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(54) **PROCESS FOR PRODUCING AN ACTIVE CATHODIC ANTI-CORROSION COATING ON STEEL ELEMENTS**

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(57) **ABSTRACT**

The invention relates to a process for producing an active anti-corrosion coating on steel components.

In order to develop an active anti-corrosion coating that can be applied on an industrial scale using conventional means (e.g. dipping, spraying or flooding) and is intended for hot-formed and, in particular, press-hardened steel parts provided with antiscaling means, the invention proposes a process comprising the following process steps:

- a. Using a steel element provided with an antiscaling layer;
- b. Annealing the steel element at a temperature above 600° C. in an annealing furnace for the purpose of hardening, semi-hot or hot forming or press hardening and thus producing a reaction layer;
- c. Applying an anti-corrosion coating to the annealed reaction layer.

**PROCESS FOR PRODUCING AN ACTIVE
CATHODIC ANTI-CORROSION COATING ON
STEEL ELEMENTS**

[0001] The invention relates to a process for producing an active anti-corrosion coating on steel components.

[0002] Hot-forming processes are being used increasingly to manufacture high-strength steel components of the sort required, for example, as structural body components for vehicle construction. One particular type of hot forming is the process referred to as press hardening, during which specialty steels (usually manganese-boron steels) are heated to austenizing temperature, hot-formed and quench-hardened in the forming tool. A martensitic microstructure of high mechanical strength is obtained, which makes it possible to manufacture components that are thin and therefore light in weight, yet high in strength. Austenizing takes place at temperatures above 850° C. At this temperature, pronounced scale formation occurs at the steel surface. The scale forms so quickly that even parts which are heated in an atmosphere of protective gas, e.g. in a continuous furnace, will undergo scale formation when they come into contact with atmospheric oxygen on being transferred from the furnace to the forming tool. In the case of production lines configured for the forming of piece numbers in vehicle manufacturing, it is not justifiable either from economical or constructional aspects to operate the entire section of the line—from heating to forming—under protective gas.

[0003] As it forms, the scale is apt to flake off, and is rough and brittle. It therefore damages components as well as forming tools, and has to be removed at high cost from the component following press hardening, for example by blasting. The regular cleaning of the forming tools which is necessary substantially increases cycle times, and the material removed by blasting has to be compensated for by using thicker metal sheet. For press hardening, therefore, it is usual to use steel sheet which has been provided with a coating that protects against scaling.

[0004] The EP 1 013 785 A1 describes the use of hot-dip aluminized steel types. These are coated with an approximately 20-30 µm thick layer of an Al—Si alloy, which is applied by hot-dip coating. This Al—Si coating does indeed offer a certain degree of corrosion protection for hot-dip aluminized sheet steel while it is in storage, which means that sheets and coils need not be oiled for storage and transport purposes; however, after the annealing process employed during hot-forming, the anti-corrosive effect of the coating is very much reduced. This becomes evident when, for example, hot-dip aluminized steel sheet that has been annealed at 950° C. is examined using the salt spray test according to German standard DIN 50021. After just a few days, red-rust formation is apparent over the entire surface. After the entire vehicle body has been assembled and phosphated, the affected parts can be subjected to cathaphoretic dip-coating. This provides them with adequate corrosion protection for use in certain applications. However, if the cathaphoretic dip coating is damaged, no adequate active corrosion protection is ensured anymore. Under normal conditions of direct press-hardening, the electrical resistance of hot-dip aluminized sheet is in the region of <1 mOhm following the hardening process.

[0005] Another form of protection against scaling, which is described in the WO 2006/040030 A1, is based on the wet-chemical coating of steel sheet or coil with a coating compo-

sition consisting of an organosilicon binder, aluminium particles and solid lubricants. This can be hot- or cold-formed and protects against scaling during hot-forming. After the hot-forming (press-hardening) process, the inorganic reaction layer is removed by blasting. The time and energy needed to do so is markedly less than that required to remove scale. Removal of this layer by blasting is necessary because it does not have the required electrical conductivity for the subsequent resistance spot welding. After the bare metal sheets have been welded, these too are phosphated and subjected to cathaphoretic dip-coating.

