# United States Patent

Greaves

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## [54] VAPOR DEPOSITION OF ALLOYS


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[52] **U.S. Cl.** ..... **117/107,** 29/187.5, 117/93.3, 117/106

[51] **Int. Cl.** ..... **C23c 13/02,** D21h 1/18, C23c 11/00

[58] **Field of Search** ..... 117/107, 106, 93.3; 29/187.5



[56] **References Cited**

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| 3,024,761 | 3/1962 | Bertelsen | 117/107 X |
| 3,205,087 | 9/1965 | Allen | 117/93.3 X |
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L. Holland, Vacuum Deposition of Thin Films, Wiley & Sons, Inc., N.Y., 1956 p. 197.



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[57] **ABSTRACT**

In the coating of substrates with alloys containing elemental constituents characterized by significant differences in melting point and vapor pressure under the coating conditions, the material to be coated is provided as a plurality of individual elements comprising the coating constituents and the time-temperature relationship for each constituent in the melting cycle is adjusted to compensate for the varying degrees of difficulty in vaporizing the respective constituents.


**7 Claims, 3 Drawing Figures**

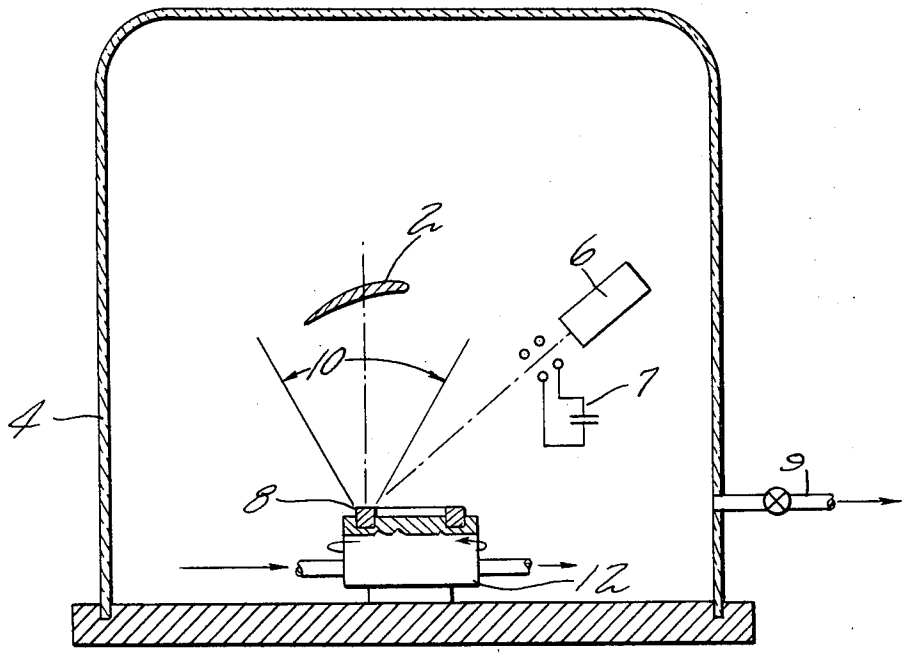


FIG. 1

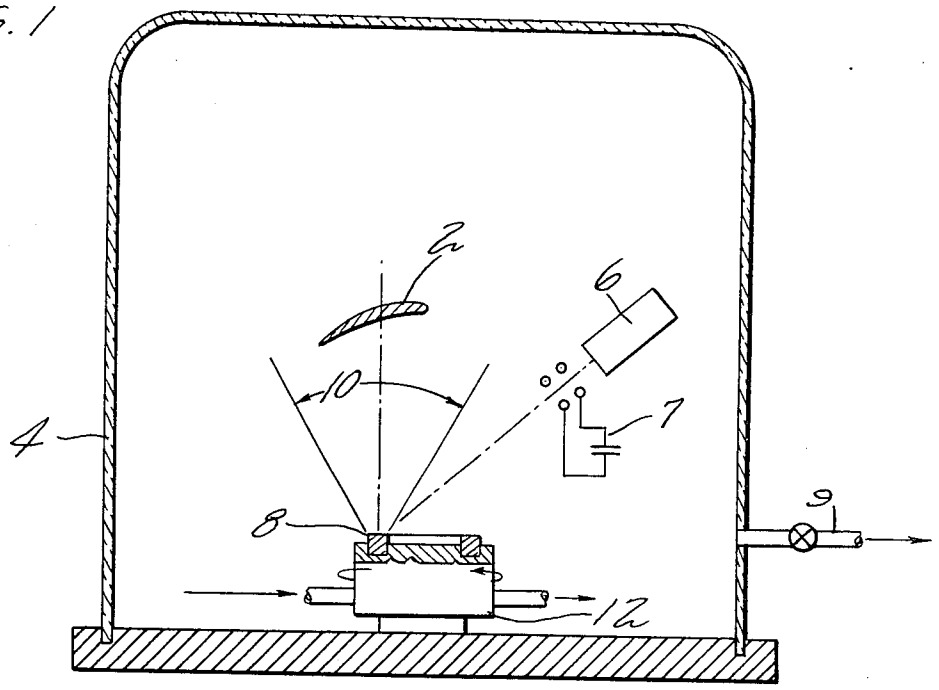



FIG. 3

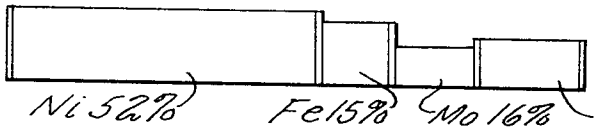
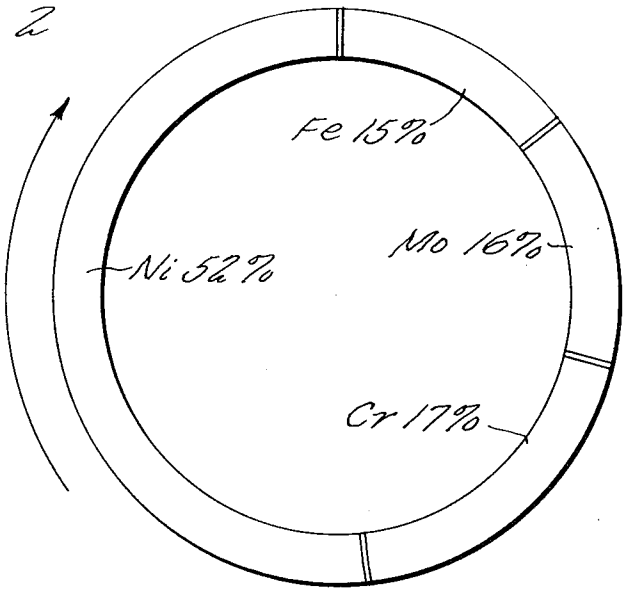



FIG. 2




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# VAPOR DEPOSITION OF ALLOYS

