The present invention is related to a steel composition intended to be used in a process including a cold rolling step, for the production of uncoated, electro-galvanized or hot dip galvanized TRIP steel products, the composition being characterized by a specific addition of phosphorus. The latter is added in order to reach the desired mechanical properties (high tensile strength in combination with high elongation) while keeping a good weldability by sufficiently reducing the carbon content. The invention is further related to a process for producing a steel product, and to the steel product obtained, said product having the composition of the invention.
STEEL COMPOSITION FOR THE PRODUCTION OF COLD ROLLED MULTIPHASE STEEL PRODUCTS

FIELD OF THE INVENTION

[0001] The present invention is related to a steel composition comprising phosphor, to be used for the production of TRIP steel products. The invention is equally related to the process of production of said products, and to the end products themselves.

STATE OF THE ART

[0002] In the automotive industry there is a need for weight reduction, which implies the use of higher strength materials in order to be able to decrease the thickness of the parts without giving up safety and functional requirements. Ultra high strength steel (UHSS) sheet products and in particular TRIP steel products, showing a remarkable combination of high strength and good formability, can provide the solution for this problem. Additionally, an increased corrosion resistance of these steel sheet products by means of electro or hot dip galvanising, is frequently asked for.

[0003] Several documents are describing such UHSS products. EP-A-1096029 is related to the production of a tempered martensite TRIP steel, whose chemical composition is silicon-manganese based and contains (in wt %) 0.05-0.20% C, 0.3-1.8% Si and 1.0-3.0% Mn as well as one or more of the following additions (in wt %): 0.05-1% Cr+Mo, ≤0.003% B, 0.01-0.1% Ti+Nb+V and ≤0.01% Ca+REM. The cold rolling production process consists of three consecutive annealing steps. In the first step, the sheet is completely austenised during at least 5 seconds and subsequently rapidly cooled (>105 °C/s) below the Ms (Martensite start) temperature in order to produce lath martensite. The second and third step are combined in a continuous annealing or galvanising line and consist of reheating the sheet in the intercritical region (Ac1 < T < Ac3) during 5 to 120 seconds, cooling (>5 °C/s) to 500 °C or lower and then subjecting the sheet to a galvanising or galvannealing treatment. There are two main drawbacks associated with this invention. The first one being the additional annealing step that is required to produce the lath martensite starting micro-structure. This extra process step will not only increase the total processing cost, but it will also complicate logistics as well as weldability at the entrance of the continuous annealing or hot dip galvanising line. Cracks that are initiated in the weld or heat affected zone, will easily propagate into the hard and brittle martensite structure, leading to a high risk on complete rupture of the weld between two coils. The second major drawback is related to the rather high Si content in these steels. From about 0.5% Si on, these high Si contents are well known to provoke problems as to surface quality because of the presence of Si-oxides which after pickling create a surface with irregular and very high roughness. Moreover, in view of corrosion protection, hot dip galvanising of such a high Si-containing substrate in general leads to insufficient surface appearance for automotive applications, with moreover a very high risk on the presence of bare spots on the surface.

[0004] EP-A-0922782 also describes the production of a cold rolled Si—Mn based TRIP steel which contains (in wt %) 0.05-0.40% C, 1.0-3.0% Si, 0.6-3.0% Mn, 0.02-1.5% Cr, 0.01-0.20% P and 0.01-0.3% Al. As opposed to the previous invention, this product does not require the use of an additional annealing step. Cr is added to the analysis in order to retard the bainite formation and promote acicular ferrite and martensite formation as it is thought by the inventors that bainite is detrimental to the crushing behaviour in Si—Mn based TRIP steels. P is added to avoid pearlite formation and to increase the strength of the ferritic phase. The maximal P content is limited to 0.2% because of weldability. The high Si content in this invention will however again impair hot dip galvanisability resulting in an insufficient surface appearance and a very high risk on bare spots. The occurrence of red scale which is difficult to remove, on the hot strip, due to the higher Si content, is also expected to cause processing difficulties.

[0005] EP-A-0796028 describes the production of an Al-based Dual Phase steel which contains (in wt %) 0.05-0.3% C, 0.8-3.0% Mn, 0.4-2.5% Al and 0.01-0.2% Si. Additionally the steel can contain one of the following elements (in wt %) ≤0.05% Ti, <0.8% Cr, <0.5% Mo, <0.5% Ni, <0.05% Nb and <0.08% P. After cold rolling with a reduction rate higher than 40%, the material is intercritically annealed at temperatures between 740 and 850 °C and subsequently cooled at a cooling rate of 10 to 50 K/s to the Zn-bath temperature. As compared to both previous analyses, the latter, nearly Si-free analysis, readily allows the steel to be hot dip galvanised and avoids the formation of the detrimental red scale. However, Al, as opposed to Si, does not produce a strong solid solution strengthening effect. This implies the use of rather high Al-contents in order to reach medium high strength levels (e.g. Rm ~700 MPa). These high Al levels are however known to cause stickers during continuous casting and impair weldability due to the presence of Al-oxides in the welded area. This is especially detrimental for the crash behaviour of welded structures. In order to avoid the casting problems an adapted very fine casting powder is required that could cause health problems. Steelmaking plants are therefore in general not willing to produce this kind of compositions because the workers have to carry masks and a lot of special precautions have to be taken.

