METHOD FOR COATING A SUBSTRATE CONTAINING COBALT, NICKEL AND/OR IRON WITH A CORROSION-RESISTANT LAYER

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ABSTRACT

A method is provided for corrosion-proofing substrates made of materials containing cobalt, nickel and/or iron, in which cracking in the material and in a corrosion-proofing layer can be avoided. For this purpose, a slurry containing aluminium is applied to a substrate and the substrate, together with the applied slurry, is then subjected to a brief annealing of the surface layer at reduced temperature. Due to the heating of the surface layer of the substrate and of the slurry during the annealing of the surface layer, an exothermic reaction between the aluminium and the substrate metal takes place on the surface of the substrate, so that aluminium phases are formed which produce an aluminide diffusion layer on the substrate. Above this layer remains a residual layer of unused slurry.
METHOD FOR COATING A SUBSTRATE CONTAINING COBALT, NICKEL AND/OR IRON WITH A CORROSION-RESISTANT LAYER

BACKGROUND AND SUMMARY OF THE INVENTION

[0001] The invention relates to a method for coating a substrate that contains cobalt, nickel and/or iron with a corrosion-resistant layer.

[0002] Substrates, such as components and elements, that will be used at high temperatures, e.g., equipment parts for use in the chemicals industry, must be protected against corrosion. It therefore is generally necessary to produce cost-efficient and effective coatings for components and elements of this type.

[0003] The technique most frequently used for preventing hot gas corrosion and oxidation of components involves applying aluminum-rich surface layers to substrates, a process referred to as aluminizing. In this process, the surfaces of components that will be used at high temperatures and exposed to strong corrosive forces are equipped with conventional aluminide coatings, weld cladding layers or highly alloyed thermal spray coatings.

[0004] Aluminum forms intermetallic bonds with preferably nickel, cobalt and iron. Phases that have a lower percentage of Al, namely the aluminum-poorer phases NiAl and/or CoAl or FeAl, are preferable to the extremely brittle phases such as Fe₄Al₃₆ [Xiang et al.] or Fe₃Al₃ [Perez et al., Rohr et al.], Ni₅Al₃ or Ni₃Al and/or Co₅Al₃, as the former phases are less susceptible to cracking. A protective oxide layer, which also forms on the aluminum-poorer intermetallic bonds, comprises slow growing, highly adherent and highly stable aluminum oxide.

[0005] Various methods and coatings that are based on the principle of aluminum enrichment in the material surface are known.

[0006] In this context there are two different types of coatings: surface coatings, which are applied to the substrate surface, and diffusion coatings, which are provided by the diffusion of elements such as aluminum, chromium or silicon into the surface zone of the substrate.

[0007] One option is the chemical vapor deposition (CVD) method, in which aluminum or other elements are deposited from a gas phase onto the material surface by means of halogen activators. This method is known as the "pack cementation" process and has been described in numerous patents, Wochsell et al. U.S. Pat. No. 3,257,230 or Boone et al. U.S. Pat. No. 3,544,348.

[0008] A second option involves the application of aluminum-rich metal (Fe, Ni, Co)-chromium aluminum yttrium (MCrAlY) coating layers. These layers are generally applied, e.g., by means of weld cladding or thermal spraying. During use, these layers likewise form protective aluminum oxide on the surface. However, they also contain additional elements that contribute to protection against oxidation, e.g. chromium and yttrium. Therefore, the aluminum content in these layers can be lower than is necessary for diffusion layers. In this manner, other alloys can also be applied to materials that are susceptible corrosion. However, this method is relatively complex and costly.

[0009] Slurry coatings offer another alternative; these are already being used as commercial coatings, and have been described, e.g., by Allen et al. in U.S. Pat. No. 3,248,251 or Mosser et al. in U.S. Pat. No. 5,650,235. In the slurry method, intermetallic coatings are produced by way of reaction and interdiffusion between the substrate and a metal-containing powder, which is applied together with a binder to the component surface, see, e.g., Joseph U.S. Pat. No. 3,102,044. The layers that are produced are similar to those produced by means of pack methods and, due to the high temperature during the interdiffusion step, also contain the elements of the base material, in addition to the elements of the slurry.