## BACKGROUND OF THE INVENTION

The present invention relates in general to coating processes and, more particularly, to coating processes involving the vacuum vapor deposition of alloys of complex chemistry.

It has become increasingly advantageous, particularly in certain advanced gas turbine engine applications, to provide coatings on selected components in processes involving the vaporization and deposition of alloys of complex chemistry. One such coating alloy is that identified in the industry as Hastelloy X, particularly formulated as follows:

MAJOR CONSTITUENT PROPERTIES

Hastelloy X

| Element | % Desired in Coating | Melting Point, °F | Heat of Vaporization Cal/$W_A$ |
|---|---|---|---|
| Mo | 9 | 3950 | 117,400 |
| Cr | 21 | 2012 | 83,360 |
| Fe | 18 | 2040 | 84,620 |
| Ni | 48 | 2370 | 91,000 |

Another suitable coating is that hereinafter identified as the FeCrAlY coating at a nominal chemistry of about, by weight, 55 percent iron, 30 percent chromium, 15 percent aluminum and 0.5 percent yttrium. This material is described in detail in a copending application of the present assignee entitled "Iron Base Coating for the Superalloys," Frank P. Talboom, Jr. et al., Ser. No. 731,650, dated May 23, 1968. Such materials may advantageously be deposited on a variety of substrates, including the nickel-base and cobalt-base superalloys, by vapor deposition in a vacuum chamber. A process of this nature is disclosed in the U.S. Pat. to Steigerwald No. 2,746,420.

