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COATING METHOD AND APPARATUS THEREFOR

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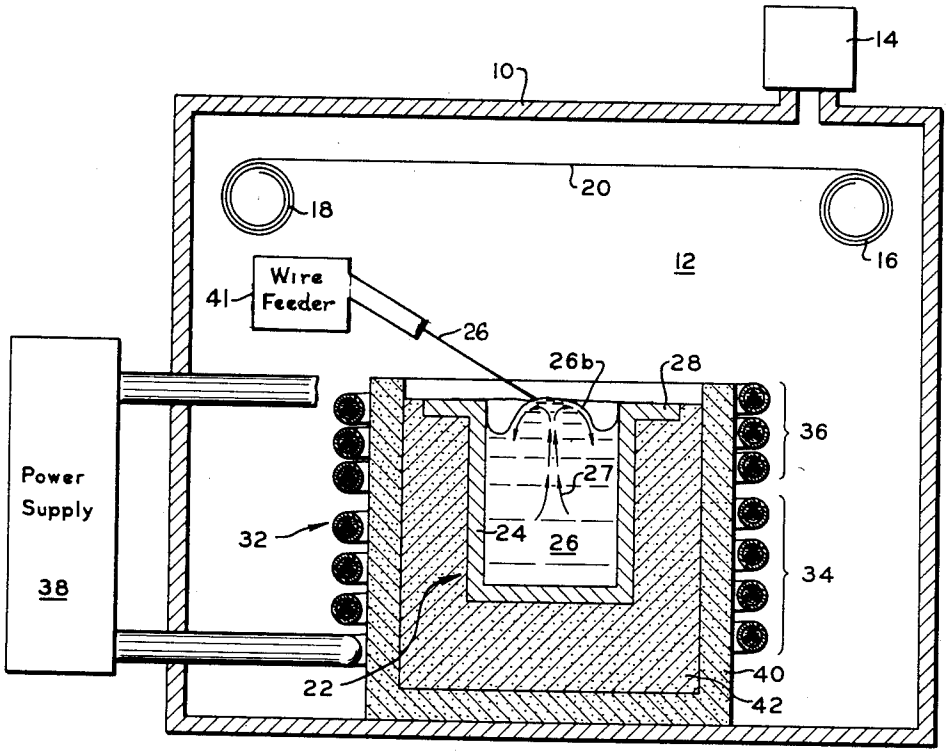


FIG. 1

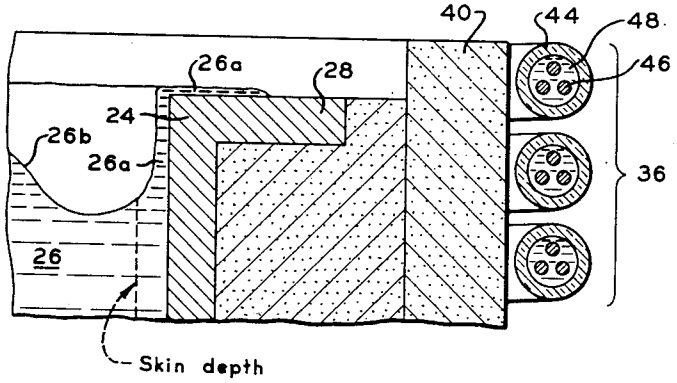


FIG. 2

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COATING METHOD AND APPARATUS THEREFOR

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2 Claims. (Cl. 117—93)

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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 our copending application, Serial No. 117,124 filed September 22, 1949.

A principal object of the present invention is to provide improved processes for evaporating molten aluminum 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 carbonaceous crucible for evaporating aluminum, the formation of aluminum carbide being rendered ineffective to create a scum which might interfere with rapid evaporation of the aluminum.

Still another object of the invention is to provide an apparatus which is particularly adapted for performing 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 apparatus possessing the construction, combination of elements and arrangement of parts, 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 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 crucible 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

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coating operation so as to provide for long periods of operation of the coating equipment. 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 of the crucible.