[0010] As with the known pack processes, slurry coatings are diffused in during a diffusion step above 800°C. During this diffusion step, which in the case of slurry coating is generally carried out in an inert atmosphere or in a vacuum, the elements of the base material and the coating diffuse into one another and form enriched mixed crystals and intermetallic bonds. More particularly, the aluminum from the slurry reacts with nickel, cobalt or iron in the base material and forms the desired aluminides. Previous methods have been limited to nickel and cobalt base materials or austenitic steels, since the temperature treatment must be performed at temperatures above 800°C; otherwise, highly aluminum-rich brittle intermetallic phases such as Fe₄Al₃ or Ni₅Al₃ will form on the surface due to the high proportion of aluminum. For this reason, coating ferritic steels with slurry coatings has never before been possible due to the temperature limits for these materials.

[0011] The previously known coatings frequently contain other elements and constituents in the slurry in addition to aluminum. The best known commercial alloy powder in this field, which is available from Sermatech Int., USA under the trade name Sermatoy 1, comprises 35% Al powder, 6% Si powder, 47% water and 12% phosphate-containing and chromium-containing binders. A further development of this coating system is described by Meelu et al. in U.S. Pat. No. 6,126,758 and/or U.S. Pat. No. 5,547,770. In this patent, Al—Si is diffused into an eutectic alloy system as a component of the slurry. All of these coatings are therefore based on the fact that the aluminum atoms of the slurry react during heat treatment with certain elements of the substrate that have a particular affinity for aluminum, forming intermetallic bonds. The substrate components nickel and cobalt, but also iron, are particularly well suited for this.

[0012] In all the previous approaches, however, the entire component must always be subjected to heat treatment at temperatures above 800°C.

[0013] Particularly in the case of slurry coatings, which involve the application of aluminum alloys in the form of a slip or a paste to the workpiece surface, the necessary heat treatment temperatures are above the typical tempering temperature for ferritic/austenitic steels, which is a maximum of 650°C. Ennis et al. have demonstrated that even at 835°C, the creep resistance of these materials is diminished substantially. Drye pond et al. have demonstrated that a CVD pack process performed at 1050°C increases particle size substantially, which has a negative impact on crack resistance at low temperatures.

[0014] Nevertheless, these temperatures are required for conventional methods, as otherwise the high proportion of aluminum near the surface, with low interdiffusion, will tend to first form the aluminum-rich, extremely brittle phases such as Fe₄Al₃ [Xiang et al.] or Fe₃Al₃ [Perez et al., Rohr et al.] on steels, which will lead to cracking. Added to this is the fact that the coefficient of thermal expansion of these damaging
phases is substantially higher than that of more conventional steel materials, resulting in an even greater tendency toward cracking.

[0015] It is known that these phases can be converted to the less brittle FeAl phases through subsequent heat treatment at high temperatures [e.g., Rohr et al.], however in many cases, cracks are already present that cannot be eliminated. Moreover, this heat treatment is generally carried out in the absence of air in order to guarantee diffusion and avoid damage to the material. At low temperatures of 650 °C, for example, several hundred hours of exposure time is required, which is a significant disadvantage.

[0016] The object of the invention is therefore to provide a cost-efficient method for corrosion-proofing substrates (components) made of materials that contain cobalt, nickel and/or iron, in which the material and the corrosion-proofing layers that are produced are not prone to cracking.

[0017] To attain this object, the invention provides that a slurry containing aluminum is applied to the substrate, and the substrate together with the applied slurry is then subjected to a brief annealing of the surface layer at a reduced temperature.

[0018] The aluminum in the slurry may be present in pure form or alloyed, e.g., in the form of an aluminum-based alloy, or as a mixture of pure or alloyed aluminum.

[0019] Annealing of the surface layer is understood as a heat treatment that acts substantially on the surface zone of the substrate and thus causes a temperature increase only in said zone, while the interior—the body—of the substrate remains substantially unaffected. Heat treatments of this type are used, e.g., for hardening the surface layers of components.

[0020] Briefly means that annealing of the surface layer lasts for less than 10 minutes.

