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[54] VAPOR RANDOMIZATION IN VACUUM DEPOSITION OF COATINGS

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[52] **U.S. Cl.** ....**117/93.4,** 117/93, 117/93.1 GD
[51] **Int. Cl.** **C23c 11/02**
[58] **Field of Search** 117/93, 93.1, 93.3, 93.4

[56] **References Cited**

UNITED STATES PATENTS

3,192,892	7/1965	Hanson et al.	117/93.3 X
3,230,110	1/1966	Smith	117/93.3 X

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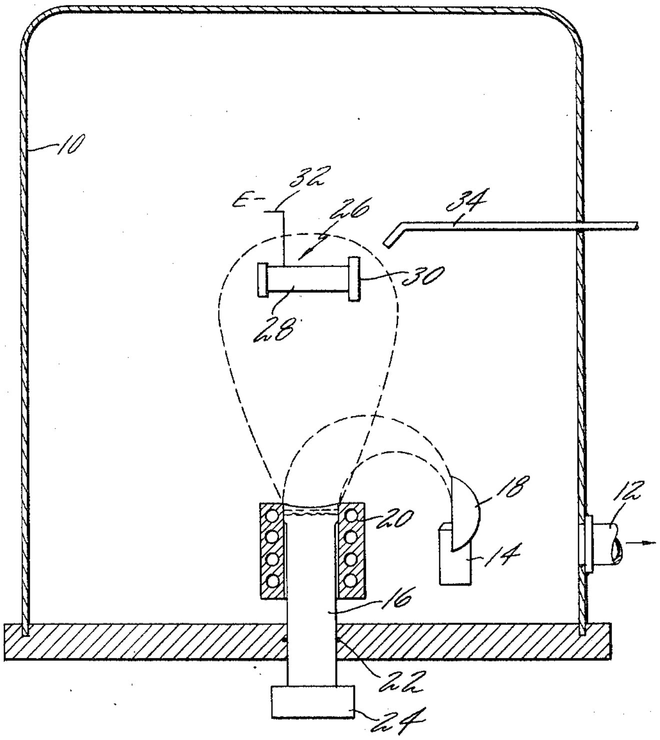
[57] **ABSTRACT**

In the processes for forming protective coatings on metal substrates, particularly the nickel-base and cobalt-base superalloys, by deposition in a vacuum, an electrically biased substrate, in conjunction with a sustained plasma discharge between the source and the substrate, is utilized to randomize the coating vapor cloud and allow non-line-of-sight deposition.