[0006] EP-A-1170391 describes the production of a low carbon (<0.08 wt %), low silicon (<0.5 wt %) and low aluminium (<0.3 wt %) TRIP steel obtained by adding a nitriding step to the processing (0.03-2 wt % N). The Al and Si contents have to be kept low in order to avoid nitride precipitation and thus loss of free N. Furthermore the Si content is preferably lower than 0.2 wt % because of hot dip galvanisability. The carbon content is kept very low because of weldability and because of the fact that the presence of nitrogen in the steel also stabilises the retained austenite. This nitrogen is incorporated in the steel sheet either during or immediately after hot finish rolling, during recrystallisation annealing, during intercritical annealing or via a combination of one or more of these processes. All of them require the steel sheet to be held for 2 sec to 10 min. in an atmosphere containing not less than 2% ammonia in the temperature range 550-800 °C. It is clear that this nitriding step makes processing a lot more difficult and requires complicated technical modifications to existing installations. At the moment this process is internationally not considered to be industrially feasible. Furthermore the very low alloying content of this steel grade, does not allow to reach tensile strength levels above 650 MPa.
U.S. Pat. No. 5,470,529 deals with the production of cold rolled TRIP steels based upon a wide variety of combined Al—Si analyses. The carbon content range is set as 0.05-0.3wt %, but more preferably is 0.1-0.2wt %. The Si-content is kept below 1.0wt % in order to avoid red scale formation, but more preferably is in the range 0.2-0.9wt %. Manganese is added in 0.005 to 4.0wt %, but more preferably 0.5-2.0wt %. As compared to traditional Si—Mn TRIP compositions, part of the Si is replaced by Al for various reasons. Like Si, Al also avoids cementite precipitation during bainitic holding. This enables to use lower Si-levels and thus avoid red scale formation. Furthermore the addition of Al increases the Ar3 temperature, leading to an increased carbon concentration in the austenite phase that is formed during intercritical annealing. This in turn stabilises the retained austenite and makes the steel less susceptible to stress-induced transformation in low stress regions, leading to an improved hole expansion ratio. Therefore the Al-range is set as 0.1-2.0wt % and more preferably as 0.5-1.5wt %. However, as Al and Si are both ferrite stabilizers, their sum is limited in order to avoid over-stabilizing the retained austenite. The Al+Si content should be in the range 0.5-3.0wt % and more preferably in the range 1.5-2.5wt %. In this invention P is considered as an incidental impurity that should be limited as much as possible. The P-limit is set at 0.1wt % or less and preferably less than 0.02wt %, Cu is added to the analysis to facilitate the removal of red scale, to improve the corrosion resistance of the as rolled product and to improve the wettability by molten Zn. Therefore the Cu-range is 0.1-2.0wt % and more preferably 0.1-0.6wt %. To avoid hot shortness problems when using Cu, Ni is added as well. For economics its content is limited to 1.0wt % and preferably 0.5wt %. The following constraints also apply: Ni (wt %)> Cu (wt %)/3 when Cu>0.5wt % and Mn+Ni>0.5wt %. Cr may be added as well to stabilise the retained austenite and to further improve corrosion resistance. It is added in the range 0.5-5.0wt % and more preferably in the range 0.6-1.6wt %. To increase tensile strength further Ti, Nb and V might be added as well. Their upper limit is preferably 0.05wt % for Nb and 0.10wt % for V. Although the maximum Si-content in this invention is limited to <1wt % in order to avoid red scale formation, most of the cold rolled example steels have a Si-content in the range 0.5-1.1wt %. The latter is considered to give rise to hot dip galvanising difficulties (bad wettability by molten Zn) and a deteriorated surface appearance (bare spots). None of these example steels contained micro-alloying additions as in high Si-TRIP steels, these are known to markedly increase the hot strip hardness, leading to strongly increased cold rolling forces. The low Si (0.2-0.4wt %) example steels on the other hand showed a high yield stress (570-590 MPa) and only moderate ultimate tensile strength (≥700 MPa) and total elongation values (AS50 ≥30%). In the latter steels no P was added additionally. A large disadvantage of these compositions is the necessity of adding Cu and Ni, elements which are considered as impurities in bulk flat carbon steel production. If a steelmaking plant has to cast this, extra logistic problems with scrap recycling occur. Moreover, the use of Ni, Cu and Cr makes the alloying cost much more expensive.

EP-A-1154028 describes the manufacturing of a P-alloyed low-Al, low-Si TRIP steel, which contains (in wt %): 0.05-0.17% C, 1.35-1.80% Mn, 0.35-0.50% Si, 0.02-0.12% P, 0.05-0.50% Al, max. 0.07% Nb, max. 0.2% V, max. 0.05% Ti, max. 0.30 ppm B and 100-350 ppm N. When the carbide forming elements Ti, Nb or V are added, the carbon content is preferably 0.16wt %. The amount of residual austenite is limited to a maximum of 10%. The combination of low Si-content and rather low C-content, results in tensile strength values which are quite low (<600 MPa). When micro-alloying elements are added, the strength level is markedly improved (800MPa), but elongations drop drastically (A80 <17%). Elongation values are in all cases rather low, which can be explained by the limited addition of Al and C, rendering the retained austenite less stable.

Barbe et al have studied the influence of phosphorus additions to several TRIP compositions, ranging from pure Si-TRIP steels over combined Al—Si TRIP steels to pure Al-TRIP steels ("Effect of phosphorus on the properties of a cold rolled and intercritically annealed TRIP-aided steel", Int. Conf. on TRIP-Aided High Strength Ferrous Alloys, Ghent, Jun. 19-21, 2002). They found that the TRIP-aided steel composition which contained (in wt %) 0.24% C, 1.66% Mn, 0.6% Al, 0.4% Si and 0.073% P resulted in an excellent combination of mechanical properties (A80=28.4% and UTS=788 MPa). Lab-experiments performed by the inventors of the present invention have however shown that Al-additions as low as 0.6wt %, render the obtained mechanical properties very sensitive to process parameter variations such as line speed and overaging temperature. This can lead to a non-compatibility between different galvanising lines (with e.g. different lengths of the levelling zone around 490-460°C) or even to strongly thickness-dependent mechanical properties. This can be explained by the insufficient stabilisation of the retained austenite and the shift of the optimum overaging time to noticeably longer times due to the too low Al-additions.

O. Yakubovsky et al have studied the stress-strain behaviour and bake hardening behaviour of several TRIP compositions, ranging from pure Si-TRIP steels over combined Al—Si TRIP steels to pure Al-TRIP steels ("Stress-strain behaviour and bake hardening of TRIP and TRIP-aided multiphase steels", Int. Conf. on TRIP-Aided High Strength Ferrous Alloys, Ghent, Jun. 19-21, 2002). In all cases the carbon content was limited to (in wt %) 0.15% and the manganese content to 1.5%. Amongst the steels studied was also a (in wt %) 0.25-0.45% Si, 1.5-2.0% Al and 0.05-0.10% P TRIP steel. No mechanical properties were mentioned in the article for the latter composition. Based upon the tensile strength versus carbon content relationship that was established from industrial production and laboratory research by the inventors of the present invention, the proposed chemical composition is insufficiently alloyed in carbon to reach tensile strengths in the range 700-850 MPa. Furthermore the high Al-content requires the use of an adapted very fine casting powder that can give rise to health problems. Furthermore the weldability can be impaired due to the presence of Al-oxides in the welded area, a consequence of the high Al-contents.

