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COATING DEVICE AND METHOD

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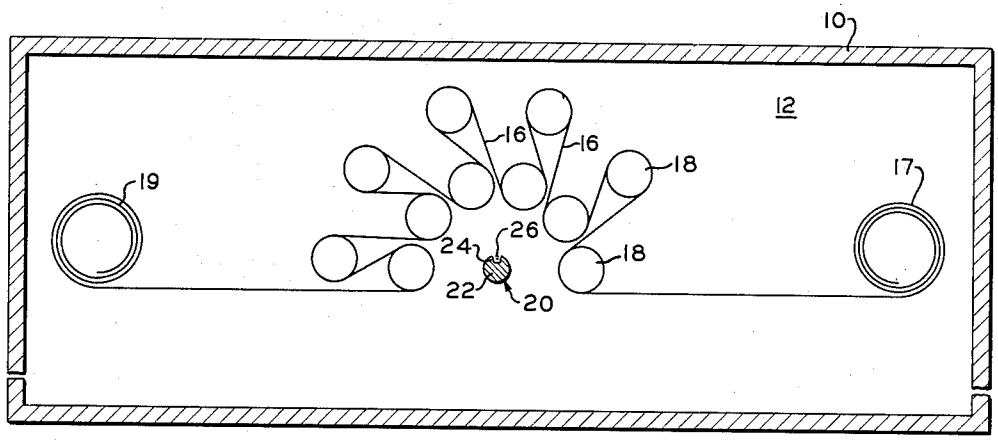


FIG. 1

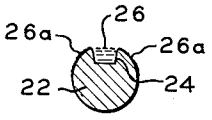


FIG. 1a

FIG. 2

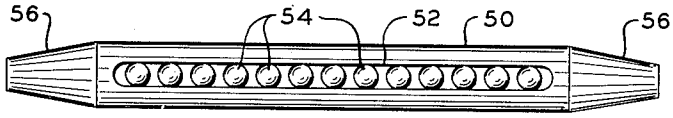


FIG. 3

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COATING DEVICE AND METHOD

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6 Claims. (Cl. 117—22)

This invention relates to coating and more particularly to the coating of substrates by vacuum evaporation of aluminum with deposition of the aluminum vapors on the substrate. This invention is particularly directed to improvements in sources for aluminum vapors in such vacuum-coating processes.

It is a principal object of the present invention to provide an improved source of aluminum vapors for use in a vacuum coating process.

Another object of the invention is to provide such a source which is cheap, reliable, and capable of long periods of operation with the generation of large quantities of aluminum vapors.

Another object of the invention is to provide a support for molten aluminum during the evaporation thereof, this support being readily wettable by molten aluminum and being relatively inert to molten aluminum.

Still another object of the invention is to provide an improved method for manufacturing such supports.

Still another object of the invention is to provide improved coating processes and apparatus embodying such improved aluminum vapor sources.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others, and the apparatus possessing the construction, combination of elements and arrangement of parts which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Fig. 1 is a diagrammatic schematic sectional view of one form of coating apparatus utilizing the present invention.

Fig. 1*a* is an enlarged view of a portion of Fig. 1.

Fig. 2 is a diagrammatic schematic sectional view of an apparatus useful in preparing the novel aluminum supports of the present invention.

Fig. 3 is a schematic top view of one type of aluminum support element particularly useful for batch coating operations.

In one preferred embodiment of the invention there is provided a vacuum chamber in which a substrate to be coated may be moved past a source of metal vapors, these metal vapors being preferably aluminum, and the invention being primarily described in connection with the coating of aluminum on flexible and other substrates. One preferred type of aluminum vapor source comprises an elongated element which acts as a support for aluminum, this element having a surface which is readily wet by molten aluminum and which is relatively inert to molten aluminum. For reasons of economy and because of its structural strength at high temperatures, this elongated support preferably comprises carbon, the surface of this carbon element having a coating of one of the metals tungsten or molybdenum. This metal coating preferably includes a substantial amount of a corresponding carbide, these two metals and their carbides being readily wet by molten aluminum and their carbides being relatively inert to molten aluminum. In the process of practicing the present invention some of the metal, at least at the beginning of the use of the carbon element, may not be completely converted to a carbide. At the temperatures preferably employed for vaporizing aluminum, i. e., 1300° to 1500° C., both molybdenum and tungsten have extremely low vapor pressures.

