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G. R. FONDA

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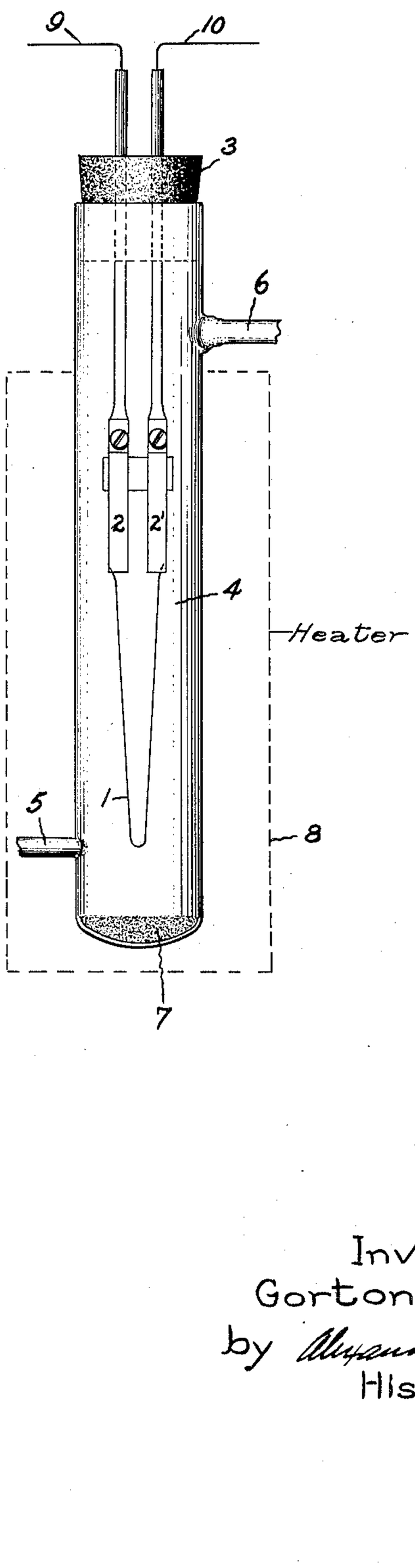

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ZIRCONIUM ALLOY.

Application filed August 30, 1924. Serial No. 735,075.

This application is a continuation in part of my prior application filed July 29, 1920, Serial No. 399,798.

The present invention relates to the formation of alloys of zirconium and in particular to the formation of zirconium alloy of a highly refractory metal, such as tungsten. My invention is particularly applicable to the manufacture of wire-shaped or filamentary bodies of zirconium alloy and in particular to the manufacture of lighting filaments comprising a preponderant amount of tungsten and a lesser proportion of zirconium.

It has been suggested heretofore to prepare alloys of tungsten and zirconium by mixing these metals in finely powdered form, consolidating the same by heating and finally forming wires by swaging and drawing. My experience has indicated that an alloy of tungsten and zirconium cannot be easily worked into the form of filamentary bodies by such mechanical process.

In accordance with my invention these alloys are prepared more conveniently by first coating a foundation metal, such as tungsten, with a layer of zirconium in a dense, finely crystalline, adherent form, and thereupon at a higher temperature causing diffusion of the zirconium into the foundation metal. Under these conditions I find that a substantial homogeneous alloy is formed of the foundation metal and the zirconium coating.

The accompanying drawing shows in elevation and in simplified form, an apparatus for carrying out the coating process.

My invention will be illustrated by describing the manufacture of lighting bodies suitable for use in incandescent lamps, and consisting of a preponderant amount of tungsten and a lesser amount of zirconium. In the production of such lighting bodies, wires or filaments of tungsten are first prepared, for example, by the procedure described in Coolidge Patent No. 1,082,933 of December 30, 1913. A tungsten filament of suitable thickness, say of about one to four mils in diameter, on which zirconium is to be deposited, is heated in an enclosed space in contact with a mixture of a halogen compound of zirconium, such as the chloride and a gaseous reducing agent, for example, hydrogen. The reduction may be carried out in an enclosed space, such as a treating bottle, of the type well known in lamp filament manufacture. As shown in the drawing, a filament 1 is mounted upon spring clip terminals 2, 2′ supported from a stopper 3 within a container 4 having gas inlet and outlet tubes 5, 6. A simple hair-pin shaped filament has been shown for purpose of illustration but of course, the filament may have any desired shape. The reduction zone is maintained at a temperature of about 300° C. or somewhat higher, for example, by a suitable external heater as indicated by the dotted outline 8. The hydrogen is passed through the bottle at the speed best adapted to give a finely crystalline deposit on the filament. For example, in a bottle about 1½ inch in diameter, a stream of hydrogen is conducted over the zirconium compound 7 and in contact with the tungsten filament at a rate of about 150 to 200 cc. per minute. At a lower rate of hydrogen flow the deposit becomes feathery or fuzzy, at a higher rate of flow the alloy becomes coarsely crystalline and poorly adherent. Neither condition is well adapted for the subsequent alloying step. The tungsten filament should be heated to a temperature between bright redness and a white incandescence (about 1500° C.) for example by passage of current supplied by the conductors 9, 10. Here likewise a lower temperature tends to produce a feathery deposit. A higher temperature produces a coarsely crystalline deposit. After the required amount of zirconium has been deposited, reduction is interrupted, and the coated filament is removed.

