METHOD FOR DEPOSITING AN ANTICORROSIVE COATING

Applicants: Werner Krommer, Landshut (DE); Andreas Trautmann, Munich (DE)

Inventors: Werner Krommer, Landshut (DE); Andreas Trautmann, Munich (DE)

Appl. No.: 14/272,602

Filed: May 8, 2014

Foreign Application Priority Data
May 16, 2013 (DE) .................. 102013008517.9
Jun. 25, 2013 (EP) ..................... 13003229.5
Jul. 30, 2013 (DE) .................. 102013012662.2

Publication Classification

Int. Cl.
C23C 4/08 (2006.01)
C23C 4/12 (2006.01)

U.S. Cl.
C23C 4/08 (2013.01); C23C 4/125 (2013.01)
USPC ........................................ 427/456

ABSTRACT

A method for depositing an anticorrosive coating on components, wherein an aluminum-zinc coating is used as an anticorrosive coating, and wherein the anticorrosive coating is deposited by thermal spraying, wherein an inert carrier gas with a reducing gas component is used for the thermal spraying.
METHOD FOR DEPOSITING AN ANTICORROSIVE COATING

CROSS REFERENCE TO RELATED APPLICATIONS


BACKGROUND OF THE INVENTION

[0002] The invention relates to a method for depositing an anticorrosive coating on components, wherein the anticorrosive coating is constituted at least in part as an aluminium-zinc coating; a use of a gas mixture containing a reducing gas for depositing an anticorrosive coating on components, as well as a use of an aluminium-zinc coating as a component part of an anticorrosive coating for components.

[0003] In a method for thermal spraying, spray particles are directed onto a workplace with the aid of a carrier gas. The spray particles form a coating on the workplace. The spray particles adhere on the workplace surface and to one another on account of the kinetic energy and the heat, which they exhibit when they strike the workplace. Active corrosion protection by means of an anticorrosive coating of aluminium and/or zinc is the largest area of application of thermal spraying. Approximately 20,000 tonnes of wire from these materials are processed each year, with an increasing trend. The spraying application of both materials, also in combination, is in part standard in the commercial, offshore sector, for example. In the area of offshore wind energy plants, there is the particular requirement to keep maintenance intervals as long as possible, which can be achieved, amongst other things, by the use of durable surface coatings. Spray metallisation has hitherto been used on offshore wind energy plants essentially on components subject to high mechanical load, e.g., flanges, frames, rivet holes, bolt holes and support surfaces, etc.

[0004] The use of a gas mixture for thermal spraying is known from EF 1 674 590 A1. The spray material, is fused in an arc in the course of arc spraying and atomised in a carrier gas to form spray particles. A gas mixture containing hydrogen is used as a carrier gas. For example, the gas mixture contains 1 to 30% by volume of hydrogen.

[0005] For this invention, hydrogen is used as a pure carrier gas in order to bind atmospheric oxygen.

[0006] EP 2 186 593 A1 discloses a gas mixture, comprising a mixture of argon, helium nitrogen, carbon dioxide or hydrogen or mixtures thereof with a hydrocarbon gaseous under normal conditions. The gas mixture is used, amongst other things, for thermal, spraying and/or surface treatment by means of an arc. In this invention, the mixtures are used in each case as a pure carrier gas.

[0007] A problem of thermal spraying, however, is the influence of oxygen on the spray material. On account of the high temperatures, the spray material becomes highly oxidised in the presence of oxygen. Oxygen can get to the spray material either through the carrier gas, for which compressed air is often used, or through the ambient air being swirled round with the carrier gas. Depending on the available energy, the fused and atomised spray particles combust completely or the metal particles oxidise to form, metal oxides. The completely combusted spray particles are no longer available for the coating, when one speaks of erosion. The erosion consequently reduces the efficiency of the deposition of the spray material onto the workplace. Efficiency is defined as the ratio between the spray material forming the coating and the spray material fused as a whole. The metal oxides, on the other hand, arrive together with the metallic spray particles at the workplace and there become a component of the coating.

[0008] In the case of anticorrosive coatings, however, these metal oxides lead to an impairment of the resistance of the coating in the presence of corrosive ambient conditions. In order to prevent this impairment of the quality of the anticorrosive coating, nitrogen can be used as a carrier gas. Nitrogen reduces the oxidation of the spray particles. However, the oxidation is suppressed only to an insufficient extent by the use of nitrogen and the coatings then often do not meet the requirements made in respect of quality.

[0009] The problem underlying the invention is to deposit, an anticorrosive coating on workpieces or components, wherein as high a degree of efficiency as possible is to be enabled for the deposition of the anticorrosive coating and oxidation of the anticorrosive coating due to the process of depositing the anticorrosive coating is to be prevented.