[0021] At a reduced temperature means that the temperature of the surface layer and in the slurry during annealing of the surface layer is between 550 °C and 800 °C.

[0022] The heating of the surface layer of the substrate and of the slurry during the annealing of the surface layer induces an exothermic reaction between the aluminum and the substrate metal (iron or nickel) on the surface, so that aluminide phases are produced, forming the coating.

[0023] It is therefore possible to furnish, e.g., nickel-containing substrates with aluminide coatings for corrosive conditions. By applying a method for surface layer hardening to a substrate with aluminum-rich slurry, a brief heat treatment of the surface layer, lasting several minutes, in the open air causes the aluminum of the slurry to react with the galvanic nickel of the substrate surface, thereby producing a coating. As a result, the method is also extremely well suited for coating components directly on site, or for use as a repair method.

[0024] As a significant difference from the diffusion coatings described in the prior art, therefore, with the new coating the layer is formed not by interdiffusion with the substrate during heat treatment of the entire component, but by a reaction of the components of the slurry with the nickel of a galvanic layer and/or of the material during heating of the surface layer, and optionally only in the contact zone with the substrate below the nickel-plating.

[0025] The new method offers several advantages:

[0026] 1. Heat can be introduced by means of classic surface layer heat treatment methods—such as flame hardening, induction hardening, conductive heating using heating strips, laser beam hardening and electron beam hardening.

[0027] 2. The new method even allows a first coating to be produced on site in industrial plants, and allows recoating to be performed as part of maintenance operations.

[0028] 3. The lower reaction temperature between the aluminum of the slurry and the nickel, combined with the use of surface layer heat treatment methods with correspondingly rapid heating to between 400 °C and 700 °C, allows processes to be performed in the open air.

[0029] 4. The exothermic, rapid reaction between aluminum and the substrate also allows non-metallic particles, e.g., oxides, to be introduced, finely distributed, into the layers, in contrast to conventional diffusion layers. As a result, e.g., the chemical layer composition can be optimized for the specific case or can be adapted to the coefficient of thermal expansion of the layers of the specific substrate.

[0030] 5. The optimization of the composition of the slurry and the simple option of introducing additional elements enables the suppression of the formation of iron-rich and aluminum-rich intermetallic bonds, which are known to be extremely brittle and in conventional coatings necessitate a high diffusion temperature to prevent cracking.

[0031] 6. The temperatures and times required for the heat treatment are substantially lower than for conventional diffusion methods (<800 °C, seconds/minutes rather than hours).

[0032] 7. For many substrates, additional subsequent thermal treatment can be dispensed with, including treatment to avoid excessive interdiffusion with the substrate.

[0033] The invention enables the application of corrosion proofing to steels or nickel alloys that are exposed to corrosive forces, e.g., in high temperature ranges as a result of oxidation, sulfidization or hot gas corrosion. The invention is particularly suitable for steels which, as iron-based materials, offer a cost advantage over nickel- and cobalt-based materials for many applications in the chemicals industry and in power engineering.

[0034] With the procedure according to the invention, specifically heating only the surface zone of the substrate, only the surface is thermally stressed, while the metallic interior of the substrate remains practically unchanged. The coatings are therefore particularly useful for the more temperature-sensitive ferritic/martensitic steels, but are also generally useful for components made of austenitic steels and nickel- or cobalt-based alloys, since the production costs are substantially lower than those for full heat treatment, and the parts can be cost-effectively aluminized directly in the open air.

[0035] To ensure that the layer produced by heat treatment adheres securely to the substrate, the substrate is heated during the annealing of the surface layer to a temperature that is above the melting point of the aluminum in the slurry.

[0036] The melting point of the aluminum relates to the respective form of the aluminum (pure or alloyed) in the slurry.

[0037] The duration of surface layer annealing may be shortened and the process may be conducted in air if the slurry contains the aluminum as a metal powder with a particle size of 5-100 μm, in which the aluminum may be present in pure form, alloyed, or as a mixture thereof. Due to the optimized particle size, the aluminum will melt in a controlled manner, but will react easily with the substances in the substrate.

[0038] The surface of the substrate is cleaned before the slurry is applied. Cleaning can preferably be performed by sand blasting or shot blasting.
The invention further provides that the surface of the substrate can be precoated galvanically or by means of thermal spraying before the slurry is applied.

