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(54) **METHOD FOR PRODUCING A STEEL STRIP WITH AN ALUMINIUM ALLOY COATING LAYER**

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Description

[0001] The invention relates to a method for producing a steel strip with an aluminium alloy coating layer in a continuous coating process. The invention also relates to a steel strip coated with an aluminium alloy coating layer that can be produced in accordance with the method, the use of such a coated steel strip and the product made by using the coated steel strip.

[0002] It is known in the art to use an aluminium-silicon alloy for coating a steel strip for producing hot-formed articles. One of the early patent applications filed in this respect is EP0971044. It has been found in practice that the products produced by hot-forming of blanks cut from this aluminium-silicon coated steel strip suppress scale formation during the hot-forming process, due to the presence of the aluminium-silicon coating. The prior art aluminium-silicon coating contains about 9 to 10 wt. % silicon. It is noted that when reference is made to an aluminium-silicon coating, a.k.a. an Al-Si coating, that Al and Si are deemed characteristic elements, but that other elements may be, and usually are, present in the coating as well. By means of non-limiting example: due to the high temperature of the coating process and the hot-forming process iron will dissolve from the steel substrate into the coating.

[0003] However, despite its use in hot-forming processes, it has also been found that during the hot-forming process the aluminium-silicon coating melts at about 575 °C when the coated blank is heated to a temperature above the Ac1 temperature of the steel, causing sticking of the molten aluminium-silicon to transport rolls in the radiation oven in which the blanks are heated. Because of the high reflectivity of these coatings for thermal radiation the blanks only heat up slowly, and therefore a long time is needed for the coating to saturate with iron by diffusion from the steel substrate. This is exacerbated by the melting of the coating which further increases the reflectivity.

[0004] Several attempts have been made to solve these problems. For instance, EP2240622 discloses that a coil of aluminium-silicon coated steel can be heated in a bell type annealing furnace during several hours at a certain temperature to achieve alloying of the coating with iron. EP2818571 discloses that a coil of aluminium-silicon coated steel is placed on a decoiler, and the strip is transported through a furnace at a certain temperature and during a certain time period to achieve alloying of the coating with iron. After this pre-diffusion blanks can be produced from the pre-diffused strip. However, both these methods require an additional process step, additional use of equipment, additional time and additional energy. For these reasons, the alloying of the strip or blanks before heating in the hot-forming furnace is not used in practice.

[0005] It is an object of the invention to provide a method for producing an aluminium-alloy coated steel strip which is easy and cost-effective to use, and which provides an aluminium-alloy coating that does not stick to transport rolls during use in a furnace for hot-forming.

[0006] It is a further object of the invention to provide a method for producing aluminium-alloy coated steel strip wherein blanks produced therefrom can be heated fast.

[0007] It is another object of the invention to provide a method for producing an aluminium-alloy coated steel strip that can be implemented in existing production lines.

[0008] It is another object of the invention to provide a method for producing an aluminium-alloy coated steel strip that can be implemented in production lines that incorporate heating equipment that make use of inductive or conductive heating means.

[0009] It is another object of the invention to provide an improved aluminium-alloy coated steel strip for use in a hot-forming process.

[0010] It is moreover an object of the invention to provide the use of the above mentioned steel strip to in a hot-forming process.

[0011] It is furthermore an object of the invention to provide the product resulting from the use of the steel strip according to the invention.

[0012] One or more of these objects can be reached with a method for producing a steel strip coated on one or both sides with an aluminium alloy coating layer in a continuous hot-dip coating and a subsequent pre-diffusion annealing process, said process comprising a hot-dip coating stage in which the steel strip is passed with a velocity v through a bath of a molten aluminium alloy to apply an aluminium alloy coating layer to one or both sides of the steel strip, and a pre-diffusion annealing stage, wherein

- the thickness of the applied aluminium alloy coating layer on the one or both sides of the steel strip is between 5 and 40 μm and wherein the aluminium alloy coating layer comprises 0.4 to 4.0 weight% silicon, and wherein
- the aluminium alloy coated steel strip enters the pre-diffusion annealing stage while at least the outer layer of the aluminium alloy coating layer or layers is above its liquidus temperature, and the strip is annealed at an annealing temperature of at least 600 and at most 800 °C for at most 40 seconds to promote the diffusion of iron from the steel strip into the aluminium alloy coating layer or layers to form a substantially fully-alloyed aluminium-iron-silicon coating layer or layers;

followed by cooling the pre-diffusion annealed coated steel strip to ambient temperatures.

[0013] The fully-alloyed aluminium-iron-silicon coating layer or layers consists substantially entirely of iron-aluminides with silicon in solid solution. In relation to this invention iron-aluminides with silicon in solid solution are deemed to include iron-aluminium intermetallics such as Fe_2Al_5 and FeAl_3 , as well as iron-aluminium-silicon intermetallics such as τ -phase (Fe_2SiAl_2).

[0014] It should be noted that the continuous hot dip coating is performed by leading a strip through the bath of a molten aluminium alloy. The subsequent pre-diffusion annealing can be performed in line with the hot dip coating, i.e. immediately after the hot dip coating or (much) later off-line. The pre-diffusion annealing can also be performed at a later time on sheets or blanks taken from the steel strip coated on one or both sides with an aluminium alloy coating layer. Preferred embodiments are provided in the dependent claims.

[0015] The aluminium alloy coating layer on the coated steel strip or sheet prior to heating and hot-forming and the pre-diffusion comprises at least three distinct layers, as seen from the steel substrate outwards:

- intermetallic layer 1, consisting of Fe_2Al_5 phase with Si in solid solution;
- intermetallic layer 2, consisting of FeAl_3 phase with Si in solid solution;
- outer layer, solidified aluminium-alloy with the composition of the molten aluminium alloy bath, i.e. including the inevitable presence of impurities and dissolved elements from the preceding strips

[0016] The composition of the fully alloyed coating layer after the pre-diffusion annealing stage consists substantially entirely of iron-aluminium intermetallics. There may be insignificant amounts of other components in the microstructure but these do not adversely affect the properties of the fully-alloyed aluminium-iron-silicon coating layer which is obtained in the method according to the invention after the pre-diffusion annealing stage. The intention is that the fully alloyed coating layer after the pre-diffusion annealing stage consists entirely of iron-aluminium intermetallics, and that thus a fully alloyed aluminium-iron-silicon coating layer or layers is/are obtained.

[0017] The inventors believe that the prior art aluminium-silicon coating is difficult to alloy with iron due to the high silicon content in the aluminium coating. Without being bound by theory, it is thought that the presence of silicon blocks diffusion paths of iron and slows down the growth of Fe-Al intermetallics. The inventors have found that when the silicon amount in the coating is lowered according to the invention that the silicon still present will not substantially prevent the diffusion of the iron into the aluminium-alloy coating layer. Compared to the prior art aluminium-silicon layers the diffusion of iron is therefore not impeded at all, or only to a relatively ineffective extent.

[0018] After experimentation, the inventors have found that a silicon content of between 0.4 and 4.0 % (all percentages are in weight percent (wt.%) unless otherwise indicated) in the aluminium alloy coating layer must be used to allow the diffusion of iron into the aluminium-alloy coating in the pre-diffusion annealing stage immediately following the coating of the steel strip with the aluminium alloy coating layer. The diffusion can then be performed within a short time of at most 40 seconds, and in this time period the iron from the steel strip will have diffused over the full thickness of the coating. The time has to be short to enable fitting the annealing cycle into existing hot dip coating lines or line concepts. The diffusion should take place at an annealing temperature between 600 and 800° C, so the diffusion of iron in the liquid aluminium alloy coating layer will be fast. After dipping the steel strip in the molten aluminium alloy the outer layer of the coated steel strip exiting the bath of molten aluminium alloy is still liquid. So the annealing temperature is above the melting temperature of the aluminium alloy coating layer. In the pre-diffusion annealing stage the diffusion of iron from the steel strip into the aluminium alloy coating layer is promoted to form a fully-alloyed aluminium-iron-silicon, substantially entirely consisting of iron-aluminides with silicon in solid solution (e.g. Fe_2Al_5 , FeAl_3 , τ -phase (Fe_2SiAl_2)). The diffusion annealing can be performed quickly after the continuous coating without the need to provide any substantial cooling or heating between the hot-dip coating stage and the pre-diffusion annealing stage because the annealing temperature is preferably in the same range as the temperature for continuous coating. The pre-diffusion annealing stage must be executed while the applied coating layer is still liquid to enable the fast diffusion of iron into the coating layer. The diffusion of iron in an already solidified coating layer would be much too slow. The slow diffusion of iron into a solidified aluminium alloy coating layer is one of the reasons why the heating stage in the conventional hot-forming process takes so long. The high reflectivity of the solidified coating is the other contributing factor. The incorporation of the pre-diffusion annealing stage in the continuous coating and annealing line as depicted in Figure 1A allows the diffusion annealing to take place quickly, because of the molten state of the coating layer, and it does not require an additional process step of reheating and cooling, because it is integrated in the continuous coating line. Such an additional process step would also have the disadvantages of having to start the diffusion from an already solidified coating layer, so this process would suffer from the same problems as the heating up stage in a hot-forming process (reflectivity, slow diffusion). The process according to the invention can be integrated in existing lines, because it goes so fast, and thus requires relatively little space, capital expenditure and operational costs.

[0019] In the invention the hot-dip coated steel strip or sheet is subjected after coating to a pre-diffusion treatment. This shortens the hot-forming step in the sense that the diffusion of iron into the aluminium alloy coating layer has already

happened and that the aluminium alloy coating layer has been converted into a fully-alloyed Al-Fe-Si coating layer consisting essentially of iron-aluminides with silicon in solid solution. It may also improve consistency of the product because the pre-diffusion treatment may be performed in a more controlled environment, e.g. in a separate continuous annealing line or in an annealing section immediately following the hot dip coating step. It also allows the use of an induction furnace rather than a radiation furnace for annealing the blanks prior to hot-forming because there is no liquid phase anymore when annealing a pre-diffused coated sheet or strip according to the invention.

[0020] In an embodiment of the invention the aluminium alloy coating layer on the coated steel strip or sheet prior to heating and hot-forming and the optional pre-diffusion comprises at least three distinct layers, as seen from the steel substrate outwards:

- intermetallic layer 1, consisting of Fe_2Al_5 phase with Si in solid solution;
- intermetallic layer 2, consisting of FeAl_3 phase with Si in solid solution;
- outer layer, solidified aluminium-alloy with the composition of the molten aluminium alloy bath, i.e. including the inevitable presence of impurities and dissolved elements from the preceding strips.

[0021] Figure 9A shows this layer system with the dark grey upper layer being the outer layer, the black matter with the capital A being the embedding material, the lightest material being the metal substrate and the FeAl_3 and Fe_2Al_5 between the outer layer and the metal substrate.

[0022] Although ideally the intermetallic layers consist only of the mentioned compounds, it is possible that there may be insignificant amounts of other components present as well as inevitable impurities or intermediate compounds. The dispersed τ -phase (Fe_2SiAl_2) at higher silicon contents would be one such inevitable compound. However, these insignificant amounts have been found to have no adverse effects on the properties of the coated steel substrate. The intention is that the fully alloyed coating layer after the pre-diffusion annealing stage consists entirely of iron-aluminides with silicon in solid solution, and that thus a fully alloyed aluminium-iron-silicon coating layer or layers is/are obtained.

