

3,227,431

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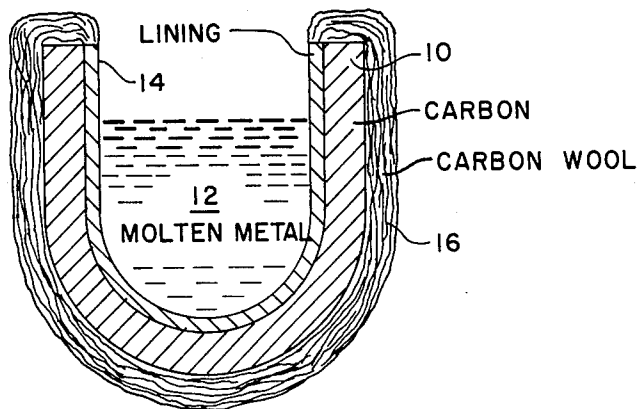


FIG. 1

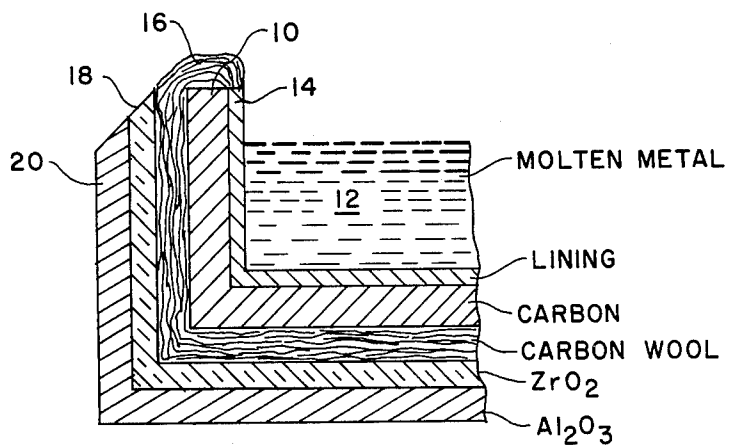


FIG. 2

INVENTOR.
Robert W. Steeres
BY Oliver W. Hayes
Edward A. Gordon

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**CRUCIBLE EXTERNALLY LINED WITH
FILAMENTARY CARBON**

Robert W. Steeves, Nahant, Mass., assignor, by mesne assignments, to National Research Corporation, Cambridge, Mass., a corporation of Massachusetts

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2 Claims. (Cl. 263-48)

This invention relates to coating and more particularly to evaporation sources for metals useful for coating a substrate by vapor deposition.

A principal object of the present invention is to provide a thermally insulated metal vapor source having uniform evaporation and a long life at elevated temperatures on the order of 1300° C. and above.

Still another object of the invention is to provide a source of metal vapors of the type described above which is simple to manufacture and use.

Another object of the invention is to provide a source of the above type which can be produced from relatively inexpensive material.

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

The invention accordingly comprises the apparatus possessing the features, properties, and the relation of components which are described 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 drawing wherein:

FIG. 1 is a diagrammatic, schematic, sectional view of one embodiment of the invention;

FIG. 2 is a diagrammatic, schematic, partially-sectional view of another embodiment of the invention.

From the standpoint of structural strength at elevated temperatures and freedom from decomposition at elevated temperatures, carbon or graphite is a preferred material of construction for metal vapor sources. Additionally, graphite is relatively inexpensive and can be easily machined into a crucible of any desired shape or structure.

In connection with carbon crucibles, however, there seems to be no practical means for thermally insulating the crucible, and the heat radiated from the high temperature body has been found to constitute a serious problem for several reasons. For example, the extremely high temperatures drive off even traces of adsorbed and absorbed moisture from the 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 high degree of vacuum essential for satisfactory coating operations. Furthermore, when the substrate or surface being coated is a heat sensitive material such as paper or plastic film the heat radiated from a carbon crucible at elevated temperatures is damaging to such materials and constitutes a definite limitation on the types of materials which can be coated. Additionally, maximum efficiency of the vapor source is not achieved when the vapor source is not insulated.

Heretofore attempts have been made to thermally insulate carbon base crucibles with refractory materials such as aluminum oxide and zirconium oxide. This method of insulating the carbon crucible proved undesirable in that such refractory oxides when applied adjacent to the carbon crucible react with the carbon crucible at elevated temperatures and reduced pressures with the resultant formation of gaseous products such as carbon monoxide.

At a temperature of about 1600° C., aluminum oxide and carbon, for example, have a reaction pressure of about 1.5 mm. When the temperature is lowered to about

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1150° C. the reaction pressure is about 1 micron. At a temperature of about 1600° C. the reaction pressure of zirconium oxide and carbon is about 250 microns. When the temperature is lowered to about 1425° C. the reaction pressure is about 6 microns. Formation of gases such as carbon monoxide are a disadvantage in vacuum coating since the presence of such reactive gases affect not only the degree of vacuum obtained but also the quality of the coating.