4 Claims, 1 Drawing Figure



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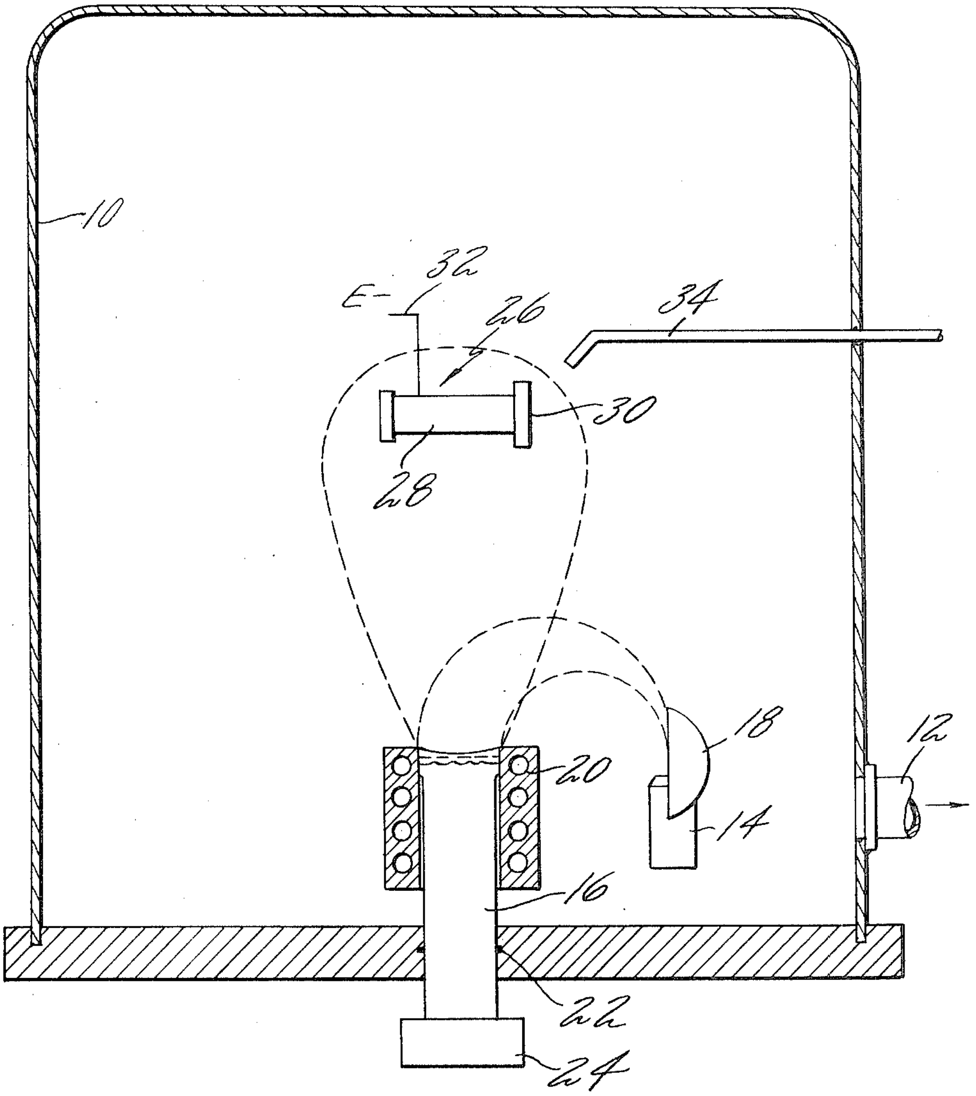

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VAPOR RANDOMIZATION IN VACUUM DEPOSITION OF COATINGS

BACKGROUND OF THE INVENTION

The present invention relates in general to metal coating processes and apparatus therefor, and more particularly, to vacuum deposition processes.

It is well known that the conventional nickel-base and cobalt-base superalloys do not in and of themselves exhibit sufficient oxidation-erosion resistance to provide component operating lives of reasonable duration in the dynamic oxidizing environments such as those associated with the operation of gas turbine engines. Accordingly, it has been the usual practice to provide these alloys with a protective coating in such applications.

Although the aluminide coatings, such as that described in the patent to Joseph U.S. Pat. No. 3,102.044, have in the past displayed satisfactory performance, it is well known that these coatings, because of their dependence upon the availability of substrate elements, often are characterized by a composition less than optimum.

Many of the more advanced coatings developed for the next generation of jet engines depend in the first instance on the deposition of a high-melting-point coating alloy with a concurrent or subsequent reaction with the substrate to attain the desired end composition, microstructure or adherence. These new alloys generally demand the application of special coating techniques to provide the right species in the right amounts at the surfaces to be protected.

Several coating compositions of current interest are described in detail in copending applications of the present assignee. Among these compositions is that hereinafter referred to as the FeCrAlY coating at a nominal composition of, by weight, 30 percent chromium, 15 percent aluminum, 0.5 percent yttrium, balance iron, as discussed in the copending application of Frank P. Talboom, Jr., et al. entitled "Iron Base Coating for the Superalloys," Ser. No. 731,650 filed May 23, 1968 now U.S. Pat. No. 3,508,805. Another such composition is the CoCrAlY composition at about, by weight, 21 percent chromium, 15 percent aluminum, 0.7 percent yttrium, balance cobalt.