[0023] In the method according to the invention the strip is not cooled to ambient temperatures between the hot-dip coating stage and the pre-diffusion annealing stage. Preferably there is no active cooling whatsoever between the hot-dip coating stage and the pre-diffusion annealing stage. The strip may have to be reheated to the pre-diffusion annealing temperature of between 600 and 800 °C to compensate for the cooling of the strip after leaving the bath and the cooling effect of the thickness controlling means, such as air knives. Only after the pre-diffusion annealing stage the strip is cooled to ambient temperature. This cooling usually takes place in two steps, wherein the cooling immediately after the annealing is intended to prevent any sticking or damage of the fully-alloyed coating layer to turning rolls, and is usually executed with an air or mist cooling at a cooling rate of about between 10 and 30 °C/s and further on in the line the strip with the fully-alloyed Al-Fe-Si coating layer is cooled quickly, usually by quenching in water. It is noted that the effect of the cooling is largely thermal to prevent damage to the line and the fully alloyed Al-Fe-Si coating layer, and that the effect of the cooling on the properties of the steel substrate are negligible.

[0024] The minimum silicon content of the aluminium alloy coating layer is 0.4 wt.%. Below 0.4% there is an increased risk of forming a finger-like interface between the initial alloy layer after the hot dipping stage and the remnants of the as yet unalloyed aluminium alloy coating layer still having the composition of the molten aluminium alloy due to irregular growth of the alloy layer. Above 0.4% this irregular growth is avoided. Above 4.0% Si the presence of Si makes rapid alloying impossible.

[0025] The low silicon content in the aluminium alloy coating layer (0.4 - 4.0 wt.% Si) according to the invention as compared to the prior art aluminium-silicon coating layer (9 - 10 wt.% Si) enables the full alloying to be completed in a timeframe which is sufficiently short (at most 40 seconds) for it to enable implementation in existing hot-dip coating lines.

[0026] The fully-alloyed aluminium-iron-silicon coating layer after the pre-diffusion annealing stage can also be referred to as a pre-diffused aluminium-iron-silicon coating layer, because the required diffusion of the iron into the aluminium alloy coating layer and the saturation with iron has already taken place. In the prior art process this iron diffusion and the formation iron-aluminide consisting substantially entirely of iron-aluminium intermetallics has to take place during the heating stage before the hot forming step, and therefore this prior art heating stage is considerably longer than the heating stage required when using the pre-diffused aluminium-iron-silicon coating layer according to the invention. It should be noted that the heating stage of the forming step, which heats to a higher temperature (typically between 850 and 950 °C) for a longer time (typically in the order of 4 to 10 minutes) than the pre-diffusion annealing stage (600 to 800 °C for at most 40 seconds) results in a change in the structure of the coated strip irrespective of whether the strip is a fully alloyed Al-Fe-Si coating layer or a freshly dipped and still unalloyed coating layer. As soon as the coating layer is saturated with Fe the Al starts to diffuse into the steel substrate, thereby enriching the steel with Al. As soon as sufficient Al has diffused into the steel substrate, the surface layer of the steel substrate remains ferritic during hot forming. This layer of high Al-ferrite is very ductile and prevents any cracks in the aluminium alloy coating layer from reaching the steel substrate. Examples of this ductile layer of high Al-ferrite are shown in Figure 8.

[0027] There are two variants of hot forming: direct and indirect hot stamping. The direct process starts with a coated

blank that is heated and formed, while the indirect process uses a preformed component from a coated blank that is subsequently heated and cooled to obtain the desired properties and microstructure after cooling. In the direct method a steel blank is heated in a furnace to a temperature sufficiently high for the steel to transform into austenite, hot-forming it in a press and cooling it to obtain the desired final microstructure of the product. The inventors found that the method according to the invention is very well suited to be used to coat a steel strip of any steel grade that results in improved properties after the cooling of the hot-formed product. Examples of these are steels that result in a martensitic microstructure after cooling from the austenitic range at a cooling rate exceeding the critical cooling rate. However, the microstructure after cooling may also comprise mixtures of martensite and bainite, mixtures of martensite, retained austenite and bainite, mixtures of ferrite and martensite, mixtures of martensite, ferrite and bainite, mixtures of martensite, retained austenite, ferrite and bainite, or even ferrite and very fine pearlite. The fully-alloyed aluminium-iron-silicon coating layer protects the steel strip against oxidation during heating, hot-forming and cooling and against decarburization and provides adequate paint adhesion to and corrosion protection of the final formed product to be used in, e.g., automotive applications.

[0028] The steel strip may be a hot-rolled strip, or a cold-rolled strip. Preferably the steel is a full hard cold-rolled steel strip. Prior to the immersion in the molten aluminium alloy the full hard cold-rolled strip may have been subjected to a recrystallisation annealing or a recovery annealing. If the strip was subjected to a recrystallisation annealing or a recovery annealing then it is preferable that this recrystallisation or recovery annealing is continuous and hot-linked to the hot-dip coating stage. The thickness of the steel strip is typically between 0.4 and 4.0 mm, and preferably at least 0.7 and/or at most 3.0 mm.

[0029] The coated steel strip according to the invention provides good protection against oxidation during the hot forming on the one hand, and provides excellent paint adhesion of the finished part on the other. It is important that if there is τ -phase present in the surface layer that it is present in the form of embedded islands, i.e. a dispersion, and not as a continuous layer. A dispersion is defined as a material comprising more than one phase where at least one of the phases (the dispersed phase) consists of finely divided phase domains embedded in the matrix phase. The improvement of the paint adherence is the result of the absence or the limited presence of τ -phase which the inventors found to be responsible for the bad adhesion of the known coatings. Within the context of this invention, a phase is considered to be a τ -phase if the composition is in the following range $\text{Fe}_x\text{Si}_y\text{Al}_z$ phase with a composition range of 50-70 wt.% Fe, 5-15 wt.% Si and 20-35 wt.% Al. τ -phase forms when the solubility of silicon is exceeded as a result of the diffusion of iron into the aluminium layer. As a result of the enrichment with iron, the solubility of silicon is exceeded and τ -phase, such as Fe_2SiAl_2 , forms. This occurrence imposes restrictions to the duration of the annealing and the height of the annealing temperature during the hot-forming process. So the formation of τ -phase can be easily avoided or restricted primarily by controlling the silicon content in the aluminium alloy layer on the steel strip or sheet and secondarily by the annealing temperature and time. The added advantage of this is that the duration of the blanks in the furnace can be reduced as well, which may allow shorter furnaces, which is an economical advantage. The combination of annealing temperature and time for a given coating layer is easily determined by simple experimentation followed by routine microstructural observation (see below in the examples). It should be noted that the percentage of τ -phase is expressed in area%, because the surface fraction is measured on a cross section of the coating layer. Preferably the coating layer is free from τ -phase. Because of the influence of the presence of τ -phase on paint adhesion, it is preferable that there is no τ -phase in the coating layer, or at least no τ -phase in the outermost surface layer where the paint would be in contact with the coating layer.

[0030] Contiguity (C) is a property used to characterize microstructure of materials. It quantifies the connected nature of the phases in a composite and can be defined as the fraction of the internal surface of an α phase shared with other α phase particles in an α - β two-phase structure. The contiguity of a phase varies between 0 and 1 as the distribution of one phase in the other changes from completely dispersed structure (no α - α contacts) to a fully agglomerated structure (only α - α contacts). The interfacial areas can be obtained using a simple method of counting intercepts with phase boundaries on a polished plane of the microstructure and the contiguity can be given by the following equations: where C_α and C_β are the contiguity of the α and β phases, $N_L^{\alpha\alpha}$ and $N_L^{\beta\beta}$ are the number of intercepts of α/α and β/β interfaces, respectively, with random line of unit length, and $N_L^{\alpha\beta}$ is the number of α/β interfaces with a random line of unit length. With a contiguity C. of 0, there are no α -grains touching other α -grains. With a contiguity C. of 1, all α -grains touch other α -grains, meaning that there is just one big lump of α -grains embedded in the β -phase.

[0031] Preferably the contiguity of the τ -phase, if present, in the surface layer is less than $C_\tau \leq 0.4$. In an embodiment of the invention the composition of the fully-alloyed aluminium-iron-silicon coating layer is 50-55 wt.% Al, 43-48 wt.% Fe, 0.4-4 wt.% Si and inevitable elements and impurities consistent with the hot dip coating process. It is noted that some elements are known to be added to the melt for specific reasons: Ti, B, Sr, Ce, La, and Ca are elements used to control grain size or modify the aluminium-silicon eutectic. Mg and Zn can be added to the bath to improve corrosion resistance of the final hot-formed product. As a result, these elements may also end up in the aluminium alloy coating layer and consequently also in the fully-alloyed aluminium-iron-silicon coating layer. Preferably the Zn content and/or the Mg content in the molten aluminium alloy bath is below 1.0 wt% to prevent top dress. Elements like Mn, Cr, Ni and

Fe will also likely be present in the molten aluminium alloy bath as a result of dissolution of these elements from the steel strip passing through the bath, and thus may end up in the aluminium alloy coating layer. A saturation level of iron in the molten aluminium alloy bath is typically between 2 and 3 wt.%. So in the method according to the invention the aluminium alloy coating layer typically contains dissolved elements from the steel substrate such as manganese, chromium and iron up to the saturation level of these elements in the molten aluminium alloy bath.

[0032] In an embodiment of the invention the molten aluminium alloy contains between 0.4 and 4.0 wt.%

$$C_{\alpha} = \frac{2N_L^{\alpha\alpha}}{2N_L^{\alpha\alpha} + N_L^{\alpha\beta}}$$

$$C_{\beta} = \frac{2N_L^{\beta\beta}}{2N_L^{\beta\beta} + N_L^{\alpha\beta}}$$

silicon, and the molten aluminium alloy bath is kept at a temperature between its melting temperature and 750 °C, preferably at a temperature of at least 660 °C and/or of at most 700 °C. Preferably the temperature of the steel strip entering the molten aluminium alloy is between 550 and 750 °C, preferably at least 660 °C and/or at most 700 °C. This enables the strip to pass from the hot-dip coating stage to the pre-diffusion annealing stage without substantial heating or cooling, and preferably without any active cooling between the hot-dip coating stage and the pre-diffusion annealing stage. Active heating will only be required to compensate for any loss in temperature due to passive cooling after leaving the bath and due to the (unintended) cooling effect of the thickness controlling means. The temperature in the pre-diffusion annealing stage is between 600 and 800 °C, preferably at least 630, more preferably at least 650 °C and/or at most 750 °C. Typically the temperature in the pre-diffusion annealing stage is between 680 and 720 °C.

[0033] In a preferred embodiment the steel strip is led through the hot-dip coating stage and the pre-diffusion annealing stage at a velocity v of between 0.6 m/s and 4.2 m/s, preferably of at most 3.0 m/s, more preferably a velocity of at least 1.0 and/or at most 2.0 m/s. These speeds are industrial speeds for a hot-dip coating line, and the method according to the invention allows maintaining this production speed.

[0034] In an embodiment the aluminium alloy coating layer contains at least 0.5 wt.% Si, preferably at least 0.6 wt.% Si, or even 0.7 or 0.8 wt.%. In an embodiment the aluminium alloy coating layer contains at most 3.5, preferably at most 3.0 wt.% Si, or even at most 2.5 wt.%.

[0035] In an embodiment the aluminium alloy coating layer contains 1.6 to 4.0 wt.% silicon, preferably at least 1.8 wt.% and/or at most 3.5, 3.0 or 2.5 wt.% silicon. This embodiment is particularly suitable for thin coating layers, typically of below 20 μm .

[0036] In another embodiment the aluminium alloy coating layer contains 0.4 to 1.4 wt.% silicon, preferably 0.5 to 1.4 wt.% silicon, more preferably 0.7 to 1.4 wt.% silicon. A suitable maximum value is 1.3 wt.% silicon. This embodiment is particularly suitable for thicker coating layers, typically of 20 μm or thicker.