[0006] A refined form of the wet-chemical antiscaling coating described, which is the subject of the WO 2007/076766 A2, does possess the required electrical conductivity for resistance spot welding and cathaphoretic dip-coating and can thus remain on the component after it has been press-hardened. Under normal conditions of press-hardening, the electrical resistance of these sheets is in the region of <5 mOhm following the hardening process. If the component is subsequently to be subjected to a welding process, in particular a resistance spot welding process, or to cathaphoretic hot-dip coating, the observance of process parameters that will lead to the formation of electrically conductive reaction layers when the steel sheet with its antiscaling coating is annealed is particularly important. The use of a protective-gas atmosphere (e.g. nitrogen or argon) or of a furnace atmosphere with a reduced oxygen content (~10%) has proved advantageous. Short heating times likewise lead to high electrical conductivity and hence to low electrical resistance in the <3 mOhm range, thus promoting weldability. After welding, phosphating and cathaphoretic dip-coating, the parts in question show adequate corrosion protection for use in certain areas. However, in this case too, there is no active corrosion protection that will protect the steel in the event of damage to the cathaphoretic dip-coating.

[0007] A general advantage of the wet-chemical antiscaling coatings described over hot-dip aluminizing is that on heating to austenizing temperature, no diffusion layer needs to be formed and therefore cycle times are shorter. Besides, on heating, there is no danger in this case of any melting, meaning that inductive or conductive heating methods may be used during press-hardening.

[0008] The applications WO 2005/021820 A1, WO 2005/021821 A1 and WO 2005/021822 A1 describe methods of manufacturing various hardened steel parts. In each case, a protective coating consisting of zinc combined with another element having an affinity for oxygen (especially aluminium) is applied to the steel. In the WO 2005/021821 A1, this protective coating is applied by means of a hot-dip process, in the WO 2005/021820 A1 and WO 2005/021822 A1 by means of a hot-dip or an electroplating process. However, these coatings, which contain zinc as the main element, are extremely susceptible to oxidation and vaporisation at the austenizing temperatures required for a press-hardening process. Even traces of dirt (e.g. dust) on the surface will burn and lead to rejection of the part. The three applications cited are based on the AT 412878 B ("High-strength corrosion-protected sheet-steel component"), in which the cathodic anti-corrosion effect of the coating is explicitly described. In practice, however, even if suitable components with undamaged surfaces are obtained within a narrow processing window, the cathodic anti-corrosion effect of the zinc is no longer the same after annealing as it was originally, and the diffusion of iron from the base material into the coating causes the components

to corrode and form red rust relatively easily. The same applies to the zinc coating described in EP 1439240A1, which is protected from vaporizing under press-hardening conditions by an additional layer of zinc oxide.

[0009] The object of the invention is to develop an active anti-corrosion coating that can be applied on an industrial scale using conventional means (e.g. dipping, spraying, flooding or rolling) and is intended for hot-formed and, in particular, press-hardened steel parts provided with antiscaling means.

[0010] This object is established according to the invention by a process according to the preamble and comprising the following process steps:

[0011] a. Using a steel element provided with an antiscaling layer;

[0012] b. Annealing the steel element at a temperature above 600° C. in an annealing furnace for the purpose of hardening, semi-hot or hot forming or press hardening and thus producing a reaction layer;

[0013] c. Applying an anti-corrosion coating to the annealed reaction layer.

[0014] In an alternative embodiment this object is established by a process according to the preamble and comprising the following process steps:

[0015] a. Using a steel element provided with an antiscaling layer;

[0016] b. Applying an anti-corrosion coating to the antiscaling layer.

[0017] c. Annealing the steel element at a temperature above 600° C. in an annealing furnace for the purpose of hardening, of semi-hot or hot forming or of press hardening and thus producing a reaction layer.

[0018] The invention is thus based on using a special antiscaling coating on steel in order to prevent scale formation during hot-forming and particularly during press-hardening at temperatures above 600° C.

[0019] Surprisingly, it was found that special coating compositions consisting of a metal oxide and metal pigment, in particular zinc pigment or zinc pigment and aluminium pigment, protect steel effectively against corrosion even when the layer thickness is in the lower µm range and irrespective of whether these coating compositions are applied directly onto the metallic steel surface or onto the reaction layer formed from the antiscaling coating during annealing. Highly resistant edge protection is imparted to the component, and the anti-corrosion coating can also be overpainted, phosphated or dip-coated, especially by the process of cathodic dip-coating, without any problem.

[0020] An embodiment of the invention consists in that annealing is effected at a temperature above 850° C.

[0021] According to the invention, hardenable steels are annealed conductively or inductively in gas-operated or electrically-operated annealing furnaces.

