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PROCESS FOR DEPOSITING AN ALUMINUM FILM
ON A SUBSTRATE BY THERMAL VAPORIZATION
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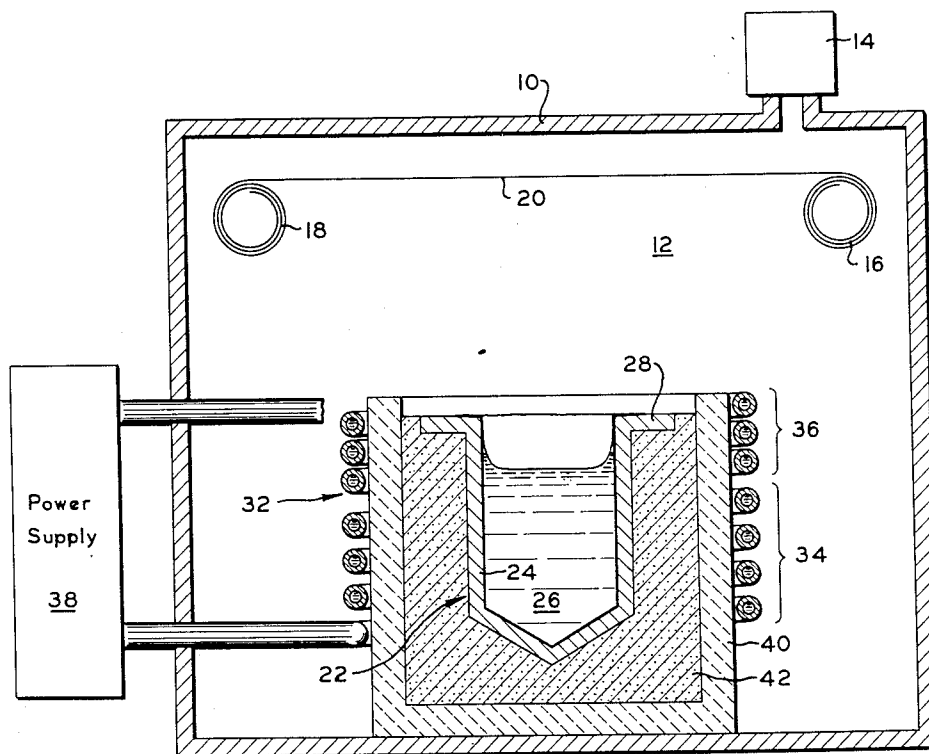


FIG. 1

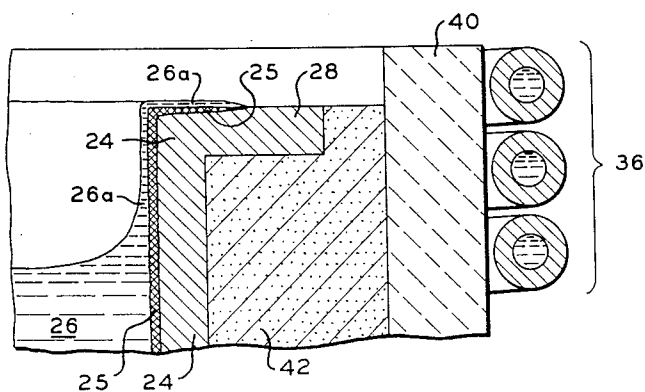


FIG. 2

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PROCESS FOR DEPOSITING AN ALUMINUM FILM ON A SUBSTRATE BY THERMAL VAPORIZATION

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11 Claims. (Cl. 117—107)

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This invention relates to coating and more particularly to the coating of various substrate materials with aluminum by vacuum evaporation and deposition of aluminum. This application is a continuation-in-part of the copending application of Earl E. Chadsey, Jr., Philip J. Clough, and Philip Godley II, Serial No. 117,124, filed September 22, 1949.

A principal object of the present invention is to provide improved processes for evaporating molten aluminum in a vacuum for the purpose of providing a coat of aluminum on a substrate positioned in a vacuum chamber.