[0037] Preferably the thickness of the aluminium alloy coating layer is at least 10 and/or at most 40 μm , preferably at least 12 μm , more preferably at least 13 μm , preferably at most 30, more preferably at most 25 μm . There is a balance between the thickness of the coating layer in terms of alloying costs on the one hand and the speed of the annealing process and resistance to oxidation at the other. The inventors found that the ranges above allow for a balanced choice. The optimal window from this point of view is between 15 and 25 μm . Furthermore it should be noted that the thickness on one side of the steel strip may be different from the thickness on the other side, and in an extreme case there may be only an aluminium alloy coating layer on one side of the steel strip and none on the other. However, this takes additional precautions during the hot-dip coating, and therefore the normal case will be that there is an aluminium alloy coating layer on both sides, optionally with different thicknesses.

[0038] In a preferred embodiment the thickness d (in μm) of the fully-alloyed aluminium-iron-silicon coating layer in dependence of the silicon content (in wt.%) of the fully-alloyed aluminium-iron-silicon coating layer is enclosed in the Si-d space by the equations (1), (2) and (3):

$$(1) d \geq -1.39 \cdot \text{Si} + 12.6 \text{ and}$$

$$(2) d \leq -9.17 \cdot \text{Si} + 43.7 \text{ and}$$

$$(3) \text{Si} \geq 0.4 \text{ \%}$$

[0039] The higher the silicon content, the lower the thickness d of the coating layer, and the smaller the operational window.

[0040] In a preferred embodiment the annealing time in the pre-diffusion annealing stage is at most 30 seconds. The

shorter the annealing time, the shorter the annealing means in the pre-diffusion annealing stage, and therefore the lower the capital and operational costs to install. Preferably the annealing means comprise, or consist of, an induction type furnace. This type of heating is quick, clean and reactive. There is no complicated furnace atmosphere to be maintained which would be the case when burners are used. Also the environmental impact of induction furnaces is lower in comparison to other types of furnace. Contact heating or resistance heating may achieve the same benefits. An additional advantage of induction heating and resistance heating is that the heat is generated in the strip and therefore comes from within, which is beneficial to promote the iron diffusion from the steel strip into the aluminium-alloy coating layer. Alternative furnaces to induction, or in addition thereto, may be radiant tube furnaces, direct fire furnaces or electrically heated furnaces, or mixtures thereof. Preferably the annealing time in the pre-diffusion annealing stage is at least 2 and preferably at least 5 seconds, and preferably at most 25 seconds. A typical minimum annealing time is 10 seconds, a typical maximum annealing time is 20 seconds. The entrance of the pre-diffusion annealing stage is as close to the aluminium alloy coating layer thickness controlling means, such as air knives, as practically possible because the pre-diffusion annealing stage must be executed while at least the outer layer of the aluminium alloy coating layer is still liquid. Practically, the entrance of the pre-diffusion annealing stage will be about 0.5 to 5.0 m after the thickness controlling means.

[0041] The time of the immersion of the steel strip in the molten aluminium alloy bath is between 2 and 10 seconds. A longer time requires a very deep bath or complicated trajectory therein, or a very slow running line, which is all undesired, whereas there must be sufficient time to build up the layer thickness. A typical minimum immersion time is 3 s, and a typical maximum is 6 s.

[0042] Upon exiting the molten aluminium alloy bath, the thickness of the aluminium layer on the steel strip is controlled by thickness controlling means, such as air knives which blow air, nitrogen or another suitable gas at high pressure through a nozzle slit onto the freshly dipped steel strip. By altering the pressure, the distance from the steel strip or the height of the nozzles over the molten aluminium alloy the coating thickness can be adjusted depending on the requirements.

[0043] According to a second aspect the invention is also embodied in a steel strip according to claim 10. Preferred embodiments are provided in claims 11 and 12.

[0044] In an embodiment of the invention the steel strip has a composition comprising (in wt.%)

C: 0.01-0.5	P: ≤ 0.1	Nb: ≤ 0.3
Mn: 0.4 - 4.0	S: ≤ 0.05	V: ≤ 0.5
N: 0.001 - 0.030	B: ≤ 0.08	Ca: ≤ 0.05
Si: ≤ 3.0	O: ≤ 0.008	Ni ≤ 2.0
Cr: ≤ 4.0	Ti: ≤ 0.3	Cu ≤ 2.0
Al: ≤ 3.0	Mo: ≤ 1.0	W ≤ 0.5

the remainder being iron and unavoidable impurities. These steels allow very good mechanical properties after a hot-forming process, whereas during the hot forming above Ac1 or Ac3 they are very formable. Preferably the nitrogen content is at most 0.010%. It is noted that any one or more of the optional elements may also be absent. i.e. either the amount of the element is 0 wt.% or the element is present as an unavoidable impurity.

[0045] In a preferable embodiment the carbon content of the steel strip is at least 0.10 and/or at most 0.25 %. In a preferable embodiment the manganese content is at least 1.0 and/or at most 2.4 %. Preferably the silicon content is at most 0.4 wt.%. Preferably the chromium content is at most 1.0 wt.%. Preferably the aluminium content is at most 1.5 wt.%. Preferably the phosphorus content is at most 0.02 wt.%. Preferably the sulphur content is at most 0.005 wt.%. Preferably the boron content is at most 50 ppm. Preferably the molybdenum content is at most 0.5 wt.%. Preferably the niobium content is at most 0.3 wt.%. Preferably the vanadium content is at most 0.5 wt.%. Preferably nickel, copper and calcium are under 0.05 wt.% each. Preferably tungsten is at most 0.02 wt.%. These preferable ranges can be used in combination with the steel strip composition as disclosed above individually or in combination.

[0046] In a preferred embodiment the steel strip has a composition comprising (in wt.%)

C: 0.10 - 0.25	P: ≤ 0.02	Nb: ≤ 0.3
Mn: 1.0 - 2.4	S: ≤ 0.005	V: ≤ 0.5
N: ≤ 0.03	B: ≤ 0.005	Ca: ≤ 0.05
Si: ≤ 0.4	O: ≤ 0.008	Ni ≤ 0.05
Cr: ≤ 1.0	Ti: ≤ 0.3	Cu ≤ 0.05
Al: ≤ 1.5	Mo: ≤ 0.5	W ≤ 0.02

the remainder being iron and unavoidable impurities. Preferably the nitrogen content is at most 0.010%. Typical steel grades suitable for hot forming are given in table A.

Table A - Typical steel grades suitable for hot forming.

Steel	C	Si	Mn	Cr	Ni	Al	Ti	B	N	C _{eq}
B-A	0.07	0.21	0.75	0.37	0.01	0.05	0.048	0.002	0.006	0.148
B-B	0.16	0.40	1.05	0.23	0.01	0.04	0.034	0.001	-	0.246
B-C	0.23	0.22	1.18	0.16	0.12	0.03	0.04	0.002	0.005	0.320
B-D	0.25	0.21	1.24	0.34	0.01	0.03	0.042	0.002	0.004	0.350
B-E	0.33	0.31	0.81	0.19	0.02	0.03	0.046	0.001	0.006	0.400
N-A	0.15	0.57	1.45	0.01	0.03	0.04	0.003	-	0.003	0.243
N-D	0.14	0.12	1.71	0.55	0.06	0.02	0.002	-	-	0.258
N-C	0.19	0.55	1.61	0.02	0.05	0.04	0.003	-	0.006	0.291
N-D	0.20	1.81	1.48	0.04	0.03	0.04	0.006	-	-	0.337

[0047] According to a third aspect of the invention the fully-alloyed aluminium-iron-silicon coated steel strip according to the invention is used to produce a hot-formed product in a hot-forming process. Because the to be hot-formed blank has undergone the diffusion process already according to the invention, i.e. it is pre-diffused, the absence of any liquid layers during the heating up stage in the hot forming process allows for a cleaner process without sticking risks. Also, the reflectivity of the fully-alloyed aluminium-iron-silicon coated steel strip is much lower than that of the prior art (with 10 wt.% Si) aluminium-silicon coated steel strip, leading to faster heating of blanks if a radiation furnace is used, and thus to potentially fewer or smaller reheating furnaces, and less damage of the product and pollution of the equipment due to roll build-up. The Fe_2Al_5 phase is darker in colour, and this causes the lower reflectivity and the higher absorption of heat in a radiation furnace.

[0048] In addition, other heating means, like induction heating and infrared heating means can be used for very fast heating. These heating means can be used in a stand-alone situation or as a fast heating step prior to a short radiation furnace.

[0049] In addition, the hot-formed coated steel product provides better paint adhesion. Induction heating of a prior art aluminium-silicon coated steel strip with 10 wt.% Si will lead to a bad surface quality, because the outer layer of these steels will be liquid during the reheating of the steel in the heating furnace of the hot-forming line. The liquid layer will react to the induction field and become wavy, rather than smooth. With the fully-alloyed aluminium-iron-silicon coated steel strip according to the invention the diffusion of iron has already happened in the pre-diffusion annealing stage so the total annealing time in the heating furnace of the hot-forming line is further reduced in addition to the faster heat-up rate due to the lower reflectivity of the fully-alloyed aluminium-iron-silicon coated steel strip.

[0050] In Figure 1 an embodiment of the process according to the invention is summarised. The steel strip is passed through an optional cleaning section to remove the undesired remnants of previous processes such as scale, oil residue etc. The clean strip is then led through the optional annealing section, which in case of a hot rolled strip may only be used for heating the strip to allow hot-dip coating (so-called heat-to-coat cycle) or in case of a cold-rolled strip may be used for a recovery or recrystallisation annealing. After the annealing the strip is led to the hot-dip coating stage where the strip is provided with the aluminium-alloy coating layer according to the invention. Thickness control means for controlling the thickness of the aluminium-alloy coating layer are schematically shown disposed between the hot-dip coating stage and the subsequent pre-diffusion annealing stage. In the pre-diffusion annealing stage the aluminium-alloy coating layer is transformed into the fully-alloyed aluminium-iron-silicon layer after which the coated strip is post-processed (such as optional temper rolling or tension levelling) before being coiled.

[0051] In Figure 1 the process according to the invention is summarised. The steel strip is passed through an optional cleaning section to remove the undesired remnants of previous processes such as scale, oil residue etc. The clean strip is then led through the optional annealing section, which in case of a hot rolled strip may only be used for heating the strip to allow hot-dip coating (so-called heat-to-coat cycle) or in case of a cold-rolled strip may be used for a recovery or recrystallisation annealing. After the annealing the strip is led to the hot-dip coating stage where the strip is provided with the aluminium alloy coating layer according to the invention. Thickness control means for controlling the thickness of the aluminium alloy coating layer are shown disposed between the hot-dip coating stage and the subsequent optional pre-diffusion annealing stage. In the optional pre-diffusion annealing stage the aluminium alloy coating layer is transformed into a fully-alloyed aluminium-iron-silicon layer. The cooling of the coated strip after the thickness controlling

means usually takes place in two steps, wherein the cooling immediately after the thickness controlling means is intended to prevent any sticking or damage of the aluminium alloy coating layer to turning rolls, and is usually executed with an air or mist cooling at a cooling rate of about between 10 and 30 °C/s and further on in the line the strip with the aluminium alloy coating layer is cooled quickly, usually by quenching in water. It is noted that the effect of the cooling is largely thermal to prevent damage to the line and the aluminium alloy coating layer, and that the effect of the cooling on the properties of the steel substrate are negligible. The strip or sheet produced in accordance with Figure 1 (i.e. as-coated or pre-diffused) can then be used in a hot-forming process according to the invention.