S. Papaefthymiou et al. studied the microstructure development and mechanical behaviour of two Al—Si-TRIP steels that were uni-axially deformed to different strain levels directly after intercritical annealing ("Microstructure development and mechanical behaviour of Al-containing TRIP-Steels", Int. Conf. on TRIP-Aided High Strength Ferrous Alloys, Ghent, Jun. 19-21, 2002). As a consequence of
this special treatment and because of the non-standard sample geometry, the mechanical properties mentioned in the article are not comparable. The two Al containing TRIP steels that were studied can be divided in a low-Al and a high-Al steel. These contain (in wt %): low-Al steel: 0.19% C, 1.5% Mn, 0.26% Si, 0.086% P and 0.52% Al; high-Al steel: 0.17% C, 1.46% Mn, 0.26% Si, 0.097% P and 1.81% Al. As already explained before, the low-Al steel will suffer from mechanical properties that are very sensitive to process parameter variations such as line speed and overaging temperature. This can lead to a non-compatibility between different galvanising lines or even to strongly thickness-dependent mechanical properties. The high-Al steel on the other hand again requires the use of an adapted casting powder that can give rise to health problems. Furthermore the weldability will be impaired due to the presence of Al-oxides in the welded area.

A. Pichler et al. ("Correlation between thermal treatment, retained austenite stability and mechanical properties of low-alloyed TRIP steels", Int. Conf. on TRIP-Aided High Strength Ferrous Alloys, Ghent, Jun. 19-21, 2002) studied the influence of different annealing process parameters on the retained austenite stability and mechanical properties of a low-alloyed TRIP-steel that contained (in wt %): <0.2% C, ~1.6% Si+Al, ~1.5% Mn, <0.5% Cr+Mo, <0.04% P, <0.01% S and <0.05% Ti+Nb. As no specifications were given related to the Al/Si ratio in this analysis, it is not possible to conclude about the galvanisability. The mentioned P-content is insufficient for obtaining the desired mechanical properties (high tensile strength in combination with high elongation), whilst maintaining a good weldability (sufficient carbon content reduction).

Aims of the Invention

It is the aim of the present invention to provide a high strength, low Si, high Al, P-alloyed TRIP steel composition for the production of steel products, produced by cold rolling that can readily be galvanised.

It is a further aim to propose a process for the manufacturing of such products, and to propose finally the products themselves, wherein said composition, said process and said products do not suffer from prior art problems.

SUMMARY OF THE INVENTION

The present invention is related to a cold rolled Al—Si P-alloyed TRIP steel composition intended to be used as uncoated, electro-galvanised or hot dip galvanised material. Said composition is characterised by the following contents:

- C: between 1300 ppm and 2600 ppm
- Mn: between 10000 ppm and 22000 ppm
- Al: between 8000 ppm and 15000 ppm
- Si: between 2000 ppm and 6000 ppm
- P: between 400 and 1000 ppm
- S: maximum 120 ppm
- N: maximum 200 ppm
- Ti: maximum 1000 ppm
- Nb: maximum 1000 ppm
- V: maximum 1000 ppm
- B: maximum 10 ppm

the remainder being substantially iron and incidental impurities.

Likewise, three more specific embodiments are related to the same subranges for carbon content which are related to the strength level that is aimed at, but having furthermore the following specific chemical composition:

- Mn: between 13000 ppm and 22000 ppm
- Al: between 8000 ppm and 14000 ppm
- Si: between 2500 ppm and 4500 ppm
- P: between 600 and 1000 ppm
- S: maximum 120 ppm
- N: maximum 150 ppm
- Ti: maximum 200 ppm
- Nb: maximum 100 ppm
- V: maximum 100 ppm
- B: maximum 5 ppm

Likewise, three more specific embodiments are related to the same subranges for carbon content which are related to the strength level that is aimed at, but having furthermore the following specific sub-range for aluminium: 9000-13000 ppm. The subranges for the other alloying elements are kept the same as in paragraph [0017].

The present invention is equally related to a process for manufacturing a cold rolled TRIP steel product, comprising the steps of:

- preparing a steel slab having a composition according to the invention,
- hot rolling said slab, wherein the finishing rolling temperature is higher than the Ar3 temperature, to form a hot-rolled substrate,
cooling said substrate to a coiling temperature (CT) between 500°C and 680°C,

coiling said substrate at said coiling temperature,

pickling said substrate to remove the oxides,

cold rolling said substrate to obtain a reduction of thickness, with a minimum reduction of 40%.

According to a first embodiment, the process of the invention further comprises the steps of:

soaking said substrate at a temperature between 760°C and 850°C,

cooling said substrate with a cooling rate higher than 2°C/s to a temperature in the range 360°C to 450°C,

holding said substrate in said temperature range for a time less than 700s,

cooling said substrate to room temperature at a cooling rate higher than 1°C/s.

subjecting said substrate to a skinpass reduction of maximum 1.5%.

According to a second embodiment, the process of the invention further comprises an electrolytic zinc coating step.

According to a third embodiment, the process of the invention further comprises the following processing steps after the cold rolling step:

soaking said substrate at a temperature between 760°C and 850°C,

cooling said substrate with a cooling rate higher than 2°C/s to the temperature of a Zn-bath,

holding said substrate in the temperature range between 490°C and 460°C for less than 200 seconds.

hot dip galvanising said substrate in said Zn-bath,

cooling said substrate to room temperature at a cooling rate higher than 2°C/s.

The process comprising a hot dip galvanising step may further comprise the step of subjecting said substrate to a skinpass reduction of maximum 1.5%.

The invention is equally related to a steel product produced according to the process of the invention and having a microstructure comprising 30-75% ferrite, 10-40% bainite, 0-20% retained austenite and possibly 0-10% martensite.

