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54 **Erosion resistant coatings.**

57 **Two-layer erosion-resistant coatings which may be applied to gas turbine compressor components comprise a first layer applied directly to the substrate and comprises palladium or nickel, and an overlayer containing tantalum or chromium, and boron. The coefficients of thermal expansion of the whole system (substrate, first layer and over layer) are matched closely to reduce residual stress and accompanying strains, whereby the fatigue life of the substrate is not deleteriously effected. Additional gains in fatigue life retention are achieved by using low coating deposition temperatures (425-760°C) (800 to 1400°F).**

EROSION RESISTANT COATINGS

This invention relates, in general, to coatings for metallic substrates and more particularly to novel two-layered erosion-resistant coatings which may be applied to gas turbine engine compressor blades without an attendant loss in fatigue life.

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Gas turbine engine compressor blades are conventionally fabricated from metallic substrates such as stainless steel or titanium alloys. The blades are subjected to severe erosion when operated in sand and dust environments. Blade erosion reduces compressor efficiency, requiring premature blade replacement.

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There are presently available a wide variety of erosion resistant coatings such as tungsten and carbon (U.S. 4,147,820), platinum metals (U.S. 3,309,292; U.S. 3,890,456) and boron (U.S. 2,822,302). However, these coatings which have been identified by the art for imparting erosion resistance to substrates such as titanium and stainless steel alloy compressor blades promote sharp drops in fatigue properties of the substrates creating the initiation of cracks and fractures with an attendant reduction in the service

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life of the substrate. This effect of the fatigue life of the coated substrate is believed due to the fact that the erosion-resistant coatings of the prior art are hard materials which produce residual stress and accompanying strains in the substrate thereby accelerating a reduction in fatigue strength of the substrate.

Therefore, there exists a need in the art for erosion-resistant coating systems which do not deleteriously affect the fatigue life of the substrate to which they are applied.

It is, therefore, an object of the present invention to provide a novel coating which is devoid of the above-noted disadvantages.

It is another object of the present invention to provide a two-layered coating which has good erosion resistance and does not exhibit a sharp drop in thermal fatigue resistance.

It is still another object of this invention to closely match the coefficient of thermal expansion of the substrate being coated, the first layer overcoating the substrate and the overlayer overcoating said first layer, in order to reduce residual stress and accompanying strains so as not to deleteriously affect the fatigue life of the coated substrate, the first layer also acting as a barrier layer to protect the substrate during coating application of the overlayer.

It is still another further object of this invention to

provide a two-layered coating which may be used in hot, corrosive, atmospheres of the type found in gas turbine compressor components.

The foregoing objects, and others, are accomplished in accordance with this invention, generally speaking, by providing two-layered coatings wherein the first layer which is applied directly to a substrate, comprises palladium, platinum or nickel and the second layer, which overlies said first layer, comprises tantalum or chromium boride. The coefficients of thermal expansion of the whole system, i.e., substrate, first layer and over layer, are matched closely to reduce residual stress and accompanying strains, whereby the fatigue life of the coated substrate is not deleteriously affected. Additional gains in fatigue life retention are achieved by using low coating deposition temperatures.

Fatigue failure is believed to be the result of the application of fluctuating stresses over a long period of time, In the case of an erosion-resistant coated article, a major source of stress results from the difference in the coefficient of thermal expansion between the substrate material and the coating material. This difference in the coefficient of thermal expansion results in the coating being stressed by the substrate during thermal coating process

cycling.

The erosion-resistant coatings of the present invention ameliorate the problem of thermal expansion by using coating layers which have closely matched coefficients of thermal expansion so that it approaches the coefficient of thermal expansion of typical metallic alloy substrate materials. This is illustrated in the Table below which contains the coefficient of thermal expansion of several different coating materials and commonly used substrate materials.

