

Feb. 4, 1958

P. ALEXANDER ET AL

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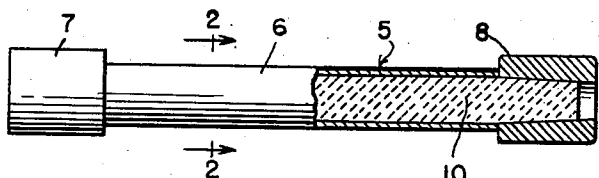
VACUUM METALLIZING AND APPARATUS THEREFOR

Filed June 3, 1952

2 Sheets-Sheet 1

FIG. 1.

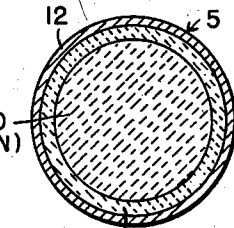
FIG. 2.



(HAFNIUM or ZIRCONIUM)

FIG. 3.

(CARBON)



(HAFNIUM CARBIDE or ZIRCONIUM CARBIDE)

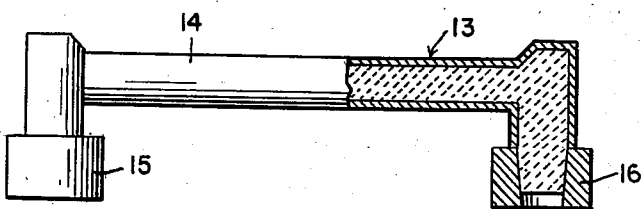


FIG. 4.

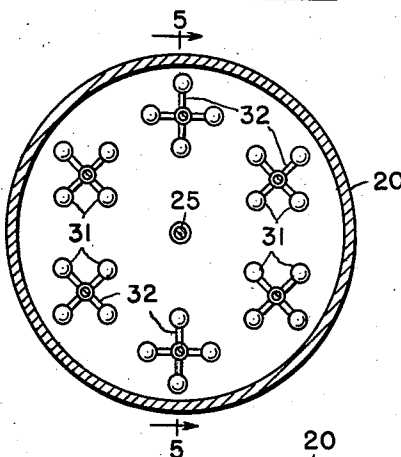
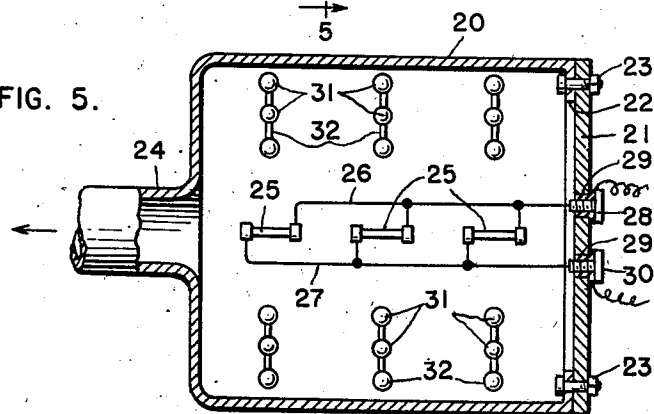


FIG. 5.



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2 Sheets-Sheet 2

FIG. 6.