In a preferred method for manufacturing such an elongated carbon element having a surface stratum of a carbide of one of the elements, molybdenum and tungsten, a coating of the corresponding metal is first created on the surface of the carbon rod. Thereafter the carbon rod with the metallic coating is heated in an air-free atmosphere for a sufficient length of time to convert a substantial proportion of the metal coating to a corresponding carbide. This heating may be achieved in an inert atmosphere, such as argon, but it is preferred that this heating be accomplished under a vacuum, since it simultaneously serves to drive from the carbon element those materials which might subsequently be volatilized when the rod is heated to the relatively high temperatures required for vaporizing aluminum in the vacuum-coating system. This heating process may thus serve the dual function of converting the metallic coating to a corresponding metal carbide and also of outgassing the carbon element so that it will not interfere with the subsequent aluminum coating process.

In a preferred embodiment of this aspect of the invention the metal coating is put on the carbon element by contacting the surface of the carbon element with a finely divided solid carbonyl of the metal to be applied to the carbon element. The interface between the carbon element and the carbonyl is then heated to a temperature on the order of 300° C. for a sufficient time to decompose the carbonyl and to form a dense adherent coating of the metal on the carbon element. The surface of the element is then freed of the carbonyl and is heated, as mentioned previously, to convert this metallic coating to the corresponding carbide.

Referring now to Figs. 1 and 1*a* there is shown one preferred embodiment of the invention as applied to a continuous coating apparatus. This apparatus generally includes a vacuum-tight housing **10** defining therewithin a vacuum-coating chamber **12** which is arranged to be evacuated by a vacuum-pumping system not shown. Within this chamber the substrate **16** to be coated is guided from a supply **17** thereof past a plurality of guiding rolls **18** to a take-up spool **19**. If desired, the rolls **18** may be cooled by suitable means. During the passage of the substrate from the supply **17** to the take-up spool **19**, it passes in a series of convolutions near a source **20** of metal vapors, these vapors being preferably aluminum vapors. The guiding rolls **18** are preferably driven and are so arranged that they do not "see" the vapor source. Thus the guiding rolls are not coated by the vapors from the source, and are not exposed to direct heat radiation from the source. This arrangement of rolls permits sufficient cooling during and between aluminum coating steps and provides a minimum of outgassing of heat-sensitive substrate. The source **20** preferably comprises an elongated carbon rod having a groove **24** in the upper surface thereof, this groove being preferably maintained full of molten aluminum **26**. This carbon rod is preferably supported in a manner similar to that illustrated in the copending application of Clough and Godley, Serial No. 171,432, filed June 30, 1950.

Aluminum in either liquid or solid form may be fed to the groove in the rod, as pointed out more fully in the above-mentioned application.

In the operation of the device shown in Figs. 1 and 1*a*, roll **17** of the substrate **16** is positioned within the vacuum chamber **12** and the substrate is guided around the various rolls **18** and connected to the take-up spool **19**. A coolant, such as cooling water at about 40° F. or lower, is then circulated through the rolls **18** by suitable piping (not shown) so as to chill the rolls **18**. The vacuum chamber **12** is then evacuated to a low pressure on the order of less than one micron, by means of the vacuum pumping system. When the requisite low pressure is achieved the substrate is advanced, preferably by driving the take-up spool **19** and the various guiding rolls **18**. Aluminum is fed to the slot **24** in the carbon rod **22** and both the rod and the aluminum carried thereby are heated to a high temperature, on the order of between 1300° and 1500° C., by passing a high amperage electric current through the rod and the aluminum supported thereby. During evaporation, the molten aluminum wets a substantial portion of the rod surface outside of the groove so that aluminum is evaporated from all hot surfaces of the rod that "see" the substrate. This wetting by the molten aluminum is shown at **26***a* in Fig. 1*a*.

In a preferred embodiment of the invention described above, the rod **22** preferably comprises dense carbon, several preferred grades of dense carbon rod being those manufactured by Becker Bros. under the designation "B–4," by National Carbon under the designation "G–A," and by Stackpole under the designation "C1H." These carbon rods may have a diameter of about .50 inch and the groove **24** may be approximately ¼ inch wide by 1/16 inch deep. The coating on the carbon rods comprises molybdenum or tungsten carbide which has been prepared in accordance with the techniques described more fully hereinafter.

