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(71) Applicant : **GENERAL ELECTRIC COMPANY**
1 River Road
Schenectady, NY 12345 (US)

(72) Inventor : **Beltran, Adrian Maurice**
RD Nr. 2, Peaceable
Ballston Spa, New York 12020 (US)
Inventor : **Spriggs, Donald Robert**
978 Inman Road
Schenectady, New York 12309 (US)

(74) Representative : **Pratt, Richard Wilson et al**
London Patent Operation G.E. Technical Services Co. Inc. Essex House 12/13 Essex Street
London WC2R 3AA (GB)

(54) Pre-oxidation of alloy powder coatings.

(57) Corrosion- and erosion-resistant coatings are thermal spray deposited onto metallic substrates, especially Co- and Ni-containing alloys, by thermal spray depositing metal particles partially pre-oxidized prior to application the metal substrate to be protected. Coatings rich in desired protective oxide and reduced non-protective, voluminous oxides result.

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Jouve, 18, rue Saint-Denis, 75001 PARIS

This invention relates to forming protective metal oxide films using conventional particle coating processes on metal alloy substrate surfaces susceptible to aggressive conditions including corrosion, erosion, oxidation, and/or wear. Particles of metal alloys prepared under controlled conditions with a thin metal oxide film thereon and suitable for use in such a metal coating process are also described.

Procedures for applying a corrosion, oxidation, erosion and/or wear-resistant coating on metal substrates using powdered metal alloys applied by conventional particle coating processes are described. These metal alloy powders have a previously-formed protective oxide film on the particle surface or metal oxide dispersed within the alloy particle itself. Metal alloy powders having a thin, adherent, protective oxide film on each particle surface and suitable for use in a high-temperature powder coating process are also described.

BACKGROUND OF THE INVENTION

Equipment for conducting chemical reactions, steam generating apparatus, gas turbine parts and the like are constantly subjected to aggressive conditions and often require protection from such conditions. A frequently used protective technique is to apply a metal oxide film to the surface of the article to be protected such as by thermal decomposition of a volatile metal alloy to deposit a metal oxide layer on the substrate requiring protection. Various proposals have been made to improve the deposition process including oxidizing the surface of the article to be protected prior to application of metal or metal oxide on the part such as described in Foster et al, U.S. patent 4,297,150. Maeda et al in U.S. patent 4,532,109 proposes to construct an apparatus for treating hydrocarbons at high temperature without carbon deposits of a special aluminum-containing alloy which itself is adapted to oxidize and form an oxide film coating directly on its surface either prior to or upon exposure to aggressive, oxidizing conditions. Nickel-base superalloys adapted to oxidize selectively to form a protective oxide Al_2O_3 adherent to their own surface are described in U.S. patent 3,754,902 to Boone et al.

Replacements for aluminide coatings such as coatings based upon MCrALY alloys, where M is Ni or Co or both, which are themselves corrosion-protective and do not depend for their protective effect on the deoxidized base metal substrate on which they are deposited, are described in U.S. patent 3,918,139 to Felten. Particles of the alloy are deposited by plasma spraying, vapor deposition or the like.

Protective oxide coatings provided by previous procedures do not afford a uniform, dense coating of the desired protective metal oxide or oxides and often contain voluminous, non-desired, non-protective oxides as the normal result of the thermal spraying process. Such non-protective films are not only superfluous, they in fact detract from the mechanical integrity and mechanical properties of the deposit. Unwanted oxides dilute/reduce the concentration of the desired, corrosion-resistant oxides often leading to a less than satisfactory coating.

As protective coatings of metal oxides are formed under volatile temperature and environmental (in terms of reactive gases) conditions, gross oxidation during the coating process is also a significant concern, again reducing the concentration of the protective oxide.

These conventional procedures feature application of the metal alloy directly onto the substrate surface and rely upon the deposition conditions of high temperatures and oxidizing environments to oxidize the alloy during the coating process and/or at the time of impact on the substrate being coated. This leads to the disadvantageous results as summarized above.

DETAILED DESCRIPTION OF THE INVENTION

Described is a process of depositing a protective film on a metal substrate by applying to that substrate to be protected particles of an alloy containing the oxide-forming reactive elements Cr, Al or Si, at least a portion of which have been previously oxidized prior to application to the substrate. The partially-oxidized metal alloy particles are applied by a convenient particle coating process such as plasma spraying, flame spraying, thermal spraying, vacuum plasma spraying and isostatic pressing. Desirably, the alloy particles prior to application have a thin, adherent oxide film substantially uniformly distributed over their surface. The particles preferably contain a dispersion of Cr, Al or Si oxides.

