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(54) A method of producing a surface coating upon a substrate.

(57) A method of forming a layer of a nitrogenous alloy upon a substrate body including the operation of depositing upon the substrate particles of a powder including an alloy containing a nitride-forming material and a thermally decomposable nitrogen donor material and heating the particles to a temperature such that the nitrogen donor dissociates to provide free nitrogen which reacts with the nitride former and the particles fuse to form a layer of a nitrogenous alloy upon the substrate.

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The present invention relates to a method of depositing a surface coating upon a substrate and more particularly to depositing a hard surface alloy coating upon a metal substrate.

For many purposes it may be desirable to provide a metal substrate body with a surface coating having properties which differ from those of the substrate. For example, it may be desirable to make the surface of the substrate metal more wear or corrosion resistant. Many techniques are used to deposit such coatings. Examples are:- electro-plating, flame and plasma spraying, ion bombardment and the use of lasers to fuse a coating powder. Favoured materials for producing hard corrosion resistant surface coatings are nitrides which can be produced either by heating the substrate in a nitrogenous environment or by the direct implantation of nitrogen ions. One such method for producing nitrogen-containing alloys in a particulate form is described in our co-pending European patent application publication number EPO 363047 A1. In the above application, there is described a method of forming alloy particles in which particles of the starting metal are heated together with a nitrogen donor material which dissociates to provide free nitrogen which dissolves in the metal particles to provide particles of the desired alloy.

According to the present invention there is provided a method of forming a layer of a nitrogenous alloy upon a substrate including the operation of depositing upon a surface particles of an alloy material including a nitrogen donor material and a nitride forming element, wherein the particles during at least a part of their passage to the substrate are arranged to be at a temperature such that at least a proportion of the nitrogen donor is dissociated to provide free nitrogen which reacts with the nitride former to form a nitrogenous alloy prior to the deposition of the particles upon the substrate and causing the particles to form an adherent non-porous layer of nitrogenous alloy upon the substrate.

The particles may be arranged to be at least plastic when they impinge upon the substrate so that they coalesce to form the non-porous layer, or the coated substrate may be subjected to a densification process such as hot rolling or hot isostatic pressing.

Preferably the particles are formed by atomising a molten precursor material, or by the use of high-temperature deposition techniques such as flame or plasma spraying.

In addition to forming a coating layer of nitrogenous alloy, the free nitrogen will diffuse into the substrate with which it preferably reacts so as to provide an interfacial region with a graded concentration of nitrogen thereby to improve the properties of the surface layer. The substrate may contain a nitrogen former to facilitate this process.

Preferably there is included the operation of subjecting the coated substrate to a heat treatment such as to enhance the dissociation of the nitrogen donor and provide a desired variation of the physical properties of the alloy surface coating and the adjacent surface region of the substrate. The heat treatment may be combined with a densifying operation as part of a hot isostatic pressing process. This will then ensure the complete dissociation of the nitrogen donor and form a dense layer.

The nitrogen donor may comprise chromium nitride (either CrN or Cr_2N) and the nitride former may comprise titanium. Preferably a dispersant may be included in the particles or introduced into the surface alloy layer. A suitable dispersant is titanium nitride itself.

The alloy from which the surface layer is formed may comprise an iron, nickel or cobalt based alloy, for example stainless steel and the substrate may comprise similar alloys, but more usually an alloy of leaner composition.

The deposition of the powder may be carried out in the presence of a nitrogenous gas. Such a nitrogenous gas may comprise pure nitrogen, nitrogen plus less than $5^{v}/_{o}$ hydrogen, or nitrogen plus an inert carrier gas such as argon which acts as a diluent.