I prefer to deposit sufficient zirconium upon the filament to produce an alloy which may vary within the limits of 0.5 to 4 per cent of zirconium content, although the preferable percentage is in the neighborhood of about 3 per cent. The amount of zirconium may be accurately predetermined by trial and will depend upon the conditions of the reduction, such as the rate of flow of the hydrogen, the temperature and therefore the vapor pressure of the zirconium compound and the temperature of the filament. In case of the above mentioned conditions 3 per cent of zirconium is deposited in a few seconds.

The zirconium coated filament, after being removed from contact with the reduction mixture, is heated preferably in contact with a gas, such as hydrogen or argon which is inert with respect to the coated filament, or in vacuum, to a temperature at which a homogeneous alloy is formed while the filament remains intact. In the case of the described tungsten filament coated with about 3 per cent of zirconium, the filament preferably should be heated to about 2600° C. for a few minutes to bring this about. This is a temperature well above the ordinary operating temperature of an incandescent lamp when emitting light at an efficiency of about one watt per candle which is about 2150° C. When a temperature less than 2600° C. is employed the length of time of heating should be lengthened accordingly. If desired the unalloyed composite filament of tungsten and zirconium may be mounted directly in an incandescent lamp in the usual well understood manner and the alloyage then will occur during the normal operation of the lamp. If the lamp is operated at an efficiency of about one watt per candle the alloyage will require several hours to become complete. Of course, as the lamp in the meantime is being used in a normal manner, this slow alloyage is not objectionable.

The presence of the zirconium in the filament lowers the rate of evaporation during operation at incandescence as compared with an unalloyed tungsten filament.

When operating in a lamp at bright incandescence, at a given efficiency the alloyed zirconium lengthens the life of the filament or if the same average life is desired as obtainable with the unalloyed tungsten filament, the zirconium alloy filament may be operated at a higher efficiency.

When a zirconium alloy filament is used in a gas-filled lamp, such as described in Langmuir Patent No. 1,180,159, issued April 18, 1916, the filament burns to a greater decrease in weight before burning out than an unalloyed tungsten filament.

Metallic zirconium may be deposited on the foundation by methods other than chemical deposition. The zirconium layer may be mechanically deposited. For example, a filament of tungsten, or other metal alloyable with zirconium may be coated with a suspension of finely divided zirconium in a suitable medium such as a solution of "film stock" which consists mainly of cellulose acetate or other cellulose compound. The coated filaments are dried and then subjected as above indicated to an alloying temperature.

Although I have described my invention with particular reference to the formation of zirconium alloys of tungsten, I wish it to be understood that my invention is not limited to the preparation of tungsten alloys.

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

1. The process of preparing an alloy of tungsten and zirconium which consists in forming on tungsten a layer of zirconium by the thermal decomposition of a zirconium compound, interrupting the reaction and thereupon heating the tungsten and zirconium to a higher temperature at which alloyage occurs in an environment inert with respect to said metals.

2. The process of preparing filamentary bodies comprising an alloy of tungsten and zirconium which consists in heating the filament of tungsten in the presence of the vapor of a zirconium compound and a reducing agent at a temperature at which the metallic zirconium is deposited on said filament, removing the coated filament from contact with the zirconium compound, and then heating to a temperature at which alloyage occurs between the tungsten filament and zirconium coating.

3. The process of preparing an alloy of tungsten and zirconium which consists in depositing metallic zirconium on a foundation of tungsten at a temperature of about 1500° C. and then heating to a materially higher temperature in an environment which is inert with respect to said metals.

4. The process of preparing a filamentary body consisting of an alloy of tungsten and zirconium which consists in depositing on a tungsten filament a layer of zirconium by heating said filament to about 1500° C. in contact with a gaseous mixture of a zirconium compound and a reducing agent, and thereupon heating the coated filament to a temperature of at least about 2600° C. to cause diffusion and alloyage of the zirconium.

5. The process of preparing an alloy of zirconium with a highly refractory metal which consists in depositing a layer of zirconium on said metal by reduction of a vaporized zirconium compound at a temperature at which the zirconium is deposited as a dense, adherent, unalloyed layer and then heating to a higher temperature at which an alloy of substantially uniform composition is formed.

6. The process of preparing an alloy of tungsten and zirconium which consists in heating a tungsten filament in contact with a current of zirconium halide and hydrogen gas, maintaining the temperature of said filament, and the rate of flow of said gas at such values that a dense, adherent, finely crystalline coating of zirconium is formed and heating said coated filament to a temperature sufficiently high to cause alloyage.

7. The process of preparing a filamentary body consisting of an alloy of tungsten and zirconium which consists in heating a tung-

sten filament in a mixture of zirconium chloride and hydrogen, maintaining said gaseous mixture in motion at such rate and maintaining the temperature of said filament at such value that a finely crystalline coating of zirconium is formed, interrupting the deposition when a desired quantity of zirconium has been deposited and heating the coated filament out of contact with said gaseous mixture at a temperature sufficiently high to cause diffusion and alloyage of the zirconium in the tungsten.

In witness whereof, I have hereunto set my hand this 28th day of August, 1924.

GORTON R. FONDA.