[0022] An advantageous embodiment of the invention consists in that the oxygen content in the annealing-furnace atmosphere is 0-10%.

[0023] It is also within the scope of the invention that the antiscaling layer consists of an aluminium alloy, aluminium pigments, a coating containing an aluminium pigment, a magnesium alloy, magnesium pigments, a coating containing a magnesium pigment, a zinc alloy, zinc pigments or a coating containing a zinc pigment;

[0024] It is also within the scope of the invention that, after the forming process, the antiscaling layer has a maximum electrical resistance of 10 mOhm, preferably a maximum of 5 mOhm.

[0025] It is additionally to advantage that the finished component has a maximum electrical resistance of 10 mOhm, preferably a maximum of 5 mOhm.

[0026] The two preceding measures ensure that resistance spot welding is possible.

[0027] It is furthermore expedient that the anti-corrosion layer is applied to the annealed reaction layer from the liquid phase in a wet-chemical process, in particular in a spraying, flooding, rolling or dipping process.

[0028] According to the invention, the layer thickness of the anti-corrosion layer is less than 50 µm, preferably less than 20 µm and best of all less than 10 µm.

[0029] It is within the scope of the invention that the anti-corrosion layer is diluted with solvents prior to application.

[0030] In an embodiment of the invention the anti-corrosion layer, once applied, is dried at a temperature between room temperature and 400° C., preferably between room temperature and 250° C.

[0031] It is furthermore within the scope of the invention that the anti-corrosion layer contains a binder and metallic pigment.

[0032] In this connection it has proved advantageous that the anti-corrosion layer contains between 10 and 100 wt. %, preferably between 50 and 100 wt. % and best of all between 70 and 95 wt. % metallic zinc pigment and/or magnesium pigment.

[0033] It is also to advantage in this connection that the anti-corrosion layer contains up to 50 wt. % metallic aluminium pigment.

[0034] A preferred embodiment of the invention consists in that the binder used in the anti-corrosion layer contains 5 to 100 wt. % metal oxides, in particular titanium, aluminium or zirconium oxides.

[0035] It is also within the scope of the invention that the binder used in the anti-corrosion layer contains up to 50 wt. % binder produced by the sol-gel process, silicones, siloxanes or waxes.

[0036] It is furthermore within the scope of the invention that the anti-corrosion layer contains solid-state lubricants, in particular graphite or boron nitride.

[0037] The invention consists in that the steel element is in the form of sheet, coil, component or other solid body.

[0038] A special embodiment of the invention consists in that the coated substrate is a steel element that has undergone a hardening process.

[0039] It is also within the scope of the invention that the steel element was shaped in a hydroforming process.

[0040] Another special embodiment consists in that the coated substrate is a steel element that has been provided with an antiscaling layer which is of a kind customary for the hardening process and which remains on the component.

[0041] It is furthermore within the scope of the invention that the steel element consists of an assembly of components made of diverse alloy steels—with or without metallic coatings such as aluminium or zinc coatings or coatings containing metal pigments—and joined together by way of standard joining processes, such as welding, bonding, bolting or riveting.

[0042] A preferred embodiment of the invention consists in that, prior to being annealed, the steel element is provided

wholly or partially with a coating that influences the heating-up behaviour of the steel part or of parts thereof.

[0043] It is possible in this context to provide the steel element with a homogeneous, heat-absorbing coating, for example a black one, in order to reduce the heating-up time, the furnace time and/or the diffusion time, or with an inhomogeneous coating with heat-absorbing and heat-reflecting areas distributed over the surface of the steel element, for example a partial black coating and a partial silver coating so that, by way of this variation in the absorption of infrared rays at the surface, the energy input may be selectively controlled from area to area, allowing, for example, the formation of different hardening zones. This measure may of course be combined with the previously described assembly, where the steel element comprises diverse components joined together.

[0044] An embodiment of the invention consists in that the components or assemblies of components provided with the anti-corrosion layer can be welded with each other, with customarily weldable alloy steels or with steel grades provided with metallic coatings.

[0045] A special embodiment of the invention consists in that the electrical resistance of the steel element used is not influenced significantly by the anti-corrosion layer.