In these processes, utilizing an electron beam heat source, the coating materials have in the past generally comprised either elemental sources or alloys of relatively simple chemistry. In the melting of the more complex alloys, serious problems arise because the elemental constituents comprising the coating alloy are characterized by widely differing melting points and vapor pressures at the coating conditions. It has been found, for example, in the deposition of the FeCrAlY coating, that the chemistry of the molten pool differs considerably from that of both the coating ingot and the finished coating. Furthermore, without special techniques, no satisfactory coating takes place in such a system until equilibrium is achieved which in many cases required up to several hours at the coating conditions.

In one system, a consumable ingot having a chemistry corresponding to the coating chemistry is continually fed into a water cooled crucible at a rate corresponding to its rate of consumption in the coating process and, at any one time, only the head end of the ingot is in a molten condition. In order to minimize the time required to establish an equilibrium pool, the end of the ingot to be first melted is enriched in that element or those elements characterized by the lower vapor pressures at the coating conditions. In the case of the FeCrAlY alloy, for example, salting of the upper end of the ingot with elemental yttrium was found to permit arrival at equilibrium within 15–30 minutes instead of several hours as is typical without ingot pretreatment.

In another system, such as that described in the U.S. Pat. to Allen No. 3,205,087, a number of separate vaporizable materials are positioned in the path of the electron beam to effect multiple deposits of material on the substrate surface.

## SUMMARY OF THE INVENTION

The present invention contemplates a vacuum vapor deposition process, particularly for use in connection with the deposition of coating alloys, wherein the ingot or coating source material is heterogeneous, the chemical composition of the coating source varying from location to location in the ingot. In a preferred embodiment, the coating source is made up of blocks of elemental coating constituents arranged end-to-end. The system is then adjusted to provide, at least in the initial stages of the process, a lesser time-temperature relationship for the more easily vaporized materials and a greater time-temperature relationship for the more difficult to vaporize components and thus to provide a coating vapor cloud of the desired composition.

In one embodiment, the system is adjusted to provide that those most easily vaporized materials be exposed to the heat source for a short duration and those most difficult to vaporize be exposed for a longer duration. In another embodiment, the location of the coating materials relative to the focal point of an electron beam power source is varied as a function of the ease of vaporization of the constituent, the more easily vaporized materials receiving relatively less heat than the more difficult to vaporize materials.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a simplified, somewhat schematic view of apparatus utilized in the vacuum vapor deposition of coatings.

FIG. 2 is an illustration of a ring ingot of a representative alloy formed according to the present invention.

FIG. 3 is a view, taken in elevation, of a linear ingot utilizing height variation in the ingot materials for selective electron beam defocusing.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a typical vacuum vapor deposition process as shown in FIG. 1, the part to be coated 2 is mounted in a vacuum chamber 4 exposed to the vapors emanating from a molten pool of the coating material. Inasmuch as the coating process basically involves line-of-sight coating, the part is frequently rotated to provide protective coverage of all surfaces lying in the plane of rotation. A heat source, such as an electron beam gun 6, with suitable focusing and deflection magnetics 7, is mounted in the system such that the beam is focused on the coating alloy ingot 8. A vacuum is established and maintained within the vacuum chamber by connection to port 9, and the coating material vaporized during the melting process proceeds from the ingot toward the parts in roughly a conically shaped cloud 10.

A prime consideration in the formation of alloy coatings by these techniques is the generation of a vapor cloud having a composition yielding the correct coating. In many instances the composition of the vapor cloud will correspond to that described in the finished coating. However, as previously mentioned, the basic problem, particularly in the initial stages of the coating process, relates to the difficulty of establishing the proper vapor cloud because of differences in melting points and vapor pressures between the various elemental constituents desired in the coating as applied.

The technique described herein contemplates the provision of the coating material in the form of a heterogeneous source or ingot wherein the alloy constituents are provided as individual segments. Either the temperature applied to each alloy constituent, the time at temperature, or both, are adjusted to provide a lesser time-temperature relationship for the easily vaporized materials and a greater time-temperature relationship for the more difficult to vaporize elements.