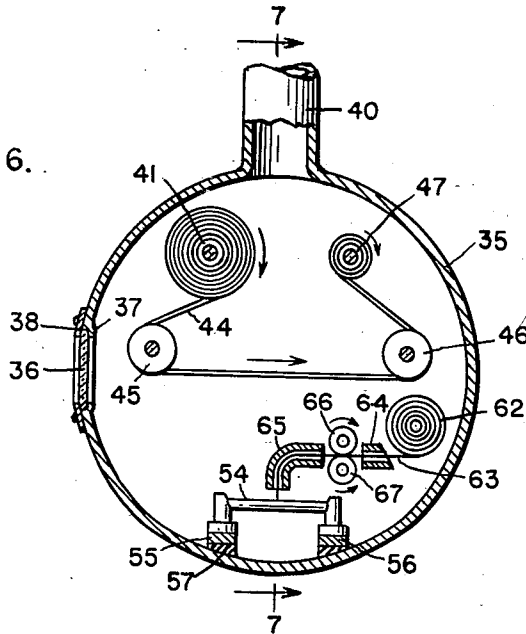
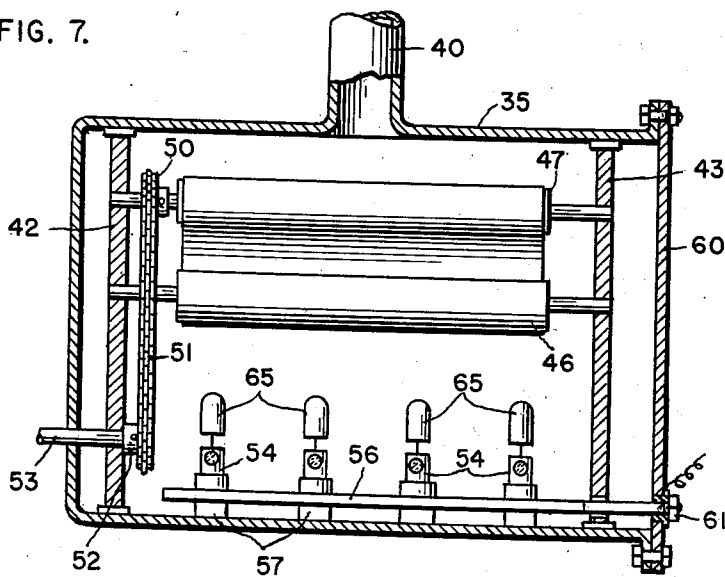


FIG. 7.



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2,822,301

VACUUM METALLIZING AND APPARATUS THEREFOR

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Application June 3, 1952, Serial No. 291,506

13 Claims. (Cl. 117—217)

The present invention relates to improvements and innovations in methods of and apparatus for applying metal coatings to surfaces by evaporation of the metals in vacuum at elevated temperature. More specifically, the invention pertains to novel heaters to be used for evaporating the metals in such methods and apparatus, and to novel methods of preparing and using such heaters. This application is a continuation-in-part of our co-pending application Serial No. 208,162, filed January 27, 1951, now Patent 2,756,166.

A number of patents have issued which are directed to the process of applying extremely thin films of metals to surfaces by evaporating the metals in vacuum at elevated temperatures. In addition to the patent literature, there have been papers and articles in the technical literature which pertain to various aspects of the art of vacuum metallizing. A great deal of research and development effort has been devoted to the production of apparatus wherein the vacuum metallizing process could be carried out satisfactorily in an economical manner. One of the critical portions of such apparatus is the pumping system since the metals to be evaporated must ordinarily be evaporated in unusually good vacuums in the order of 1×10^{-5} mm. (mercury column). Diffusion pumps have been perfected to a point where the obtainance of such vacuums no longer constitutes a problem. In like manner, other portions of the apparatus have been developed so that fairly satisfactory equipment is now procurable except for the heater elements which constitute a physically small but vital part of such equipment and apparatus. In fact, at the present time continued commercial growth and development of the vacuum metallizing process is largely dependent upon the provision of much better heaters than have been heretofore available.

While the number of metals may be vacuum evaporated for application to various objects and surfaces, aluminum is presently the most important metal from the commercial standpoint. Other metals of importance include gold, silver, copper and zinc. Various alloys of aluminum and the other metals may also be vacuum evaporated.

U. S. Patents Nos. 2,153,786, granted April 11, 1939, and 2,444,763, granted July 6, 1948, disclose methods and apparatus for vacuum evaporating aluminum wire which is fed onto a heater element. In these patents the preferred heater element is disclosed as being a tungsten filament and, in general, tungsten has heretofore been considered the preferred heater material for vacuum evaporating aluminum on a commercial scale. When aluminum is vacuum evaporated from a tungsten heater element, the tungsten is eroded away at a rather rapid rate and in order to obtain tungsten heaters which will last for as long as in the order of one-half to an hour of continuous operation, it has been found necessary to make the tungsten heater elements rather long and then carry out the evaporation from a number of points on the surface of the heater in order to prolong the life thereof. When a metal such as aluminum is being

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evaporated from one place on the tungsten heater element, only this relatively small area is covered with the molten aluminum metal while the major surface of the heater element is bare and is in an incandescent condition at a temperature substantially higher than the temperature of the localized area where the metal evaporation takes place.