The surface annealing is carried out in a vacuum, in an inert gas atmosphere or preferably in the open air.

Because the method can be carried out in the open air, equipment expenses are low. The method is therefore also well suited for producing coatings on exposed pipes in power plants.

To stabilize the coating that is produced, it is further provided that the slurry contains an organic solvent and a binder system that can be thermally decomposed.

The binder system preferably contains a synthetic, water soluble or dispersible polymer that contains no inorganic chromates, phosphates, molybdates or wolframates, which are known to be environmentally harmful.

To stabilize the aluminum powder, the binder system contains amphiphiles, low-molecular phenols, aromatic acids, surface-active alkyl phosphates and/or high-molecular polyelectrolytes.

Furthermore, the particles of the metal powder are optionally coated with a silicon-containing compound, e.g. with alkoxides, such as tetraethoxysilane as a silicon-containing precursor.

To burn off organic fractions, the substrate is heated to 400°C. prior to the surface annealing in which the aluminum phases that form the coating are formed.

The metallic powder preferably contains, in addition to the aluminum, at least one of the following elements in the indicated maximum concentrations: Si (10 wt%), Ce (20 wt%), Cr (25 wt%), Ti (2 wt%), Ta, V or Mo (5 wt% each), B (2 wt%), Fe (10 wt%), Co (20 wt%), and Ni (30 wt%).

To achieve an improved oxide coating adhesion, the slurry contains tin (up to 30 wt%), Si (up to 10 wt%), Pt (up to 10 wt%), Mg (up to 20 wt%), Ca (up to 20 wt%), one or more elements from the group comprising lanthanum, cerium, zirconium, hafnium and yttrium) (<1 wt%), or oxides thereof.

A percentage of tin, in particular, allows the invention to be used in metal-dusting environments. The additives Si, Pt, Mg and Ca and oxides thereof particularly protect against hot gas corrosion.

The elements from the group comprising lanthanum, cerium, zirconium, hafnium and yttrium) and oxides thereof increase the adhesion of oxide layers that form on components during the operation thereof.

The substrate is preferably a steel or a nickel-based alloy or the nickel-plated surface of a component.

FIG. 4a a transverse section of the outer coating of a pipe made of authentic steel and
FIG. 4b a transverse section of the inner coating of a pipe made of authentic steel following implementation of the method according to the invention by means of induction, according to FIG. 1.

EXPLANATION OF THE DRAWINGS

In the heat treatment process, differentiation is made between surface layer hardening and thermochemical diffusion treatment. In surface layer hardening, the chemical composition of the surface layer is not altered. Methods for surface layer hardening include: induction hardening, flame hardening, hardening by conductively heating the surface layer and hardening by means of high-energy heating.

The invention provides for the use of such a method, however it does not provide for the hardening of the surface layer, and therefore, the method as used in conjunction with the present invention is also referred to as surface layer annealing.

FIG. 1 shows a schematic representation of a device for induction hardening. A substrate 1, in this case a pipe, is provided on its outer surface with a slurry 2 of aluminum particles. The pipe is passed through a cooling system 3, in which electrical currents are induced in the surface of the pipe, heating the surface, and converting slurry 2, by the reaction that is thereby induced, to form an aluminate layer 4.

FIG. 2 shows a schematic representation of a device for flame hardening. A substrate 1, in this case a plate, is provided on its surface with a slurry 2 of aluminum particles. One or more burner flames 5 are directed over the surface of the plate, heating the plate, and converting slurry 2 to an aluminate layer 4.

To apply an aluminum-rich coating to iron-, nickel- or cobalt-based alloys on the surface of a component, first the surface of the component to be coated is cleaned and all dirt and grease removed. The surface may also be blasted e.g. with glass beads or sand prior to coating.

A slurry is applied to the cleaned surface. For this purpose, a metal powder is mixed with binder and a solvent, preferably water. The binder is preferably an organic polymer; however, silicone-containing binders or additives are also conceivable. The metal powder in the slurry is composed substantially of aluminum or an aluminum alloy. Additional alloy elements in elemental or oxide form may also be admixed or alloyed to the aluminum powder.