SUMMARY OF THE INVENTION

[0010] This problem is solved by a method for depositing an anticorrosive coating on components, a use of a gas mixture containing a reducing gas for depositing an anticorrosive coating on components, as well as a use of an aluminium-zinc coating as a component part of an anticorrosive coating for components. Advantageous embodiments emerge from the sub-claim and the following description.

[0011] In one embodiment of the invention, there is disclosed a method for depositing an anticorrosive coating on components, wherein an aluminium-zinc coating is used at least as a component part of an anticorrosive coating, characterised in that the aluminium-zinc coating is deposited by thermal spraying, wherein an inert gas with, a reducing gas component is used for the thermal spraying.

[0012] An aluminium-zinc coating is used at least as a component part, of an anticorrosive coating for a method according to the invention. This component part of the anticorrosive coating is deposited on the components by means of thermal spraying, wherein an inert carrier gas with a reducing gas component is used for the thermal spraying. This coating is also referred to in the following as a “spray-metallised coating”.

[0013] The term “components” is understood to mean both individual components as component parts of larger installations or machines, as well as workplaces which are not yet installed in installations or machines and are coated according to the invention in the course of their production process.

[0014] The corrosion protection effect of various anticorrosive coatings that were deposited on components using different methods was investigated within the scope of the invention. Aluminium-zinc coatings and aluminium coatings were in each case deposited on components in different layer thicknesses and forms using different methods and were sealed on a case-by-case basis and provided with a multilayer organic coating system. The main aim was to produce a more oxide-free anticorrosive coating that is superior in its effect to the layers oxidised by the process.

[0015] In the course of the invention, considerable advantages of an aluminium-zinc coating as a component, part of an
anticorrosive coating that is deposited by thermal spraying were discovered, wherein an inert carrier gas with, a reducing gas component is used for the thermal spraying.

[0016] When a corrosive attack occurs, the aluminium-zinc coating goes into solution and thus protects the underlying material of the component, for example iron. The electrochemical potential of an aluminium-zinc coating thermally sprayed with the reducing gas component is higher than that of an aluminium-zinc coating that has been thermally sprayed without, a reducing gas component, for example under conventional air. The corrosion protection effect of the aluminium-zinc coating thermally sprayed with the reducing gas component is based on a combination of the cathodic protection of the aluminium-rich phases, a selective corrosion of the zinc combined with formation of voluminous corrosion products (aluminium hydroxides and zinc hydroxides). The latter become deposited in the pores, which raises the density of the overcoat. When a corrosive attack occurs, the aluminium atoms present in the outermost molecular layer are oxidised first on account of their affinity with oxygen which is double that of zinc. A zinc oxide formation does not yet occur at this point. Aluminium oxides are formed which are surrounded by zinc atoms. Once this has taken place with all the aluminium atoms present in the first molecular layer, zinc oxide is also formed, which is readily soluble and is “flushed out” of the surface. An adherent, dense and very stable aluminium oxide layer remains, which protects the underlying aluminium-zinc coating. Moreover, a cathodic remote effect can be achieved via gaps in the damaged aluminium-zinc coating.

[0017] A basic pre-requisite for the emergence of these properties, which are decisive for the anticorrosive effect, is that the deposited aluminium-zinc coating is not already completely oxidised, by the process of the deposition and that the oxide is able to form at the surface in order to achieve its full effect. In the case of methods for the deposition of the aluminium-zinc coating without a reducing gas component, for example with air, each particle is already oxidised before it strikes the component. Very pure aluminium-zinc coatings with little oxide content are formed with aluminium-zinc coatings thermally sprayed, with the reducing gas component.

[0018] The parameters of the thermal spraying primarily determine the properties of the aluminium-zinc coating. The selection of the nozzle system as well as parameters such as for example voltage, current or the type of carrier gas influence the spray particles when they are detached at electrodes and in their flight phase and therefore the aluminium-zinc coating formed therefrom. Finely atomised melt droplets at the same time signify a large specific surface and therefore the promotion of the oxide content in the aluminium-zinc coating. This oxidation can be reduced considerably by the use of inert carrier gases with a reducing gas component.

[0019] A second coating, in particular one or more coloured layers, is advantageously deposited over the aluminium-zinc coating. A corrosion protection system comprising at least two layers is thus produced. The aluminium-zinc coating according to the invention forms the first layer, a so-called primer. The second coating forms the second layer. The resistance capacity of the corrosion protection can be further increased by the combined action of the first anticorrosive coating and the second coating. The adhesiveness of the second coating is improved considerably by the presence of the anticorrosive coating according to the invention, on the one hand compared to a “second” coating without an underlying anticorrosive coating and on the other hand compared to an anticorrosive coating that has not been thermally sprayed with the reducing gas component.

