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(54) **Method of galvanising a steel strip in a continuous hot dip galvanising line**

Verfahren zum Verzinken eines Stahlstreifens in einer kontinuierlichen Feuerverzinkungsanlage

Procédé de galvanisation de bande d'acier dans une ligne de galvanisation à chaud en continu

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Description

[0001] The invention relates to the continuous galvanizing of steel strips especially high strength steels with high content of elements like silicon, manganese, aluminium and chromium and, in particular, to the facilities comprising a direct fire or non oxidising furnace and radiant tubes furnace.

[0002] New steel grades with a very high yield point having a high elongation capacity have been developed over the years to meet the demands of higher safety and lower weight in the car industry. Such steels, sometimes referred to as Advanced High Strength Steels (AHSS) comprise families of steel such as "DP" or Dual Phase steels (DP) and or TRAnsformation Induced Plasticity steels (TRIP). Unfortunately these steels raise some problems for steel manufacturers because some of their alloying elements such as manganese, silicon, aluminium, chromium may result in a thin layer of oxides on the steel surface during the annealing operation preceding the dipping in the galvanizing bath. This (selective) oxidation harms the zinc "wettability" and thus the quality of the coating. These phenomena are due to diffusion processes of the highly oxidisable alloy components towards the strip surface where they can oxidize even in the furnaces radiant tubes zones wherein the atmosphere is yet reducing for the iron oxides.

[0003] A solution which has been proposed is to subject the strips surface to temperatures and atmosphere conditions fit for quickly and deeply oxidizing the alloy components in the direct fired (DFF) part of the annealing furnace, thereby avoiding later migration of the oxidisable elements towards the surface followed by reducing the iron oxide back to iron in the radiant tube section (RTF). For this oxidation to take place it is necessary that direct fired furnace zones are used.

[0004] However, the galvanizing furnaces do not comprise all the required DFF zones to easily perform the oxidizing and many are only using radiant tubes. Now these furnaces, despite their controlled atmosphere, do not prevent the selective oxidizing of the alloy components. Patent WO 2005/017214 recommends two possibilities to solve the problem. The first one consists in using a direct flame combustion chamber separated from the RTF annealing furnace and from which the burnt gases are collected in order to inject them in the furnace. This method requires adjusting the air to combustible gas ratio to provide excess oxygen after combustion which is then subsequently used for oxidation of the steel strip surface. The second one consists in setting up a direct flame burner in a section of the furnace enclosure. In both cases, the burnt gasses supply the necessary oxidizing atmosphere. The subsequent reduction of the oxides is then commonly obtained by going passing the strip through a nitrogen and hydrogen mixture. These two possibilities require a modification of the existing facilities.

[0005] FR-A1-2920438 or US-B-3936543 disclose the

control of air or of oxygen to fuel in DFF in galvanizing lines. A radiant tube furnace after DFF is also foreseen.

[0006] The object of this invention is to provide an improved method of avoiding selective oxidation of alloying elements in AHSS in a direct fire or non oxidising furnace and radiant tube fired continuous hot dip galvanising line.

[0007] One or more of these objects are reached by a method according to claim 1.

[0008] The invention consists in projecting an oxidizing medium consisting of a gas mixture of nitrogen and oxygen or a gas mixture of nitrogen and air onto one or both of the surfaces of the uncoated strip exiting the non-oxidising or direct fired furnace section. In the prior art the air to combustible gas ratio had to be adjusted in the DFF-section which leads to a compromise between the conditions in the DFF section and the subsequent oxidation of the strip. This leads to control problems and stability problems, leading in turn to bad oxide homogeneity across the strip width caused by the burner pattern. By using a separate nozzle system dedicated to injecting either 1). a gas mixture of nitrogen and air or 2). a gas mixture of nitrogen and oxygen so that a controlled oxygen content is injected into the furnace to cause the oxidation of the hot steel strip to take place in a controlled manner and to prevent selective oxidizing of the steel alloy components. To that end the nozzles are designed such as to distribute the gas mixture evenly thereby causing the hot steel strip surface to oxidise evenly and reproducibly.