TABLE

	Metal, <u>Compound</u>	Coefficient of linear expansion (0° - 1200°C) $\cdot 10^6 / ^{\circ}\text{C}$
5	Ni	13.14
	Pd	11.52
	TaB ₂	11.40
	Cr-B	11.10
10	Pt	9.10
	AM350 Steel	12.96
	C450 Steel	12.95
	Ti-6Al-4V	10.44
	Ti-(3.8 Al)-(1.5 Mo)	10.08
15	Ti-Mn Alloy	10.80
	Ti-Al-Mn Alloy	9.72

As can be seen from the Table, Ni, Pt, Pd, TaB₂ and CrB₂ have coefficients of thermal expansion which are closely matched to each other and also closely approach the coefficient of thermal expansion of a variety of stainless steel and titanium alloy substrates commonly used in gas turbine engine components. As will hereinafter be illustrated, the coated substrates of the present invention exhibit excellent erosion-resistance with no deleterious reduction in fatigue life and this result is believed to be due to the close matching of the coefficient of thermal expansion between the coating layers and the substrate composition.

The coatings of the present invention are thus distinguished from erosion resistant coatings of the

prior art which exhibit sharp drops in fatigue properties, thus creating the initiation of cracks and fractures. Illustrative of this prior art is McCaughna, U.S. Patent No. 2,882,302 which discloses
5 the plating of a refractory metal (e.g., tungsten, molybdenum or tantalum) with boron. At Column 2, lines 13-17, it is disclosed that a platinum interlayer may be placed between the refractory metal and the boride layer to act as a barrier. In the instant invention,
10 palladium or nickel acts as an interlayer between the substrate material (e.g., stainless steel) and the overlayer (i.e. boron and tantalum or chromium).

Glaser, U.S. Patent No. 2,862,828, discloses the use of
15 refractory diborides, such as tantalum diborides, in turbine components. There is no disclosure, however, to the use of a soft palladium or nickel interlayer underlying the refractory dibromides.

20 Andrews et al, U.S. Patent No. 3,309,292, discloses coatings of platinum metals (i.e., palladium, ruthenium, rhodium, osmium, iridium and platinum) on refractory metals such as tungsten and molybdenum for preparing rocket components, turbine blades,
25 atmospheric re-entry vehicles and the like.

Friedrich et al, U.S. Patent No. 3,574,572 discloses coating techniques using high-temperature alloys. Overcoating tantalum with silicides, aluminides, etc.
30 are disclosed at Column 2, line 36.

Glaski, U.S. Patent 3,890,110, discloses an electrocladding technique for coating a base metal with

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tantalum. No interlayer is present and the disclosure is not directed to infusion of the tantalum with boron or related materials.

5 Dils, U.S. Patent No. 3,890,456 discloses a coating technique for depositing layers of various materials on turbine blades. At column 3, lines 44-47, Dils discusses deposition of a noble metal, such as platinum, rhodium or palladium.

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The scope of the present invention, as further disclosed in the present specification and defined in the appended claims, patentably distinguishes over the foregoing art taken individually or in combination one
15 with another. No reference discloses or suggests a coating system wherein palladium, platinum or nickel is coated with tantalum or chromium boride coated on steel and titanium alloys.

20 Any suitable substrate material may be used with the two-layered coatings of the present invention. Typical substrate materials include stainless steel alloys, nickel, titanium and cobalt base superalloys, dispersion-strengthened alloys, composites, single
25 crystal and directional eutectics. While any suitable substrate material may be used, particularly good results are obtained when stainless steel, e.g. C450 type is used with the novel two-layer coatings disclosed herein.

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The first layer of the coating of this invention is a ductile layer containing palladium, platinum or nickel. While any suitable palladium, platinum or nickel-

containing metal may be used, about 100% palladium or a palladium alloy containing up to about 10%, by weight, ruthenium is preferred, especially when stainless steel is used as the substrate material being coated. This
5 palladium, platinum or nickel-containing layer acts as a barrier layer to protect the substrate during further coating with the hard second layer, i.e. the boride-containing layer containing tantalum or chromium and boron in the form of tantalum or chromium diboride.

10

The layers comprising the coating of this invention may be of any suitable thickness. Particularly good results are obtained with the palladium, platinum or nickel-containing layer being between about 0.0001
15 inches to about 0.002 inches and the tantalum or chromium diboride layer being between about 0.001 inches and 0.003 inches. Optimum results are obtained when the palladium or nickel-containing layer is about between 0.0003 and about 0.001 inches and the tantalum
20 or chromium boride overlayer is about 0.002 inches.