[0020] The first layer “heals” damage, for example cracks, by flow. The second layer limits this flow of the first layer in order that this “healing” can take place and, the loss of material from the first layer due to flow is limited.

[0021] In the present invention, therefore, an anticorrosive coating containing a spray-metallised layer is deposited on workpieces or components, which in particular is carried out in process technical terms in such a way that further coloured layers are/have been deposited on this spray-metallised anticorrosive coating in downstream or upstream process steps, so that, as a result of the combined action of the spray-metallised layer and the further coloured layers, a high-quality corrosion protection results for the workpieces or components coated in this way, said corrosion protection also withstanding the most challenging corrosive media and environmental conditions. The highest possible degree of efficiency for the deposition is enabled by the invention for the deposition of the spray-metallised layer and oxidation of the anticorrosive coating due to the process of depositing the anticorrosive coating is prevented according to the invention.

[0022] Hydrogen is preferably used as a reducing gas component. Nitrogen is also advantageously used as a carrier gas. A hydrogen-nitrogen mixture is particularly preferably used. The proportion of the reducing gas component, in the gas mixture preferably amounts to between 0.1% and 10%, in particular between 2% and 4%.

[0023] A use of the gas mixture containing hydrogen disclosed in EP 1 674 590 A1 from the same applicant is also conceivable. In this regard, reference should be made expressly to this specification with regard to the corresponding disclosure. In particular, such a gas mixture, which contains 3% to 7% by volume of hydrogen, is suitable for a method according to the invention. In this invention, however, hydrogen only was used as a carrier gas in order to bind atmospheric oxygen (e.g. from the ambient air).

[0024] A gas mixture according to EP 2 186 593 A1, also from the same applicant, is also conceivable. In this regard, reference should be made expressly to this specification with regard to the corresponding disclosure. Such a gas mixture comprises a mixture of argon, helium, nitrogen, carbon dioxide or hydrogen or mixtures thereof, with a hydrocarbon gaseous under normal conditions. In particular, this gas mixture contains metered quantities of NO and/or NO₂. In this invention, the mixtures are used in each case as a pure carrier gas.

[0025] Arc spraying is preferably used for the thermal spraying, in the case of arc spraying, two wires are fused in an arc and atomised with the aid of a carrier gas to form spray particles and then conveyed to the component. The electric arc burns between the two wires, which are constituted as anode and cathode. Only electrically conductive materials therefore come into question as wires. The two wires can be made from the same or from different materials. Instead of wires, use can also be made of two small metallic tubes. The arc is usually generated between the two wires ends by the application of a voltage with a contact ignition, said wires ends being fed towards one another in the spray gun. Filler wires can also be processed, as a result of which it is also possible to deposit hard material-containing layers for protection against wear, said layers containing for example oxides, nitrides, carbides or borides. Up to 20 kg per hour for
example can be processed for an aluminium-zinc coating. Arc spraying has ideal pre-requisites for the deposition of a metallic anticorrosive coating. Easy handling, use of favourable materials (through the use of wire), high deposition rate with high efficiency, as well as the covering of large areas in a short time.

The adhesiveness of the spray-metallised aluminium-zinc coating preferably amounts, on average, to between 50 μm and 150 μm, in particular between 75 μm and 120 μm, more especially 100 μm.

The anticorrosive coating is preferably deposited on components that are exposed to a sea water atmosphere (C5-M) or a maritime atmosphere (lm2), e.g. or drilling rigs or on coastal installations, and/or on components that are exposed to other corrosive chemical atmospheres (C5-I), e.g. in chemical plants. The anticorrosive coating is also suitable for components that are exposed to an extreme climate, in particular a tropical climate, e.g. metallisations of propane bottles for a tropical climate.

In a particularly preferred embodiment of the invention, the anticorrosive coating is deposited on components of a wind energy plant, in particular an offshore wind energy plant. The anticorrosive coating is particularly suitable for being deposited on wind towers of wind energy plants or offshore wind energy plants. The anticorrosive coating can be deposited according to the invention particularly easily on components subject to high mechanical load, such as flanges, frames and support surfaces. Maintenance intervals can be kept as long as possible due to the adhesiveness and the durability of the anticorrosive coating deposited according to the invention.

Furthermore, the invention relates to a use of a gas mixture containing a reducing gas component for depositing an anticorrosive coating on components, as well as a use of an aluminium-zinc coating as an anticorrosive coating for components. Embedments of these uses according to the invention emerge in an analogous manner from the above description of the method according to the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be explained farther with the aid of the appended drawings. In the figures:

FIG. 1 shows a component without an anticorrosive coating.

FIG. 2 shows a component with an aluminium-zinc coating, which has been deposited with air as a carrier gas.