In accordance with the present invention the above objects are achieved and the disadvantages of the prior art overcome by applying a layer of carbon in the form of fine flexible fibers or filaments adjacent the outer surface of the carbon crucible.

The carbon layer is preferably applied in the form of carbon wool consisting of the fine flexible carbon fibers. In accordance with the present invention, the thickness of the carbon fibers is less than about 10 mils. (.010 inch) and preferably less than about 1 mil. Carbon wool such as grade FRC consisting of fine flexible fibers and having a density of .05 g./cm.³ produced by the Carbone Company, Boonton, N.J., is suitable for forming the carbon layer. The flexible fibers can be produced as described in Mechanical Engineering, 120, June 1959 at pg. 121. Several additional methods of forming suitable fibrous carbon products are shown in the prior art, such as, for instance, the method of forming carbon wool shown in the U.S. Patent 2,796,331 to Kauffman et al., granted June 18, 1957.

In one preferred embodiment of the present invention (referring to FIG. 1) a container for confining a molten metal at elevated temperatures is provided by furnishing a refractory base 10 which is in the form of a crucible or other structure suitable for confining a substantial pool of molten metal 12. The refractory base 10 is preferably formed of graphite, carbon, or mixtures thereof. Adjacent to the outer surface of the refractory base 10 there is applied a layer 16 of carbon wool. The thickness of the layer of carbon wool can be varied and depends on the degree of thermal insulation desired. The layer of carbon wool 16 can be supported against the refractory base 10 by a thin sheet or layer of ceramic paper not shown wrapped around the outer surface of the carbon wool. A ceramic paper suitable for supporting the carbon wool is an aluminum-silicate paper sold by The Carborundum Company under the name "Fiberfrax." In the form of fine fibers, the carbon wool layer 16 essentially will not be electrically conductive and hence will not be heated by electrical induction for example. Thus the carbon wool will provide an effective thermal barrier during the evaporation of metals.

Where tin is the metal to be evaporated the whole interior surface of the refractory base 10 which is to be exposed to molten tin is preferably coated with a thin layer 14 of molybdenum metal as set forth in the copending application of Clough et al., Serial No. 130,647, now abandoned, filed August 10, 1961. Briefly stated, the molybdenum coating is preferably applied by flame spraying techniques. In this manner excellent mechanical bonding of molybdenum to the refractory base is obtained. Since the molybdenum coating is wet by tin metal at elevated temperatures a large mass of molten tin can be maintained in the crucible even though induction currents are created in the molten metal. Additionally the thin molybdenum coating provides uniform thermal distribution to the tin metal.

In a similar manner where aluminum is a metal to be evaporated, layer 14 is preferably a coating of boron nitride which is prepared and applied as set forth in the copending application of Baer et al., Serial No. 24,238, now Patent 3,084,060 filed April 25, 1960. In this case

the whole interior surface of the crucible which is to be exposed to the molten aluminum is coated with a slurry of boron nitride. This slurry is then dried such as by baking in an oven at a sufficiently elevated temperature to drive off the water or other medium for forming the liquid phase in the slurry.

A crucible thus prepared is positioned in the vacuum chamber and suitably supported so as to be heated preferably by an induction coil. Such crucibles provide for smooth even evaporation of the metal and have an extremely long life at elevated temperatures.

In another preferred embodiment of the invention (referring to FIG. 2) the layer of nonconducting carbon wool 16 is applied to the outer surface of base 10. By providing a nonconducting layer of carbon wool of sufficient thickness adjacent the refractory carbon base a sufficient temperature gradient is obtained to permit one or more refractory oxides such as zirconium and aluminum oxides to be sequentially applied adjacent the layer of carbon wool without chemical reaction. Thus, refractory oxides can be applied adjacent to the carbon wool to provide support for the carbon wool and also provide additional thermal barriers. In the present preferred embodiment layer 18 which is preferably zirconium oxide is then applied adjacent to layer 16. A zirconium oxide layer can be conveniently prepared by first forming a slurry of zirconium oxide powder with water and a suitable binder such as ethylsilicate, containing a catalyst such as morpholine. The zirconium oxide mixture thus can be applied by painting or in the form of a cast. The mixture is then heated sufficiently to effect conversion of the ethylsilicate to silica which bonds the zirconium oxide powder together. Alternatively, the zirconium oxide layer may be first prepared in cast form conforming to the shape of the refractory base 10, sufficient allowance being made in the size to provide a space in which the carbon wool may be placed. Externally adjacent to layer 18 there is preferably provided a layer 20 of refractory material having, in addition to a high melting point, high mechanical stability. Preferably this layer is aluminum oxide.