[0009] The gas mixture must have a oxygen content such that the steel surface can be oxidised in a controlled way and a controlled oxide thickness. This allows alloy components like silicon, manganese, aluminium and chromium to be oxidized and to not have the possibility to migrate towards the surface anymore during further annealing. To reach this goal, the inventors found that the mixture had to be 1). a mixture of nitrogen and air or 2). a mixture of nitrogen and oxygen. In the first case there is additional nitrogen from the air as well as smaller amounts of other gases present in air. These smaller amounts do not affect the oxidation process. In the second case residual amounts of other gases may be present as a result of their presence in the oxygen and nitrogen to be mixed. These residual amounts also do not affect the oxidation process. It was found that the gas mixture resulting from the combustion of an overstoichiometric air or of an oxygen enriched air or of an oxygen/fuel in a burner like those proposed in the prior art was inadequate to provide a controlled oxidation.

[0010] The inventors found that the oxygen content of the gas mixture needed to be between 2 and 4.5% in volume. At oxygen values above 10% the oxide layer did not have the desired composition and the growth rate of the oxide layer is too high, resulting in thick oxide layers. At oxygen values below 0.5% the oxidation process was too slow and the oxide layer remained too thin.

[0011] In an embodiment a spray bar with specifically designed nozzle is mounted in the connection chamber

between the DFF and PTF, on one or on both sides of the strip which sprays a jet of oxidising medium onto the strip surface so that the strip surface is evenly oxidised. An illustration of the system is provided in a schematic drawing in figure 1.

[0012] According to the invention the maximum oxygen content is 4.5%. This results in an oxide layer of consistent composition, thickness and homogeneity to provide a good quality galvanised coating. In the present invention the gas mixture comprises an oxygen content of between 2 to 4.5%.

[0013] In an embodiment a method is provided wherein the control of the oxidation of the steel strip surface or surfaces is based on the measurement of the oxygen content in the mixture. This measurement can be performed by oxygen transducers set up a fixed way and running in closed loop with the flow control valves regulating the flow rate of the mixture injected by the nozzles. This results in an oxide layer of consistent composition, thickness and homogeneity to provide a good quality galvanised coating.

[0014] According to the invention the oxidation of the steel strip surface or surfaces takes place between 650°C and 900°C. In a preferred embodiment the oxidation of the steel strip surface or surfaces takes place at a temperature of at most 800°C and more preferably of at most 750°C.

[0015] By means of non-limiting examples commercial trials were performed on 1 and 1.5 mm thick and 1200 mm wide coiled strip material of the DP600 and DP800 type. The dew point during the trials was between -30 and -24°C. The oxygen content of the gas mixture was varied between 2.26 to 3.61%. The results in terms of strip wettability and coating adhesion after the annealing and coating were excellent.

[0016] In figure 2 a schematic indication is given where the oxidation of the steel substrate, for instance using the system in figure 1, is performed in a furnace comprising a direct fired furnace and a radiant tube furnace.

Claims

1. Method of galvanizing a steel strip in a continuous hot dip galvanizing line comprising a direct fired furnace section or non oxidising furnace and a subsequent radiant tube furnace section, the method comprising injecting an oxidizing medium consisting of a gas mixture of nitrogen and air or a gas mixture of nitrogen and oxygen into the galvanizing furnace by projecting the oxidizing medium onto one or both of the surfaces of the uncoated strip exiting the nonoxidizing or direct fired furnace section by a nozzle system to cause one or both of the steel strip surfaces to oxidise in a controlled manner in the connection chamber between the direct fired furnace section or non-oxidising section and the radiant tube section, wherein the nozzles are designed such as to distrib-

ute the gas mixture evenly, the method further comprising at least partly reducing the oxide back to iron in the radiant tube furnace section and the method further comprising hot dip galvanizing the steel strip in the hot dip galvanizing line, wherein the gas mixture comprises an oxygen content of 2 to 4.5% in volume, wherein the oxidation of the steel strip surface or surfaces takes place between 650°C and 900°C.

2. Method according to claim 1, wherein the oxidation of the steel strip surface or surfaces takes place at a temperature of at most 750°C.