Referring now to Fig. 2 there is shown one preferred method of manufacturing a carbon rod having a carbide surface of the type mentioned above. In this figure, **30** represents a container such as a glass beaker which confines a quantity of powdered carbonyl **32**, this container being closed by a stopper **35**. The carbon element **22** is heated by a high frequency induction coil **36** connected to a suitable power supply **37**. If desired a thermocouple **38** may be utilized for indicating, by means of a meter **39**, the temperature of the carbon element during the treatment thereof. The container **30** is preferably vented through a tube **40** containing a quantity of copper oxide **41**. The tube also includes a calcium chloride water vapor barrier **42**, a pressure surge tank **46**, and another container **48**, the end of tube **40** being below the level of a water solution of potassium hydroxide **47** held in container **48**.

In one preferred example of this aspect of the process of the present invention, the powdered carbonyl **32** is prepared by powdering molybdenum hexacarbonyl, $Mo(Co)_6$. The crusted grains of carbonyl powder are preferably of a size at least as small as 60 mesh, this small grain size being particularly desirable for assuring uniform coating in the slot **24** in the carbon rod **22**. Powdered carbonyl **32** is then placed in a container **30** and the carbon rod **22** is inserted therein. In this connection it is desired to tap the container **30** so as to insure intimate contact between the powdered carbonyl and all surfaces of the rod. The high frequency coil is then energized to heat the carbon rod to a temperature above the decomposition temperature of the carbonyl. This temperature is preferably on the order of approximately 300° C. This temperature is preferably maintained for about 10 seconds, the temperature being lowered to about 150° C. at the end of the 10 seconds and then again raised to 300° C. This cycle is repeated until the total time of heating to a temperature near 300° C. equals about 180 seconds. During the operation of the carbonyl decomposition apparatus the copper oxide **41** is preferably heated to about 320° C. to convert to carbon dioxide the carbon monoxide resulting from decomposition of the carbonyl. One convenient method of operating the apparatus of Fig. 2, without the use of a thermocouple for directly reading the rod temperature, is to replace the hydroxide solution **47** with water. Coil **36** is then energized until a rapid series of bubbles appears in the water **47**. This indicates that decomposition of the carbonyl is taking place, the bubbles being carbon dioxide. The coil is deenergized and the carbon rod **22** is allowed to cool slightly for a few seconds. The coil is energized again until another group of bubbles appears in water **47**. Again the power is turned off. This cycle can be repeated until the total time for generating the bubbles equals about 180 seconds. At the end of either of the above heating periods the coil **16** is deenergized and the carbon rod is removed.

In a preferred embodiment of the invention, particularly when manufacturing support elements for batch coating operations, the carbon rod may be, in the form illustrated at **50** in Fig. 3, about two inches long, about ¼ inches in diameter. This rod has a slot **52** therein approximately 1¾" long. This carbon rod is preferably formed of a dense carbon, such as Grade B–4 sold by Becker Bros. The slot **52** in the rod may be about ⅛ inch wide by 1/16 inch deep. A supply of aluminum in the slot **52** is shown in the form of balls **54**. The ends **56** of the rod are preferably tapered to provide low resistance contacts with a rod holder, not shown, to permit the rod to be heated by passing an electrical current therethrough. After coating such a rod, by heating in intimate contact with powdered molybdenum hexacarbonyl at a temperature of about 300° for approximately 180 seconds, the rod is found to be coated with a dense uniform layer of molybdenum which appears to be slightly less than .001 inch thick. This coating is strongly adherent to the carbon element. Metallographic examination indicates that the molybdenum coating is in the form of a laminar deposit. This coating is essentially molybdenum with some carbon (less than 5%) in solution. This coated carbon element, after removal from the carbonyl coating container, is heated in a vacuum furnace to approximately 1250° C. until the pressure in the vacuum chamber can be maintained at about .1 micron Hg abs. Metallographic examination after treatment indicates that the molybdenum coating has undergone recrystallization with considerable diffusion of carbon into the molybdenum coating, particularly at the interface between the molybdenum coating and the carbon element. This diffusion of carbon appears to create an interface layer of molybdenum carbide, but metallographic examinations alone cannot confirm this fact. A rod **50**, prepared as above, was placed in a batch vacuum coater and the slot **52** was loaded with about .33 gram of aluminum. Prior to the first evaporation the temperature of the rod was gradually raised to slightly below the melting point of aluminum during the evacuation of the vacuum chamber to remove any adsorbed water vapor from the rod. During this preliminary heating the pressure was maintained below about 5 microns Hg abs. When the operating pressure of approximately .1 micron Hg abs. was obtained in the vacuum coater, the rod containing the aluminum was heated to about 1400° C. to evaporate all of the aluminums. This heating was preferably achieved by passing about 200 amps through the rod. On subsequent coatings the rod, reloaded with aluminum, is brought up to temperature (about 1400° C.) as soon as the desired coating pressure of about .1 micron has been obtained. This coating procedure was repeated for fifty times, approximately .33 gram of aluminum being evaporated on each coating cycle. At the end of fifty batch coating operations the rod was still in excellent shape.