There seems to be no practical means for shielding the bare areas of the tungsten heater elements and the heat radiated therefrom at high temperature has been found to constitute a serious problem for several reasons. Thus, the extremely high temperatures drive off even traces of adsorbed and absorbed moisture from exposed portions of the apparatus itself as well as from the materials to be metal coated, and the water vapor formed interferes with the obtaining and maintaining of the low degree of vacuum essential for satisfactory operation. Furthermore, when the object or surface being coated is a material such as paper or plastic film, the heat radiated from the bare areas of the tungsten heaters is damaging to such materials and constitutes a definite limitation on the types of materials which can be coated in accordance with this process.

In accordance with the present invention, we have discovered and developed novel heater elements for the vacuum metallizing process which are markedly superior to the tungsten heater elements and other types of heater elements which have previously been used. We have also discovered and developed novel methods of preparing and using our new heater elements. Briefly, our novel heater elements for use in vacuum metallizing apparatus and operations comprise a carbon core or internal support member, the surface of which is provided with a coating or sheathing of zirconium carbide or hafnium carbide wherein at least some free zirconium or hafnium metal, respectively, is exposed to the surface. The sheathing may be composed of both zirconium and hafnium carbides and small amounts of the free metals. Our novel method of making such heaters involves the utilization of zirconium hydride as the source material for zirconium, and hafnium hydride as the source of hafnium. Some commercial grades of zirconium hydride contain small associated quantities of hafnium hydride. In our novel method of using the heaters to vacuum evaporate metals such as aluminum, the metal to be evaporated is allowed to melt and film out over all or most of the heated surface of the heater element. These and other features of the invention will be fully disclosed and illustrated in the following detailed description and the accompanying drawings.

One important object of the invention is a novel heater for use in vacuum metallizing apparatus which lasts several times longer than the tungsten heater elements which are now used and which has a heating surface uniformly wetted by the metal to be evaporated so that the heater operates at nearly uniform temperature throughout. This object of the invention is satisfied by our heaters made with carbon cores or supports and provided with a heating surface of zirconium carbide wherein there is a substantial content of free zirconium metal, or of hafnium carbide wherein there is a substantial content of free hafnium metal.

An important object of the invention is a novel method of making a heater element for vacuum metallizing apparatus by decomposing zirconium hydride or hafnium hydride in a vacuum at elevated temperature on a carbon core and decomposing a sufficient amount of the zirconium hydride or hafnium hydride to produce a substantial amount of free zirconium metal in the zirconium carbide coating, or of free hafnium in the hafnium carbide coating, respectively, which is formed on the carbon support.

Another important object of the invention is an im-

proved method of vacuum evaporating a metal such as aluminum at elevated temperature in a vacuum chamber by evaporating the metal from a heater having a heating surface formed of zirconium carbide or hafnium carbide containing an appreciable amount of free zirconium or hafnium metal, respectively, the molten metal being evaporated covering most of the heated evaporating surface of the heater element so that the temperature of the heater element is maintained substantially uniform throughout and there is little if any bare incandescent heating area which is not coated with a film of the metal being evaporated.

Certain other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

For a more complete understanding of the nature and scope of our invention, reference may now be had to the following detailed description thereof taken in connection with the accompanying drawings, wherein:

Fig. 1 is a side elevational view, partly in section, of a carbon core heater element made in accordance with the present invention;

Fig. 2 is an enlarged sectional view taken on line 2—2 of Fig. 1 and showing diagrammatically the outer coating or sheathing of either zirconium carbide and free zirconium metal or of hafnium carbide and free hafnium metal, which serves as the heating surface thereof;

Fig. 3 is a side elevational view partly in vertical section of a modified form of heater element made in accordance with the present invention;

Fig. 4 is a diagrammatic vertical cross sectional view through one form of apparatus for vacuum evaporating metals so as to deposit a film of the metal on the surfaces of individual objects;

Fig. 5 is a sectional view taken on line 4—4 of Fig. 4;

Fig. 6 is a partially diagrammatic vertical cross sectional view through a vacuum metallizing apparatus designed for the continuous coating of a web of material such as paper or plastic, certain parts being shown in elevation; and

Fig. 7 is a longitudinal vertical sectional view partly in elevation taken on line 6—6 of Fig. 6.