Any suitable coating technique may be used to apply the first layer of the coating to the substrate material. Typical methods include electroplating, sputtering,
25 ion-plating, pack coating, and vapor deposition, among others. While any suitable technique may be used, it is preferred to employ an electroplating, ion plating, sputtering or chemical vapor deposition (CVD) process. Any suitable technique, likewise, may be used to apply
30 the erosion-resistant tantalum or chromium boride layer to the palladium or nickel interlayer, a CVD or sputtering process being preferred.

In practicing the coating procedure of the present invention, the surface of the substrate to be coated is first shot peened to provide compressive stresses therein. The shot peened surface is then thoroughly
5 cleaned with a detergent, chlorinated solvent, or acidic or alkaline cleaning reagent to remove any remaining oil or light metal oxides, scale or other contaminants.

10 To insure good adherence of the first layer of palladium or nickel, the cleaned substrate is activated to effect final removal of adsorbed oxygen. As already indicated, the first layer is applied to the surface of the substrate by such conventional coating
15 techniques as electroless-plating, CVD or sputtering. If electroplating is the coating method chosen, then activation of the substrate surface is conveniently accomplished by anodic or cathodic electrocleaning in an alkaline or acidic cleaning bath by the passage
20 therethrough of the required electrical current. Plating is then accomplished using conventional plating baths such as a Watts nickel sulfate-chloride bath or a palladium diamino nitrite bath. If CVD is elected for the coating application, then activation is
25 accomplished by the passage of a hydrogen gas over the substrate surface. CVD is then accomplished using the volatilizable halide salt of the metal to be deposited and reacting these gases with hydrogen or other gases at the appropriate temperature, e.g. 500^o to 1850^oF to
30 effect deposition of the metallic layer.

If sputtering is chosen as the method of coating application, bias sputtering can be used to activate

the substrate. Deposition of the first metallic interlayer is accomplished with sputtering or ion-vapor plating using high purity targets of the desired metal coating material.

5

Coating application of the second layer of tantalum or chromium boride over the first metallic layer preferably is accomplished at a temperature not exceeding 1900°F by CVD, sputtering, pack or other conventional coating processes.

10

Thus, stress in the coating system is a function of the difference in the coefficients of thermal expansion between coating ($\Delta\alpha$) and the difference in temperature between the substrate (room temperature) and the coating deposition temperature (ΔT). Thus stress (σ) in the coating system can be represented by the formula

15

$$\sigma = \Delta \alpha \times \Delta T$$

In view of the formula, stress in the coating can be reduced by reducing the $\Delta\alpha$ by using a coating material having a coefficient of expansion closely corresponding to that of the substrate and reducing the ΔT by using a lower temperature at which the coating is deposited. Tantalum or chromium boride coatings are conventionally applied at 1000 - 1900°F. In a preferred embodiment of the present invention, the tantalum or chromium boride erosion-resistant coating is applied at a lower temperature i.e. a temperature between about 800°F and about 1400°F whereby improved fatigue life of the substrate is achieved.

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If CVD is chosen for the deposition of the tantalum or chromium boride, a gaseous mixture of a tantalum

halide, e.g. $TaCl_5$, a boron halide, e.g. BCl_3 , hydrogen gas and an inert gaseous diluent such as argon is flowed into a reaction chamber containing the first layer coated substrate heated to a temperature of about
5 1800 - 2000^oF and the gaseous mixture is allowed to react and deposit on the heated substrate.

If a physical vapor deposition process, such as sputtering, is chosen for the deposition of the high
10 purity targets of a tantalum-boron alloy, suitable alloy materials are fabricated and sputter coating equipment is used to coat the first layer of the coated substrate with the target material.

15 Other methods of depositing the tantalum or chromium boride coatings include electroplating Ta or Cr metal from a plating bath on the substrate. The coatings are then boronized by pack methods to form the metal boride compound wherein the Ta or Cr metal coated substrate is
20 packed in a boron coating mixture containing boron powder and a suitable reactive agent, e.g., potassium fluoride and then heating the packed substrate at 1700^oF for 1-2 hours to obtain the boronized substrate. Alternatively pack methods may be used to deposit Ta or
25 Cr and then the deposited metal is boronized by pack methods to form tantalum or chromium boride.

Several of the above discussed coating techniques have been utilized in connection with the present invention
30 which are described in the following Example which is illustrative of the invention.

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EXAMPLE

The surfaces of individual C450 stainless steel substrates were first thoroughly cleaned free of all dirt, grease and other objectionable foreign matter followed by conditioning by means of shot peening. The cleaned surface of the substrate was then electroplated with a 0.5 - 1.5 mil coating of nickel using a Watts nickel sulfanate plating bath.