In another aspect, the invention includes a process of coating a Ni- or Co-based superalloy substrate with a protective coating on the surface by applying particles of a metal alloy containing at least one of the oxide-forming reactive elements Cr, Al or Si in it. At least a portion of the particles contain up to 20 weight percent of an oxide of Cr, Al or Si prior to application. The resulting adherent protective coating being corrosion-, erosion-, oxidation- and wear-resistant, is rich in the protective Cr, Al or Si oxides and substantially devoid of voluminous, non-protective oxides. Ni- or Si-based superalloy articles having a thin, adherent, corrosion, erosion, oxidization and wear-resistant protective coating there are also included as are particles of an Fe-, Ni-, Co-based metal alloy containing Cr, Al or both having a thin, adherent, protective oxide film of Cr, Al or both Cr and Al on their surfaces.

This invention relates to thermal pre-treatment of prealloyed metallic powders and to subsequently thermally spraying these particles onto metallic substrates to form protective layers or coatings on the substrate for corrosion, oxidation, erosion or wear resistance. The particles are applied by such techniques as plasma spraying or flame spraying. The invention is applicable to alloys containing strong oxide-forming reactive elements such as Cr, Al and Si.

This invention provides a superior powder metallurgy deposit by selectively preoxidizing the powder, prior to thermal spraying, to produce a thin, adherent, protective oxide film on each powder particle surface. Pre-oxidation conducted under controlled conditions of time, temperature and environment to produce a preferred oxide composition of minimal thickness on the alloy particles. Examples of suitable particle-forming alloys for this invention are alloys containing greater than about 10 wt. % Cr and/or 3 wt. % Al, having base elements of Fe, Ni or Co, or mixtures of these. The aim is to preclude the formation of voluminous, non-protective oxides which normally form during the thermal spraying process. The presence of these oxides in the deposit reduce the integrity and mechanical properties (strength and ductility) of the deposit. Gross oxidation during deposition also alters the compositional balance of the deposit, since various elements might be involved in the oxidation reactions. If the deposit's main function is to provide oxidation, corrosion or wear resistance, this ability may be impaired by uncontrolled and otherwise unavoidable gross oxidation during thermal spraying.

Thermal spraying by conventional oxyacetylene, or other combusted gases, or plasma spray processes subjects the metallic powder to extremely high temperatures, as much as 3000°F or higher, in oxidizing environments for very short intervals. High gas stream velocity and the elevated temperatures produced by plasma formation transfer momentum and heat to the powder particles which become molten in flight. Impactions of this material with the substrate cause adiabatic heating, gross plastic deformation of the droplets and fracture of the powder surface oxides. High solidification rates and the dissipation of heat into the substrate and surroundings however, minimize the extent of deposit in-situ oxidation, provided that preheating of the substrate is minimal. This tends to minimize post-deposition oxidation of the deposit.

Classic oxidation theory and experimental evidence for bulk materials indicate that oxidation of Fe, Ni and Co-base alloys containing Cr and/or Al may occur in three stages. The initiation of oxidation involves linear reaction rates to form base metal oxides, i.e., FeO, NiO or CoO due to the high concentrations of these elements in the prealloyed powder, often 55 to 75 wt. %. The reactive elements Cr and/or Al also begin to react immediately, and may participate in a second oxidation stage involving the formation of spinel oxides such as MCr_2O_4 or MAl_2O_4 (where M is Fe, Ni or Co). Commercial alloys such as the 300 series austenitic stainless steels, i.e., 304ss (18Cr-8Ni) or 310ss (25Cr-20Ni), or the 400 series ferritic steels, i.e., 446ss (25Cr), contain sufficient Cr to eventually form a protective oxide film Cr_2O_3 at the oxide metal interface during the third stage of oxidation; stages II and III may actually be reversed in some systems. Once this film forms, the oxidation reaction rate becomes parabolic (Δ W/M = $k_pt^{-2} + c$) and oxide film thickness growth is governed by the diffusion rate of Cr^{+3} through Cr_2O_3.

Little is really known of the powder particle oxidation phenomena in a high velocity gas stream. Because of the high temperatures generated in the arc-plasma and oxycetylene spray systems, most of the powder particles become molten. Diffusion rates are in general two or three orders of magnitude higher in the liquid state, hence, the oxidation process undoubtedly involves reaction-limited linear kinetics, and the formation of a solid oxide surface film to favor diffusion-limited parabolic kinetics may be impossible in current systems. Of course, some undefined fraction of the particles do not melt during flight; these may oxidize at somewhat lower reaction rates. Some of the fine submicron particles probably volatilize and do not enter into the coating and oxidation process.

Although the plasma spray effluent is generated with inert gases such as Ar, He or stable gases such as H_2, the effluent itself is not necessarily unreactive. Because the gases leave the plasma gun at high velocity and with a rapid pressure drop, the surrounding atmosphere, i.e., air, is drawn into the main gas stream. Measurements by researchers [A. Hasui, S. Kitahara, T. Fukushima, Tran. Nat. Res. Inst. Metals (Japan) 1965, 7 (5), 21] have indicated the arc gas to be as much as 90% air at a distance of 10 cm. from the plasma-gun nozzle. This contamination can result in oxidation, decarburization, or nitrogen absorption of the powder coating alloys contained in the stream. These oxides or other reaction products that form during spraying are complex and are rarely established as a continuous film. Thus, in-flight particle oxidation reactions are gross and uncontrolled.