In Figs. 1 and 2 a heater element is indicated generally at 5 which comprises a cylindrical rod 6 provided with metallic terminals 7 and 8 on opposite ends thereof. The rod 6 consists of an inner core or support made of carbon and indicated at 10 in Fig. 2 and having an exterior surface consisting of a layer or sheathing of zirconium or hafnium carbide 11 bearing free zirconium or hafnium metal, respectively, 12 on the exterior thereof. The exact dimensions and shape of the rod 6 are not critical. The core 10 may, for example, have a diameter of about one-quarter of an inch and a length of two inches. The coating of zirconium or hafnium carbide 11 and the skin of zirconium or hafnium metal 12 are so thin that they do not add appreciably to the diameter of the carbon core 10.

The heater 5 may be suitably made in accordance with the following example when the sheath 11 is zirconium carbide and the skin 12 is zirconium metal:

Example 1

The terminals 7 and 8 are applied to the opposite ends of any desired number of carbon rods. A suitable grade of carbon for this purpose is the compressed amorphous carbon such as is used with a binder for making the electrodes for arc lamps. The carbon rods are preferably first heated in a vacuum in the order of 1×10^{-1} mm. (mercury column) or better for at least about 2 minutes and preferably for about 5 minutes, at a temperature of at least about 2000° C. It has been found that this preliminary heat treatment of the carbon rods results in substantially superior heaters.

A suspension of finely divided zirconium hydride is prepared by dispersing the zirconium hydride powder in alcohol, or if desired in some other vehicle such as acetone

or water. The carbon rods are now coated with the suspension of zirconium hydride either by dipping the rods into the suspension or by brushing or spraying the suspension onto the rods. After the initial coating of zirconium hydride has thus been applied, the rods are heated in a vacuum in the order of 1×10^{-3} mm. at a temperature of around 2050° C. for about 1 minute. Under these conditions the zirconium hydride decomposes into zirconium metal and hydrogen gas. The zirconium metal reacts immediately as it is formed with the carbon making up the surface of carbon rods so as to form zirconium carbide thereon. The amount of hydrogen gas given off is not sufficient to interfere with the maintenance of the vacuum but it does tend to provide a reducing atmosphere which is beneficial in protecting the free zirconium metal as it is formed.

It has been discovered that superior heaters can be made by giving the carbon rods or supports at least two coatings of zirconium hydride followed in each instance by heating in vacuum to decompose the zirconium hydride into the metal and hydrogen gas. Normally, only two coatings and subsequent heating in vacuum are required to form a skin or coating of zirconium carbide on the carbon support or core together with an appreciable amount of zirconium metal in the surface of the zirconium carbide. The second heating of the heater element after it has received its second application of zirconium hydride suspension may be carried out at approximately the same vacuum and temperature conditions as the first heating of the zirconium hydride but it is preferable to regulate the time of heating during the second operation by noting when a film of zirconium metal appears on the surface of a heater and then to discontinue further heating.

When the carbon rods are provided with terminals, the heating to the elevated temperatures in the vacuum chambers may be accomplished by passing electric current therethrough. However, the carbon support may be heated by other methods if desired.

Certain commercial grades of zirconium hydride contain small amounts of hafnium hydride. When such hydride is used, a mixture of the respective carbides and the free metals is obtained and this is not normally very objectionable. If hafnium hydride is present, the coated carbon rods or supports should be heated somewhat higher than 2050° C. (e. g. 2100° C.) in view of the higher melting point of hafnium.

Example 2

In making heater 5 with a sheath 11 of hafnium carbide and a coating 12 of free hafnium metal, the procedure outlined in Example 1 may be followed using hafnium hydride suspension in place of zirconium hydride and heating to 2250° C. in each instance instead of to 2050° C.

The free zirconium or hafnium metal on the surface of the zirconium or hafnium carbide coating, respectively, is desirable from two standpoints. In the first place, since the carbide is formed by reaction of the metal, as it is formed on the decomposition of the hydride, with the carbon surface of the core or rod, it is desirable that there be at least some excess of the zirconium or hafnium metal in order to insure that the carbon surface of the rod is completely coated with the corresponding carbide and no unreacted carbon is left at the surface. The carbon itself if left exposed will react with the metal being evaporated, e. g. aluminum, and then the aluminum or other carbide will decompose at the operating temperature so as to form the metal vapor and carbon smoke which will spoil the coating or deposit of the metal on the object or surface to be coated. By having at least some excess of zirconium or hafnium metal formed, the substantially complete coating of the carbon rod with the corresponding carbide will be insured.