A crucible prepared in accordance with the foregoing embodiments provides for a substantial reduction in the loss of heat by conduction and radiation and thus provides a more efficient vapor source. Since crucibles prepared in accordance with the present invention are effective to minimize heat radiation from the portions of the crucible which are not covered by molten metal, heat sensitive substrates can be coated in close proximity to the vapor source. Also, due to the inert nature of the crucible, metals can be evaporated to produce uncontaminated vapors which in turn provide improved coatings. Additionally, the inert nature of the crucible permits high vacuum conditions to be maintained at elevated crucible temperatures. Crucibles prepared in accordance with the present invention when used as vapor deposition sources provide brilliant reflecting metal coatings.

The invention will now be described by way of non-limiting examples thereof.

Example 1

A rectangular graphite crucible having inside dimensions of 13 by ½ by 2 inches with a ½ inch wall was coated on the inner surface with molybdenum metal by flame spraying as described in the above Clough et al. application. The molybdenum coating was about .0001 inch thick. A layer of carbon wool approximately ½ inch thick consisting of carbon fibers of less than 1 mil thick and having a density of about .05 g./cm.³ was applied to the outer surfaces of the crucible. A layer of Fiberfrax paper was wrapped around the carbon wool to support it against the crucible. The crucible was placed inside an induction coil (which, for example, may be of the type shown in U.S. Patent No. 3,049,431) connected to a 9600 c.p.s. generator. The crucible, which contained a solid

charge of tin, and the coil assembly were mounted in a vacuum chamber such as the type shown in U.S. Patent No. 2,665,224 for vapor coating substrate. The vacuum chamber was then pumped down to a pressure of about 1 micron Hg abs. After the power was turned on there was coupling to the crucible and the crucible became heated. As the crucible temperature was raised the tin became molten and at a temperature of about 1200° C. the tin started to wet the inner surface of the crucible. The wetting of the crucible took approximately 15 minutes. The temperature was then raised to about 1500 to 1600° C. At the same time a substrate consisting of Mylar (polyethylene terephthalate) and positioned 4 inches above the crucible was passed through the tin vapors. The chamber was easily maintained at about 5 microns Hg abs. at the operating temperature. Smooth even evaporation of the tin was maintained during the run. The tin was deposited on the substrate as a brilliant, specular coating of high quality. Examination of the crucible after numerous runs did not indicate any damage or attack.

Example 2

This example was similar to Example 1 in all respects except that the layer of carbon wool was not applied adjacent to the graphite crucible. Adjacent to the graphite crucible there was applied a layer of aluminum oxide. During the coating operation the lowest pressure that could be maintained in the chamber varied between 80 and 120 microns Hg abs. Reaction of the graphite crucible with the adjacent aluminum oxide layer resulted in carbon monoxide evolution which seriously affected the chamber pressure and the coating deposit obtained. The tin coating obtained was cloudy and generally not of good specular quality.

While preferred embodiments of the invention have been set forth above, it is apparent that many other modifications thereof may be practiced without departing from the spirit of the invention. Where the word "carbon" is used in the specification and claims, it is intended to include graphite as well as amorphous carbon.

For example, when it is desirable to provide lateral or downward evaporation from the crucible a deflecting top or cover is provided over the crucible, a suitable opening being left between one portion of the cover and the main body of the crucible as a vapor outlet.

While the non-conducting insulating layer of carbon has been described as flexible fibers in the form of carbon wool, the fibers can be employed in other forms. For example, the fibers can be entwined or woven together to form a composite cloth-like body which can then be applied to the carbon base crucible such as by wrapping to the desired thickness.

Also, the crucible may be formed into any desired shape or suitable structure. For example, where it is desired to vapor deposit a coating of tin on a substrate in sheet form, the crucible can be an elongated boat extending across the width of the substrate and containing a long molten pool of the metal to be evaporated. The boat or crucible can also be constructed to have a small aperture or slit through which the metal vapors flow. This provides a source which produces a concentrated stream of metal vapors traveling from the source.

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

What is claimed is:

1. A carbon crucible capable of being heated by a 9600 c.p.s. induction coil to a temperature above 1400° C. in a vacuum system, a layer of fine flexible carbon fibers surrounding said crucible, said individual fibers having a thickness less than 10 mils and being nonconducting to a 9600 c.p.s. induction field, and a layer of

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insulation material surrounding said layer of fine carbon fibers.

2. A carbon crucible capable of being heated by a 9600 c.p.s. induction coil to an elevated temperature above 1400° C. in a vacuum system, a layer of fine flexible carbon fibers surrounding said crucible, said individual fibers having a thickness less than 10 mils and being nonconducting to a 9600 c.p.s. induction field, and a layer of refractory insulation material surrounding said layer of fine carbon fibers, said refractory insulating material being reducible under vacuum by carbon at said elevated temperature, said layer of fine carbon fibers being sufficiently thick so that the interface between said carbon fibers and said insulating material is below the temperature at which appreciable reaction occurs.

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CHARLES A. WILLMUTH, *Primary Examiner*.
RICHARD D. NEVIUS, WILLIAM D. MARTIN,
Examiners.