[0046] Finally, the scope of the invention extends to use of the process according to the invention for producing anti-corrosive components or assemblies for machine construction, in particular for vehicle construction, building, in particular steelwork, for process engineering, aerospace, power plants and power-plant engineering, electrical engineering, medical engineering, sports equipment, horticulture and landscape gardening, toolmaking, agricultural machinery, furniture, kitchens, household appliances, toys, sports articles, camping equipment, caravans, window and door frames, heating installations, heat exchangers, air conditioners, escalators, conveyors, oil platforms, jewellery, locomotives, rails, transport systems, cranes, furnaces, engines and engine attachments, pistons, sealing rings, exhaust systems, ABS and braking systems, brake discs, chassis components, wheels, rims, sanitary articles, lamps and design articles.

[0047] The invention is described below by reference to embodiments.

EXAMPLE 1

[0048] Degreased 22MnB5A steel strip moving at 60 m/min is roll-coated in a coil coating line with a coating material according to WO 2007/076766 A2. The coating material is hardened at a PMT (Peak Metal Temperature) of 200-250° C. The coated steel strip is cut into tailored blanks and pre-drawn in a cold-forming process to a preform. The preform is heated in a nitrogen atmosphere having a maximum oxygen content of 10 vol. % to a temperature of 950° C. in an electrically operated continuous furnace for 4 minutes, transferred to the forming tool and hot-formed there, and then quench-hardened by cooling to 200° C. within 20 s.

[0049] A suitable anti-corrosion coating for the press-hardened parts described is produced as follows:

[0050] 23.6 g of an aluminium pigment paste (e.g. Decomet Hochglanz Al 1002/10 from Schlenk) and 138.1 g of a zinc pigment paste (Stapa TE Zinc AT from Eckart) are stirred into 74.4 g of 1-butanol solvent and mixed in homogeneously for 20 minutes using a dissolver running at a speed of 1000 rpm. 163.3 g tetrabutylorthotitanate (from Fluka) are stirred into this solution. Prior to further processing, 5 g of Byk 348 wetting agent (from Byk Chemie) are added.

[0051] The coating solution is applied to the entire surface of the press-hardened part using a paint spray gun (e.g. Sata Jet, 1.2 mm nozzle) such as to produce a layer thickness of 3-10 µm after drying and hardening. The coating solution hardens at room temperature within an hour of application, or within 20 minutes at 180° C.

EXAMPLE 2

[0052] A component provided with an aluminium antiscaling coating (e.g. Usibor) is subjected as in Example 1 to a press-hardening process.

[0053] A suitable anti-corrosion coating for this component is produced as follows:

[0054] 138.1 g of a zinc pigment paste (Stapa TE Zinc AT from Eckart) are stirred into 400 g of 1-butanol solvent and mixed in homogeneously for 20 minutes using a dissolver running at a speed of 1000 rpm. 163.3 g tetrabutylorthotitanate (from Fluka) are stirred into this dispersion.

[0055] A mixture of 40 g methyltriethoxysilane (from Fluka) and 10 g tetraethoxysilane (from Fluka) is hydrolysed by stirring 15 g of 1% orthophosphoric acid into it. After 5 hours of stirring, the reaction mixture is single-phase and is stirred into the aforementioned dispersion to produce a homogeneous solution.

[0056] The coating solution is prepared in a quantity sufficient to fill a suitably controlled dip tank. The component is lowered by means of a crane into the dip tank filled with coating solution, and after its entire surface has been homogeneously wetted, is lifted out again. After any excess coating solution has dripped off, the component is transferred to a furnace where the coating is hardened for 20 minutes at 180° C.

[0057] After the treatment, the composite entity comprising steel, aluminium and anti-corrosion layer has a resistance of <10 mOhm and can be joined readily with other sheets by means of resistance spot welding.

EXAMPLE 3

[0058] Body components are produced by means of press-hardening from steel blanks with an Al—Si dip-coating and from steel blanks coated according to the WO 2007/076766 A2. These are joined with uncoated steel components by means of resistance spot welding to form an assembly.

[0059] A suitable anti-corrosion coating for this assembly is produced as follows:

[0060] 33.0 g of an aluminium oxide powder (e.g. Aeroxide Alu C from Degussa), 41.3 g of a zinc powder (e.g. Standart Zink Flake AT from Eckart) and 4.5 g Aerosil R 972 (from Degussa) are added to 250 g of 1-butanol solvent. Prior to further processing, 20 g of a suitable powdered wax (e.g. Licowax C from Clariant) are added to the mixture and mixed in homogeneously for at least two hours using a dissolver.