3. Method according to any one of the preceding claims wherein the control of the oxidation of the steel strip surface or surfaces is based on the measurement of the oxygen content of the gas mixture.

Patentansprüche

1. Verfahren zum Verzinken eines Stahlbands in einer kontinuierlichen Feuerverzinkungsanlage, umfassend einen direkt befeuerten Ofenabschnitt oder einen nicht oxidierenden Ofen und einen nachfolgenden Strahlungsrohrfurnabschnitt, das Verfahren umfassend ein Einspritzen eines Oxidationsmediums, das aus einem Gasgemisch aus Stickstoff und Luft oder einem Gasgemisch aus Stickstoff und Sauerstoff besteht, in den Verzinkungs-Ofen, durch Abschleudern des oxidierenden Mediums auf eine oder beide der Oberflächen des unbeschichteten Bands, das aus dem nicht oxidierenden oder direkt befeuerten Ofenabschnitt austritt, durch ein Düsensystem, um zu bewirken, dass eine oder beide der Stahlbandoberflächen auf geregelte Weise in der Verbindungskammer zwischen dem direkt befeuerten Ofenabschnitt oder dem nicht oxidierenden Abschnitt und dem Strahlungsrohrfurnabschnitt oxidieren, wobei die Düsen so ausgelegt sind, dass sie das Gasgemisch gleichmäßig verteilen, das Verfahren ferner umfassend mindestens ein teilweises Reduzieren des Oxids zurück zu Eisen in dem Strahlungsrohrfurnabschnitt, und das Verfahren ferner umfassend ein Feuerverzinken des Stahlbands in der Feuerverzinkungsanlage, wobei die Gas Mischung einen Sauerstoffgehalt von 2 bis 4,5 Vol.-% umfasst, wobei die Oxidation der Stahlbandoberfläche oder -oberflächen bei zwischen 650 °C und 900 °C erfolgt.
2. Verfahren nach Anspruch 1, wobei die Oxidation der Stahlbandoberfläche oder -oberflächen bei einer Temperatur von höchstens 750 °C erfolgt.
3. Verfahren nach einem der vorstehenden Ansprüche, wobei die Steuerung der Oxidation der Stahlband-

berfläche oder -oberflächen auf der Messung des Sauerstoffgehalts des Gasgemischs basiert.

Revendications

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1. Procédé de galvanisation d'une bande d'acier dans une ligne continue de galvanisation par immersion à chaud comprenant une section de four à combustion directe ou de four sans oxydation et une section de four à tubes rayonnants ultérieure, le procédé comprenant l'injection d'un milieu oxydant constitué d'un mélange gazeux d'azote et d'air ou d'un mélange gazeux d'azote et d'oxygène dans le four de galvanisation en projetant le milieu oxydant sur l'une ou les deux surfaces de la bande non revêtue sortant de la section de four sans oxydation ou à combustion directe par un système de buses pour amener l'une ou les deux surfaces de la bande d'acier à s'oxyder de manière régulée dans la chambre de liaison entre la section de four à combustion directe ou la section sans oxydation et la section à tubes rayonnants, dans lequel les buses sont conçues de manière à distribuer le mélange gazeux uniformément, le procédé comprenant en outre la réduction au moins partielle de l'oxyde à nouveau en fer dans la section du four à tubes radiants et le procédé comprenant en outre la galvanisation par immersion à chaud de la bande d'acier dans la ligne de galvanisation par immersion à chaud, dans lequel le mélange gazeux comprend une teneur en oxygène de 2 à 4,5 % en volume, dans lequel l'oxydation de la surface ou des surfaces de la bande d'acier a lieu entre 650 °C et 900 °C.
2. Procédé selon la revendication 1, dans lequel l'oxydation de la surface ou des surfaces de la bande d'acier a lieu à une température d'au plus 750 °C.
3. Procédé selon l'une quelconque des revendications précédentes, dans lequel la régulation de l'oxydation de la surface ou des surfaces de la bande d'acier est basée sur la mesure de la teneur en oxygène du mélange gazeux.