A second, and very important function of the free zirconium or hafnium metal on the surface is that it

increases the wettability of the heater surface by such molten metals as aluminum. Since one of the important advantages of the heaters of the present invention is the ability to evaporate the molten metal from the entire area thereof, it is very beneficial to increase the wettability or ease with which the molten metal spreads out and wets the heater surface.

It has also been further found in practice that the free zirconium or hafnium metal serves to make the heaters "self-healing" should cracks or breaks develop in the carbide coating. That is, the free zirconium or hafnium metal present will react with the exposed carbon if the breaks are not too large, and will thereby form protective zirconium or hafnium carbide either of which is resistant to attack by the molten aluminum or other metal.

While the method of forming the carbide-free metal coatings described above in connection with Examples 1 and 2 is the presently preferred one, these coatings may be made by other techniques and methods. Thus, free zirconium or hafnium metal powder itself or mixtures thereof may be used in place of the hydride. This method has the disadvantage that it is difficult to obtain and then prevent oxidation of the finely divided zirconium or hafnium powder and the protective action of the hydrogen gas is not present as it is when metal hydride is used. Another technique that may be used is the heating of the carbon rods or supports to temperatures of around 2100° C. in closed chambers in atmospheres of zirconium iodide. Apparently this compound decomposes as the zirconium reacts with the carbon surface of the heated elements to form zirconium carbide and if heating is continued sufficiently long in such an atmosphere, a free zirconium metal coating is ultimately obtained. Hafnium iodide would be used to obtain a hafnium carbide-free hafnium metal coating.

While it is convenient to use carbon rods as the cores for heaters made in accordance with the present invention, the carbon supports may be made in other shapes, for example, as shown in Fig. 3 of the drawings. The heater in Fig. 3 is indicated generally at 13 and is in the form of a bridge-shaped carbon support 14 suitably coated with a sheathing of metal carbide-free metal as described above in connection with Examples 1 and 2. Metallic terminals 15 and 16 are applied to the opposite ends of the support 14. A block of carbon may be suitably machined so that it has a cross section corresponding to the elevation of the carbon support 14 as shown in Fig. 3. Such a block may then be sliced crosswise into a number of the supports 14. The horizontal portion of the support 14 will thus be rectangular in cross section and heaters having widths of one-quarter of an inch and thicknesses of one-eighth of an inch have been found to be suitable although these dimensions are not critical.

The heaters 5 and 13 shown in Figs. 1 and 3, respectively, are suitable for self-heating by passing electric currents therethrough. It will be understood that heaters may be made in accordance with the present invention which have other shapes and cross sections and which may be heated indirectly by induction or electron bombardment.

At the present time vacuum metallizing operations are conducted either as a batch or a continuous type process depending upon the particular surfaces or articles to be coated. Where small individual articles are to be coated (e. g. jewelry, toys, Christmas tree ornaments, etc.), the metal is vacuum evaporated in a batch type process in apparatus suitably designed for this type of operation. Where the surface or object to be coated is of a large area such, for example, as a web or roll of paper or plastic, the metal is vacuum evaporated in a continuous type process wherein the web is continuously unrolled from a supply roll and rewound after a coating on another

roll while the metal to be evaporated is continuously fed onto the heater elements. The use of heaters of the present invention in a batch type vacuum metallizing apparatus will be described in connection with Figs. 4 and 5 of the drawings. In these figures the vacuum chamber is indicated at 20 and may take the form of a horizontal bell jar which may be formed either of metal or glass. The chamber 20 is provided on one end with a removable door 21 which may be bolted onto a flange 22 by means of suitably spaced bolts 23—23. It will be understood that a suitable gasket may be used in order to insure tightness of the chamber 20 when closed. At the opposite end, the chamber 20 is provided with a neck or connection 24 which leads to the pumping system. Since the pumping system may be of any suitable known design which will have adequate capacity and provide the suitable vacuum, it will not be shown or described in the present application.

The heater elements, which may, for example, correspond to the heater element 5 shown in Figs. 1 and 2, are indicated at 25—25 in Figs. 4 and 5. These heaters 25 are suitably supported in the chamber 20 approximately on the longitudinal axis thereof and the opposite terminals of the heaters are suitably connected to the buses 26 and 27 which are supported from the door 21 and have exterior terminals 28 and 30 respectively suitably insulated from the door 21 by bushings 29—29.