It has been found that refractory carbonaceous materials, such as elemental carbon, for example amorphous carbon, graphite and, particularly, mixtures of amorphous carbon and graphite, have certain excellent characteristics such as cheapness, ease of 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. As long as the aluminum carbide remains in solution, it does not seriously interfere with the coating operation. However, the surface of the molten aluminum from which the evaporation takes place is cooler than the main body of the molten aluminum. Therefore, at this surface, the aluminum carbide tends to come out of solution 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 makes the scum formation even more readily apparent. The cool metal, being heavier than the hot metal, sinks rapidly to the bottom of the crucible where it reacts with more 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. The melt continuously remains saturated with aluminum carbide and more and more scum is formed as the solid aluminum is fed to the melt. After a relatively short period the scum forma-

tion may be so severe as to completely stop evaporation of aluminum.

It has been found that the above-mentioned disadvantages may be overcome, and that greatly increased evaporation rates and greatly increased evaporating times may be achieved by providing for a stirring of the molten aluminum during the evaporation thereof. This stirring has the effect of maintaining the temperature more nearly uniform throughout the body of the molten aluminum and, additionally, has the effect of breaking up any scum which commences to form on the surface of the aluminum, carrying the formed crystals of aluminum carbide down to the hotter portions of the melt where they are again partially dissolved. The stirring thus acts to keep the aluminum melt saturated with aluminum carbide previously formed, rather than by the formation of new aluminum carbide resulting from the addition of fresh aluminum metal.

In a preferred form of the invention the stirring is achieved by inducing eddy currents in the molten aluminum melt, these eddy currents being preferably produced by an induction coil which serves also to heat the crucible and the melt to the desired high temperature necessary for rapid evaporation of the aluminum. Since the carbonaceous materials employed for the crucible act as an electromagnetic shield for the melt, it is necessary to provide, in a preferred form of the invention, a thickness of crucible wall that is less than the skin depth of the induced current. In this way part of the induced current flows within the aluminum itself. As a result of the induced current flowing in the molten aluminum, liquid currents are generated which maintain stirring of the molten aluminum.

Skin depth of an induced current is a function of both the frequency of the current being used and the resistivity of the crucible material. Skin depth may be calculated by the method shown on page 34 of "Radio Engineer's Handbook" by Terman, First Edition, McGraw-Hill, 1943. The equation given by Terman is as follows:

$$\text{skin depth in cm.} = 5{,}033\sqrt{\frac{\rho}{\mu f}}$$

where ρ is resistivity in ohms per cm. cube, f is cycles per second and μ is magnetic permeability. Another standard text (Stratton "Electromagnetic Theory" First Ed. p. 403, McGraw-Hill) gives a similar method of calculating skin depth. The following table gives the skin depth of induced currents with carbon and graphite at 1300° C. at several different frequencies.

TABLE I

Skin depth in inches (1300° C.)

Frequency	Carbon	Graphite
9,600 cycles/sec	.88	.63
100,000 cycles/sec	.27	.20
150,000 cycles/sec	.23	.17

In the present invention the crucible wall is preferably made of such a thickness as to be only about two-thirds to three-quarters of the calculated skin thickness of the induced current at the frequency and temperature to be employed during the evaporation of the aluminum. As a result of this, considerable eddy currents flow within the melt, these eddy currents setting up an electromagnetic field which causes physical flow of the molten aluminum, this flow being generally axially of the crucible, the metal tending to concentrate in the center of the crucible.

In a preferred form of the invention the agitation of the molten aluminum is not sufficient to cause splashing of the aluminum out of the crucible. However, the stirring is sufficiently vigorous so as to provide for thorough remixing of aluminum carbide crystals formed on the surface of the melt so that these crystals do not collect as a scum on the melt surface.

Referring now to Figs. 1 and 2, there is shown one preferred embodiment of the invention wherein **10** represents a vacuum-tight housing 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, carbonaceous 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**. 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 metal to the crucible are also preferably provided. Such means may comprise a wire-feeding mechanism schematically indicated at **41** which feeds wire to the crucible at a rate equal to the rate of evaporation of the aluminum.

In a preferred form of the invention, the metal-holding crucible **22** is preferably formed of a current-conducting, carbonaceous material, such as carbon, graphite or a graphite-carbon mixture 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, in a preferred form, comprises a refractory tubing **44**, such as Pyrex, quartz, or the like, within which is positioned a multistranded copper conductor **46**, there being sufficient space between the copper conductor **46** and the wall of the tubing **44** to permit the circulation of cooling water **48** therebetween. This arrangement has the particular advantage of preventing arc discharge between

the turns of the coil at the relatively high vacuum employed. 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 0.2 inch at the temperature employed. The wall of the crucible is thus preferably made slightly thinner than 0.2 inch (for example .125 inch) so that some of the induced current flows in the molten aluminum charge.