The basic problems associated with the deposition of these coating alloys relates to their high melting points and the difficulty of providing the right amount of all of the alloy species in the coating as applied. Satisfactory results have been attained through the use of vacuum vapor deposition techniques, such as that suggested in the patent to Steigerwald U.S. Pat. No. 2,746,420. These processes, which have in the past been primarily directed toward the application of relatively low-temperature materials of relatively simple composition, are in the present instance characterized by extreme sensitivity to variations in the process parameters and, accordingly, reproducibility as well as processing expense is a problem.

The vacuum vapor deposition of electron beam melted metals in existing low-evaporation rate, production-type systems, such as high cyclic speed or stripline coaters, has essentially been limited to line-of-sight coating from the source (molten pool of coating metal) to rotating or linearly moving substrates. Recently, several techniques have been developed to improve the versatility of the basic process through collimation or densification of the vapor cloud. In one such method, a gas cascade or multiorificed nozzle surrounding the pool of molten coating material is utilized to introduce a high-velocity inert gas inwardly at an angle to the vapor cloud to densify the direction of the metal vapor atoms thus permitting increased coating rates of line-of-sight areas. In another such method, a high mass, high-temperature reflector is utilized to the same end.

SUMMARY OF THE INVENTION

The present invention contemplates an electron gun vacuum deposition process which utilizes the electrical bias of the substrate in conjunction with the creation of a vapor plasma discharge to attract the coating material vapor ions. For this purpose, an inert gas leak is utilized to ionize the vapor cloud and sustain a gas plasma. The present technique provides for an accelerated level of vapor impact onto the substrate with a resulting higher, more adherent coating bond as well as a randomization of the direction of flight of the metal vapor coating material to cause, in essence, coating of non-line-of-sight areas.

Prior to the present invention, it had been expected that a substrate located in close proximity to an electron beam heated vapor source and biased to a significant fraction of the electron beam acceleration voltage would cause deflection of the beam and failure of the vapor source. It has been determined however that the introduction to the system of a gas in an amount sufficient to sustain a glow discharge but insufficient to cause dispersion of the electron beam, results in no significant electrostatic interaction between the electron beam and the biased substrate. It was found that the voltage drop at a negatively biased substrate in a glow discharge occurs almost wholly within a few millimeters of the substrate surface and hence electrostatic forces can operate only within that space. There is thus herein provided an improved technique for ion plating which advantageously incorporates electron beam vapor source-heating means.

BRIEF DESCRIPTION OF THE DRAWING

An understanding of the invention will become more apparent to those skilled in the art by reference to the following detailed description when viewed in light of the accompanying drawing, wherein is shown a schematic illustration, partially in section, of vacuum vapor coating apparatus in accordance with this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In one particular embodiment as illustrated in the drawing, there is shown a vacuum chamber **10** having an exit port **12** leading to a suitable high-vacuum pump, preferably of the diffusion type, for the rapid and continuous evacuation of the chamber. Located inside the chamber, there is shown an electron gun **14** for generating a beam of charged particles to impinge upon and vaporize an ingot of source metal **16**. It will be appreciated by those skilled in the art that the electron beam is suitably directed by conventional magnetic deflection pole pieces **18**. Of course, the arrangement of the electron beam gun within the vacuum chamber is a function of design. A 30-kilowatt electron beam unit has provided satisfactory deposition rates with a 2-inch diameter ingot of FeCrAlY coating material, the depth of the molten pool usually being one-fourth–one-half inch.

The ingot **16** is made movable and is slidably received at its upper end by an annular water-cooled crucible **20**. The ingot is normally continuously fed upwardly into the crucible through a heat-resistant vacuum seal **22** in the chamber wall at a controlled rate by a chuck **24** to maintain a constant pool height. In this way, the focused electron beam will impinge only on the desired pool surface area. Furthermore, since coating efficiency, composition and uniformity are very susceptible to pool height changes, a constant height relationship between the pool and the part to be coated is preferred.