To minimize gross oxidation of the powder particles in flight, this invention provides a selective oxidation pre-treatment to generate a thin, controlled oxide, such as Cr_2O_3 or Al_2O_3, on the particle surface. Conditions of time, temperature and environment are chosen to preclude the formation of base metal oxides and to generate a uniform, adherent protective surface oxide in a reasonable time, with minimal impact upon the composition, microstructure or particle topography. An important variable-in this process is the choice of environment, which must produce an atmosphere reducing to FeO, NiO or CoO, i.e., below the dissociation pressure for these oxides but above that for these two groups of oxides, selective oxidation pre-treatment is readily accomplished. Metal-metal oxide stability in a H_2O/H_2 atmosphere (and in vacuo) as a function of temperature and dew point as depicted in a graph by N. Bredzs (1969) based upon data from Kubaschewski and Evans (1967). Any point to the right of a given equilibrium curve indicates metal stability, i.e., oxide will not form. For example, oxidation pre-treatment of 446ss (25 Cr - balance Fe) at 2000°F and dew points between -20°F and 80°F, for example, will form Cr_2O_3; FeO and Fe_3O_4 will not form.

This invention provides economic and commercial significance in the following applications:

The primary area of interest is conventional thermal spraying which utilizes prealloyed metallic powders containing reactive elements such as Cr, Al or Si, as discussed above. Deposits may be utilized to provide oxidation, corrosion, erosion or wear resistance. Recent developments in the plasma spray field center upon vacuum plasma spraying in a large chamber at reduced pressures (10 - 100 Torr) to minimize oxidation of the powder to enhance structure and properties of the deposit. While of particular benefit of Al-containing MCrAlY coating compositions used on superalloys in the gas turbine industry, substantial process,capitalization and cost premiums are associated with this approach.

Selective preoxidative treatment of the MCrAlY materials according to this invention may provide a substantial cost advantage through conventional plasma spray processing. The commercial utility of the MCrAlY materials thus are enhanced and expanded. For example, large articles that are difficult or impossible to enclose in vacuum would become McrAlY-coatable and thus render resistant to oxidation and corrosion.

Selective preoxidative treatment of some Cr, Al or Si containing powder alloy compositions may be controlled to generate a very fine dispersion of internal oxide, as opposed to a thin surface oxide layer. Discrete sub-micron aluminum oxide (Al_2O_3) particles are known to significantly enhance the mechanical properties and microstructural stability in a number of alloy systems. Hence, surface coatings or monolithic structures utilizing this material would exhibit inherent hardness or strength advantages. Pre-treated powder could be vacuum plasma sprayed onto a substrate or sacrificial mandrel using available VPS equipment and processing parameters, or could be consolidated to the desired shape via hot isostatic pressing followed by thermal-mechanical processing.

Powder treatment to produce controlled oxides either as internal oxide particles or surface layers may also be useful as erosion or wear-resistant coatings, particularly in solid-particle erosion environments. Oxide type, volume percent loading and morphology are tailored for a specific application environment. Application for parts coated with this process include steam turbine surfaces exposed to boiler scale carry-over during start-up, or to gas turbine gas-path components operating in the effluent of a coal-fired pressurized, fludized bed combustor (PFBC) among other countless applications.

Claims

1. A process of depositing a protective film on a metal substrate comprising applying to the substrate to be protected particles of an alloy containing the oxide-forming reactive elements Cr, Al or Si at least a portion of which particles have been previously oxidized prior to application to the substrate.

2. The process of claim 1, in which the partially-oxidized metal alloy particles are applied by a particle coating process selected from the group consisting of plasma spraying, flame spraying, thermal spraying, vacuum plasma spraying and isostatic pressing.

3. The process of Claim 1 or Claim 2, in which the alloy particles prior to application have a thin, adherent oxide film substantially uniformly distributed over the surface thereof.

4. The process of any preceding claim, in which the particles contain a dispersion of Cr, Al or Si oxides therein.

5. The process of any preceding claim, in which the particles contain at least about 10 weight % Cr therein.

6. The process of any preceding claim, in which the particles contain at least about 3 weight percent Al therein.

7. The process of any one of Claims 1 to 6, in which the metal substrate is a Ni-based superalloy.

8. The process of any one of Claim 1 to 6, in which the metal substrate is a Co-based superalloy.

9. The process of any one of Claim 1 to 6, in which the metal substrate is an Fe-based alloy.

10. A process of applying to a Ni- or Co-based superalloy substrate a protective coating, said process comprising applying particles of a metal alloy containing at least one of the oxide-forming reactive elements Cr, Al or Si therein and at least a portion of said particles containing on the surface thereof up to 20 weight percent of an oxide of Cr, Al or Si prior to application, the resulting adherent protective coating being corrosion-, erosion-, oxidation- and wear-resistant rich in the

protective Cr, Al or Si oxides and substantially devoid of voluminous, non-protective oxides.