Another object of the invention is to provide a process of the above type which permits high evaporation rates over long periods of operation of an aluminum-evaporating crucible.

Still another object of the invention is to provide a process of the above type which permits the use of a crucible of elemental carbon, this crucible being so treated as to have a high resistance to attack by molten aluminum.

Still another object of the invention is to provide for high aluminum evaporation rates by the prevention of the formation of aluminum carbide scum on the surface of molten aluminum being evaporated in a carbonaceous crucible.

Still another object of the invention is to provide an improved crucible for use in processes of the above type.

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

The invention accordingly comprises the product possessing the features, properties and the relation of components, and 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 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 an exaggerated, diagrammatic, partially sectional view of one preferred form of apparatus embodying the invention; and

Fig. 2 is an exaggerated, enlarged, sectional view of a portion of Fig. 1.

In the coating of materials, such as paper, synthetic plastics and the like, with an aluminum film by vacuum evaporation of the aluminum, it is desirable to use a relatively small cru-

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cible so that radiant heat from the area of the molten aluminum does not unduly raise the temperature of the substrate to be coated. It is also desirable to feed aluminum into the crucible during the coating operation so as to provide for long periods of operation. It is additionally advantageous to employ crucible materials which are relatively inexpensive and which have a relatively long life. Additionally, it is extremely desirable to have crucible materials which are not readily subject to heat shock so as not to unduly lengthen the warm-up and cool-off periods.

It has been found that materials comprising elemental carbon, such as amorphous carbon, graphite, and particularly mixtures of amorphous carbon and graphite have excellent characteristics, such as cheapness, machinability, and resistance to heat shock when used as crucibles for coating aluminum. However, molten aluminum, when raised to temperatures on the order of 1200° to 1300° C., rapidly attacks such crucibles with the formation of aluminum carbide. This aluminum carbide is soluble in molten aluminum, but the concentration thereof quickly approaches the saturation point. Since the surface of the molten aluminum on which the evaporation takes place is cooler than the main body of the molten aluminum, the aluminum carbide tends to come out of solution at this surface with the formation of small crystals of aluminum carbide. These crystals, being lighter than aluminum, float on the surface of the molten aluminum in the form of a scum. This scum decreases the effective area from which the aluminum can be evaporated, thereby cutting down the evaporation rate. This defect is particularly noticeable in those cases where solid aluminum is fed to the molten bath during the course of evaporation. Since the solid aluminum is at a temperature considerably below the temperature of the bath, chilling of the surface occurs when the solid aluminum strikes the bath. This chilling rapidly increases the rate of scum formation. The cool metal, being heavier than the hot metal, sinks rapidly to the bottom of the crucible where it reacts with more elemental carbon to form additional aluminum carbide. Thus the feeding of aluminum to the molten pool of aluminum first causes the precipitation of aluminum carbide in the form of a scum and, additionally, forms more aluminum carbide which is dissolved in the melt. Thus the melt continuously remains saturated with aluminum carbide and more and more scum is formed as the solid aluminum is fed to the melt.

It has been found that all of the above-mentioned disadvantages may be overcome, and greatly increased evaporation rates and greatly lengthened crucible life may be achieved by providing, in addition to the aluminum in the crucible, a material which forms a carbide which is substantially insoluble in the molten aluminum at the evaporating temperatures. It has been found that the group IVa and group Va metals are particularly advantageous from this standpoint. By the group IVa and group Va metals we mean those metals in groups IVa and Va shown on the "Periodic Chart of the Atoms," W. F. Meggers, 1947 published by W. M. Welch Manufacturing Company. Generally, the effectiveness of these additional metals for preventing scum formation lies in the following order of decreasing effectiveness: hafnium, zirconium, titanium, tantalum, columbium and vanadium. Of these zirconium, because of its relative abundance, is preferred.

