bond other materials to them. The present invention solves such problems as these. For example, in making an ohmic contact between silicon and molybdenum, it is desirable to use a gold and antimony alloy (gold 99%–antimony 1%); however, heretofore, it has been a problem to make a good adherent coating of the gold-antimony alloy to the surface of a molybdenum plate. By the technique of the present invention, it is possible to produce an excellent coating of gold antimony on the surface of the molybdenum plate. The other side of the molybdenum plate may be coated with copper as described above to provide an external surface which may be easily soldered to.

I, therefore, intend in the appended claims to cover all changes and modifications of the examples of my invention herein chosen for purposes of disclosure which do not constitute departures from the spirit and scope of the invention.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. The method of providing an adherent coating on an article composed of a substance selected from the group consisting of tungsten, molybdenum, tungsten and molybdenum-based alloys and graphitic carbon comprising the steps of coating a surface of said article with molybdenum trioxide, reducing the molybdenum trioxide on said surface to molybdenum, applying to said reduced surface a material to be coated thereon selected from the group consisting of copper, gold, tin, indium, germanium, silver, iron and nickel and alloys thereof at the melting temperature of said material.

2. The method of providing an adherent coating on an article composed of a substance selected from the group consisting of tungsten, molybdenum, tungsten and molybdenum-based alloys and graphitic carbon comprising the steps of coating a surface of said article with a solution including molybdenum trioxide as solute, removing the solvent to leave said surface coated with molybdenum trioxide, reducing the molybdenum trioxide on said surface to molybdenum, applying to said reduced surface a material to be coated thereon selected from the group consisting of copper, gold, tin, indium, germanium, silver, iron and nickel and alloys thereof at the melting temperature of said material.

3. The method of prividing an adherent coating on an article composed of a substance selected from the group consisting of tungsten, molybdenum, tungsten and molybdenum-based alloys and graphitic carbon comprising the steps of coating a surface of said article with a water solution of molybdenum trioxide, removing the solvent to leave said surface coated with molybdenum trioxide, reducing the molybdenum trioxide on said surface to molybdenum, applying to said reduced surface a material to be coated thereon selected from the group consisting of copper, gold, tin, indium, germanium, silver, iron and nickel and alloys thereof at the melting temperature of said material.

4. The method of providing an adherent coating on an article composed of a substance selected from the group consisting of tungsten, molybdenum, tungsten and molybdenum-based alloys and graphitic carbon comprising the steps of coating a surface of said article with an ammonium hydroxide solution of molybdenum trioxide, removing the solvent to leave said surface coated with molybdenum trioxide, reducing the molybdenum trioxide on said surface to molybdenum, applying to said reduced surface a material to be coated thereon selected from the group consisting of copper, gold, tin, indium, germanium, silver, iron and nickel and alloys thereof at the melting temperature of said material.

5. The method of providing an adherent coating on an article composed of a substance selected from the group consisting of tungsten, molybdenum, tungsten and molybdenum-based alloys and graphitic carbon comprising the steps of coating the surface of said article with molybdenum trioxide, reducing the molybdenum trioxide on said coated article to molybdenum, applying to said surface in a non-oxidizing atmosphere a material to be coated thereon selected from the group consisting of copper, gold, tin, indium, germanium, silver, iron and nickel and alloys thereof at the melting temperature of said material.

6. The method of providing an adherent coating on an article composed of a substance selected from the group consisting of tungsten and molybdenum and tungsten and molybdenum-based alloys and graphitic carbon comprising the steps of coating a surface of said article with molybdenum trioxide, raising the temperature of said surface in non-oxidizing atmosphere to a temperature in excess of substantially 600° C. for a time to reduce the molybdenum trioxide on said surface to molybdenum, thereby forming a coating of fine particles of molybdenum metal distributed on said surface of the metal, applying to said surface in a non-oxidizing atmosphere a material to be coated thereon selected from the group consisting of copper, gold, tin, indium, germanium, silver, iron and nickel and alloys thereof at the melting temperature of said material.

7. The method of providing an adherent coating on an article composed of molybdenum comprising the steps of oxidizing a surface of said article to form molybdenum trioxide thereon, reducing the molybdenum trioxide on said surface to form a coating of fine particles of molybdenum distributed on said surface, applying to said surface in a non-oxidizing atmosphere a material to be coated thereon selected from the group consisting of copper, gold, tin, indium, germanium, silver, iron and nickel and alloys thereof at the melting temperature of said material.

8. The method of providing an adherent coating on an article composed of graphitic carbon comprising the steps of coating a surface of said article with molybdenum trioxide, reducing the molybdenum trioxide on said surface in a non-oxidizing atmosphere to form a coating of fine particles of molybdenum on said surface, applying to said surface in a non-oxidizing atmosphere a material to be coated thereon selected from the group consisting

of copper, gold, tin, indium, germanium, silver, iron and nickel and alloys thereof at the melting temperature of said material.

9. An article of manufacture produced by the practice of the process recited in claim 1.

10. The method of providing an adherent coating of an article composed of molybdenum comprising the steps of coating a surface of said article with molybdenum trioxide, reducing the molybdenum trioxide on said surface to form a coating of fine particles of molybdenum distributed on said surface, applying to said surface in a non-oxidizing atmosphere a material to be coated thereon selected from the group consisting of copper, gold, tin, indium, germanium, silver, iron and nickel and alloys thereof at the melting temperature of said material.

11. The method of providing an adherent coating on an article composed of tungsten comprising the steps of coating a surface of said article with molybdenum trioxide, reducing the molybdenum trioxide on said surface to form a coating of fine particles of molybdenum distributed on said surface, applying to said surface in a non-oxidizing atmosphere a material to be coated thereon selected from the group consisting of copper, gold, tin, indium, germanium, silver, iron and nickel and alloys thereof at the melting temperature of said material.

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