[0052] In an embodiment of the invention the hot-dip-coated strip is pre-diffused immediately prior to the hot-forming operation instead of immediately after the hot-dip coating. This pre-diffusion may be performed on the uncoiled strip prior to blanking, sheets cut from the strip, or on blanks cut from the strip or sheet. This embodiment mitigates the risk of damage of the pre-diffused strip during coiling, transport, uncoiling and handling because the substantially fully-alloyed aluminium-iron-silicon coating layer or layers, substantially entirely consisting of iron-aluminium intermetallics on the steel substrate tend to be brittle. The pre-diffusion can be done using induction because there is no liquid material on the surface as a result of the low silicon content. The blanks, either taken from the pre-diffused strip, or pre-diffused individually have a coating after pre-diffusion containing Fe_2Al_5 .

EXAMPLES

[0053] The invention will now be further explained by means of the following, non-limitative examples. The steel substrate for the experiments had the composition as given in Table 1.

Table 1 - Composition of steel substrate, balance Fe and inevitable impurities. 1.5 mm, cold-rolled, full-hard condition.

C	Mn	Cr	Si	P	S	Al	B	Ca
wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	ppm	ppm
0.20	2.18	0.64	0.055	0.010	0.001	0.036	0	17

Example 1

[0054] Two aluminium-alloy coated steels were produced. Sample A was produced by hot-dipping a steel strip in a molten aluminium alloy bath comprising 0.9 wt.% Si. Sample B was produced by hot-dipping in a prior art aluminium alloy bath comprising 9.6 wt.% Si. Both baths were saturated with Fe (about 2.8 wt.%). The steel grade used is a 1.5 mm cold rolled steel, in full hard condition and having a composition suitable for hot forming applications. Prior to hot-dipping the steels were recrystallisation annealed. Immediately following the recrystallisation annealing the steels were immersed in the respective aluminium alloy bath for a period of 3 seconds, which is consistent with a line speed of about 120 m/min. The strip entry temperature in the bath was 680 °C, and the bath temperature was 700 °C. After hot dipping the layer thickness of the coating was adjusted by wiping with nitrogen gas at 20 µm. The steels were annealed in the pre-diffusion annealing stage for 20 s at 700 °C to obtain pre-alloying and then cooled down by forced nitrogen gas.

[0055] Figure 2 shows the annealed aluminium-alloy coating layers. The coating on sample A is a fully-alloyed aluminium-iron-silicon coating layer while the coating on sample B consists of an alloyed layer of less than 10 µm thick (with a different composition than the fully-alloyed aluminium-iron-silicon coating layer on sample A!) with a non-alloyed layer with the coating bath composition on top. Additional experiments with sample B with varying annealing times in the pre-diffusion annealing stage at 700 °C show that the growth rate of the alloyed layer is very slow (see table 1). The remainder of the coating layer is still liquid.

[0056] In figure 9 the build-up of the layers in an annealed Al-Si coating layer of 3.0% Si and 1.6% Si is shown [AB1].

[0057] The right hand column shows the development of the different layers of intermetallic compounds during heat treatment of an steel substrate provided with an aluminium alloy coating comprising 1.6 wt.% Si. Figure A shows the as-coated layer, with the layers that are formed immediately after the immersion, and the top layer having the composition of the bath, B shows the development during reheating once the sample has reached 700 °C and C is the situation after annealing at 900 °C for 5 minutes. In sample C the diffusion zone is now clearly visible, and the top layer having the composition of the bath has completely vanished (EDS: acceleration voltage (EHT) 15 keV, working distance (wd) 6.0, 6.2 and 5.9 mm).

[0058] The layer for the 1.6 wt.% Si layer (figure 9 - right) consists mainly of Fe_2Al_5 with on top a thin layer of FeAl_3 is present at the substrate interface as illustrated in figure 9A-right. In contrast to a standard 10wt% Si coating no Fe_2SiAl_7 layer is present. During heating the Fe_2Al_5 layer, with on top a thin FeAl_3 layer, is growing towards the surface. The solubility limit of Si in Fe_2Al_5 is not exceeded and therefore no Si rich phases precipitate, see figure 9B- right. The Fe_2Al_5 continues to grow to the surface without any Fe_2SiAl_2 precipitation and closer to the steel base a more iron rich phase,

identified as FeAl_2 , develops, see figure 9C- right.

[0059] Figure 9 (left-hand column) shows the development of the different layers of intermetallic compounds during heat treatment of an steel substrate provided with an aluminium alloy coating comprising 3.0 wt.% Si (EHT 15 keV, wd 6.6, 6.5, 6.2 mm respectively). Figure A shows the as-coated layer, with the layers that are formed immediately after the immersion, and the top layer having the composition of the bath, B shows the development during reheating once the sample has reached 850 °C and C is the situation after annealing at 900 °C for 7 minutes. In sample C the diffusion zone is now clearly visible, and the top layer having the composition of the bath has completely vanished. Also visible is a degree of τ -phase (Fe_2SiAl_2) which is dispersed in the Fe_2Al_5 layer, and does not form a continuous layer.

[0060] For a coating dipped into a bath with 3wt% an almost similar layer development can be observed during the first stages of heat treatment, as illustrated in figure 3. However the Si solubility limit is just exceeded and Fe_2SiAl_2 precipitation in the form of globules takes place at the end of heat treatment.

Enrichment of Fe_2SiAl_2 at the surface is not observed

[0061] Both alloy contents result in a fully alloyed coating layer substantially entirely consisting of the intermetallics Fe_2Al_5 , FeAl_2 , and, depending on the Si-content, and Fe_2SiAl_2

Table 1: thickness measurements of alloy layer on Sample B annealed at 700°C

Sample ID	i	ii	iii	iv
Heat treatment time [s]	0	10	20	60
Alloy layer thickness [μm]	5	7	9	11

[0062] So a prior art coating with 9.6wt.% Si is not suitable for inline pre-alloying according to the invention, because the pre-diffusion annealing stage does not produce a fully-alloyed aluminium-iron-silicon coating layer. The coating with 0.9% Si on the other hand shows a fully alloyed layer of 20 μm thickness already after 20 seconds.

Example 2

[0063] Sample A from Ex. 1 (recrystallised cold-rolled 1.5 mm thick strip) was hot-dip coated in aluminium-alloy baths with different Si concentrations according to the invention, varying between 0.5, 0.9, 1.1 and 1.6 wt.% and pre-diffusion annealing times ranged from 0 to 30 seconds. The pre-diffusion annealing temperature was 700°C. The coating layer thickness was adjusted at 30 to 40 μm by nitrogen jets after exiting the coating bath. Producing relatively thick layers was a deliberate choice as the purpose of these examples was to determine the maximum achievable pre-alloying thickness without a limiting effect of the applied coating thickness. The steels were treated the same as in Ex. 1, except for the varying annealing time. In figure 3 cross sections (SEM) of the produced coatings are shown. The images clearly reveal an increased alloy layer thickness at lower Si levels and longer heat treatment times. Alloy layer thickness are presented in figure 4. Measurements demonstrate that depending on Si concentration and heat treatment time the alloy layer thickness ranges from 10 to 35 μm . Based on the measurements and extrapolation of the measurements a triangle is drawn in figure 4 that displays the thickness of fully alloyed coatings that can be produced with dipping times of 3s in combination with heat times between 0 and 30s.

Example 3

[0064] Hot-forming steel (1.5 mm) coated with an aluminium alloy coating layer with 0.9 wt.% Si and 2.3 wt.% Fe with immersion times in the molten aluminium alloy bath of 3, 5 and 10 seconds. After exiting the coating bath the layers thickness was controlled at 25 μm by wiping with nitrogen. Next the steels were cooled down with forced nitrogen. Bath and strip entry temperature were as before. The thickness of the alloy layer thicknesses are given in table 2. The increase of alloy layer thickness at longer dipping times, i.e. lower line speeds, is clearly illustrated.

Table 2: thickness measurements (0.9 wt.% Si)

Sample ID	v	vi	vii
Dipping time[s]	3	5	10
Alloy layer thickness [μm]	13	15	18

[0065] By changing the dipping time the fabrication window of Ex.3 (figure 4) can be enlarged. Combining data of both examples resulted in a production window of fully alloyed coatings as shown in figure 5.

Example 4

[0066] Hot-forming steel (1.5 mm) coated with an aluminium alloy coating layer with 1.9 wt.% Si and 2.3 wt.% Fe with immersion times in the molten aluminium alloy bath of 3, 5 and 10 seconds. After exiting the coating bath the layers thickness was controlled at 25 μm by wiping with nitrogen. Next the steels were cooled down with forced nitrogen. Bath and strip entry temperature were as before. The thickness of the alloy layer thicknesses are given in table 3. The increase of alloy layer thickness at longer dipping times, i.e. lower line speeds, is clearly illustrated.

Table 3: thickness measurements in μm (1.9 wt.% Si)

pre-diffusion annealing time (s)	Dipping time 3 s	Dipping time 5 s	Dipping time 10 s
0	9	10	12
10	14	16	18
20	20	21	23

Example 5

[0067] The layer structure of sample A after pre-diffusion annealing (for 20 s at 700 °C, according to the invention) and B as hot-dipped (so no pre-diffusion annealing, which is the prior art situation) are compared in figure 6 (SEM cross section images). Sample A shows a fully-alloyed aluminium-iron-silicon coating layer, whereas the coating on sample B is a thin alloy layer at the steel interface, while the top part of the coating is not alloyed and has an average composition equal to the coating bath composition. As a consequence the top layer starts to melt at a temperature of about 575°C. The steels in this condition were heat treated in a radiation furnace set at 900°C with a thermocouple welded to the strips to record the heat-up rates. The heating curves of both steels (see figure 7) clearly illustrate the faster heat up rate of the pre-alloyed sample A compared to comparative sample B. Especially at lower temperatures the heating rate is improved by pre-alloying as during this stage the reflection of radiation is markedly reduced by the dull appearance of the pre-alloyed coating. Faster heating rate enables higher throughput with the same furnace. Alternatively shorter furnaces can be used requiring a smaller foot print and lower investment. Samples taken at temperatures of 700, 800, 850°C during the heating of sample B revealed that only at after reaching a temperature of 850°C a fully alloyed layer is obtained. This means that the outer part of the coating layer remained liquid over the entire temperature range of 575 to 850°C. During the time the coating is molten roll build up during contact with the furnace rolls occurs. Roll build up not only leads to increased maintenance and furnace down time but is also a source of product damage. Sample A with the non-melting pre-alloyed coating is not causing any roll build up at any temperature.

Example 6.

[0068] Sample A (1.1 wt.% Si) and sample B sheets (9.6 wt.% Si) were heated in a radiation furnace set at 900 °C. At various time intervals samples were taken out of the furnace for examination in cross section to determine the growth rate of the diffusion layer, which is a ductile layer having aluminium in solid solution. A thickness of the diffusion layer of 10 μm is considered to be a proper diffusion zone with good crack propagation resistance. The investigation showed that a thickness of 10 μm was achieved for sample A after 170 seconds at 900 °C and for sample B after 400s. With sample A (according to the invention) a furnace time saving of more than 50% is achieved compared to sample B (prior art). The relevant images are shown as figure 8A and B.

Claims

1. Method for producing a steel strip coated on one or both sides with an aluminium alloy coating layer in a continuous hot-dip coating and a subsequent pre-diffusion annealing process, said process comprising a hot-dip coating stage in which the steel strip is passed with a velocity v through a bath of a molten aluminium alloy to apply an aluminium alloy coating layer to one or both sides of the steel strip, and a pre-diffusion annealing stage, wherein

- the thickness of the applied aluminium alloy coating layer on the one or both sides of the steel strip is between

5 and 40 μm and wherein the aluminium alloy coating layer comprises 0.4 to 4.0 weight% silicon, and wherein
 • the aluminium alloy coated steel strip enters the pre-diffusion annealing stage while at least the outer layer of the aluminium alloy coating layer or layers is above its liquidus temperature, and the strip is annealed at an annealing temperature of at least 600 and at most 800 °C for at most 40 seconds to promote the diffusion of iron from the steel strip or sheet into the aluminium alloy coating layer or layers to form a substantially fully-alloyed aluminium-iron-silicon coating layer or layers;

followed by cooling the pre-diffusion annealed coated steel strip to ambient temperatures.