The substrate to be coated is disposed within the vacuum chamber **10** vertically above the ingot **16** and is illustrated as a gas turbine blade **26** having an airfoil section **28** and a shroud section **30**. Since the coating process is fundamentally line-of-sight, the part is typically mounted to effect rotation about its longitudinal axis, that is, the longitudinal axis of the airfoil **28**, usually utilizing a pass-through (not shown) through the vacuum chamber to an external drive system. Of course, more than one part may be coated at a time. In such a case, in order to minimize nonuniformity of coating between each of the plurality of parts, each part is normally mounted in a plane of vapor isodensity or roughly along an arc defining a zone of constant vapor concentration, the parts closest to the vertical passing through the center of the molten pool being located slightly farther from the pool surface than those positioned at an angle with respect to the said vertical. Whether coating a single part or a plurality of parts however, each substrate is further positioned as close as possible to the surface of the molten source pool for maximum coating efficiency but far enough removed therefrom to prevent coating contamination by splash from the pool. The substrate height varies with each system but for a 2-inch diameter pool and a deposition rate of about 0.3 mils per minute with a FeCrAlY coating material, a mean height of about 10 inches has been found satisfactory.

As mentioned previously, the vacuum vapor-coating process is essentially line-of-sight. Although axial rotation of the part is successful in effecting deposition along its entire length, it does not alleviate the problem of coating the remaining end portions. This is particularly unsatisfactory in a part having an enlarged end portion such as the shroud **30** of the turbine blade **26**. In accordance with the present invention, there is provided an electrical lead line **32** suitably connected between the part **26** and a voltage source (not shown) to maintain the part at a negative bias potential. There is also provided an inert gasline **34** adjacent the outer surface of the shroud **30**. The line **32** admits an inert gas, preferably argon, at a low velocity, controlled leak rate from a position generally above and outwardly from the shroud in a direction generally downwardly and inwardly theretoward. The exact location of the inert gas admittance, insofar as the creation of a plasma glow discharge is concerned, is not critical and the gas can be introduced anywhere within the chamber **10** so long as the system pressure is raised to a level high enough to ionize the metal vapor atoms and ensure plasma generation. As will be described hereinafter, however, selective placement of the gasline **34** as in the preferred location described above will result in further process advantages.

During the ordinary course of source metal evaporation by electron gun melting, a localized glow discharge frequently occurs due to the ionization of some of the vapor metal atoms by the electron beam itself. By introducing an inert gas such as argon into the vapor cloud, further ionization occurs until, at a predetermined system pressure, a plasma glow discharge extending from the molten source pool to the substrate, will be sustained. With the substrate at a negative electrical bias, the positively charge metal and argon ions will be attracted thereto. The force of attraction will vary, of course, with the amount of electrical bias on the substrate. It was found, for example, that at a bias potential of 3,000 to 5,000 volts negative and a partial pressure of argon gas between $1-5\times10^{-2}$ mm. Hg, the vapor ions were accelerated toward the substrate at a sufficiently increased rate to cause significantly higher impact and a consequently improved bond with the substrate. Thus the establishment of a negative bias at the substrate was found to not only increase the coating rate but also to improve the quality of its bond. The grain morphology of the coating material, unlike the typical columnar structure characteristic of straight vapor deposition, is equiaxed in structure. A further advantage which derives from the establishment of the electrical bias in the substrate is a heating effect on the substrate, shown in table I with the result that conventional radiation preheating components can be eliminated. In one series of tests, with the part **26** at a negative bias potential of 3,500 volts and a sustained plasma discharge evidencing 100 ma. of current flow, there resulted a substrate heating of from 1,400°–1,800° F. The energy input in watts to the substrate, as a consequence of the electrical bias and resulting discharge, is utilized mainly in heating the substrate. Approximately 95 percent of the kinetic energy of the ion bombardment is converted into heat. The remaining 5 percent of the power input to the substrate surface as a result of the ion bombardment is utilized to give a sputtering effect wherein contaminants from the chamber are cleaned off of the advancing coating surface and the coating metal is redistributed. The result is increased deposition and mitigation of oblique incidence, such as that encountered in straight evaporation.