[0061] The coating solution is applied to the entire surface of the press-hardened assembly using spray painting equipment (e.g. HVLP pressurized-air nozzles with a diameter of 1.2 mm) such as to produce a layer thickness of 3-10 µm after drying and hardening. The solution is also sprayed particularly into cavities, gaps and joints. Hardening is effected for 20 minutes at a temperature of 180° C.

RESULT

[0062] The components and assemblies from the examples 1-3 are each coated with a 3-10 µm thick silver-grey anti-

corrosion layer that adheres firmly to the substrate. After being exposed in a salt-spray test as per DIN EN ISO 9227 for 1000 h, the coatings showed no red-rust formation, neither on the surface nor at the cruciform injury site. The coated components and assemblies have an electrical resistance of <10 mOhm and can be welded to other steel parts, for example to assemble a vehicle body.

1-22. (canceled)

23. Process for producing an active cathodic anti-corrosion coating on steel elements, comprising the following process steps:

- a. Using a steel element provided with an antiscaling layer, said antiscaling layer consisting of an aluminum alloy, a coating containing an aluminum pigment, a magnesium alloy, a coating containing a magnesium pigment, a zinc alloy or a coating containing a zinc pigment;
- b. Annealing the steel element at a temperature above 600° C. in an annealing furnace for the purpose of hardening, semi-hot or hot forming or press hardening and thus producing a reaction layer;
- c. Applying an anti-corrosion coating containing a binder and a metallic pigment to the annealed reaction layer.

24. Process according to claim 23, wherein annealing is performed at a temperature above 850° C.

25. Process according to claim 23, wherein annealing is performed conductively or inductively in gas-operated or electrically-operated annealing furnaces.

26. Process according to claim 23, wherein the oxygen content in the annealing-furnace atmosphere is 0-10%.

27. Process according to claim 23, wherein the anti-corrosion layer is applied to the annealed reaction layer from the liquid phase in a wet-chemical process, in particular in a spraying, flooding, rolling or dipping process.

28. Process according to claim 27, wherein the layer thickness of the anti-corrosion layer is less than 50 µm, preferably less than 20 µm and best of all less than 10 µm.

29. Process according to claim 27, wherein the anti-corrosion layer is diluted with solvents prior to application.

30. Process according to claim 23, wherein after the anti-corrosion layer has been applied, it is dried at a temperature between room temperature and 400° C., preferably between room temperature and 250° C.

31. Process according to claim 23, wherein the anti-corrosion layer contains between 10 and 100 wt. %, preferably

between 50 and 100 wt. % and best of all between 70 and 95 wt. % metallic zinc pigment and/or magnesium pigment.

32. Process according to claim 23, wherein the anti-corrosion layer contains up to 50 wt. % metallic aluminum pigment.

33. Process according to claim 23, wherein the binder used in the anti-corrosion layer contains 5 to 100 wt. % metal oxides, in particular titanium, aluminum or zirconium oxides.

34. Process according to claim 23, wherein the binder used in the anti-corrosion layer contains up to 50 wt. % binder produced by the sol-gel process, silicones, siloxanes or waxes.

35. Process according to claim 23, wherein the anti-corrosion layer contains solid-state lubricants, in particular graphite or boron nitride.

36. Process according to claim 23, wherein the steel element is in the form of sheet, coil, component or other solid body.

37. Process according to claim 23, wherein the steel element consists of an assembly of components made of diverse alloy steels—with or without metallic coatings such as aluminum or zinc coatings or coatings containing metal pigments—and joined together by way of standard joining processes, such as welding, bonding, bolting or riveting.

38. Process according to claim 23, wherein, prior to being annealed, the steel element is provided wholly or partially with a coating that influences the heating-up behavior of the steel part or of parts thereof.

39. Use of the process according to claim 23 for producing anti-corrosive components or assemblies for machine construction, in particular for vehicle construction, building, in particular steelwork, for process engineering, aerospace, power plants and power-plant engineering, electrical engineering, medical engineering, sports equipment, horticulture and landscape gardening, toolmaking, agricultural machinery, furniture, kitchens, household appliances, toys, sports articles, camping equipment, caravans, window and door frames, heating installations, heat exchangers, air conditioners, escalators, conveyors, oil platforms, jewelry, locomotives, rails, transport systems, cranes, furnaces, engines and engine attachments, pistons, sealing rings, exhaust systems, ABS and braking systems, brake discs, chassis components, wheels, wheel rims, sanitary articles, lamps and design articles.

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