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[54] **VACUUM DEPOSITION OF
MULTI-ELEMENT COATINGS AND FILMS
WITH A SINGLE SOURCE**

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[63] Continuation-in-part of Ser. No. 209,359, Dec. 17, 1971, abandoned.

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[51] Int. Cl. **C23c 13/02**

[58] Field of Search **117/93.3, 106 R, 107, 131; 118/49.1, 49.5; 219/121 EB**

[56]

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[57]

ABSTRACT

Multi-element coatings and films having a composition substantially the same as that of a precast ingot of source material are prepared by continuously and rapidly sweeping a high intensity electron beam over the source surface so that only a small volume is heated at any one instant, completely evaporated and vacuum deposited on a desired substrate as a coating of great uniformity in volume and thickness.

8 Claims, No Drawings

VACUUM DEPOSITION OF MULTI-ELEMENT COATINGS AND FILMS WITH A SINGLE SOURCE

This is a continuation-in-part of our copending patent application Ser. No. 209,359 filed Dec. 17, 1971, assigned to the assignee hereof and now abandoned.

This invention relates to a method of forming multi-element coatings and films from a single source, and to a product produced thereby, and in more particular relates to the formation of coatings by vacuum deposition of predictable compositions essentially identical to that of the source material.

Coatings according to the invention find utility, for example, as applied to parts of gas turbine engines.

BACKGROUND OF THE INVENTION

The electron beam heating of source materials for vacuum deposition of coatings and films is a well established processing technique. Commercially available types of equipment for this processing generally employ a maximum electron accelerating voltage of 10-20 KV. This type of equipment has proven to be excellent for depositing single element layers. However, when multi-element layers are required, control of deposit composition is difficult because of the differing vapor pressures of the elements at any given temperature. If a single source is used, the element or elements having the higher vapor pressure are distilled preferentially from a molten pool of the source material, giving rise to deposits of substantially different composition than that of the source. Additionally, the rates at which elements diffuse into such a melt can differ considerably with the result that the melt composition rapidly shifts away from that of the original source material which leads to further disproportion in the deposited coating.

SUMMARY OF THE INVENTION

In accordance with the present invention, a small, high energy intensity electron beam during operation is continuously and rapidly swept over a surface of the source material so that evaporation takes place under highly nonequilibrium conditions. As a consequence, at any instant only a small volume (a few cubic millimeters) will be heated and evaporated without forming a persisting melt, thus overcoming the problem of the varying vapor pressures of the elemental components as well as that of different diffusion rates.

The coating produced is highly uniform throughout its thickness and volume as a result of control of the power density and beam sweep rate, which together determine the temperature of the incremental surface volume at the point of impact of the electron beam such as to achieve a vapor pressure for the least volatile constituent of the alloy of at least 10^{-2} torr.

Accordingly, an object of the invention is to provide a uniform thin film coating which is economical to apply and durable in use.

Another object of the invention is to provide a coated turbine blade which will resist hot corrosive conditions longer than coated blades heretofore known.

Still another object of the invention is to provide a coating on a turbine engine part which will resist attack under severe conditions of operation to which it is subjected including severe oxidation and hot corrosion.

DESCRIPTION OF PREFERRED EMBODIMENTS

In accordance with the invention, a multiple component source contains at least two elements, preferably selected from the group iron, cobalt, nickel, chromium, aluminum, yttrium and silicon. The power density of the electron beam is controlled within the limits of 10^4 to 10^{10} watts/sq. inch for these preferred alloys. The sweep rate of the electron beam across the surface of the source material must be fast enough to avoid spattering and the formation of persisting liquid phase, but slow enough to effect the evaporation from the source. The sweep rate can range from about 100 to 3,600 linear inches/min. A preferred range of power density and sweep rate for multiple alloy sources of the above named preferred group of metals is within the range of 10^8 to 10^9 watts/sq. inch power density, and when the power density is 2×10^8 watts/sq. inch, the sweep rate should be about 100 linear inches per minute. Stated in terms of exposure time or electron beam residence interval, the travel of the beam will be such that the beam will impinge upon any given point on the source material surface from about one three-hundredth second to about one twelve-thousandth second. Thus the beam may be moved back and forth along a line across the source material surface impinging upon a given point tens or even hundreds of times every second and each time cause heating, melting, evaporation and refreezing of the melt residue. Alternatively, the beam may be moved to define a raster-like pattern across the source material surface so that the interval between beam exposures at any given point on that surface is considerably longer.