The invention is equally related to a steel product produced according to the process of the invention and having a carbon content between 1300 ppm and 1900 ppm. Said product has a yield strength between 320 MPa and 480 MPa, a tensile strength above 590 MPa, an elongation A80 higher than 26% and a n-value (this is the strain hardening coefficient, calculated between 10% and uniform elongation) higher than 0.2.

The invention is further related to a steel product produced according to the process of the invention and having a carbon content between 1700 and 2300 ppm. Said product has a yield strength between 350 MPa and 510 MPa, a tensile strength above 700 MPa, an elongation A80 higher than 24% and a n-value (calculated between 10% and uniform elongation) higher than 0.19.

The invention is further related to a steel product produced according to the process of the invention and having a carbon content between 2000 ppm and 2600 ppm. Said product has a yield strength between 400 MPa and 600 MPa, a tensile strength above 780 MPa, an elongation A80 higher than 22% and a n-value (calculated between 10% and uniform elongation) higher than 0.18.

The invention is further related to a steel product produced according to the process of the invention and having a carbon content between 2000 and 2600 ppm. Said product has a yield strength between 450 MPa and 700 MPa, a tensile strength above 980 MPa, an elongation A80 higher than 18% and a n-value (calculated between 10% and uniform elongation) higher than 0.14.

A steel product according to the invention may have a bake hardening BH2 higher than 40 MPa in both longitudinal and transversal directions.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, a steel composition is proposed for the production of a P-alloyed Al—Si TRIP steel product. Application of the broadest chemical composition ranges which are indicated, will be able, in combination with the right process parameters, to result in products having a desired TRIP microstructure, good weldability as well as excellent mechanical properties, with very high values of the product of tensile strength and total elongation (this value is characteristic for a high energy absorption potential in case of a crash). The preferred ranges are related to more narrow ranges of mechanical properties, for example a guaranteed minimum tensile strength of 780 MPa, or to more stringent requirements on weldability (maximum of C-range, see next paragraph).

C: between 1300 ppm and 2600 ppm. A first preferred subrange is 1300-1900ppm. A second preferred subrange is 1700-2300 ppm. A third preferred subrange is 2000-2600 ppm. The minimum carbon content per subrange is needed in order to ensure the strength level as carbon is the most important element for the hardenability. The maximum of the claimed range per sub-range is related to weldability. The effect of carbon on mechanical properties is illustrated by exemplary composition A, B, C and D (tables 1, 3-8). The effect of carbon content on spot weldability is illustrated by reference compositions B, C and D (table 2). Two specific subranges for carbon are characteristic for two specific embodiments: 1350-1900ppm and 1400-1900ppm. These subranges are aimed at ensuring an Ultimate Tensile Strength of at least 600 MPa.

Mn: between 10000 ppm and 22000 ppm, preferably between 13000-22000 ppm. Manganese acts as an austenite stabiliser and thus decreases the Ms temperature of the retained austenite. Furthermore Mn suppresses pearlite formation and also contributes to the overall strength level of the steel by solid solution hardening. Adding excess Mn results on the other hand in insufficient ferrite formation upon cooling from the soaking temperature and thus to
insufficient carbon concentration in the retained austenite, rendering the latter less stable. Too much Mn will also increase the hardness of the weld and will enhance the formation of detrimental banded microstructures.

[0074] Al: between 8000 ppm and 15000 ppm, preferably between 8000-14000 ppm and most preferably between 9000-13000 ppm. Aluminium is added because, to an even stronger degree than Si, it is a ferrite stabiliser and thus enhances the ferrite formation during soaking and during cooling from the soaking temperature, thereby stabilising the retained austenite. The latter is stabilised even more by the fact that Al also suppresses the precipitation of carbon from the retained austenite during the overaging stage. Unlike Si, Al has no detrimental effect on galvanisability. Al-contents above 15000 ppm are however known to require the use of an adapted very fine casting powder that can cause health problems. Furthermore weldability can deteriorate due to the presence of Al-oxides in the welded area. A minimum Al content is however required to allow the material to be processed on different hot dip galvanising lines with different lengths of the levelling zones and to ensure a high process robustness.

[0075] Si: between 2000 ppm and 6000 ppm, preferably between 2500-4500 ppm. Silicon has essentially the same function as Al, albeit slightly less pronounced. That is, Si is a ferrite stabiliser and prevents carbide precipitation during the overaging stage, thereby stabilising the retained austenite at room temperature. Besides this, Si also contributes to the overall strength level of the steel by solid solution hardening. The maximum Si-content is however limited as Si is well known to provoke problems as to surface quality because of the presence of Si-oxides which after picking can create a surface with irregular and very high roughness. Moreover, in view of corrosion protection, hot dip galvanising of high Si-containing substrates in general leads to insufficient surface appearance for automotive applications, with moreover a high risk on the presence of bare spots on the surface.

[0076] P: between 400ppm and 1000 ppm, preferably between 600-1000 ppm. Phosphorous is added primarily to allow the carbon content to be decreased to obtain improved weldability, while maintaining the same tensile strength level. Furthermore, P in combination with Si, is known to enhance the retained austenite stability by suppressing carbide precipitation during the overaging stage. In this respect P additions below 400 ppm do not allow a sufficiently large reduction of C-content. When adding more than 1000 ppm P, the risk on segregation defects increases and weldability is again deteriorated.

[0077] S: maximum 120 ppm. The S-content has to be limited because a too high inclusion level can deteriorate the formability.

[0078] N: maximum 200 ppm, preferably maximum 150ppm otherwise too much AlN and/or TiN precipitates can form which are detrimental to formability.

[0079] Ti: maximum 1000 ppm, preferably below 200 ppm for products produced according to the present invention having a tensile strength below 980 MPa. Titanium can be added in order to increase the tensile strength of the steel by grain refinement and precipitation strengthening. However for tensile strengths below 980 MPa, even without adding Ti, using the appropriate processing parameters, will result in the targeted mechanical properties per carbon sub-range and thus avoid an increase in analysis cost or extra processing difficulties (e.g. rolling forces).