It has been found that these group IVa and group Va metals may be utilized in conjunction with the molten aluminum in an elemental carbon crucible in a number of ways. The metals can be added, before or during the evaporation, in the form of compounds which are reduced by the molten aluminum to the metal with the subsequent formation of the carbide, or they can be added in the form of the metal. Since these metals have relatively low vapor pressures at the temperatures employed for evaporating aluminum, they do not contaminate the aluminum coat on the substrate.

The group IVa and Va metals operate in several ways to prevent scum formation. When the metal, such as zirconium, is employed, it acts to form zirconium carbide from aluminum carbide in the melt. Since the zirconium carbide is relatively insoluble in molten aluminum, it is precipitated out of the solution. This zirconium carbide, being heavier than aluminum, sinks to the bottom of the melt and does not form a scum. Additionally, the zirconium forms a film of zirconium carbide at the interface between the molten aluminum body and the elemental carbon crucible wall. When this film is about 0.5 mm. thick it is substantially impermeable to molten aluminum and thereby prevents attack of the crucible wall by the aluminum.

Referring now to Fig. 1, one preferred form of apparatus utilizing the present invention is shown. This apparatus comprises a vacuum-tight housing 10 providing a vacuum chamber 12, this chamber being kept at a pressure in the micron range by means of a vacuum pumping system schematically indicated at 14. Within the chamber 12 there is provided a means for supporting a base material to be coated, this means being shown schematically as a first spool 16 and a second spool 18 carrying therebetween the base material 20.

The means for vaporizing the metal comprises a metal-holding crucible 22 having a main body portion 24 in which the aluminum 26 is to be held in molten condition and heated to a temperature sufficient to vaporize the aluminum at a high rate under the pressure existing in the vacuum chamber 12. Extending from the top of the main body portion 24, there is provided a lip 28 which is preferably formed integrally with the body portion 24. For providing heat to the aluminum 26 and the metal-holding crucible 22, there is included a heating means, schematically indicated at 32. This heating means preferably comprises an induction coil having a portion 34 for

heating the main body of the crucible and the aluminum carried thereby and a portion 36 for heating the lip 28 of the metal-holding crucible. A suitable power supply 38 is provided for furnishing a high frequency current to the induction coil 34, 36. The induction coil 34, 36 is preferably a water-cooled coil, such as a copper tubing, through the interior of which water is adapted to be circulated. As can be seen from Fig. 1, the turns in portion 36 of the coil, adjacent the lip 28, are closer together than are the turns in portion 34 of the coil, adjacent the main body portion of the crucible.

For preventing radiation heat loss from the crucible 22, there is provided an outer crucible 40, preferably made of a refractory material which does not conduct electricity, and a refractory packing 42 between the metal-holding crucible 22 and the outer refractory crucible 40. Means for feeding aluminum to the crucible are also preferably provided but not illustrated. Such means may comprise a wire-feeding mechanism which feeds wire to the crucible at a rate equal to the rate of evaporation of the aluminum. Additionally, the aluminum may be fed to the crucible in the form of pellets by the use of a pellet-feeding mechanism of the type described in the application of Earl E. Chadsey, Jr., Serial No. 130,453, filed December 1, 1949, and now Patent No. 2,635,579.

In a preferred form of the invention the metal-holding crucible 22 is preferably formed of an elemental carbon, such as amorphous carbon, graphite, or a mixture of graphite and amorphous carbon of the type commercially available under the trade name "Graphitar." The outer crucible 40 preferably comprises a refractory material, such as silica, while the refractory packing 42 preferably comprises zirconia or beryllia. The induction coil is preferably provided with a suitable source of high frequency current of approximately 9,000 to 150,000 cycles per second from a usual high frequency power source. When a "Graphitar" crucible 22 is employed for vaporizing aluminum, and a frequency of about 100,000 cycles is used, the skin depth of the induced current is approximately .2 inch at the temperature employed. The wall of the crucible is preferably made slightly thinner than .2 inch so that some of the induced current flows in the molten aluminum charge.