As a result of the induced eddy currents in the melt, the aluminum is subjected to an alternating electromagnetic field which tends to concentrate the aluminum in the center of the crucible. The action of gravity prevents complete concentration so that the top central portion of the melt rises up into the cone **26***b*, with the creation of circulatory flow of aluminum in the general direction shown by the arrows **27**. This flow of aluminum causes a thorough mixing of the melt which prevents the formation of a scum of aluminum carbide crystals and also acts to carry the formed crystals of aluminum carbide from the surface of the melt down into the body thereof where at least some redissolving of the aluminum carbide takes place.

As can be seen best in Fig. 2, a portion of the molten aluminum tends to creep up the side of the crucible **24** and onto the lip **28**, this creeping meniscus of aluminum being indicated at **26***a*. In the preferred form of arrangement of crucible lip and heating coil **36**, the lip **28** is maintained substantially hotter than the body portion of the crucible **24** so that aluminum in the creeping meniscus **26***a* is evaporated prior to the time when it can creep across the surface of the lip **28**. This feature of the invention is described more fully and claimed in the above-mentioned application, Serial No. 117,124, filed September 22, 1949.

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

What is claimed is:

1. In a process for the coating of a substrate with aluminum by the vapor deposition of aluminum in a vacuum chamber wherein the aluminum is evaporated from a carbonaceous crucible which is formed of elemental carbon selected from the group consisting of amorphous carbon, graphite and mixtures thereof, the improvement which comprises heating the crucible and the molten aluminum therein to a temperature above about 1200° C. so that the vapor pressure of the aluminum is above the free air pressure in the vacuum chamber while supplying induced heating current to the crucible and the aluminum therein, maintaining said induced heating current at a frequency between about 9600 and 150,000 cycles per second, said frequency and the crucible wall thickness being so related that the skin depth of the induced current is substantially greater than the thickness of the crucible wall to cause a substantial stirring of said molten aluminum, thereby carrying into the body of the melt aluminum carbide crystals floating on the surface of the melt and thus maintaining the surface of the aluminum melt free of substantially all aluminum carbide scum, and depositing on said substrate aluminum vapors emanating from the surface of the molten aluminum.

2. Apparatus for coating a base material with aluminum by vapor deposition techniques, said apparatus comprising a vacuum-tight chamber, means for positioning said base material within said chamber, means for evacuating said chamber to a low free air pressure, a carbonaceous crucible for melting and vaporizing said aluminum, said carbonaceous crucible being formed of elemental carbon selected from the group consisting of amorphous carbon, graphite and mixtures of amorphous carbon and graphite, an induction coil for heating said crucible and the aluminum held thereby to a temperature above about 1200° C. so that the vapor pressure of the aluminum is above the free air pressure in said chamber, means for feeding aluminum to said crucible, means for advancing said substrate past the source of aluminum vapors to coat said substrate with aluminum, and a source of alternating current energy for said induction coil, the frequency of said current being between about 9600 and 150,000 cycles per second, the thickness of the crucible being about ⅔ to ¾ the skin depth of the electric current induced in the crucible and the molten aluminum, whereby a substantial proportion of the induced current flows in the molten aluminum to cause a thorough stirring of the molten aluminum with remixing into the body of the molten aluminum of aluminum carbide scum floating on the surface of the molten aluminum.

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References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,601,523	George	Sept. 28, 1926
1,694,792	Northrup	Dec. 11, 1928
1,872,990	Linnhoff	Aug. 23, 1932
2,255,549	Kruh	Sept. 9, 1941
2,378,476	Guellich	June 19, 1945
2,384,500	Stoll	Sept. 11, 1945
2,467,058	Tama	Apr. 12, 1949
2,513,082	Dreyfus	July 27, 1950
2,584,660	Bancroft	Feb. 5, 1952

FOREIGN PATENTS

Number	Name	Date
590,537	France	Mar. 19, 1925