EPO patent specification number 363047 A1 describes the use of the Osprey process as means of obtaining a metal preform in which the donor powder is contained. This is achieved by injecting the donor powder into the atomising gas used in the Osprey process during spraying so as to be dispersed into the preform. A natural consequence of this process is that the metal powder that does not impinge on the substrate to form a preform, termed "overspray", also contains donor material encapsulated within the metal powder particles. This overspray powder can also be consolidated as per the methods stated in the above patent or by using a hot isostatic pressing operation to produce dissociation of the donor and formation of the nitride. In addition if the metal-donor co-spray powder is not allowed to impinge on a substrate, but is collected as a powder, then the process can be used to produce quantities of powder consisting of donor material encapsulated within the metal. This powder can then be used to provide coatings by methods embodying the present invention and as described later.

The invention will now be described, by way of example, with reference to the following examples:

Example 1

Particles of a powder comprising an alloy having the general formula MCrA1Y where M may be iron, cobalt or nickel, have incorporated within them a nitrogen donor such as CrN. The particles are applied to a stainless steel substrate body by plasma spraying. During the deposition process the CrN dissociates to provide free nitrogen which reacts with aluminium or yttrium from the MCrA1Y to form the appropriate nitrides and also provides a source of nitrogen for additional coating and substrate hardening.

The MCrA1Y alloy is arranged to contain sufficient aluminum to ensure that after pre-oxidation there will continue to be in use oxidation protection by the formation of alumina scale. The MCrA1Y alloy also may contain up to 3 $^{v}/_{o}$ titanium, which will react to form a nitride before the aluminium thus ensuring that some aluminium remains in the MCrA1Y alloy to enable an alumina scale to form in use.

The CrN may be incorporated into the MCrA1Y alloy particles by the method disclosed in our co-pending European patent application EPO 363047 A1 to which previous reference has been made. Alternatively it can be incorporated by the already mentioned use of "Osprey" process overspray material, or it can be incorporated by a technique called Mechano Fusion where the donor CrN coats the alloy powder by a mechanical fusing process.

Example 2

In this case, the powder is made of the cobalt based hard surfacing alloy known as Stellite produced by Deloro Stellite Limited. Again, chromium nitride is incorporated as a nitrogen donor and titanium is included as a nitride forming material. As before the powder is applied by means of plasma spraying, or some other powder deposition technique and the dissociation of the chromium nitride is achieved thermally during the deposition phase, or subsequently.

A further heat treatment step such as a thermal anneal, laser glaze or hot isostatic pressing process may be found to be necessary to achieve the complete dissociation of the chromium nitride and the formation of the titanium nitride.

Example 3

In this case, the powder is made of the nickel-based alloy known as Deloro, also produced by Deloro Stellite Limited. Again, chromium nitride and titanium are used as the nitrogen donor and the nitride former respectively, and the deposition process is as before.

Example 4

In this case the powder is made of the iron-based alloy known as Delchrome, again produced by Delloro Stellite Limited, but as before the nitrogen donor is chromium nitride and the nitride former is titanium. The deposition process is as for examples 2 and 3.

In Examples 2 to 4, the deposition can be done in an atmosphere of nitrogen or nitrogen-containing gas. Excess nitrogen donor material will provide an excess of nitrogen in solid solution in the final alloy layer and the interface region of the substrate upon which it is deposited. This excess of nitrogen will provide strengthening of the coating and the interfacial region of the substrate as well as the bond between them. Also the corrosion resistance of the alloy coating will be improved.

TiN/N strengthening phases can be used as well as, or instead of, the strengthening phases which usually are incorporated in the above mentioned alloys. TiN/N strengthening will enhance the performance of cobalt, nickel and iron-based hard facing alloys in the following ways;

a) By providing a nitride dispersion which is thermodynamically more stable than some of the carbides which are used in the above alloys, so extending the application temperature range to higher values than had hitherto been possible.

b) A fine dispersion of TiN in the alloy layer will in its own right provide an increment in strength and creep strength. A hard alloy will be more wear resistant.

c) Nitrogen in solid solution will provide solid solution strengthening of the deposited layer and also improve the corrosion resistance of the deposited layer.

The mixture of nitrogen donor and titanium containing alloy for spraying may be obtained also by a blending of appropriate particles, or by the use of a hollow tube made of a titanium-containing alloy packed with the nitrogen donor material and adapted for use as a plasma spraying consumable in a known manner.