10

A second coating of tantalum boride or chromium boride was applied to the electroplated surface by either CVD or pack coating as follows:

A second coating consisting of a 1 - 2 mil(s) thick tantalum boride layer was applied using a CVD technique wherein the nickel plated substrate was preheated to 1850-1950^oF for about 30 minutes before tantalum boride deposition and this temperature was maintained throughout the coating operation. The CVD coating operation utilized the reduction of gaseous TaCl₅ and BCl₃ with the deposition on the substrate surface of TaB₂. TaCl₅ was formed in situ by the reaction of chlorine gas flowed over tantalum chips at a flow rate of (300 cm³/min)² in a heated enclosure above the main reaction chamber. The flow rate of the other gaseous components were as follows:

30 BCl₃.....50-600cm³ /min.
 Argon (carrier gas).....1000 cm³/min.

The reaction chamber was maintained at 200 torr. The deposit was made at a rate of 0.0003 to 0.001in/hr to

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the required coating thickness.

A second coating consisting of a 0.5 to 1.5 mil thick Cr-B alloy was applied to the nickel plated substrate surface using a packing technique. The nickel plated substrate was successively put in a Cr powder pack and heated to about 1900°F followed by a boron powder pack at about 1400°F.

10 The DPH hardness of the Cr-B pack process coated substrate cross-section was as follows:

	Cr-B- - - - -	-1700 kg/mm ²
	Ni- - - - -	700 kg/mm ²
15	Substrate - - - - -	270 kg/mm ²

I. Erosion Resistance of the Coated Substrate

The coated substrate specimens were tested for erosion-resistance using S.S. White erosion testing equipment. When using this equipment, the coated specimen is subjected to a pressurized blast of sand, which is impinged on the specimen from a 0.5 inch diameter nozzle spaced from the specimen. The conditions under which the erosion testing was performed were as follows:

	Sand- - - - -	S.S. White #10, 50µm
	Air Pressure- - - - -	30 psi
30	PowderFlow - - - - -	60AC*
	Specimen/Nozzle Spacing-	0.5 inches

*setting on S.S. White equipment, powder chamber is

vibrated 60 times per second to produce desired powder flow rate.

5 The specimens were blasted with sand at 30° and 90° sand impingement angles for 5 minutes. The erosive wear was measured as the volume of coating material lost per minute of sand impingement. The results of the erosive wear tests are recorded in Table I below.

10 For purposes of comparison, the procedure of the Example was repeated with the exception that the C450 stainless steel substrate was not coated. The results of this comparative erosive wear test is also recorded in Table I.

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TABLE I

Relative Erosion Resistance of Ni/TaB₂ and Ni/Cr-B Coated C450 Steel Alloy and Uncoated C450 Steel

20

Test Specimen Volume Loss Rate (cm³/min.x 10⁻⁵)
@ Angle of Sand Impingement

	<u>30°</u>	<u>90°</u>
25 <u>Coating</u>		
Ni/TaB ₂	2.0	3.0
Ni/Cr-B	2.5	4.0
Uncoated	70.0	65.0

30 By reference to Table I, it is immediately apparent that the uncoated specimen exhibited an erosion rate which was 16-28 times greater than the coated specimens.

II. Fatigue Life of Coated Specimens

Ni + Cr-B coated bend plate (modified Krause) specimens coated in accordance with the Example were subjected to high cycle fatigue bend testing using a bend plate machine. Both ends of the specimen were rigidly clamped in the machine. An uncoated C450 stainless steel substrate was used as a control for baseline determination. Each specimen was tested at room temperature with an A ratio (sa/sm) = 1 and were mechanically vibrated to failure at a stress level of 60-70 ksi at a frequency $f = 30$ Hz. The stress level was varied from 60 to 70 ksi. Failure was indicated by breakage of the test specimen.

15

The results of the fatigue testing are given below in Table II.