In the use of the present invention, as embodied in Figs. 1 and 2, a number of alternative methods may be employed. In one preferred embodiment of the process, a quantity of aluminum 26 is provided in the crucible 22 in the form of pellets or the like. Also included within the initial charge is a number of pellets of zirconium metal. Chamber 12 is evacuated by the pump 14 to about .2 micron pressure, and power is supplied to the induction coil 34, 36. The amount of aluminum supplied to the crucible 22 is preferably enough to fill the crucible to within about a quarter of an inch from the top thereof. As the aluminum melts, due to the applied heat, the zirconium dissolves, forming a mixture of the two metals. Both the aluminum and the zirconium attack the inner surface of the body portion 24 of the crucible, the aluminum forming aluminum carbide, most of which is dissolved in the melt, and the zirconium forming zirconium carbide, in situ, on the inner surface of the crucible. As the zirconium carbide formation progresses, it forms a substantially impermeable layer or film 25 on the inner surface of the cru-

cible, this layer preventing further reaction between the molten aluminum and the crucible body 24. Excess zirconium in the aluminum melt also acts to reduce the formed aluminum carbide to aluminum with the formation of zirconium carbide which sinks to the bottom of the crucible.

As can be seen from an examination of Fig. 2, the molten aluminum in the crucible tends to creep up the walls of the crucible and over the top surface of the lip 28 thereof. In a preferred form of the invention illustrated, the portion 33 of the heating coil 32 maintains the lip 28 hotter than the remainder of the crucible so that the aluminum tending to creep out of the crucible is vaporized before it can progress beyond the edge of the lip 28. This aspect of the invention is described in more detail and is claimed in the above-identified application of Chadsey et al., Serial No. 117,124.

The above description of the operation of the invention has been limited to one preferred form thereof, wherein zirconium metal is utilized as the material for forming the relatively insoluble carbide film 25 which protects the inner surface of the crucible. As mentioned previously, zirconia, or other reducible compounds of zirconium, may be used. In addition the other group IVa and group Va metals, hafnium, titanium, tantalum, columbium and vanadium may equally be used, either in the form of the metal or in the form of compounds reducible by aluminum at the temperature employed.

The various metals or compounds thereof, such as zirconium, titanium or the like, may be utilized in a number of different fashions. These metal compounds may be added as a slurry to the interior of the crucible prior to the loading of the aluminum therein. In this case the carbon of the crucible reduces some of the metal compound and forms the carbide directly. Equally, the metal may be deposited by vapor deposition procedures on the interior of the crucible. These vapor deposition procedures include, among others, such processes as vacuum evaporation and deposition of the metal on the inner surface of the crucible, and vapor phase thermal dissociation or reduction on this inner surface. These vapor deposition procedures are particularly advantageous in those instances where the elemental carbon is relatively porous, such as is in the case of most graphites. In this case the preforming of the relatively impermeable inner film of the group IVa or group Va metal carbide prevents permeation of the molten aluminum into the interior of the graphite crucible, and thus prevents destructive interior formation of aluminum carbide.

In still other forms of the invention the metal may be melted in the crucible to form the protective carbide on the inner surface thereof. The metal, or compound thereof, may be added in the form of pellets, powder, or rods to the initial charge or to the melt during the course of evaporation of the aluminum. When only a small charge of the metal is added with the aluminum initially, it is preferred that the metal or its compound be added during the feeding of the aluminum to the melt. When relatively large quantities of the metal are added, either in the form of a carbide skin 25 on the crucible or as a part of the initial charge, it is sometimes not necessary to add any more of the metal during long periods of vaporization. For example, when about two grams of zirconium per square inch of inner crucible surface are added with the ini-

tial charge, it has been found that the resulting carbide film 25 formed on the interior of the crucible is about 0.5 mm. thick and is sufficient to protect the crucible against attack by molten aluminum for well over five hours' operation. These excellent results are achieved in spite of chilling which occurs due to feeding of aluminum to the crucible during this time.