The objects to be coated may, for example, take the form of glass balls 31—31 such as are used for Christmas tree ornaments. These balls are supported on the ends of the spokes 32 of a number of wheels which are adapted to be rotated within the chamber 20. As the wheels rotate the balls 31 are completely exposed to the metal being evaporated from the heaters 25 and thus receive a uniform coating over their entire surfaces.

Before the heaters 25 are inserted into the chamber 20, they are first provided with a deposit of the metal to be coated, e. g. aluminum. Such a deposit may be provided thereon either by dipping the heaters 25 into molten aluminum so as to receive a film thereof or aluminum in the form of wire or foil may be wrapped around the heaters 25.

The operation of the apparatus shown in Figs. 4 and 5 in general follows conventional procedure for this type of equipment, which corresponds to that previously in use for batch vacuum metallizing operations except for the heaters 25. The open chamber 20 is loaded with the objects 31 to be coated and with the heaters 25 which are suitably provided with the metal to be coated. The cover or end 21 is then bolted in place and the vacuum is drawn until it is reduced to the desired degree, e. g. 1×10^{-5} mm. The current is then turned on and the temperature of the heaters 25 raised to the point where the metal evaporates therefrom, e. g. 1350° C., when the metal is aluminum. Normally the evaporation only requires approximately one-half minute.

While the heaters of the present invention may be used to advantage in the batch vacuum metallizing operations, they have their fullest utility and greatest advantage in connection with continuous type vacuum metallizing operations wherein a web of paper or plastic is to be coated with a metallic film. Such an apparatus and the method of operation thereof will be described in connection with Figs. 6 and 7. In these figures the vacuum chamber is indicated at 35 and is preferably formed of steel in view of the rather large size which may be as long as 6 feet and as much as 5 feet in diameter. For purposes of facilitating control, the chamber 35 is provided with at least one sight glass or window 36 secured in place in gas-tight relationship by means of inner and outer retaining rings 37 and 38 which will be suitably gasketed in known manner. A connection 40 is integrally formed on the top of the chamber 35 for connection with the pumping system.

The supply roll of sheet material to be coated is in-

licated at 41 and is suitably supported for rotation on a shaft which is journaled between vertical plates 42 and 43 as shown in Fig. 7. The web is indicated at 44 and runs over one guide roll 45 and thence over another horizontally spaced guide roll 46 from which it passes over a windup roll 47. All of these rolls are supported between the plates 42 and 43 and the windup roll 47 is positively driven. For this purpose the shaft on which the windup roll 47 is carried is provided on one end with a sprocket 50 over which runs a drive chain 51 which runs over a drive sprocket 52 carried on a drive shaft 53 which projects outwardly through the adjacent end of the chamber 35 and is suitably packed and sealed in known manner.

This arrangement serves to continuously pass the web 44 between the guide rolls 45 and 46 so that it is horizontally supported above a plurality of heaters 54—54 which may take the form of the heaters 13 shown in Fig. 3 of the drawings. Each of the heaters is supported at opposite ends on a pair of bus bars 55 and 56 which are insulatedly supported from the bottom of the chamber 35 by means of a plurality of insulating blocks 57—57. The buses 55 and 56 project through the door 60 to the chamber 35 and are provided with exterior terminals 61—61.

Since this apparatus is designed to operate continuously for periods of over an hour, an arrangement is made for continuously feeding the metal to be evaporated to the heaters 54. One suitable feeding arrangement is shown in Fig. 6. There, the metal to be evaporated in the form of a wire or strip is supported on spools 62 which are free to unwind, there being one of these spools provided for each of the heaters 54. The wire is indicated at 63 and is guided through tubular sections 64 and 65. Each of the tubular sections 65 is curved downwardly so as to bend and feed the wire 63 down onto the top surface of the adjacent heater 54. Knurled feeding rolls or wheels 66 and 67 are placed in between the tubular sections 64 and 65 so as to grip the wire 63 and feed it forwardly. The means by which the sets of rolls 66 and 67 are driven is not shown but may be of known or obvious design and preferably is regulatable from the exterior of the apparatus.