Claims

1. A method of forming a layer of a nitrogenous alloy upon a substrate including the operation of depositing upon a surface particles of an alloy material including a nitrogen donor material and a nitride forming element, wherein the particles during at least a part of their passage to the substrate are arranged to be at a temperature such that at least a proportion of the nitrogen donor is dissociated to provide free nitrogen which reacts with the nitride former to form a nitrogenous alloy prior to the deposition of the particles upon the substrate and causing the particles to form an adherent non-porous layer of nitrogenous alloy upon the substrate.

2. A method according to Claim 1 wherein the concentration of the nitrogen donor is such that free nitrogen exists in the deposited layer and the said free nitrogen is caused to diffuse into the substrate thereby to provide a nitrogenous interfacial region of the substrate.

3. A method according to Claim 2 wherein the material of the substrate includes a nitride forming element.

4. A method according to Claim 2 or Claim 3 wherein the coated substrate is subjected to a heat treatment to enhance the dissociation of nitrogen donor material present in the deposited layer.

5. A method according to any preceding Claim wherein the deposited layer is subjected to a hot densification process.

6. A method according to Claim 5 wherein the hot densification process is hot isostatic pressing.

7. A method according to any preceding Claim wherein the nitrogen donor comprises chromium nitride.

8. A method according to any preceding Claim wherein the nitride former comprises titanium.

9. A method according to any preceding Claim wherein either the particles or the deposited layer includes a dispersant for the nitride.

10. A method according to Claim 9 wherein the dispersant comprises titanium nitride.

11. A method according to any preceding Claim wherein the formation and/or the deposition of the particles is carried out in the presence of a nitrogenous gas.

12. A method according to Claim 11 wherein the nitrogenous gas comprises nitrogen, nitrogen plus less than 5 $^{v}/_{o}$ hydrogen, or nitrogen plus an inert carrier gas.

13. A method according to any preceding Claim wherein the particles and the substrate have the same general formula.

14. A method according to any preceding Claim wherein the alloy from which the particles are formed is an iron, cobalt or nickel alloy.

15. A method according to Claim 14 wherein the said alloy has the general formula MCrA1Y where M may be iron, cobalt or nickel.

16. A method according to Claim 15 wherein the said alloy includes up to 3 $^{v}/_{o}$ titanium.

17. A method according to any preceding Claim wherein the particles are formed by the atomization of a liquid precursor material.

18. A method according to Claim 17 wherein the liquid precursor material is atomised by means of one or more jets of gas and the nitrogen donor material is injected into the gas thereby to include the nitrogen donor material into the particles.

19. A method according to any of Claims 1 to 16 wherein the particles are deposited by plasma spraying utilising an electrode comprising a hollow titanium-containing alloy tube filled with the nitrogen donor material.

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EUROPEAN SEARCH REPORT

Application Number
EP 93 30 0142

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.5)
X	GB-A-1 182 242 (UNITED STATES BORAX AND CHEMICAL CORPORATION) * claims 1-4 *	1,8,11, 12	C23C4/12
A	US-A-4 961 457 (WILLIAM G. WATSON) * claims 1-7 *	1,8,11	
A	WO-A-8 905 870 (OSPREY METALS) * page 9; claims 1-14 *	1-6,8,11	
A	EP-A-0 156 760 (MANNESMANN AG) * page 4, line 19 - line 28; claims 1-6 *	1,8,11	
A	DE-A-3 808 285 (MESSER GRIESHEIM) * claims 1-10,22,23 *	1,11,13, 17	
A,D	EP-A-0 363 047 (UNITED KINGDIM ATOMIC ENERGY AUTHORITY) * claims 1-19 *	7-11, 14-18	
A	EP-A-0 456 847 (BERNEX) * claims 1,2,13,14,15,21 *	11,13, 14,17,18	TECHNICAL FIELDS SEARCHED (Int. Cl.5) C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07 MAY 1993	ELSEN D.B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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D : document cited in the application
L : document cited for other reasons

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