2. Method according to claim 1, wherein the molten aluminium alloy in the bath contains between 0.4 and 4.0 wt.% silicon, and wherein the molten aluminium alloy has a temperature of between 630 and 750 °C, preferably of at least 660 °C and/or at most 700 °C.

3. Method according to claim 2, wherein

- the temperature of the steel strip entering the molten aluminium alloy bath is between 550 and 750 °C, preferably at least 660 °C and/or at most 700 °C, and/or wherein
- the velocity v is between 0.6 m/s and 4.2 m/s, preferably of at most 3.0 m/s, more preferably of at least 1.0 and/or at most 2.0 m/s.

4. Method according to any one of the preceding claims, wherein the fully-alloyed aluminium-iron-silicon coating layer contains at least 0.5 wt.% Si and/or at most 3.5 wt.% Si.

5. Method according to any one of the preceding claims, wherein the thickness of the fully-alloyed aluminium-iron-silicon coating layer is at least 8 and/or at most 40 μm , preferably at least 10 μm , more preferably at least 12 μm , preferably at most 30, more preferably at most 25 μm , and even more preferably at most 20 μm .

6. Method according to any one of the preceding claims wherein the thickness d (in μm) of the fully-alloyed aluminium-iron-silicon coating layer in dependence of the silicon content (in wt.%) of the fully-alloyed aluminium-iron-silicon coating layer is enclosed in the Si- d space by the equations (1), (2) and (3):

- (1) $d \geq -1.39 \cdot \text{Si} + 12.6$ and
- (2) $d \leq -9.17 \cdot \text{Si} + 43.7$ and
- (3) $\text{Si} \geq 0.4 \%$.

7. Method according to any one of the preceding claims, wherein the immersion time of the steel strip in the molten aluminium alloy bath in the hot-dip coating stage is between 2 and 10 seconds, preferably at least 3 and/or at most 6 seconds..

8. Method according to any one of the preceding claims, wherein the pre-diffusion is performed immediately prior to a hot-forming operation by annealing the strip prior to blanking, or by annealing sheets cut from the strip, or by annealing blank cut from the strip or sheet, preferably wherein the annealing is performed induction heating, optionally followed by radiation heating.

9. Steel strip having a composition comprising (in wt.%):

C: 0.01 - 0.5	P: ≤ 0.1	Nb: ≤ 0.3
Mn: 0.4 - 4.0	S: ≤ 0.05	V: ≤ 0.5
N: $\leq 0.001 - 0.030$	B: ≤ 0.08	Ca: ≤ 0.05
Si: ≤ 3.0	O: ≤ 0.008	Ni: ≤ 2.0
Cr: ≤ 4.0	Ti: ≤ 0.3	Cu: ≤ 2.0
Al: ≤ 3.0	Mo: ≤ 1.0	W: ≤ 0.5

the remainder being iron and unavoidable impurities, coated on one or both sides with a fully alloyed aluminium-iron-silicon coated steel strip obtainable by the process according to any one of the preceding claims, and wherein the composition of the fully-alloyed aluminium-iron-silicon coating layer or layers is 50-55 wt.% Al, 43-48 wt.% Fe, 0.4-4 wt.% Si and inevitable elements and impurities consistent with the said process.

10. Coated steel strip according to any claim 9 wherein the alloy layer on the coated steel strip or sheet prior to the pre-diffusion annealing step, comprises at least three distinct layers, from the steel strip or sheet surface outwards:

- intermetallic layer 1, consisting of Fe_2Al_5 with silicon in solid solution
- intermetallic layer 2, consisting of FeAl_3 with silicon in solid solution
- outer layer having the composition of the molten aluminium alloy bath.

11. Coated steel strip according to claim 9 or 10 wherein the fully-alloyed aluminium-iron-silicon coating layer or layers contain between 0 and 10 area.% of τ -phase, and wherein the τ -phase, if present, is dispersed in the coating layer.

12. Use of the fully-alloyed aluminium-iron-silicon coated steel strip obtainable by the process according to one of claims 1 to 8, or the coated steel strip according to claim 9, 10 or 11, to produce a hot-formed product in a hot-forming process comprising the steps of:

- cutting the coated steel strip to obtain a blank;
- heating the blanks to above the Ac_1 temperature of the steel, optionally to above the Ac_3 temperature of the steel;
- hot-forming the blank into a product;
- cooling the hot-formed product,

13. Use of the fully-alloyed aluminium-iron-silicon coating coated steel strip in a hot-forming process according to claim 12 wherein the heating of the blanks from ambient temperature to above the Ac_1 temperature of the steel, optionally to above the Ac_3 temperature of the steel, is performed by means of induction heating, contact heating or resistance heating.

14. Use of the product according to claim 12 or 13 as a part in a vehicle, e.g. as a body part.

Patentansprüche

1. Verfahren zum Herstellen eines Stahlbands, das an einer oder beiden Seiten mit einer Aluminiumlegierungsbeschichtungsschicht beschichtet ist, in einem kontinuierlichen Schmelztauchbeschichtungs- und einem anschließenden Vordiffusionsglühprozess, wobei der Prozess eine Schmelztauchbeschichtungsstufe, in der das Stahlband mit einer Geschwindigkeit v durch ein Bad einer geschmolzenen Aluminiumlegierung geführt wird, um eine Aluminiumlegierungsbeschichtungsschicht auf eine oder beide Seiten des Stahlbands aufzutragen, und eine Vordiffusionsglühstufe umfasst, wobei

- die Dicke der aufgetragenen Aluminiumlegierungsbeschichtungsschicht auf der einen oder beiden Seiten des Stahlbands zwischen 5 und 40 μm ist und wobei die Aluminiumlegierungsbeschichtungsschicht 0,4 bis 4,0 Gew.-% Silizium umfasst, und wobei
- das mit Aluminiumlegierung beschichtete Stahlband in die Vordiffusionsglühstufe eintritt, während zumindest die äußere Schicht der Aluminiumlegierungsbeschichtungsschicht oder -schichten über ihrer Liquidustemperatur ist, und das Band bei einer Glühtemperatur von zumindest 600 und höchstens 800 °C für höchstens 40 Sekunden geglüht wird, um die Diffusion von Eisen aus dem Stahlband oder -blech in die Aluminiumlegierungsbeschichtungsschicht oder -schichten zu fördern, um eine im Wesentlichen vollständig legierte Aluminium-Eisen-Silizium-Beschichtungsschicht oder -schichten zu bilden;

gefolgt von Abkühlen des vordiffusionsgeglühten beschichteten Stahlbands auf Umgebungstemperaturen.

2. Verfahren nach Anspruch 1, wobei die geschmolzene Aluminiumlegierung in dem Bad zwischen 0,4 und 4,0 Gew.-% Silizium enthält und wobei die geschmolzene Aluminiumlegierung eine Temperatur zwischen 630 und 750 °C, bevorzugt von zumindest 660 °C und/oder höchstens 700 °C aufweist.

3. Verfahren nach Anspruch 2, wobei

- die Temperatur des Stahlbands, das in das geschmolzene Aluminiumlegierungsbad eintritt, zwischen 550 und 750 °C, bevorzugt zumindest 660 °C und/oder höchstens 700 °C ist, und/oder wobei
- die Geschwindigkeit v zwischen 0,6 m/s und 4,2 m/s, bevorzugt bei höchstens 3,0 m/s, bevorzugter bei zumindest 1,0 und/oder höchstens 2,0 m/s ist.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei die vollständig legierte Aluminium-Eisen-Silizium-Beschichtungsschicht zumindest 0,5 Gew.-% Si und/oder höchstens 3,5 Gew.-% Si enthält.

5. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Dicke der vollständig legierten Aluminium-Eisen-Silizium-Beschichtungsschicht zumindest 8 und/oder höchstens 40 μm , bevorzugt zumindest 10 μm , bevorzugter zumindest 12 μm , bevorzugter höchstens 30, bevorzugter höchstens 25 μm und noch bevorzugter höchstens 20 μm ist.

6. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Dicke d (in μm) der vollständig legierten Aluminium-Eisen-Silizium-Beschichtungsschicht in Abhängigkeit von dem Siliziumgehalt (in Gew.-%) der vollständig legierten Aluminium-Eisen-Silizium-Beschichtungsschicht in den Si-d-Raum durch die Gleichungen (1), (2) und (3) eingeschlossen ist:

$$(1) d \geq -1,39 \cdot \text{Si} + 12,6 \text{ und}$$

$$(2) d \leq -9,17 \cdot \text{Si} + 43,7 \text{ und}$$

$$(3) \text{Si} \geq 0,4 \text{ \%}.$$

7. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Eintauchzeit des Stahlbands in das geschmolzene Aluminiumlegierungsbad in der Schmelztauchbeschichtungsstufe zwischen 2 und 10 Sekunden, bevorzugt zumindest 3 und/oder höchstens 6 Sekunden ist.

8. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Vordiffusion unmittelbar vor einem Warmumformvorgang durch Glühen des Bands vor dem Stanzen oder durch Glühen von Blechen, die aus dem Band geschnitten sind, oder durch Glühen von Rohling, der aus dem Band oder Blech geschnitten ist, durchgeführt wird, wobei bevorzugt das Glühen Induktionserwärmung durchgeführt wird, optional gefolgt von Strahlungserwärmung.

9. Stahlband mit einer Zusammensetzung umfassend (in Gew.-%):

C: 0,01 - 0,5	P: $\leq 0,1$	Nb: $\leq 0,3$
Mn: 0,4 - 4,0	S: $\leq 0,05$	V: $\leq 0,5$
N: $\leq 0,001 - 0,030$	B: $\leq 0,08$	Ca: $\leq 0,05$
Si: $\leq 3,0$	O: $\leq 0,008$	Ni: $\leq 2,0$
Cr: $\leq 4,0$	Ti: $\leq 0,3$	Cu: $\leq 2,0$
Al: $\leq 3,0$	Mo: $\leq 1,0$	W: $\leq 0,5$

wobei der Rest Eisen und unvermeidbare Verunreinigungen ist, beschichtet auf einer oder beiden Seiten mit einem vollständig legierten Aluminium-Eisen-Silizium-beschichteten Stahlband, das durch den Prozess nach einem der vorhergehenden Ansprüche erhältlich ist, und wobei die Zusammensetzung der vollständig legierten Aluminium-Eisen-Silizium-Beschichtungsschicht oder -schichten 50-55 Gew.-% Al, 43-48 Gew.-% Fe, 0,4-4 Gew.-% Si und unvermeidliche Elemente und Verunreinigungen ist, die mit dem Prozess übereinstimmen.

10. Beschichtetes Stahlband nach Anspruch 9, wobei die Legierungsschicht auf dem beschichteten Stahlband oder -blech vor dem Vordiffusionsglühschritt zumindest drei unterschiedliche Schichten von der Oberfläche des Stahlbands oder -blechs nach außen umfasst:

- intermetallische Schicht 1, bestehend aus Fe_2Al_5 mit Silizium in fester Lösung
- intermetallische Schicht 2, bestehend aus FeAl_3 mit Silizium in fester Lösung
- äußere Schicht mit der Zusammensetzung des geschmolzenen Aluminiumlegierungsbad.