In a preferred embodiment, the coating material ingot is formed in the shape of an annular ring (FIG. 2) which is mounted in a water cooled crucible 12 which is mounted for rotation relative to the focal point of the electron beam. Alternatively, the beam may be programmed to traverse a stationary ingot. In either case, however, relative motion between the beam focal point and the ingot is utilized to cause sequential heating and vaporization of the respective elemental constituents. In this embodiment, to generate the basic Hastelloy

X composition on nickel-base alloy components, the nickel, iron, molybdenum and chromium constituents are arranged in the ingot to provide 52, 15, 16, and 17 percent, respectively, of the circumferential length, utilizing rings of 2–12 inches diameter rotating at 50 cycles per second.

In the most preferred embodiment as set forth in FIG. 3, the coating material ingot is formed of blocks of varying height and in blocks of different traverse length so that, in effect, both the temperature and the time at temperature of the respective elemental constituents of the coating is varied. The height variation between the elemental ingot blocks provides an automatic variation in temperature as a function of the material melting point by removing the surface of the block into or out of the focal point of the beam as the ingot is rotated beneath the beam. For the embodiment shown, the focal point at the beam and, consequently, maximum heating, is caused to occur at the surface of the molybdenum.

Alternatively, the relative rotation between the beam and the ingot may be made variable and, similarly, the desired focusing and defocusing of the electron beam may be accomplished by suitable electronic or magnetic means. In any event, the tim-temperature relationship in the heating cycle of the individual elements characterized by divergent melting or vaporization requirements is adjusted to provide a coating vapor cloud of the desired composition. The process described necessarily involves a time sequence wherein first one material then another are vaporized and, accordingly, some heterogeneity in the vapor cloud is to be expected. This heterogeneity is to be minimized, however, to prevent the buildup of layers of the individual components on the parts in such thicknesses that they cannot be readily diffused together to form a homogenous alloy coating. Accordingly, while beam dwell times may be programmed to provide greater or lesser temperature-time relationships during the traverse of the higher melting and lower melting point constituents of the coating material, the overall time required for a complete beam traverse of the ingot must be short enough to minimize the described heterogeneity in the vapor cloud to prevent an undesirable laminar coating on the parts to be protected.

The invention in its broader aspects is not limited to the exact details described, for obvious modifications will occur to those skilled in the art.

What is claimed is:

1. In the vacuum vapor deposition of coating alloys from a consumable ingot, the improvement which comprises: forming the ingot as a heterogeneous structure consisting of a side-by-side arrangement of the major elemental constituents comprising the coating alloy; and selectively heating each constituent to subject the more volatizable components to a treatment of lesser time and/or temperature and the more difficulty volatizable components to a treatment of greater time and/or temperature to establish a coating alloy vapor cloud of the desired composition.

2. In the vacuum vapor deposition of coating alloys from a consumable ingot utilizing an electron beam heat source, the improvement which comprises:

forming the ingot as a heterogeneous structure consisting of a side-by-side arrangement of the elemental constituents comprising the coating alloy;

arranging the ingot to permit relative movement thereof with respect to the electron beam whereby the beam may be caused to sequentially dwell on each of the elemental constituents;

and adjusting the dwell time of the electron beam to provide a greater degree of heating for the hard-to-vaporize constituents and a lesser degree of heating for the more easily vaporized constituents, the heating of the respective constituents being selected to provide a coating alloy vapor cloud of the desired composition.

3. The improvement according to claim 2 wherein:

the ingot is formed in the shape of a ring.

4. The improvement according to claim 3 wherein:

the ingot is caused to rotate beneath a fixed electron beam to permit the beam to traverse the ingot circumferentially.

5. The improvement according to claim 3 wherein:

the elements comprising the ingot are provided in different lengths in the ingot as a function of their ease of vaporization, the more easily vaporized materials having a shorter relative length than the more-difficult-to vaporize materials.

6. The improvement according to claim 3 wherein:

the elements comprising the ingot are provided in different heights in the ingot as a function of their ease of vaporization, the variations in height effecting a focusing-defocusing effect of the electron beam, the respective heights being selected to provide a degree of heating of the individual elements related to their melting point, the more easily vaporized materials being exposed to the more defocused beam.

7. The improvement according to claim 6 wherein:

the elements are also provided in different lengths in the ingot as a function of their ease of vaporization, the height-length relationship of each of the elements being selected to provide a vapor cloud of the desired composition.

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