The surface can then optionally be provided with a nickel layer by galvanic means.

The slurry is applied to the substrate or to the nickel layer and is then dried.

The organic constituents of the slurry are then burned off, within a temperature range of 150°C. to 400°C.

Once this is completed, the substrate together with the slurry is subjected to annealing of the surface layer in the open air, during which the reaction between iron/nickel/cobalt and aluminum to form aluminitides takes place.

With rapid heating to temperatures of between 550°C. and 700°C., when the melting point of the aluminum alloy in the metal powder in the slurry on the surface of the substrate is exceeded, a reaction with the base material occurs, and therefore a chemical bonding of the layer to the substrate. Aluminitide formation occurs after several seconds; the coating zone and the interdiffusion zone are substantially thinner than with conventional coatings (approximately 20-80 μm).
Since the iron- and/or nickel- or cobalt-rich surface regions of the substrate to be coated react with aluminum from a slurry coating to form aluminides, nearly crack-free coatings can be produced at substantially lower workpiece core temperatures than was previously possible. In addition, the new coating is more environmentally friendly than conventional coatings, since environmentally harmful halides are not required for the production process, as is the case with the pack cementation method, for example, and the new coating does not contain chromates and phosphates, as are required for most conventional slurry coatings, e.g. those described by Meedu et al. in U.S. Pat. No. 6,126,758 and/or U.S. Pat. No. 5,547,770. In fact, these constituents are expressly avoided in the implementation of the new method.

The added use of galvanic nickel plating or additional elements in the slurry allows the formation of highly iron-rich, brittle aluminide phases to be minimized. During experimentation to test the concept of this invention, a number of advantages in terms of process control over conventional slurry coatings were discovered which not only enable simpler and less costly production, but also result in improved properties of the coatings. These advantages will be described in the following.

It is also important that the coatings have a homogeneous composition, and layer formation and bonding to the substrate are achieved by exothermic aluminide formation, which takes place within the temperature range of the melting point of the aluminum alloy. As a result, a layer can be produced by heat treatment at between 550° C. and 700° C. The minimum temperature that is required for a thin layer is just below and/or just above the melting point of the aluminum powder in the slurry, i.e. the aluminum alloy used.

It is a significant advantage of the innovation that only a brief temperature treatment of the surface layer, lasting only several minutes, is sufficient to produce a coating, in contrast to conventional methods, which frequently require long process times in heat treatment furnaces. Nevertheless, in the layers produced by means of the new method, sufficient excess aluminum is present to enable a limited reaction with the substrate, and thereby ensure a secure bonding of the layer. Of crucial importance in this method is the rapid heating to between 400° C. and 700° C., as a result of which a relatively short and localized heat treatment, limited to the surface region, is sufficient.

For the slurry, the metal powder fraction is mixed with binder and solvent, preferably water. The binder is preferably an organic polymer; however, silicone-containing binders or additives are also conceivable. The powder in the slurry comprises substantially aluminum or an aluminum alloy. Additional alloy elements in elemental or oxidic form may also be admixed or alloyed to the aluminum powder or may also be deposited during the galvanic coating step.

For many substrates, additional subsequent thermal treatment can be dispensed with, including treatment to avoid excessive interdiffusion with the substrate.

**EMBODIMENT EXAMPLES OF THE INVENTION**

Samples of the austenitic AISI 347 and the ferritic P 91 alloy were shot blasted, and the surface of the samples was cleaned with ethanol. The water-based slurry, which contains polyvinyl alcohol as a binder, was then applied by “air brush spraying”. The slurry contained spherical Al particles ranging in size from 2-20 μm. The volume applied was approximately 12 mg/cm².

The coated samples were first held at 300° C. for four hours, in order to burn off the binder.

Following the burning off step, the reaction step for coating was performed in laboratory air.

**First Example**

Coating on Austenitic Iron-Based Alloy by Means of a Gas Burner

FIG. 3 shows the transverse section of an AISI 347 sample following a flame treatment, as represented in FIG. 2. Clearly visible is substrate 1, on top of which is the formed aluminide diffusion layer 4 and on top of that, a residual layer 6 of unused slurry. In this case, a brief flame application period of only five minutes was used to convert the dried slurry, from which binder had been removed, to an aluminide diffusion layer 4 in a region bordering the substrate, using a butane flame as the heat source. The layer thickness of aluminide diffusion layer 4 was approximately 25-30 μm after only 5 minutes.