[0080] Nb: maximum 1000 ppm, preferably below 100 ppm for products produced according to the present invention having a tensile strength below 980 MPa. Niobium can be added in order to increase the tensile strength of the steel by grain refinement and precipitation strengthening. However for tensile strengths below 980 MPa, even without adding Nb, using the appropriate processing parameters, will result in the targeted mechanical properties per carbon sub-range and thus avoid an increase in analysis cost or extra processing difficulties (e.g. rolling forces).

[0081] V: maximum 1000 ppm, preferably below 100 ppm for products produced according to the present invention having a tensile strength below 980 MPa. Vanadium can be added in order to increase the tensile strength of the steel by grain refinement and precipitation strengthening. However for tensile strengths below 980 MPa, even without adding V, using the appropriate processing parameters, will result in the targeted mechanical properties per carbon sub-range and thus avoid an increase in analysis cost.

[0082] B: maximum 10 ppm, preferably maximum 5 ppm. Boron is avoided because of its detrimental influence on ferrite nucleation.

[0083] The present invention is equally related to the process for producing said steel product. This process comprises the steps of:

[0084] preparing a steel slab having a composition according to the invention, such as defined above,

[0085] if necessary, reheating said slab to a temperature higher than 1000° C., preferably above 1200° C.,

[0086] hot rolling the slab, wherein the finishing rolling temperature FT at the last stand of hot rolling is higher than the Ar3 temperature,

[0087] cooling to cooling temperature CT, preferably by continuous cooling to the CT, typically at 40-50° C/s. Stepwise cooling may be used as well,

[0088] hot rolling mill coating of said substrate at a coating temperature CT comprised between 500° C. and 680° C., preferably between 600° C. and 680° C. This temperature range is chosen so as to create a hot band which is as soft as possible in order to facilitate cold rolling,

[0089] pickling the substrate to remove the oxides,

[0090] cold rolling to obtain a reduction of thickness. The cold rolling reduction is preferably higher than 40%.

[0091] According to a first embodiment of the invention, these steps are followed by an annealing treatment in a continuous annealing line, comprising the following steps:

[0092] soaking said pickled cold rolled substrate in a temperature range between 760 and 850° C. in order to create a microstructure that consists of ferrite and austenite. If the soaking temperature is chosen above 850° C., the amount of austenite formed will be too large, which leads to a less stable retained austenite in the end product. Due to the reduced austenite stability, a substantial part of it could also transform to martensite during final cooling
to room temperature which deteriorates elongation properties. If, on the other hand, the soaking temperature would be chosen too low, insufficient austenite would be formed during soaking. This could lead to over-stabilisation of the retained austenite, which again deteriorates mechanical properties.

[0093] Cooling said substrate with a cooling rate higher than 2°C/s to a holding temperature in the range 360°C to 450°C. The holding time in said temperature range is less than 700 seconds. When the holding temperature would be chosen below 360°C, a substantial part of the retained austenite will transform to martensite, leading to a DP-like behaviour (high initial n-value that decreases as a function of increasing strain) of the final product. Holding temperatures above 450°C, will on the other hand lead to a decomposition of the retained austenite by carbon precipitation. This will again deteriorate elongation properties.

[0094] Final cooling of said substrate to a temperature below 150°C with a cooling rate higher than 1°C/s.

[0095] Finally said substrate can be subjected to a skin pass reduction which is preferably in the range 0.3% to 1.5%.

[0096] A second preferred embodiment comprises the same processing steps mentioned above, but additionally also comprises an electrolytic zinc coating step.

[0097] According to a third embodiment of the invention, the cold rolling step is followed by an annealing treatment in a continuous hot dip galvanising line, comprising the following steps:

[0098] soaking said pickled cold rolled substrate in a temperature range between 760°C and 850°C in order to create a microstructure that consists of ferrite and austenite. If the soaking temperature is chosen above 850°C, the amount of austenite formed will be too large, which leads to a less stable retained austenite in the end product. Due to the reduced austenite stability, a substantial part of it could also transform to martensite during final cooling to room temperature which deteriorates elongation properties. If, on the other hand, the soaking temperature would be chosen too low, insufficient austenite would be formed during soaking. This could lead to over-stabilisation of the retained austenite, which again deteriorates mechanical properties.

[0099] cooling said substrate with a cooling rate higher than 2°C/s to the temperature of the Zn-bath.

[0100] holding said substrate in the temperature range between 490°C and 460°C for less than 200 seconds and preferably between 5 seconds and 80 seconds.

[0101] hot dip galvanising said substrate in said Zn-bath.

[0102] final cooling to room temperature at a cooling rate higher than 2°C/s.

[0103] Finally said substrate can be subjected to a skin pass reduction which is preferably in the range 0.3% to 1.5%.

[0104] The thickness of the steel substrates of the invention after cold rolling can be lower than 1 mm according to the initial hot rolled sheet thickness and the capability of the cold rolling mill to perform the cold rolling at a sufficiently high level. Thus, thicknesses between 0.3 and 2.5 mm are feasible.

[0105] The resulting cold rolled product has a multiphase structure with 30-75% ferrite, 10-40% bainite, 0-20% retained austenite and possibly amounts of martensite (0-10%) present at room temperature. The amount of martensite at room temperature should however be limited in order to maintain an n-value behaviour (constant or increasing with strain) and mechanical properties that are characteristic for TRIP-steels. Specific mechanical properties as a function of processing parameter values are given in the examples.

[0106] The cold rolled non-temper rolled product showed in all cases a yield point elongation, which is typical for TRIP-steels and indicates that no or only very small amounts of martensite are present in the microstructure. This yield point elongation can be suppressed by temper rolling the final product. Small temper rolling reductions are sufficient to avoid the occurrence of a yield point elongation and temper rolling reductions above 1.5% should be avoided in order to prevent a too large yield strength increase.

[0107] The final cold rolled product furthermore preferably exhibits a constant or increasing n-value with increasing strain. This behaviour implies that the retained austenite is gradually transformed into martensite as the tensile test progresses thereby postponing the occurrence of necking, leading to an excellent combination of tensile strength and total elongation.