TABLE II

Summary of Fatigue Bend Plate Test Data On Ni/CrB² and Uncoated C450 Steel

Test Specimen	Stress Level	No. of Cycles
<u>Coating</u>	<u>(ksi)</u>	<u>at Failure</u>
Ni/Cr-B	60	160,000
Uncoated	60	136,300
Ni/Cr-B	70	80,700
Uncoated	70	80,700

By reference to the data recorded in Table II, it is immediately apparent that the Ni/Cr-B coated C450 stainless steel specimens prepared in accordance with the present invention exhibited no degradation in

fatigue life when compared to baseline (uncoated) C450 stainless steel.

- 5 While specific components of the present system are defined above, many other variables may in any way affect, enhance or otherwise improve the coating systems of the present invention. These are intended to be included herein.
- 10 Although variations are shown in the present application, many modifications and ramifications may occur to those skilled in the art upon reading the present disclosure. These, too, are intended to be included herein.

CLAIMS:

1. A two-layered coating which comprises a first layer comprising palladium, platinum or nickel and a second layer overlying said first layer said second layer comprising tantalum or chromium and boron.
- 5 2. The coating of claim 1 wherein said first layer consists of about 100% palladium, platinum or nickel.
3. The coating of claim 1 wherein said first layer consists of up to about 10%, by weight, ruthenium and the remainder palladium.
4. The coating of claim 1 wherein said tantalum or chromium
10 and said boron are present as borides of tantalum or chromium.
5. The coating of claims 1, 2, 3, or 4 wherein the thickness of said first layer is from about .0005 inches to about .0015 inches and the thickness of said second layer is from about .0015 inches to about .003 inches.
- 15 6. The coating of claims 1, 2, 3 or 4 wherein the thickness of said first layer is from about 0.0001 to about 0.002 inches.
7. An article of manufacture comprising a substrate overcoated with the coating of any one of claims 1 to 6, wherein said first layer of said coating is in direct contact with said substrate.
- 20 8. The article of claim 7 wherein said substrate is stainless steel.
9. A method of preparing a two-layered coating comprising depositing tantalum or chromium boride on palladium or nickel.
10. The method of claim 9 wherein said nickel or palladium is
25 deposited by an electroplating or sputtering process.
11. The method of claim 9 or 10, wherein said tantalum or chromium boride is deposited by a CVD pack or by a sputtering process.
12. The method of claims 9, 10 or 11 wherein said palladium or nickel is deposited on a substrate material prior to being
30 overcoated.
13. The method of claims 9, 10, 11 or 12 wherein said substrate is stainless steel or titanium.

14. A method for imparting erosion resistance to a metallic substrate without an attendant loss in the fatigue life of the substrate which comprises applying to the substrate a first layer comprising palladium or nickel in direct contact with the substrate
5 and applying a second layer which overcoates the first layer, the second layer being comprised of a boride of tantalum or chromium.

15. The method of claim 16 wherein the second layer is deposited over the first layer at a temperature of about 452°C (800°F) to about 760°C (1400°F).



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	FR-A-2 447 980 (JOHNSON, MATTHEY & CO., LTD.) * Claims 1,2,4 *	1,14, 15	C 23 C 28/00
A	* Claims 1,2,4; page 4, line 36, example *	2,5-8, 10,12, 13	
Y	EP-A-0 015 451 (GENERAL ELECTRIC CO.) * Claims 1,4 *	1,14, 15	TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
A	* Examples 1,3 *	4,9-11	
A	FR-A-2 185 696 (UNION CARBIDE) * Claims 1,2 *	1,2,4, 8,9,13, 14	C 23 C
A	CHEMICAL ABSTRACTS, vol. 96, no. 12, March 1982, page 320, no. 90399w, Columbus, Ohio, US; & PL - A - 109 472 (OSRODEK BADAWCZO-ROZWOJOWY MASZYN WLOKIENNICZYCH alpha POLMATEX-CENARO") 30-06-1981 * Abstract *	1,14	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-03-1986	Examiner ELSEN D.B.A.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-3 824 134 (M.R. CHANCE) * Claims 1,2 *	1,4,8, 13,14	
A	FR-A-2 110 202 (LABORATOIRE SUISSE DE RECHERCHES HORLOGERES ET CIBA-GEIGY) * Claims 1,2,8,15 *	1,2,7, 8,10- 15	
A	DE-B-1 954 366 (HERAEUS) * Claims 1,5-9 *	1,4,7, 8,10, 12	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
Place of search THE HAGUE		Date of completion of the search 19-03-1986	Examiner ELSEN D.B.A.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			