11. Beschichtetes Stahlband nach Anspruch 9 oder 10, wobei die vollständig legierte Aluminium-Eisen-Silizium-Beschichtungsschicht oder -schichten zwischen 0 und 10 Flächenprozent τ -Phase enthalten und wobei die τ -Phase, falls vorhanden, in der Beschichtungsschicht dispergiert ist.

12. Verwendung des vollständig legierten Aluminium-Eisen-Silizium-beschichteten Stahlbands, das durch den Prozess nach einem der Ansprüche 1 bis 8 erhältlich ist, oder des beschichteten Stahlbands nach Anspruch 9, 10 oder 11, um ein warmumgeformtes Produkt in einem Warmumformprozess herzustellen, der die folgenden Schritte umfasst:

- Schneiden des beschichteten Stahlstreifens, um einen Rohling zu erhalten;
- Erhitzen der Rohlinge über die Ac_1 -Temperatur des Stahls, optional über die Ac_3 -Temperatur des Stahls;
- Warmumformen des Rohlings zu einem Produkt;
- Abkühlen des warmumgeformten Produkts.

13. Verwendung des mit vollständig legierter Aluminium-Eisen-Silizium-Beschichtung beschichteten Stahlbands in einem Warmumformprozess nach Anspruch 12, wobei das Erhitzen der Rohlinge von Umgebungstemperatur auf über die Ac_1 -Temperatur des Stahls, optional auf über die Ac_3 -Temperatur des Stahls, mittels Induktionserwärmung, Kontakterwärmung oder Widerstandserwärmung durchgeführt wird.

14. Verwendung des Produkts nach Anspruch 12 oder 13 als Teil in einem Fahrzeug, z. B. als Karosserieteil.

Revendications

1. Procédé permettant la production d'une bande d'acier revêtue, sur une ou les deux faces, d'une couche de revêtement d'alliage d'aluminium dans un revêtement par immersion à chaud continu et un processus ultérieur de recuit par pré-diffusion, ledit processus comprenant une étape de revêtement par immersion à chaud dans lequel la bande d'acier est passée avec une vitesse v à travers un bain d'un alliage d'aluminium fondu pour appliquer une couche de revêtement d'alliage d'aluminium sur un ou les deux côtés de la bande d'acier, et une étape de recuit par pré-diffusion,

- ladite épaisseur de la couche de revêtement d'alliage d'aluminium appliquée sur le ou les deux côtés de la bande d'acier étant comprise entre 5 et 40 μm et ladite couche de revêtement d'alliage d'aluminium comprenant 0,4 à 4,0 % en poids de silicium, et

- ladite bande d'acier revêtue d'alliage d'aluminium entrant dans l'étape de recuit par pré-diffusion pendant qu'au moins la couche externe de la couche ou des couches de revêtement d'alliage d'aluminium est au-dessus de sa température de liquidus, et ladite bande étant recuite à une température de recuit supérieure ou égale à 600 et inférieure ou égale à 800°C pendant au plus 40 secondes pour favoriser la diffusion du fer à partir de la bande ou tôle d'acier jusque dans la couche ou les couches de revêtement d'alliage d'aluminium pour former une couche ou des couches de revêtement d'aluminium-fer-silicium sensiblement complètement alliées ;

suivi du refroidissement de la bande d'acier revêtue recuite par pré-diffusion à température ambiante.

2. Procédé selon la revendication 1, ledit alliage d'aluminium fondu dans le bain contenant entre 0,4 et 4,0 % en poids de silicium, et ledit alliage d'aluminium fondu comportant une température comprise entre 630 et 750°C, de préférence supérieure ou égale à 660°C et/ou inférieure ou égale à 700°C.

3. Procédé selon la revendication 2,

- ladite température de la bande d'acier entrant dans le bain d'alliage d'aluminium fondu étant comprise entre 550 et 750°C, de préférence supérieure ou égale à 660°C et/ou inférieure ou égale à 700°C, et/ou

- ladite vitesse v étant comprise entre 0,6 m/s et 4,2 m/s, de préférence inférieure ou égale à 3,0 m/s, mieux encore supérieure ou égale à 1,0 et/ou inférieure ou égale à 2,0 m/s.

4. Procédé selon l'une quelconque des revendications précédentes, ladite couche de revêtement d'aluminium-fer-silicium complètement alliée contenant au moins 0,5 % en poids de Si et/ou inférieure ou égale à 3,5 % en poids de Si.

5. Procédé selon l'une quelconque des revendications précédentes, ladite épaisseur de la couche de revêtement d'aluminium-fer-silicium complètement alliée étant supérieure ou égale à 8 et/ou inférieure ou égale à 40 μm , de préférence supérieure ou égale à 10 μm , mieux encore supérieure ou égale à 12 μm , de préférence inférieure ou égale à 30, mieux encore inférieure ou égale à 25 μm , et idéalement inférieure ou égale à 20 μm .

6. Procédé selon l'une quelconque des revendications précédentes, ladite épaisseur d (en μm) de la couche de revêtement d'aluminium-fer-silicium complètement alliée en fonction de la teneur en silicium (en % en poids) de la couche de revêtement d'aluminium-fer-silicium complètement alliée étant enfermée dans l'espace Si- d par les équations (1), (2) et (3) :

(1) $d \geq -1,39 \cdot Si + 12,6$ et

(2) $d \leq -9,17 \cdot Si + 43,7$ et

(3) $Si \geq 0,4 \%$.

7. Procédé selon l'une quelconque des revendications précédentes, ledit temps d'immersion de la bande d'acier dans le bain d'alliage d'aluminium fondu à l'étape de revêtement par immersion à chaud étant compris entre 2 et 10 secondes, de préférence supérieur ou égal à 3 et/ou inférieur ou égal à 6 secondes.

8. Procédé selon l'une quelconque des revendications précédentes, ladite pré-diffusion étant réalisée immédiatement avant une opération de formage à chaud par recuit de la bande avant découpage, ou par recuit de tôles découpées dans la bande, ou par recuit d'ébauche découpée dans la bande ou la tôle, de préférence ledit recuit étant réalisé par chauffage par induction, éventuellement suivi d'un chauffage par rayonnement.

9. Bande d'acier comportant une composition comprenant (en % en poids) :

C : 0,01-0,5	P : $\leq 0,1$	Nb : $\leq 0,3$
Mn : 0,4 - 4,0	S : $\leq 0,05$	V : $\leq 0,5$
N : $\leq 0,001 - 0,030$	B : $\leq 0,08$	Ca : $\leq 0,05$
Si : $\leq 3,0$	O : $\leq 0,008$	Ni : $\leq 2,0$
Cr : $\leq 4,0$	Ti : $\leq 0,3$	Cu : $\leq 2,0$
Al : $\leq 3,0$	Mo : $\leq 1,0$	W : $\leq 0,5$

le reste étant du fer et des impuretés inévitables, revêtues sur une ou les deux faces d'une bande d'acier revêtue d'aluminium-fer-silicium complètement alliée pouvant être obtenue par le processus selon l'une quelconque des revendications précédentes, et ladite composition de la couche ou des couches de revêtement d'aluminium-fer-silicium complètement alliées étant de 50-55 % en poids d'Al, 43-48 % en poids de Fe, 0,4-4 % en poids de Si et d'éléments et impuretés inévitables conformes audit processus.

10. Bande d'acier revêtue selon une quelconque revendication 9, ladite couche d'alliage sur la bande ou tôle d'acier revêtue avant l'étape de recuit par pré-diffusion comprenant au moins trois couches distinctes, en allant de la surface de bande ou de tôle d'acier vers l'extérieur :

- couche intermétallique 1, constituée de Fe_2Al_5 avec du silicium en solution solide
- couche intermétallique 2, constituée de $FeAl_3$ avec du silicium en solution solide
- couche externe comportant la composition du bain d'alliage d'aluminium fondu.

11. Bande d'acier revêtue selon la revendication 9 ou 10, ladite couche ou lesdites couches de revêtement d'aluminium-fer-silicium complètement alliées contenant entre 0 et 10 % en surface de phase τ , et ladite phase τ , si elle est présente, étant dispersée dans la couche de revêtement.

12. Utilisation de la bande d'acier revêtue d'aluminium-fer-silicium complètement alliée pouvant être obtenue par le processus selon l'une des revendications 1 à 8, ou de la bande d'acier revêtue selon la revendication 9, 10 ou 11, pour produire un produit formé à chaud dans un processus de formage à chaud comprenant les étapes de :

- découpe de la bande d'acier revêtue pour obtenir une ébauche ;
- chauffage des ébauches au-dessus de la température Ac_1 de l'acier, éventuellement au-dessus de la température Ac_3 de l'acier ;
- formage à chaud de l'ébauche en un produit ;
- refroidissement du produit formé à chaud.

13. Utilisation de la bande d'acier revêtue d'un revêtement d'aluminium-fer-silicium complètement alliée dans un processus de formage à chaud selon la revendication 12, ledit chauffage des ébauches à partir de la température ambiante jusqu'à une température au-dessus de la température Aci de l'acier, éventuellement au-dessus de la température Ac_3 de l'acier, étant réalisée au moyen d'un chauffage par induction, d'un chauffage par contact ou d'un chauffage par résistance.

14. Utilisation du produit selon la revendication 12 ou 13 en tant que pièce dans un véhicule, par exemple en tant que

partie de carrosserie.

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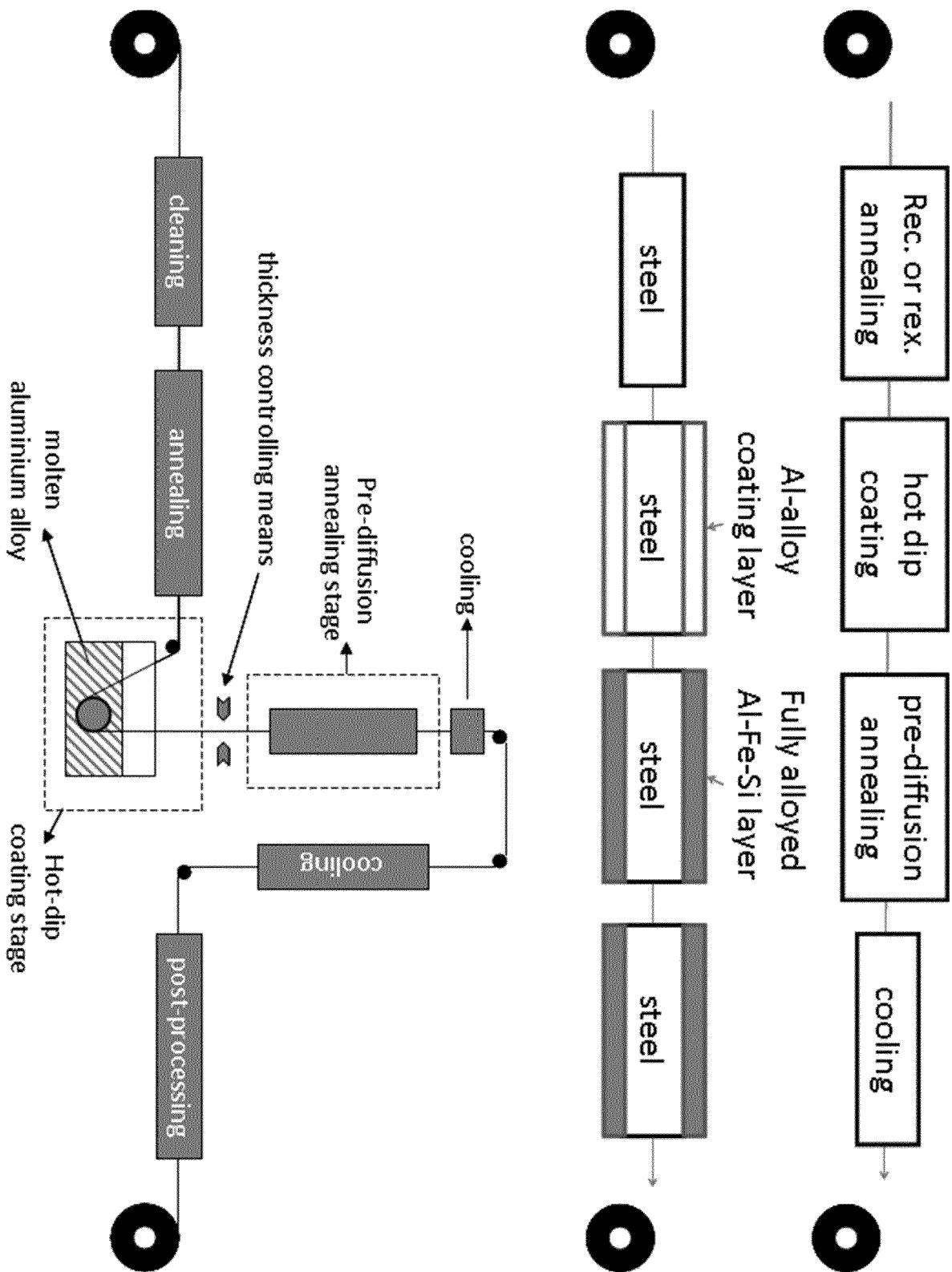