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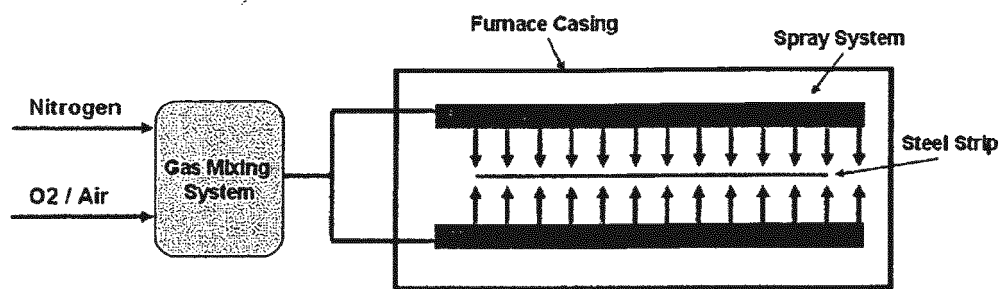


Figure 1.

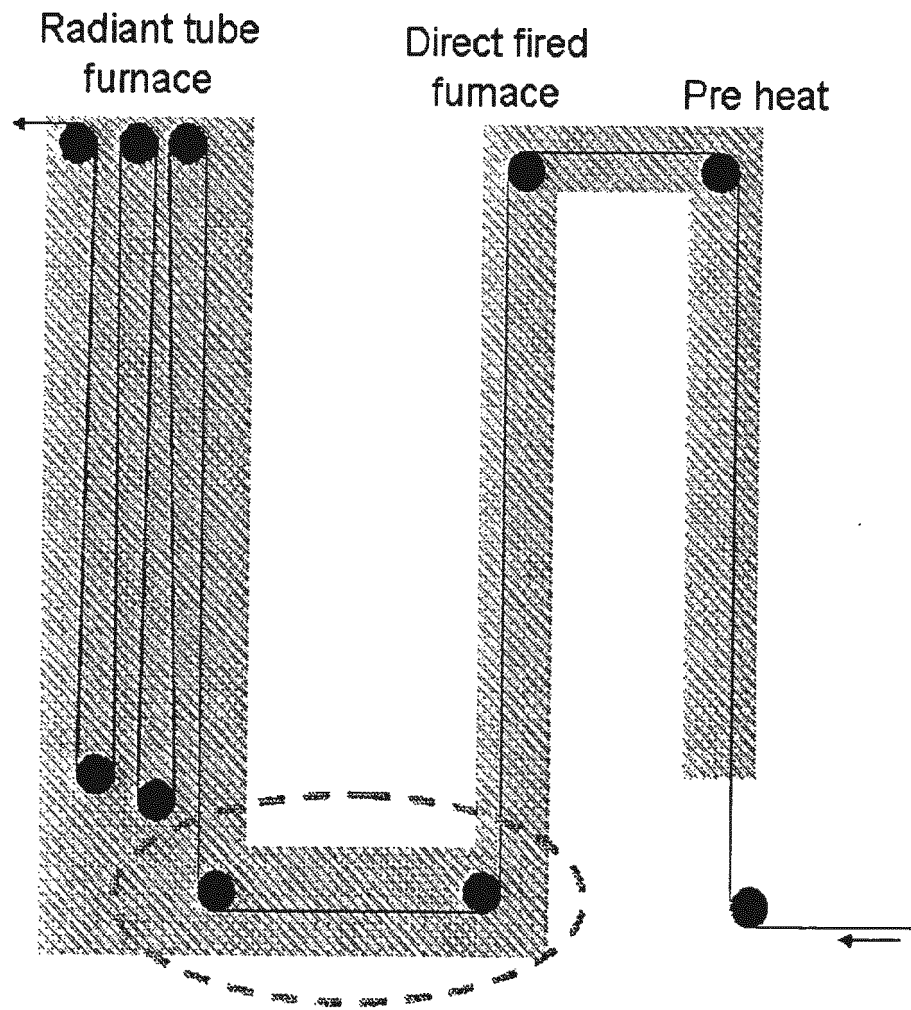


Figure 2

REFERENCES CITED IN THE DESCRIPTION

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