In general, the multiple element source in the form of an ingot or similar bulk body is placed in a vacuum chamber within the path of an electron beam and the chamber is evacuated to a pressure between 2×10^{-3} to 4×10^{-3} torr in order to avoid electric arcing in the beam gun. It is preferable to evaporate in a chamber where the pressure is below 10^{-4} torr in order to minimize gas phase collisions between the evaporating atoms from the source and the residual gas atoms in the chamber. Thus, the lower the pressure in the chamber, the better, but for reasons of economy a vacuum of 1×10^{-6} torr is preferred.

According to the invention, a uniform coating is produced wherein the variation in composition of the resulting film at any point throughout its volume is less than ± 5 percent from that of the nominal composition of the source.

By other methods of the prior art such as conventional evaporation using a stationary source, variations in nominal composition as high as ± 50 percent are frequently observed, and in no case can one achieve, reproducibly over extended periods of time, a variation of less than ± 10 percent by such prior art methods. Likewise, the traveling beam technique of the prior art has not proven to be the answer to the problem solved by this invention, the molten pool or residue formed and maintained in such an operation resulting in variations in nominal composition of the order of at least ± 10 percent.

The following typical examples demonstrate the beneficial results of the method of the present invention.

EXAMPLE 1

A vacuum melted ingot was prepared containing (nominally, by weight) 70Co-25Cr-4Al-1Y. A section cut from the ingot and serving as the source was placed in a water-cooled copper crucible in a vacuum chamber exhausted to a vacuum between 10^{-3} torr and 10^{-4} torr. An electron beam of about 0.005 inch diameter giving an energy intensity of about 10^7 watts/in.² was employed, using a Hamilton Standard electron beam welder, model W1-1 provided with GE beam deflection coils for controlling the beam sweep in X and Y directions in various desired sweep patterns to permit concentrated focusing. A beam power of about 120 KV and about 2ma was used, and the beam was swept back and forth across the source of 60 cycles/sec. along a line on the surface about one-half inch long. A film of about 2000 A. thick was deposited in about 20 seconds on a glass coupon three-fourths inch by three-fourths inch which was positioned about 4 inches from the alloy source. The alloy source was one-half inch by three-fourths inch by one-eighth inch, cut from the above described vacuum-melted ingot. The relative chemical composition of the resulting film deposited was measured by X-ray fluorescence technique and is listed in Table I. Also listed for comparison purposes, is the X-ray fluorescence analysis of a sample of the bulk material which was cut from the original ingot, as well as the analysis of a film deposited by "conventional" electron beam evaporation from a source cut from the same original ingot. The conventional evaporation was performed using a stationary beam of somewhat lower intensity, namely at a power of 17 KV and 110 ma, giving an estimated energy intensity 10^5 watt-s/in.².

TABLE I

Comparison of Relative Compositions of Deposited Films from 70Co-25Cr-4Al-1Y Source				
Method	Co	Cr	Al	Y
1. Hi Power Moving Beam (10^7 watts/in. ²)	.778	.194	.00474	.023
2. Bulk Source Alloy	.740	.225	.00038	.034
3. Conventional evaporation (10^5 watts/in. ²)	.678	.317	.00092	.0038

The comparative analyses in Table I above, as well as in Table II, was by X-ray fluorescence analysis, expressed as:

Counts per sec/2cm² of element/Total counts per sec/2cm² and is used as a relative comparison, not equivalent to weight percent nor an absolute quantitative analysis, but does give an indication for comparison purposes. From the above data in Table I, it is seen that the films deposited by method 1 are relatively closer in composition to the bulk source alloy. It is particularly relevant that the highly volatile element chromium in the films deposited in accordance with the invention are much closer to the composition of the original bulk source alloy than was the film deposited by conventional technique using a stationary beam for the evaporation.

EXAMPLE II

A section of a cast ingot (about one-fourth inch thick

by 2 1/16 inch diameter), containing, by weight, 80 percent Ni and 20 percent Cr was mounted on a water-cooled copper pedestal. A beam power of 0.67 KW (122 KV, 5.5 ma) was used to evaporate the material from the source. The moving beam was swept across the surface of the specimen in a moving circle about three-fourths inch diameter at a rate of 40 rpm instead of along a straight line, as in Example I. Initially the beam spot size was about one-eighth inch diameter, which made the beam intensity 5.5×10^4 watts/in.². At seven minutes into the run, the spot size was focused to about 0.002 inches diameter, making the beam intensity about 2×10^8 watts/in.². A series of films were deposited on glass coupons at intervals, ranging from about 2,000A to about 8,000A in film thickness. The composition of these films was analyzed, using the X-ray fluorescence technique, as in Table I, to give a relative indication. A comparison of the results shows that the high power density moving beam achieved a deposited film much closer in composition to the bulk source alloy.