[0108] The robustness of TRIP steel products produced according to this invention is ensured by the minimum Al-content specified in the preferred Al-range: 8000-14000 ppm and most preferably in the range 9000-13000 ppm. Adding less Al will render the retained austenite less stable. This will increase the risk of loss of mechanical properties by austenite decomposition through carbon precipitation and on the other hand the less stable retained austenite will more easily transform into martensite during straining, limiting the formability of the material. Adding less Al will also retard the bainite transformation kinetics. As a consequence the mechanical properties will become more dependent on processing conditions such as line speed and overaging temperature as well on the actual line lay-out (short or long overaging section). Using an Al-content within the preferred range, avoids such line dependency and loss of robustness.

[0109] Concerning weldability of the obtained cold rolled product, the addition of phosphorus allows to decrease the carbon content as compared to P-free Al—Si TRIP steels of the same tensile strength level. As in the investigated carbon range, weldability is improved by lowering the carbon content, such a carbon content reduction by P-addition can be considered as the main advantage of the current invention.

[0110] The different drawbacks described above as to the compositions described in state of the art publications are not encountered when the composition of the present invention is applied:

[0111] Si is limited in order to ensure the hot dip galvanisation. The surface appearance of the hot dip galvanised cold rolled steel of the present invention is sufficient for automotive unexposed applications whereas substrates with higher Si-contents in general lead to insufficient surface appearance for automotive applications, with moreover a much higher risk on the presence of bare spots on the surface.
Si is furthermore limited in order to avoid the need of hot charging the slabs to prevent crack formation.

The presence of red scale on the hot rolled substrate's surface is also avoided by limiting the Si-content.

A small amount of Si, which is compatible with hot dip galvanising, is added to more easily reach the targeted tensile strength levels. In comparison with Si-free Al-TRIP steels, this allows to use a lower C-content or lower Al-content.

The maximum Al-content is limited to avoid the use of an adapted very fine casting powder that could cause health problems. Furthermore in the case of high Al-contents (>1.5%) weldability could deteriorate due to the presence of Al-oxides in the welded area. A minimum Al-content however ensures a high process robustness and less sensitivity to changes in line speed, overageing temperature and lay-out of the continuous annealing or hot dip galvanising line.

For a given tensile strength level, the C content is limited as compared to other Al—Si TRIP steels in order to improve weldability, by the addition of P and without the need of micro-alloying.

No Ni, Cu or Cr are added to the steel products of the invention. This avoids logistic problems with scrap recycling and reduces the cost of the analysis.

**DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS - EXAMPLES**

1. Example Compositions

Table 1 shows examples of compositions of laboratory castings of the P-alloyed Al—Si TRIP steel product according to the present invention (codes A, E and F), and of reference compositions (B, C and D) having either a C-content which is higher than the claimed range and/or no intentionally added phosphor. Laboratory thermal cycle simulations and tensile tests were performed to obtain the mechanical properties of the test specimens of these example compositions. It is to be noted that in what follows, all mentioned tensile test mechanical properties are measured according to the standard EN10002-1.

**1.1 Cold Rolled and Continuously Annealed Product**

The processing steps were:

- Casting,
- Reheating at 1250°C for 1 hour,
- Hot rolling in the austenite region to a final thickness of 3.5 mm,
- Water cooling to the coiling temperature of 600°C,
- Cold rolling to a final thickness of 1 mm.

After the previous processing steps, tensile specimens with 80 mm gauge length parallel to the rolling direction were machined out of the sheets. These specimens were heat treated in two salt baths following a two-step thermal cycle. After annealing in the intercritical region, the samples were quenched in a salt bath at a lower temperature and isothermally held. The temperatures and holding times were adapted in order to simulate closely the process steps, including a hot dip galvanizing step. The mechanical properties are listed in Table 4 and clearly illustrate that the current invention leads to a very robust hot dip galvanized TRIP700 product: a broad variation of process parameters (IAT, IAT, BH, BH) all result in products with comparable mechanical properties. No temper rolling was applied. When comparing the mechanical properties mentioned in Table 4 (example composition A), with those mentioned in Table 6 (in particular reference composition C), it becomes clear that the addition of P in the steel of the present invention clearly allows to reduce the carbon content with 500 ppm while maintaining the tensile strength level. This C-reduction will seriously improve weldability (cfr. Table 2: difference between 0.25C and 0.20C).

Table 7 contains the mechanical properties obtained after applying several continuous annealing simulations on steel samples of compositions E and F. Looking at the data in Table 5 and 7 (in particular E compared to B), it is clear that the tensile strength is even higher for the composition of the invention, as compared to the reference composition which has 600 ppm more carbon and no intentionally added phosphor.

**TABLE 1**

<p>| Compositions (ppm) of Al—Si TRIP steels. Compositions A, E, F according to the invention. B, C and D are reference compositions |
|---------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|</p>
<table>
<thead>
<tr>
<th>Code</th>
<th>C</th>
<th>Mn</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Ti</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2000</td>
<td>16200</td>
<td>5900</td>
<td>3000</td>
<td>850</td>
<td>20</td>
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<td>12500</td>
<td>3000</td>
<td>173</td>
<td>60</td>
<td>43</td>
<td>47</td>
<td>30</td>
</tr>
</tbody>
</table>
### TABLE 1-continued

Compositions (ppm) of Al—Si TRIP steels. Compositions A, E, F according to the invention, B, C and D are reference compositions.

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<thead>
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<th>Code</th>
<th>C</th>
<th>Mn</th>
<th>Al</th>
<th>Si</th>
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<th>S</th>
<th>N</th>
<th>Ti</th>
<th>Nb</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
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<td>15000</td>
<td>12000</td>
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<td>167</td>
<td>55</td>
<td>32</td>
<td>37</td>
<td>26</td>
<td>45</td>
</tr>
<tr>
<td>D</td>
<td>2000</td>
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<td>10</td>
<td>100</td>
<td>50</td>
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<td>0</td>
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<tr>
<td>F</td>
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<td>50</td>
<td>50</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>

### TABLE 5

Mechanical properties of the cold rolled and continuously annealed reference Al—Si TRIP steels. (RD: rolling direction; TD: transverse direction)