**Second Example**

Coating on Ferritic Iron-Based Alloy by Means of an Induction Method

For the heat treatment in this case, the surface of the component (substrate 1) made of a ferritic P 91 alloy was heated for only two minutes using an induction heat source according to FIG. 1. Because in this case the wall thickness of the component was small (2 mm), the back side of the component was also heated to the point at which a slurry applied thereto also reacted. In this manner, with thin-walled components, inner surfaces can also be coated by means of heating according to the invention. The layer thickness of aluminide diffusion layer 4 on the P 91 substrate in this case is approximatively 60 μm on the exterior side (see FIG. 4a) and approximately 40-50 μm on the side that faces away from the induction coil (see FIG. 4b). In this case as well, a residual layer 6 of unused slurry remained in each case.

**LIST OF REFERENCE SIGNS**

- 1 substrate
- 2 slurry
- 3 coil system
- 4 aluminide layer
- 5 burner flames
- 6 residual layer

1. A method for coating a substrate that contains cobalt, nickel and/or iron with a corrosion-resistant layer, wherein a slurry containing aluminum is applied to the substrate, and the substrate together with the slurry is then subjected to a brief annealing of the surface layer at a reduced temperature.

2. The method according to claim 1, wherein during the annealing of the surface layer, the substrate is heated to a temperature that is above the melting point of the aluminum in the slurry.
3. The method according to claim 1, wherein the slurry contains the aluminum as a metal powder having a particle size of 5-100 μm.

4. The method according to claim 1, wherein the surface of the substrate is cleaned before the slurry is applied.

5. The method according to claim 1, wherein the surface of the substrate is precoated galvanically or by thermal spray before the slurry is applied.

6. The method according to claim 1, wherein the surface annealing is carried out in a vacuum, in an inert gas atmosphere or in the open air.

7. The method according to claim 1, wherein the slurry contains an organic solvent and a binder system which can be thermally decomposed.

8. The method according to claim 7, wherein the binder system is a synthetic, water-soluble or dispersible polymer that contains no inorganic chromates, phosphates, molybdates or wolframates.

9. The method according to claim 7, wherein the binder system contains amphiphiles, low-molecular phenols, aromatic acids, surface-active alkyl phosphates and/or high-molecular polyelectrolytes.

10. The method according to claim 1, wherein the particles of a metal powder in the slurry are coated with a silicon-containing compound.

11. The method according to claim 1, wherein prior to the surface annealing, in which the aluminide phases that form the coating are formed, the substrate is heated to 400° C.

12. The method according to claim 1, wherein the metallic powder contains at least one of the following elements in the indicated maximum concentrations: Si (10 wt %), Ge (20 wt %), Cr (25 wt %), Ti (2 wt %), Ta, V or Mo (5 wt % each), B (2 wt %), Fe (10 wt %), Co (20 wt %) and Ni (30 wt %).

13. The method according to claim 1, wherein the substrate or the slurry contains tin (up to 30 wt %), Si (up to 10 wt %), Pt (up to 10 wt %), Mg (up to 20 wt %), Ca (up to 20 wt %) and additionally one or more elements from the group comprising: lanthanum, cerium, zirconium, hafnium and yttrium or oxides thereof (<1 wt %).

14. The method according to claim 1, wherein the substrate is a steel or a nickel-based alloy, or in that the substrate is a nickel-plated surface of a component.

15. The method according to claim 2, wherein the slurry contains the aluminum as a metal powder having a particle size of 5-100 μm.

16. The method according to claim 8, wherein the binder system contains amphiphiles, low-molecular phenols, aromatic acids, surface-active alkyl phosphates and/or high-molecular polyelectrolytes.

17. The method according to claim 10, wherein the silicon-containing compound is an alkoxide.

18. The method according to claim 17, wherein the alkoxide is tetraethoxysilane as a silicon-containing precursor.