TABLE II

Comparison of Relative Compositions of Deposited Films from 20Cr-80Ni Source			
Method	Power Density watts/in. ²	Element	
		Cr	Ni
Low power (moving beam)	5.5×10^4	.0679	.932
High power (moving beam)	2×10^8	.0850	.915
Bulk Source	—	.115	.885
Conventional (stationary beam)	4.4×10^4	.187	.813

It will be noted that Table II as well as Table I shows that the high powered intensity moving beam causes a film to be deposited which is closer in composition to that of the bulk source alloys than the film deposited by the conventional evaporation process using a stationary electron beam. In both Example I and Example II, the highly volatile constituent occurs in the film at a composition which deviates much less from the desired bulk composition as compared to the film produced by the conventional evaporation method.

Thus, the two compared methods of evaporation in each example demonstrate clearly that the composition of the deposit made from the high intensity evaporation and moving electron beam conforms more nearly to that of the bulk source alloy than a comparable film deposited by conventional evaporation with a stationary beam.

Those skilled in the art will understand that the concept of this invention constitutes a basic departure from prior art practice, particularly in respect to the fact that no lasting or persisting liquid phase is produced or established at any time during the vacuum evaporating and depositing operations. As indicated above the diameter of the focussed electron beam on the bulk body source material surface is relatively small, being from about two mils to five mils (i.e., 0.002 - 0.005 inch) so that only a very small fraction of the beam travel course over the bulk body surface is exposed to the beam at any one time. Heating, melting and evaporation, as well as refreezing of any unevaporated melt, are a sequence of virtually milli-second

events which take place at each point of impingement of the beam with the bulk body surface. Thus, at each successive point of impingement, a superficial portion of the bulk body is melted and part (possibly one-half) of the melt is evaporated before the beam moves to the next successive points of impingement. Refreezing of the melt residue is virtually instantaneous and in any event so rapid as to preclude diffusion of source material constituents into the melt. Surprisingly, such melting and evaporating and refreezing can be caused to occur in the same small area of the bulk body surface over 100 times per second so that there is no persisting melt but evaporation is continuous throughout the deposition process.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The method of vacuum evaporating and depositing on the surface of a turbine engine metal part a multi-element protective coating of substantially the composition of a single metallic alloy source, which comprises the steps of cutting a section from an ingot of said alloy and placing the ingot section in a chamber evacuated to a pressure of 10^{-3} to 10^{-4} torr, sweeping a focused electron beam of power density from 10^4 to 10^{10} watts per square inch back and forth across the surface of the ingot section at 60 cycles per second along a line on the ingot section surface one-half inch long, and exposing the turbine engine part to the combined evaporated components.

2. The method of claim 1 in which the alloy source has a nominal composition of 70Co-25Cr-4Al-1Y, and in which the electron beam is operated at an intensity of about 10^7 watts per square inch.

3. The method of vacuum evaporating and depositing on the surface of a turbine engine part a multi-element

protective coating of substantially the composition of a single metallic alloy source which comprises the steps of providing a bulk body of said alloy in a chamber evacuated to a pressure less than 10^{-3} torr, continuously heating and evaporating alloy from the bulk body by sweeping an electron beam across the surface of the body at a rate such that the residence interval of the beam at each successive point of impingement of the beam on the body surface is less than one-three hundredth of a second and causing at each said successive impingement point the melting of a superficial portion of the bulk body and the evaporation of part of the resulting melt under the electron beam followed by freezing of melt residue of that superficial portion as the beam moves to the next successive points of impingement with the bulk body surface, and exposing the turbine engine part to the combined evaporated components of the said alloy.

4. The method of claim 3 in which the power density of the electron beam is from 10^4 to 10^{10} watts per square inch.

5. The method of claim 3 in which the alloy of the bulk is of at least two elements selected from the group consisting of iron, cobalt, nickel, chromium, aluminum, yttrium and silicon.

6. The method of claim 3 in which the diameter of the electron beam at the bulk body surface is between 0.002 and 0.005 inch.

7. The method of claim 3 in which the electron beam is swept across the bulk body surface in a raster-like pattern.

8. The method of claim 3 in which the residence interval of the electron beam is from one-three hundredth second to one-twelve thousandth second.

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