As a general proposition it appears that, when high evaporation rates are to be employed from an unlined crucible, it is preferable to use the group IVa or group Va metals rather than the reducible compounds thereof in the aluminum melt. This requirement is believed to be due to the fact that the reaction between the molten aluminum and the elemental carbon is faster than the reducing action of the aluminum upon the compound, such as zirconia. Therefore, the charge in the crucible becomes very rapidly saturated with aluminum carbide with the rapid formation of scum upon the feeding of cool aluminum thereto. Once the scum of aluminum carbide is formed, it has been found much easier to eliminate the scum by the addition of pure metal, such as zirconium, rather than by the addition of the compound zirconia. In all cases it is generally better to prevent excess aluminum carbide formation than to eliminate the aluminum carbide formation after scum has been created.

While preferred forms of the invention have been described above, it should not be limited thereto. For example, the crucible may be wholly formed of the carbide of one of the group IVa and Va metals. However, such crucibles are relatively expensive, are not as easily formed or machined, and are more subject to heat shock than the elemental carbon crucibles containing the inner lining of the metal carbide.

While the invention has been described in connection with a preferred type of crucible and heating element for use therewith, it should be understood that the invention is by no means limited to the particular embodiment shown. The crucible may be of the type disclosed in the application of Noble E. Hamilton, Serial No. 117,444, filed September 23, 1949, and now abandoned. Equally, other types of crucibles and heating systems of the prior art may be employed. While a crucible is preferred for holding the aluminum, in those cases where a strong electromagnetic field is utilized to hold the molten aluminum in a globular shape on a flat surface, the support for the molten aluminum may comprise elemental carbon including a surface in contact with the aluminum which comprises a carbide of one of the group IVa or group Va metals.

Since certain changes may be made in the above product and process 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 drawing, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process for the deposition of an aluminum film on a substrate by thermal evaporation of molten aluminum in a vacuum which comprises heating aluminum to a temperature sufficiently above its melting point to evaporate the aluminum, maintaining the molten aluminum, during evaporation, on an elemental carbon support, and maintaining at the interface between the support and the molten aluminum a layer of a carbide of a metal taken from the class consist-

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ing of titanium, zirconium, hafnium, vanadium, columbium and tantalum so as to prevent undue attack of the elemental carbon support by the molten aluminum, said carbide layer being formed by contacting said carbon support with a material comprising said carbide-forming metal while said support is maintained at a sufficiently high temperature to form the carbide layer.

2. The process of claim 1 wherein said metal comprises zirconium.

3. The process of claim 1 wherein said metal comprises titanium.

4. The process of claim 1 wherein said metal comprises tantalum.

5. The process of claim 1 wherein said metal comprises columbium.

6. The process of claim 1 wherein said metal comprises vanadium.

7. The process of claim 1 wherein said carbide layer is on the order of 5 mm. thick.

8. The process of claim 1 wherein said carbide surface is formed on said support prior to feeding aluminum thereto.

9. The method of eliminating formation of aluminum carbide scum and protecting an elemental carbon support against attack by high temperature molten aluminum during the vacuum evaporation of aluminum from the support which comprises dissolving in the molten aluminum a second metal selected from the class consisting of titanium, zirconium, hafnium, vanadium, columbium and tantalum, said aluminum containing said dissolved second metal being maintained at a sufficiently high temperature to form said second metal carbide layer.

10. In a process for the deposition of an aluminum film on a substrate by thermal evaporation of molten aluminum in a vacuum wherein the

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aluminum is heated to a temperature sufficiently above its melting point to evaporate the aluminum, the improvement which comprises forming a surface layer of a carbide of a second metal on an elemental carbon support by contacting said elemental carbon support with a material comprising said second metal and maintaining said material and said support at a sufficiently high temperature to form said carbide layer, said second metal being selected from the class consisting of titanium, zirconium, hafnium, vanadium, columbium and tantalum, and maintaining the molten aluminum, during evaporation, on the carbide surface layer so as to prevent attack of the elemental carbon support by molten aluminum.

11. The process of claim 10 wherein said material comprises an oxide of one of said second metals.

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