FIG. 3 shows a component with an aluminium-zinc coating with a gas mixture containing an active gas component as a carrier gas, said aluminium-zinc coating having been deposited by means of an embodiment of a method according to the invention and

FIG. 4 shows a magnified detail of the component from FIG. 3 to illustrate the effect, of the aluminium-zinc coating deposited by means of an embodiment of a method according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

FIGS. 1 to 4 show the results of the laboratory tests and test series forming the basis of the invention.

The corrosion protection effect of various duplex systems suitable for application on offshore wind energy plants was investigated in the laboratory tests. Particular attention was paid to the embodiment of the metallisations.

In the case of the pore-rich arc-sprayed anticorrosive coatings, a sealant serves to seal the anticorrosive coating in order to prevent the penetration of moisture.

The various anticorrosive coatings were prepared for the laboratory tests according to ISO 20340 with artificial damage (scratch) with an extension of 30 mm long and 2 mm wide (horizontal), in order to simulate damage to the corrosion protection system, and were subjected to a 25 week cyclical ageing test. The evaluation criteria for the quality of the various anticorrosive coatings were the degree of corrosion from the scratch, as well as the degree of blistering, the degree of rust, the degree of cracking, the degree of delamination and the degree of infiltration from the scratch.

Compared to anticorrosive coatings that had not been deposited by thermal spraying, in particular with a reducing gas component, a much better corrosion behaviour can be shown. Considerable differences in the various anticorrosive coatings were also able to be established with regard to corrosion and the influence on the bond with a coloured layer.

The arc-sprayed aluminium-zinc coating with a layer thickness of 75 μm displayed the best results in the tests. Red rust was formed here only in the vicinity of the scratch. An arc-sprayed aluminium-zinc coating with a layer thickness of 50 μm, on the other hand, starts with the formation of red rust after approx. 16 weeks.

FIG. 1 shows a component without an anticorrosive coating that has also undergone the laboratory tests described above. As can(0,9),(998,989)
adhesiveness of 4.8 MPa. The aluminium-zinc coating deposited by means of the hydrogen-nitrogen gas mixture achieves the best values. The adhesiveness of said aluminium-zinc coating lies on average at 7.6 MPa. The reason for these higher values is to be found in the better anchoring of the organic coating.

Having thus described the invention, what we claim is:
1. A method for depositing an anticorrosive coating on components, wherein an aluminium-zinc coating is used at least as a component part of an anticorrosive coating, characterised in that the aluminium-zinc coating is deposited by thermal spraying, wherein an inert gas with a reducing gas component is used for the thermal spraying.
2. The method according to claim 1, wherein a further coating is deposited on or under the aluminium-zinc layer.
3. The method according to claim 2, wherein the further coating comprises one or more coloured layers.
4. The method according to claim 1, wherein hydrogen is used as the reducing gas component.
5. The method according to claim 1, wherein nitrogen is used as the inert gas.
6. The method according to claim 1, wherein a hydrogen-nitrogen mixture is used for the thermal spraying.
7. The method according to claim 1, wherein arc spraying is used for the thermal spraying.
8. The method according to claim 1, wherein the aluminium-zinc coating layer alone or as a component part of an anticorrosive coating is deposited on areas subject to high mechanical load to reduce wear and corrosion.
9. The method according to claim 1, wherein a proportion of the reducing gas component in the inert gas amounts to between 0.1% and 10%.
10. The method according to claim 1, wherein a proportion of the reducing gas component in the inert gas amounts to between 2% and 4%.
11. The method according to claim 1, wherein a thickness of the aluminium-zinc coating amounts to between 50 μm and 150 μm.
12. The method according to claim 1, wherein a thickness of the aluminium-zinc coating amounts to between 75 μm and 120 μm.
13. The method according to claim 1, wherein a thickness of the aluminium-zinc coating amounts to 100 μm.
14. The method according to claim 1, wherein the adhesiveness of the spray-metallised aluminium-zinc layer amounts on average to between 7.0 and 8.0 MPa.
15. The method according to claim 2, wherein the adhesiveness of the further layers to the spray-metallised aluminium-zinc layer itself or of the anticorrosive coating to the coated, material amounts on average to between 7.0 and 8.0 MPa.
16. The method according to claim 1, wherein the anticorrosive coating is deposited on components that are exposed to a corrosive atmosphere.
17. The method according to claim 1, wherein the corrosive atmosphere is selected from the group consisting of a sea water atmosphere, a marine atmosphere and a chemical atmosphere.
18. The method according to claim 1, wherein the anticorrosive coating is deposited on components of a wind energy plant.
19. The method according to claim 1, wherein the wind energy plant is an offshore wind energy plant.
20. The method according to claim 1, wherein the wind energy plant is an offshore wind energy plant.