In operation: The vacuum chamber 35 is first loaded with a roll 41 of the web to be coated and this web is threaded around the rolls 45 and 46 and fastened to the windup roll 47. Heaters 54 from a previous run which appear to have been consumed to the point where they will not last for the duration of another run are replaced, and spools of wire (e. g. aluminum) are inserted and threaded through the guide sections 64 and 65 and feed rolls 66 and 67. The chamber is then closed, and the terminals 61 are connected to the source of current. The vacuum is then drawn onto the chamber 35 and when it has been suitably perfected, the apparatus is placed into operation. The metal wire is fed onto the heaters 54 at a sufficient rate so as to maintain a molten film over the evaporating surface thereof and the evaporating metal serves to deposit a uniform and continuous film of the metal onto the bottom surface of the web 44 as it passes between the support rolls 45 and 46. The operator will from time to time make whatever adjustments are necessary for controlling the rate of speed of the web 44, and the rate of speed of the aluminum wire onto the various heaters 54—54. A further adjustment which may be made as required is the amount of current fed to the heaters 54, which controls the temperatures thereof.

The two primary advantages of the heaters made in accordance with the present invention when used in continuous type vacuum metallizing operations are: (1) the comparative long life of the heaters (e. g. up to 3 hours) and the dependability thereof; and, (2) the operation of the heaters at substantially lower temperatures than were previously possible with heaters such as those of the tungsten filament type. The longer life and the greater dependability of the heaters permit the apparatus to be operated for longer periods at a single time without

failure or interruption due to failure of individual heaters or need to shut down for replacement of the heaters. The lower operating temperatures lessen the chances of altering or damaging the webs or films 44 to be coated and permit webs to be coated of a type that cannot withstand the higher temperatures encountered when heaters of the prior art such as the tungsten filament type are employed. Furthermore, the lower operating temperatures prolong the useful life of the various parts of the apparatus that are sensitive to high temperatures.

By substituting heaters made in accordance with the present invention for those previously available and used in continuous type vacuum metallizing apparatus, it has been possible to increase the productive operating time of such apparatus as much as 200%.

Since certain changes and modifications may be made in the embodiments of the invention described above in connection with the accompanying drawings and other embodiments of the invention may be made without departing from the spirit and scope thereof, the foregoing detailed disclosure of the invention is intended to be interpreted as illustrative and not in a limiting sense.

What is claimed as new is:

1. The method of making a heater adapted for use in apparatus for evaporating metal onto a surface by thermal evaporation of the metal in a vacuum, comprising, coating a carbon support with finely divided zirconium hydride, heating said support in a vacuum so as to decompose said zirconium hydride into zirconium metal and hydrogen gas, and repeating said coating and heating steps at least once.

2. The method of making a heater adapted for use in apparatus for evaporating metal onto a surface by thermal evaporation of the metal in a vacuum, comprising, heating a carbon support in a vacuum in order to drive off volatile matter therefrom, applying a coating of finely divided zirconium hydride to said carbon support, heating said support in a vacuum so as to decompose said zirconium hydride into hydrogen gas and zirconium metal, and repeating said coating and heating steps at least once.

3. The method of making a heater adapted for use in apparatus for evaporating metal onto a surface by thermal evaporation of the metal in a vacuum, comprising, heating a carbon support in a vacuum of at least about 0.1 mm. (mercury column) at a temperature of at least about 2000° C. for at least about two minutes, applying a liquid suspension of finely divided zirconium hydride over the surface of said carbon support, heating said support with said zirconium hydride thereon in a vacuum of about 1×10^{-3} mm. at about 2050° C. for about one minute, re-coating said carbon support with a suspension of finely divided zirconium hydride, and heating said re-coated support in a vacuum of about 1×10^{-3} mm. at a temperature of about 2050° C. and discontinuing the heating when a film of free zirconium metal is produced on the surface.

4. The method of making a heater adapted for use in apparatus for evaporating metal onto a surface by thermal evaporation of the metal in a vacuum, comprising, coating a carbon support with finely divided hafnium hydride, heating said support in a vacuum so as to decompose said hafnium hydride into hafnium metal and hydrogen gas, and repeating said coating and heating steps at least once.