From the above description of the invention it would seem that this carbon element containing the molybdenum-carbon surface stratum is extremely resistant to attack by molten aluminum at relatively high temperatures on the order of 1300° to 1500° C., and has an amazingly long useful life. This is particularly surprising when it is considered that a molybdenum filament, when used in a batch coating operation for evaporating aluminum, has a life of about three evaporations. An uncoated carbon rod has an equally short life and is very poorly wet by molten aluminum. The exact mechanism involved is not particularly well understood since the amount of molybdenum is extremely small. It is believed that, although there may be some slight solubility of the molybdenum or molybdenum carbide in the molten aluminum, the dissolved molybdenum or molydenum carbide is redeposited as the aluminum evaporates, thus maintaining a protective surface stratum as long as the rod is in contact with the molten aluminum.

The results utilizing tungsten carbonyl in place of molybdenum carbonyl are equivalent to those obtained when using molybdenum carbonyl. Equally a carbonyl powder diluted by an inert powder may be employed in this coating operation, the other conditions, such as temperature, etc., remaining the same. One type of diluent may comprise alumina powder of about 60 mesh or finer, the diluent being about 50% by weight of the mixed powders. Other diluents are described in the copending application of Stauffer S. N. 181,373 filed August 25, 1950.

While a preferred embodiment of the invention has been described above, where molybdenum and tungsten carbonyls have been employed in a pack technique utilizing powdered carbonyls, other less preferred embodiments of the invention may be practiced. For example, the carbonyl may be decomposed from the vapor phase, as described in British Patents 589,966 and 589,977. Additionally, the molybdenum or tungsten coating can be produced on the carbon element by thermal decomposition or reduction of volatile halides of these compounds. Such techniques are described in Journal Electro-Chemical Society 96, 318–333 (1949); van Arkel, "Reine Metalle" published by Edward Bros., Inc., Ann Arbor, Michigan (1943): Childs, Cline, Risner and Wulff, Trans. A. S. M. 43, 105–121 (1951).

These latter methods of coating the molybdenum or tungsten on the carbon element are less preferred than the powdered carbonyl technique in view of the simplicity and excellent results obtained by utilizing this powdered carbonyl.

In general, it is desirable that the carbon element be as dense as possible, and carbon or mixtures of carbon and graphite are preferred over dense graphite in view of the higher resistance of these materials to attack by molten aluminum in the event of imperfections in the coatings. Graphite also has a low electrical resistance and, for a given rod diameter, much higher electrical heating currents are required. Additionally, the rods may be formed of tungsten or molybdenum, and the surfaces thereof may be converted to the carbide by heating in contact with powdered carbon or graphite, or by thermal decomposition of simple organic compounds, such as methane. However, this alternative method of manufacturing these support elements is less preferred due to the lower electrical resistance of the resulting elements and the brittleness of the molybdenum or tungsten rods after use due to recrystallization thereof at the high temperatures required for vaporizing aluminum. Also the carbon, in the surface carbide layer, will diffuse into the molybdenum or tungsten rod during use thereof, thus adding to the brittleness of the rod. When the word "carbon" is used in the annexed claims, it is intended to include elemental carbon, graphite and mixtures of carbon and graphite.