FIGURE 1

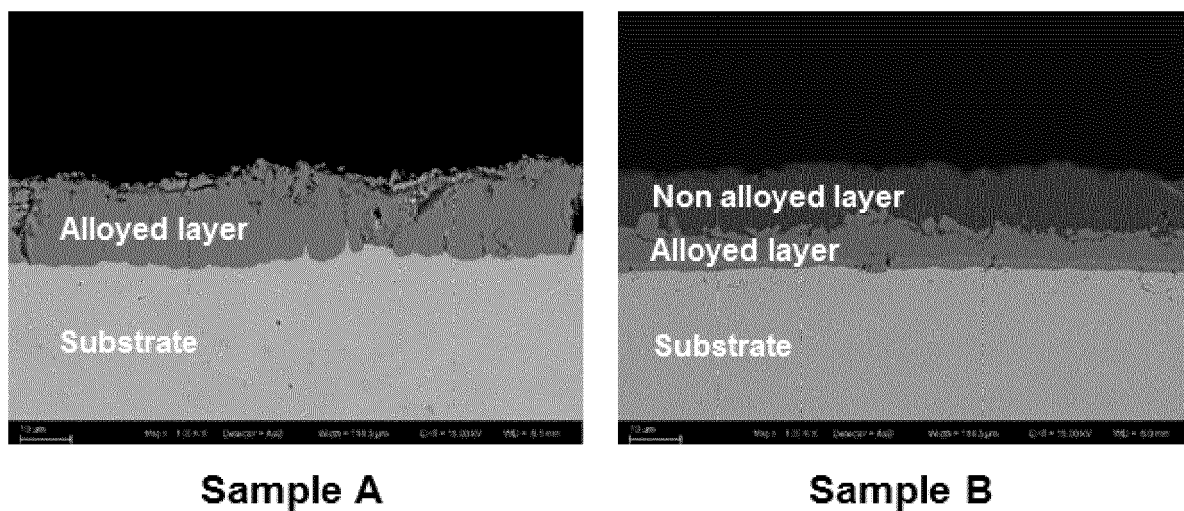


FIGURE 2

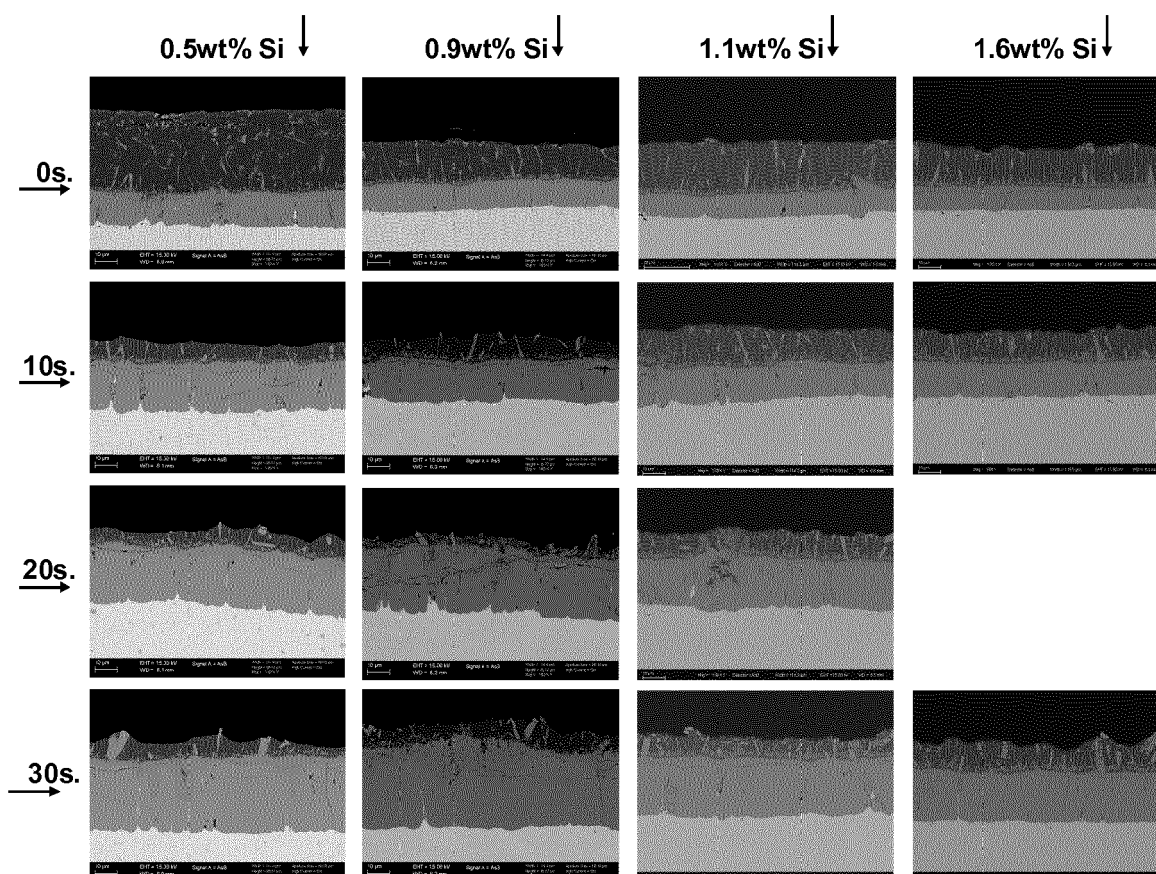


FIGURE 3

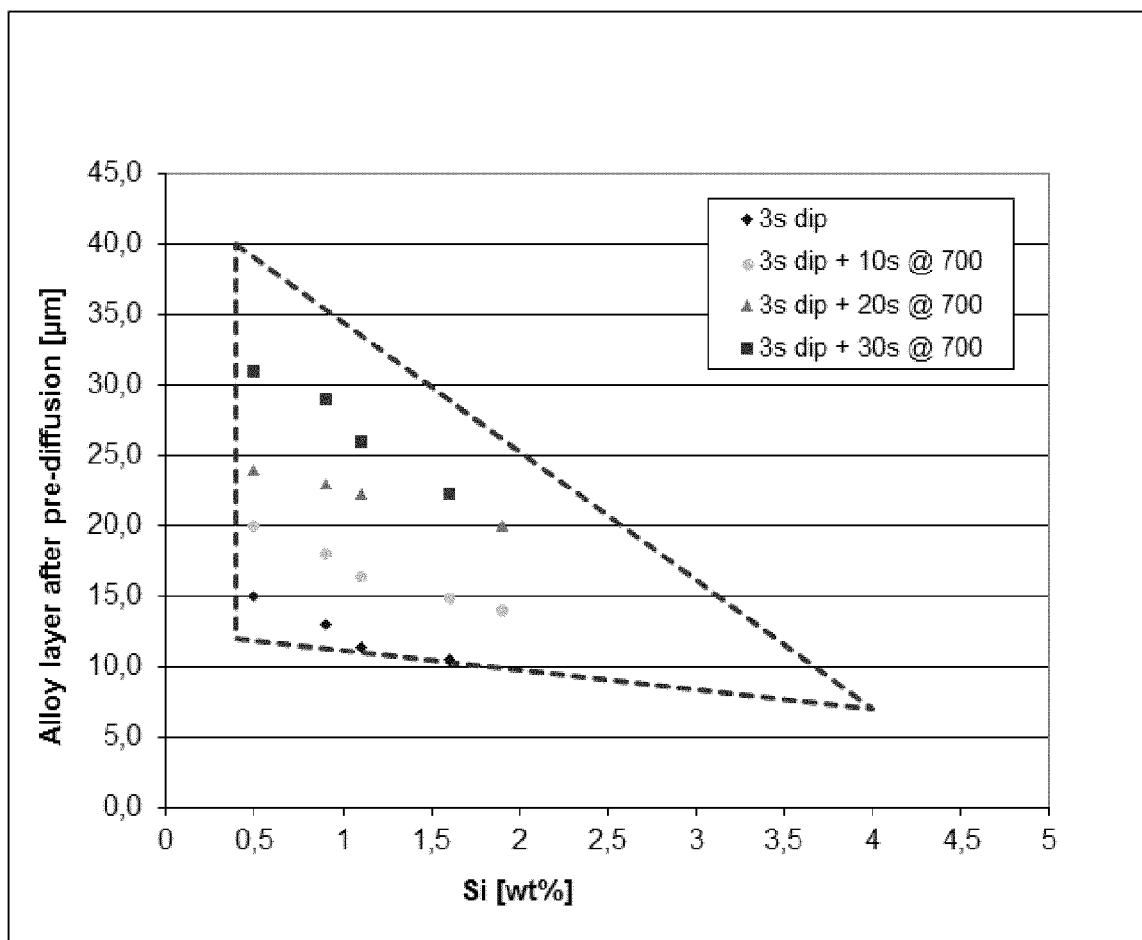


FIGURE 4

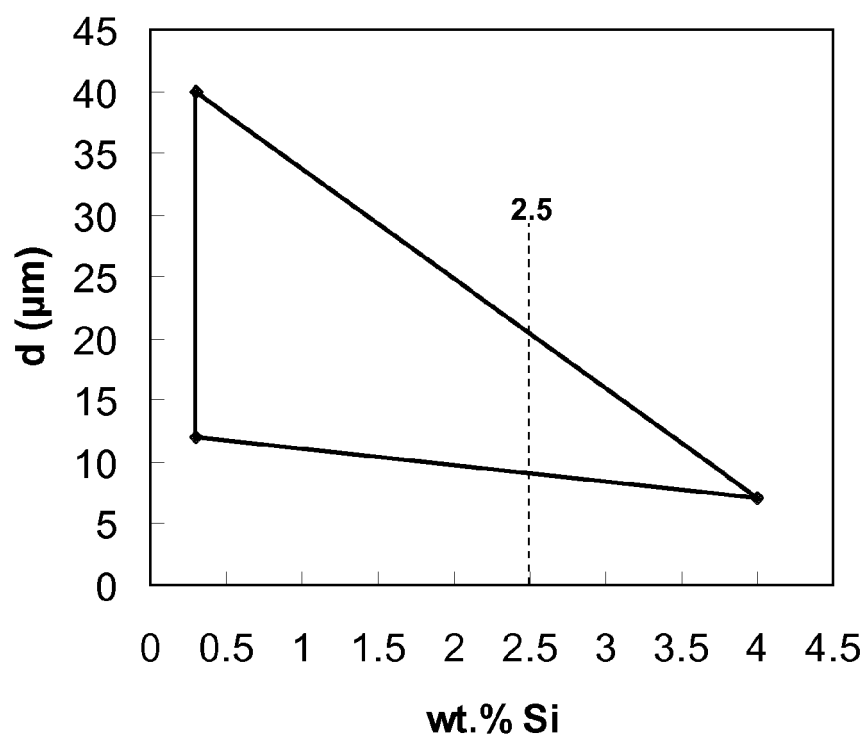


FIGURE 5

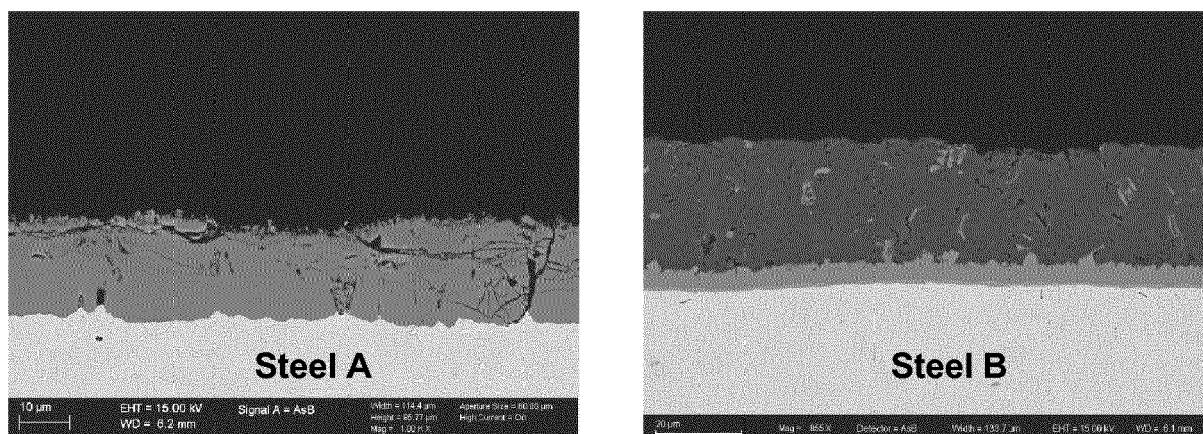


FIGURE 6