As illustrated in the drawing, introduction of the inert gas is preferred in the vicinity of the substrate and, more particularly, is preferred in the vicinity of non-line-of-sight portions of the substrate. In this way, the inert gas acts to decrease the mean free collision path of metal atoms adjacent thereto and causes randomization of the coating material. In essence, the randomization will be effected either by simple impingement without ionization and redirection by kinetic rebound or by ionization and subsequent substrate attraction or both. In any case, the metal vapor cloud is, in truth, randomized in its movements so that substrate areas both line-of-sight and non-line-of-sight, with respect to the source are coated.

In early tests, a simulated turbine blade was coated with Kanthal A–1 alloy (nominal composition, by weight: 5.5 Al, 22 Cr, 0.5 Co, bal Fe), with a system argon pressure of 5×10^{-3} mm. Hg, a bias potential of 5,000 volts and a bias current of 50 ma. The coating time was 10 minutes and 1 gram of the coating alloy was evaporated by a 3.25 kw. self-accelerating Pierce-type gun. The coating thickness was 10 microns with the grain size of the coating ranging from one-half to 1 micron. There was no deflection or other interaction of the electron beam during the tests.

A number of tests were conducted with various coating materials and various substrate alloys. In one series of tests, argon and helium gas was introduced at a pressure of 17 p.s.i. through a 0.250-inch stainless steel line having an inside diameter of 0.190 inch. The line end was oriented at an angle of approximately 45° and spaced a distance of 2 to 3 inches with respect to the shroud of a TF 30 turbine blade. When measurements were made, corresponding specimens coated with and without the electrical bias on the substrate in the presence of a sustained gas plasma showed substantial increases of coating thicknesses on non-line-of-sight areas. The typical coating procedure utilized a power setting of the electron beam gun at 21 kw. for the CoCrAlY material and at 15.5 kw. for the FeCrAlY material.

The results on one particular series of tests are set forth in the following table.

TABLE I.—FeCrAlY COATED TEST SPECIMENS

Substrate	Coating material	Avg. power, kw.	Calculated coating thickness, mils	Coating time, min.	Coating rate, mils/min.	Ingot feed rate, in./min.	Specimen bias volts-current		Specimen area, cm.^{2}	Specimen temp., ° F.	Chamber pressure, torr
2"x4" SS flat plate	FeCrAlY [1]	14.5	15.5	15.0	1.03	.0355	−2,000– −4,000	120–180	51.5	1,500	1.4×10^{-5}
PWA 663, erosion bar	FeCrAlY [2]	16.0	4.39	12.0	0.366	.0397	−4,000	120	22.4	1,880–1,650	1.2×10^{-5}
Do	FeCrAlY [2]	15.8	4.54	12.0	0.279	.0377	−1,000	70	22.4	1,300	1.4×10^{-5}
Do	FeCrAlY [2]	15.9	4.68	13.0	0.360	.0369	−1,000– −3,400	65–107	22.4	1,700–1,400	8.4×10^{-6}

[1] Ingot chemistry: 57.9 Fe, 29.5 Cr, 11.2 Al, 0.39 Y.
[2] Ingot chemistry: 64.5 Fe, 25.6 Cr, 11.8 Al, 0.73 Y.

It is to be understood that the inventive process can be practiced in other ways and on other substrates than as specifically described above. What has been set forth above is intended primarily as exemplary to enable those skilled in the art in the practice of the invention and it should therefore be understood that, within the scope of the appended claims, the invention may be practiced in other ways than as specifically described.

What is claimed is:

1. A process for coating a metallic substrate spaced opposite a source metal in a vacuum chamber comprising:
   imposing a negative electrical bias potential on the substrate;
   admitting an inert gas to the system to raise the system pressure to at least 5×10^{-3} mm. of mercury to generate and sustain a plasma;
   electron beam heating said source metal to establish a cloud of metal vapors moving generally from the source metal to the substrate, said metal vapors being ionized and attracted to said substrate to cause coating of both line-of-sight and non-line-of-sight substrate portions.

2. The method of claim 1 wherein the inert gas is admitted at a location adjacent a selected portion of the substrate.

3. The method of claim 1 wherein the inert gas is argon.

4. The method of claim 3 wherein said pressure is in the range of $1-5\times10^{-2}$ mm. Hg.

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