<table>
<thead>
<tr>
<th>Thickness</th>
<th>SKP Re (MPa)</th>
<th>Rd (MPa)</th>
<th>A80 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Code</td>
<td>(mm)</td>
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<td>TD</td>
</tr>
<tr>
<td>B</td>
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<td>C</td>
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</tr>
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<td>D</td>
<td>1.6</td>
<td>1.00</td>
<td>524</td>
</tr>
<tr>
<td>E</td>
<td>0.7</td>
<td>0.50</td>
<td>502</td>
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<tr>
<td>F</td>
<td>1.45</td>
<td>0.80</td>
<td>507</td>
</tr>
<tr>
<td>G</td>
<td>0.85</td>
<td>0.70</td>
<td>483</td>
</tr>
<tr>
<td>H</td>
<td>1.22</td>
<td>0.70</td>
<td>451</td>
</tr>
<tr>
<td>I</td>
<td>1.47</td>
<td>0.75</td>
<td>466</td>
</tr>
</tbody>
</table>

### TABLE 2

Average of max. force measured at Inmax in cross-tensile test on spot welds according to AFNOR-A87001.

<table>
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<tr>
<th>Code</th>
<th>Fmax at Inmax (N)</th>
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</thead>
<tbody>
<tr>
<td>B</td>
<td>6906</td>
</tr>
<tr>
<td>C</td>
<td>7489</td>
</tr>
<tr>
<td>D</td>
<td>9608</td>
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</tbody>
</table>

### TABLE 3

Mechanical properties of the cold rolled and continuously annealed P-allyed Al—Si TRIP steel, composition A, according to the present invention. No temper rolling applied. Thickness 1 mm.

<table>
<thead>
<tr>
<th>LAT Code</th>
<th>LAT (°C)</th>
<th>BHT (°C)</th>
<th>RH0.2 (MPa)</th>
<th>Rd (MPa)</th>
<th>Au (%)</th>
<th>A80 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>770</td>
<td>60</td>
<td>120</td>
<td>486</td>
<td>708</td>
<td>24.7</td>
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</tbody>
</table>

### TABLE 4

Mechanical properties of the cold rolled and hot dip galvanised P-allyed Al—Si TRIP steel, composition A, according to the present invention. No temper rolling applied. Thickness 1 mm. (BH = biaxial holding; holding before passing through the zinc bath)

<table>
<thead>
<tr>
<th>LAT Code</th>
<th>LAT (°C)</th>
<th>BHT (°C)</th>
<th>RH0.2 (MPa)</th>
<th>Rd (MPa)</th>
<th>Au (%)</th>
<th>A80 (%)</th>
<th>Re/Rm</th>
<th>Rm x A80</th>
</tr>
</thead>
<tbody>
<tr>
<td>770</td>
<td>73</td>
<td>460</td>
<td>20</td>
<td>411</td>
<td>738</td>
<td>23.6</td>
<td>587</td>
<td>21107</td>
</tr>
<tr>
<td>800</td>
<td>460</td>
<td>20</td>
<td>408</td>
<td>756</td>
<td>22.6</td>
<td>28.0</td>
<td>540</td>
<td>21168</td>
</tr>
<tr>
<td>830</td>
<td>460</td>
<td>14</td>
<td>427</td>
<td>746</td>
<td>24.6</td>
<td>30.2</td>
<td>527</td>
<td>22529</td>
</tr>
<tr>
<td>770</td>
<td>52</td>
<td>14</td>
<td>434</td>
<td>761</td>
<td>22.4</td>
<td>28.1</td>
<td>570</td>
<td>21384</td>
</tr>
<tr>
<td>800</td>
<td>460</td>
<td>14</td>
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<td>734</td>
<td>24.3</td>
<td>29.4</td>
<td>571</td>
<td>21580</td>
</tr>
<tr>
<td>830</td>
<td>460</td>
<td>14</td>
<td>434</td>
<td>761</td>
<td>22.4</td>
<td>28.1</td>
<td>570</td>
<td>21384</td>
</tr>
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<td>770</td>
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<td>14</td>
<td>419</td>
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<td>29.4</td>
<td>571</td>
<td>21580</td>
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<td>800</td>
<td>460</td>
<td>14</td>
<td>434</td>
<td>761</td>
<td>22.4</td>
<td>28.1</td>
<td>570</td>
<td>21384</td>
</tr>
<tr>
<td>830</td>
<td>460</td>
<td>14</td>
<td>419</td>
<td>734</td>
<td>24.3</td>
<td>29.4</td>
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<td>21580</td>
</tr>
<tr>
<td>770</td>
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<td>10</td>
<td>423</td>
<td>701</td>
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<td>30.3</td>
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<td>21240</td>
</tr>
<tr>
<td>800</td>
<td>460</td>
<td>10</td>
<td>419</td>
<td>726</td>
<td>23.8</td>
<td>28.7</td>
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<tr>
<td>830</td>
<td>460</td>
<td>10</td>
<td>423</td>
<td>755</td>
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<td>28.9</td>
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<tr>
<td>800</td>
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<td>10</td>
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<td>726</td>
<td>23.8</td>
<td>28.7</td>
<td>577</td>
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<td>830</td>
<td>460</td>
<td>10</td>
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<td>28.9</td>
<td>574</td>
<td>22195</td>
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<td>770</td>
<td>36</td>
<td>10</td>
<td>423</td>
<td>701</td>
<td>24.7</td>
<td>30.3</td>
<td>603</td>
<td>21240</td>
</tr>
</tbody>
</table>

### TABLE 6

Mechanical properties of the cold rolled and continuously annealed reference Al—Si TRIP steel. (RD: rolling direction; TD: transverse direction)

<table>
<thead>
<tr>
<th>Thickness</th>
<th>SKP Re (MPa)</th>
<th>Rd (MPa)</th>
<th>A80 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Code</td>
<td>(mm)</td>
<td>RD</td>
<td>TD</td>
</tr>
<tr>
<td>B</td>
<td>1.00</td>
<td>0.5</td>
<td>490</td>
</tr>
<tr>
<td>C</td>
<td>1.2</td>
<td>0.7</td>
<td>483</td>
</tr>
<tr>
<td>D</td>
<td>1.45</td>
<td>0.9</td>
<td>472</td>
</tr>
<tr>
<td>E</td>
<td>1.49</td>
<td>1.0</td>
<td>446</td>
</tr>
<tr>
<td>F</td>
<td>1.23</td>
<td>1.1</td>
<td>451</td>
</tr>
</tbody>
</table>
TABLE 7

Mechanical properties of the cold rolled and continuously annealed Al—Si TRIP steel, compositions E and F, according to the present invention.