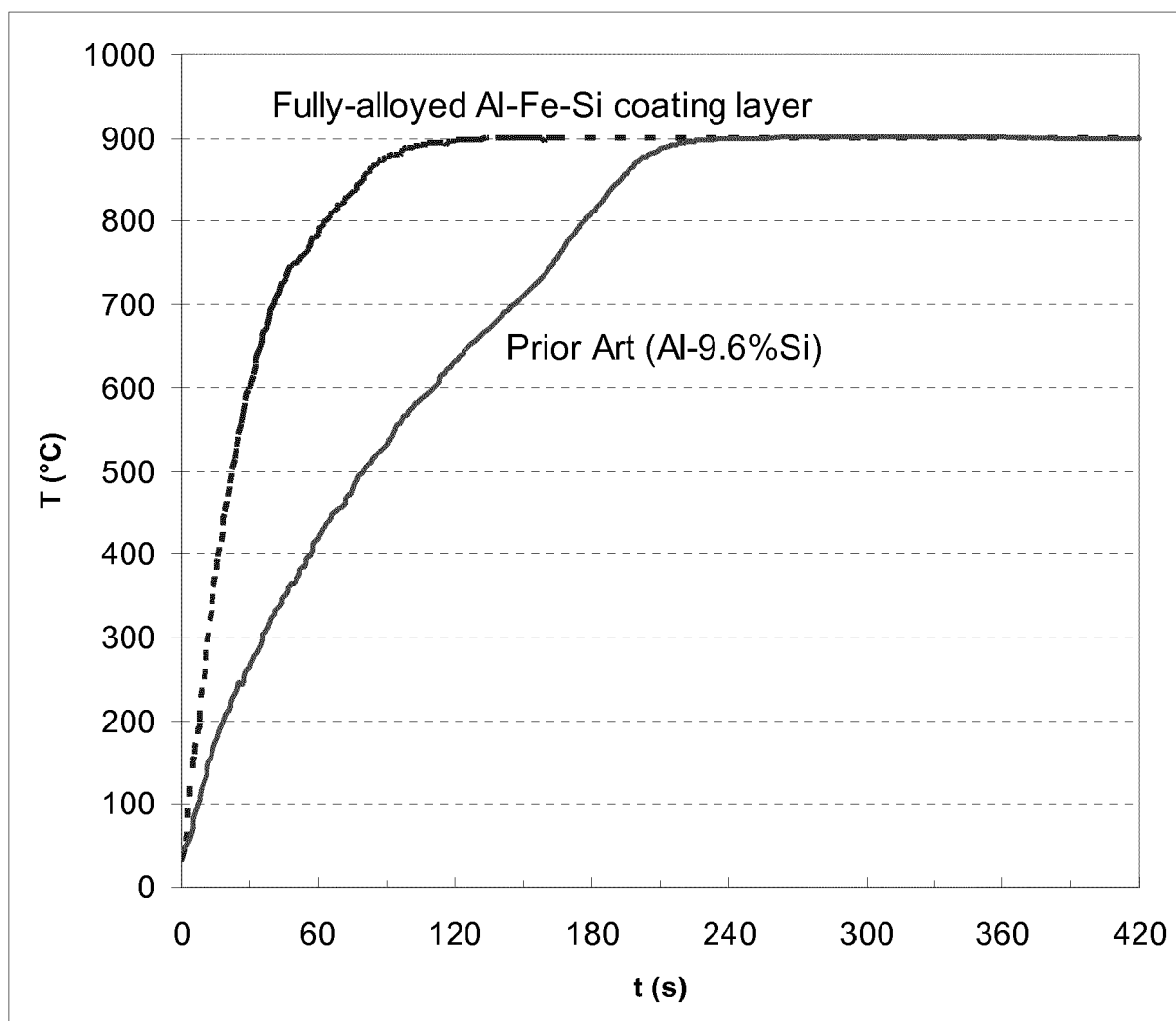


FIGURE 7

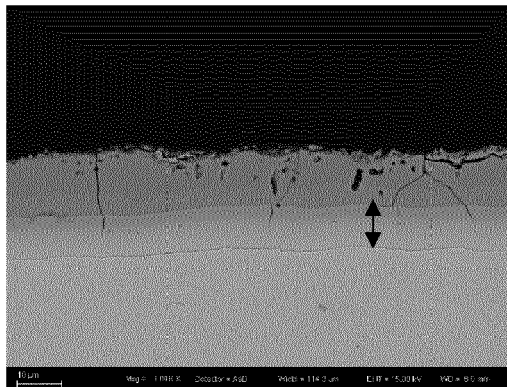
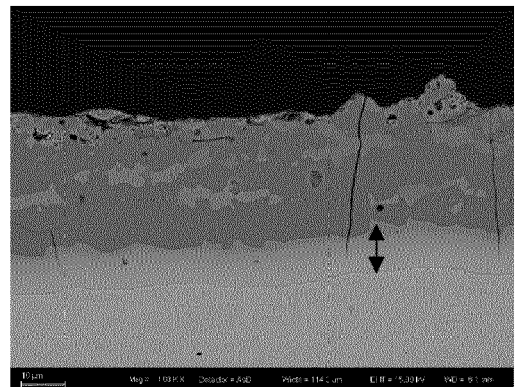
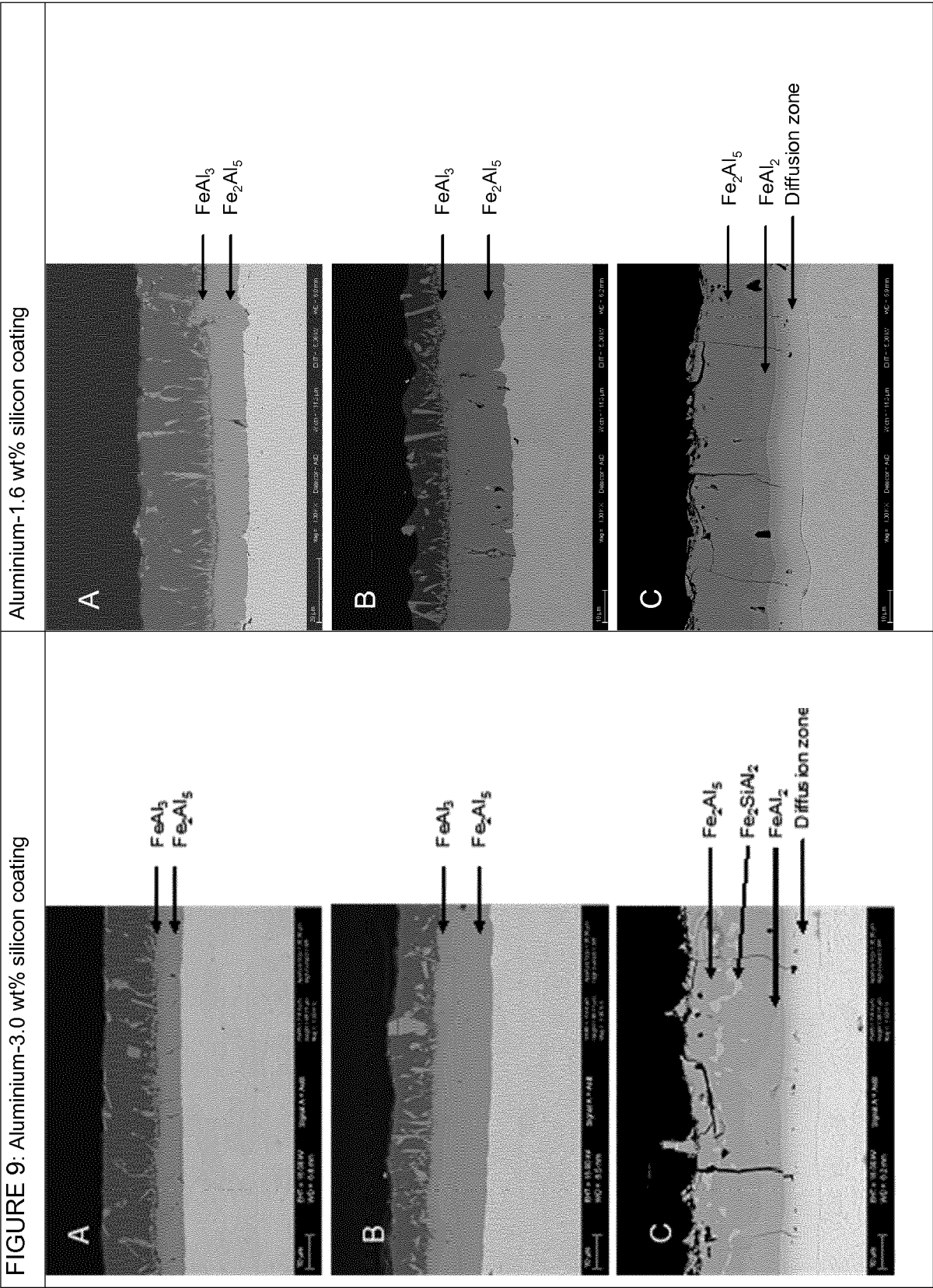


FIGURE 8 - A. Sample A



B. Sample B



REFERENCES CITED IN THE DESCRIPTION

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