Since certain changes may be made in the above process and apparatus without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description, or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of manufacturing a wick element which is readily wet by molten aluminum for use as a support for molten aluminum during the vacuum evaporation of aluminum in a vapor deposition coating process, said manufacturing process comprising the steps of providing an elongated support comprising a dense carbon element, contacting the surface of said support with a finely divided solid carbonyl from the class consisting of the carbonyls of the metals molybdenum and tungsten, maintaining the interface between said support and said carbonyl at a temperature on the order of 300° C. for a sufficient time to decompose said carbonyl and to form a dense adherent coating of said metal on said support, freeing said surface of said carbonyl, and heating said support under a vacuum of at least .001 mm. Hg abs. for a sufficient time to outgas said support and to cause at least some diffusion of carbon into said metal coating, said last named heating step being accomplished at a temperature on the order of at least 1000° C.

2. The process of manufacturing a wick element which is readily wet by molten aluminum for use as a support for molten aluminum during the vacuum evaporation of aluminum in a vapor deposition coating process, said manufacturing process comprising the steps of providing an elongated support comprising a carbon element, applying to the surface of said carbon element a dense adherent coating of a metal taken from the group consisting of molybdenum and tungsten, said coating having a thickness between about .00004 inch and .001 inch, and heating said support under a vacuum of at least .001 mm. Hg abs. for a sufficient time to outgas said support and convert at least some of said metal coating to a corresponding metal carbide, said last-named heating step being accomplished at a temperature on the order of at least 1000° C.

3. The process of manufacturing a wick element which is readily wet by molten aluminum for use as a support for molten aluminum during the vacuum evaporation of aluminum in a vapor deposition coating process, said manufacturing process comprising the steps of providing a carbon support element, contacting the surface of said support with a finely divided solid carbonyl from the class consisting of the carbonyls of the metals molybdenum and tungsten, maintaining the interface between said support and said carbonyl at a temperature on the order of 300° C. for a sufficient time to decompose said carbonyl and to form a dense adherent coating of said metal on said support, freeing said surface of said carbonyl, and heating said carbon element under a vacuum at some stage in its manufacture to a temperature of at least 1000° C. until substantially all volatiles, having a vapor pressure greater than about 0.5 micron Hg abs. at 1000° C., have been removed from said element.

4. The process of manufacturing a wick element which is readily wet by molten aluminum for use as a support for molten aluminum during the vacuum evaporation of aluminum in a vapor deposition coating process, said manufacturing process comprising the steps of providing an elongated support comprising a carbon element, depositing on said carbon element a dense adherent coating comprising a metal from the class consisting of the metals molybdenum and tungsten, heating said coated element to a temperature of at least 1000° C. in an air-free atmosphere to cause a reaction between said carbon and said metal coating, and heating said carbon element under a vacuum at some stage in its manufacture to a temperature of at least 1000° C. until substantially all volatiles, having a vapor pressure greater than about 0.5 micron

Hg abs. at 1000° C., have been removed from said element.

5. A coating device for coating substrates with aluminum by evaporation of said aluminum and condensation of said aluminum on said substrate, said apparatus comprising means defining a vacuum-tight housing, means for evacuating said housing to a free air pressure on the order of less than one micron Hg abs., an elongated support for molten aluminum within said housing, a charge of aluminum carried by said support, said support comprising a carbon element, said carbon element having thereon a dense adherent coating comprising a metal from the class consisting of the metals molybdenum and tungsten, at least a substantial portion of said metal coating on said carbon element having been converted to a carbide of said metal, and means for heating said carbon element, and the aluminum supported thereby, to a temperature on the order of above 1300° C.

6. A support for holding molten aluminum during evaporation thereof in a vacuum coating device, said support comprising an elongated carbon element, said carbon element having thereon a dense adherent coating

comprising at least one metal from the class consisting of the metals molybdenum and tungsten, said element being substantially free of all volatiles having a vapor pressure greater than about 0.5 micron Hg abs. at 1000° C., said element indicating, under metallographic examination, considerable diffusion of carbon into said metal coating at the interface between said metal coating and said carbon element.

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