5. The method of making a heater adapted for use in apparatus for evaporating metal onto a surface by thermal evaporation of the metal in a vacuum, comprising, heating a carbon support in a vacuum in order to drive off volatile matter therefrom, applying a coating of finely divided hafnium hydride to said carbon support, heating said support in a vacuum so as to decompose said hafnium hydride into hydrogen gas and hafnium metal, and repeating said coating and heating steps at least once.

6. The method of making a heater adapted for use in apparatus for evaporating metal onto a surface by thermal

evaporation of the metal in a vacuum, comprising, heating a carbon support in a vacuum of at least about 0.1 mm. (mercury column) at a temperature of at least about 2000° C. for at least about two minutes, applying a liquid suspension of finely divided hafnium hydride over the surface of said carbon support, heating said support with said hafnium hydride thereon in a vacuum of about 1×10^{-3} mm. at about 2250° C. for about one minute, re-coating said carbon support with a suspension of finely divided hafnium hydride, and heating said re-coated support in a vacuum of about 1×10^{-3} mm. at a temperature of about 2250° C. and discontinuing the heating when a film of free hafnium metal is produced on the surface.

7. In a method of applying metal coatings to surfaces wherein the metal to be deposited thereon is evaporated at an elevated temperature in a vacuum, the improvement which consists in heating in the vacuum a carbon core having a coating thereon of composite metal and metal carbide selected from the group consisting of zirconium carbide with free zirconium metal and of hafnium carbide with free hafnium metal and of mixed carbides of zirconium and hafnium with mixed zirconium and hafnium free metal, said coating having the selected carbide at the carbon core and the selected free metal at the exterior surface, said heating being to a temperature above the melting point of the metal to be deposited, bringing the metal to be deposited into contact with the said selected metal whereby the molten metal to be deposited wets and spreads upon the selected free metal and is evaporated from a film extending over substantially the entire surface of said coating, and preventing contact with the carbon core by the metal to be deposited through maintaining the coating of the selected metal carbide upon the carbon core.

8. The method as in claim 7, in which the metal is zirconium and the carbide is zirconium carbide.

9. The method as in claim 7, in which the metal is hafnium and the carbide is hafnium carbide.

10. In an apparatus for evaporating metal and depositing the metal vapor onto a surface and having an evacuated chamber surrounding the said surface and an evaporating heater in said chamber for contact with the metal to be evaporated, said evaporating heater having a core subject to attack by the molten metal to be evaporated and a heating surface for contact with the metal to be evaporated, said surface being presented by a metal wettable by the metal to be evaporated for establishing over the surface area a film of the metal to be evaporated, the improvement which consists in having said heater composed of a carbon core and an outer coating of composite free metal and metal carbide upon said core, said coating being selected from the group which consists of zirconium carbide with free zirconium metal and of hafnium

carbide with free hafnium metal and of mixed carbides of zirconium and hafnium with mixed zirconium and hafnium free metal, the selected carbide forming a sheath on the carbon core and the selected free metal being present at the exterior surface of the coating, said coating being characterized in that the molten metal to be evaporated can wet and be spread by the selected free metal present at the surface of the said coating and the carbide of said coating is effective to prevent contact with the carbon core by the metal to be evaporated.

11. The improvement as in claim 11, in which the metal is zirconium and the carbide is zirconium carbide.

12. The improvement as in claim 11, in which the metal is hafnium and the carbide is hafnium carbide.

13. In an apparatus for evaporating aluminum and depositing the aluminum vapor onto a surface and having an evacuated chamber surrounding the said surface and an evaporating heater in said chamber for contact with the aluminum to be deposited, said evaporating heater having a core subject to attack by molten aluminum and a heating surface for contact with the aluminum to be evaporated, said surface being presented by a metal wettable by the aluminum for establishing over the surface area a film of molten aluminum, the improvement which consists in having said evaporating heater composed of a carbon core and an outer coating of composite free metal and metal carbide upon said core, said coating being selected from the group which consists of zirconium carbide with free zirconium metal and of hafnium carbide with free hafnium metal and of mixed carbides of zirconium and hafnium with mixed zirconium and hafnium free metal, the selected carbide forming a sheath on the carbon core and the selected free metal being present at the exterior surface of the coating, said coating being characterized in that the molten aluminum to be evaporated can wet and be spread by the selected free metal present at the surface of the said coating and the carbide of said coating is effective to prevent contact with the carbon core by the aluminum.

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