<table>
<thead>
<tr>
<th>Code</th>
<th>LAT (°C)</th>
<th>Lat (s)</th>
<th>BHIT (°C)</th>
<th>BHIT (s)</th>
<th>Rp0.2 (MPa)</th>
<th>Rm (MPa)</th>
<th>A80 (%)</th>
<th>Re/Rm</th>
<th>Rm × A80</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>800</td>
<td>375</td>
<td>448</td>
<td>595</td>
<td>820</td>
<td>26.1</td>
<td>0.726</td>
<td>21402</td>
<td></td>
</tr>
<tr>
<td></td>
<td>425</td>
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<td>0.674</td>
<td>22434</td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td>125</td>
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<td>562</td>
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<td>375</td>
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<td>597</td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 8

Mechanical properties of the cold rolled and hot dip galvanised Al—Si TRIP steel, compositions E and F, according to the present invention. No temper rolling applied. Thickness 1 mm. (BHl = bainite holding; holding before passing through the zinc.)

<table>
<thead>
<tr>
<th>Code</th>
<th>LAT (°C)</th>
<th>Lat (s)</th>
<th>BHIT (°C)</th>
<th>BHIT (s)</th>
<th>Rp0.2 (MPa)</th>
<th>Rm (MPa)</th>
<th>A80 (%)</th>
<th>Re/Rm</th>
<th>Rm × A80</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>800</td>
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<td>460</td>
<td>496</td>
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1. A steel composition intended to be used in a process comprising a cold rolling step, for the production of uncoated, electro-galvanised or hot dip galvanised TRIP steel products, said composition comprising:

- C: between 1300 ppm and 2600 ppm,
- Mn: between 10000 ppm and 22000 ppm,
- Al: between 8000 ppm and 15000 ppm,
- Si: between 2000 ppm and 6000 ppm,
- P: between 400 and 1000 ppm,
- S: maximum 120 ppm,
- N: maximum 200 ppm,
- Ti: maximum 1000 ppm,
- Nb: maximum 1000 ppm,
- V: maximum 1000 ppm,
- B: maximum 10 ppm,

the remainder being substantially iron and incidental impurities.

2. The steel composition according to claim 1, comprising a carbon content between 1300 ppm and 1900 ppm.

3. The steel composition according to claim 2, comprising a carbon content between 1350 ppm and 1900 ppm.

4. The steel composition according to claim 2, comprising a carbon content between 1400 ppm and 1900 ppm.

5. The steel composition according to claim 1, comprising a carbon content between 1700 ppm and 2300 ppm.

6. The steel composition according to claim 1, comprising a carbon content between 2000 ppm and 2600 ppm.

7. The steel composition according to claim 2, comprising:
Mn: between 13000 ppm and 22000 ppm,
Al: between 8000 ppm and 14000 ppm,
Si: between 2500 ppm and 4500 ppm,
P: between 600 and 1000 ppm,
S: maximum 120 ppm,
N: maximum 150 ppm,
Ti: maximum 200 ppm,
Nb: maximum 100 ppm,
V: maximum 100 ppm,
B: maximum 5 ppm.

8. The steel composition according to claim 7, comprising an aluminum content between 9000 ppm and 13000 ppm.

9. A process for manufacturing a cold rolled TRIP steel product, comprising the steps of:

preparing a steel slab having a composition according to claim 1,

hot rolling said slab, wherein the finishing rolling temperature is higher than the Ar3 temperature, to form a hot-rolled substrate,

cooling said substrate to a cooling temperature (CT) between 500° C. and 680° C.,

coating said substrate at said coating temperature,

pickling said substrate to remove the oxides,

cold rolling said substrate to obtain a reduction of thickness, with a minimum reduction of 40%.

10. The process according to claim 9, further comprising the steps of:

soaking said substrate at a temperature between 760° C. and 850° C.,

cooling said substrate with a cooling rate higher than 2° C/s to the temperature of a Zn-bath,

holding said substrate in the temperature range between 490° C. and 460° C. for less than 200 seconds.

hot dip galvanising said substrate in said Zn-bath,

cooling said substrate to room temperature at a cooling rate higher than 2° C/s.

13. The process according to claim 12, further comprising the step of subjecting said substrate to a skinpass reduction of maximum 1.5%.

14. A steel product produced according to the process of claim 9 and having a microstructure comprising 30-75% ferrite, 10-40% bainite, 0-20% retained austenite and possibly 0-10% martensite.

15. A steel product produced according to the process of claim 10, said product comprising a carbon content between 1300 ppm and 1900 ppm, said product having a yield strength between 320 MPa and 480 MPa, a tensile strength above 590 MPa, an elongation A80 higher than 26% and a strain hardening coefficient, calculated between 10% and uniform elongation, higher than 0.2.

16. A steel product produced according to the process of claim 10, said product comprising a carbon content between 1700 ppm and 2300 ppm, said product having a yield strength between 350 MPa and 510 MPa, a tensile strength above 700 MPa, an elongation A80 higher than 24% and a strain hardening coefficient, calculated between 10% and uniform elongation, higher than 0.19.

17. A steel product produced according to the process of claim 10, said product comprising a carbon content between 2000 ppm and 2600 ppm, said product having a yield strength between 400 MPa and 600 MPa, a tensile strength above 780 MPa, an elongation A80 higher than 22% and a strain hardening coefficient, calculated between 10% and uniform elongation, higher than 0.18.

18. A steel product produced according to the process of claim 10, said product comprising a carbon content between 2000 ppm and 2600 ppm, said product having a yield strength between 450 MPa and 700 MPa, a tensile strength above 980 MPa, an elongation A80 higher than 18% and a strain hardening coefficient, calculated between 10% and uniform elongation, higher than 0.14.

19. A steel product produced according to claim 14, having bake hardening BH2 higher than 40 MPa in both longitudinal and transversal directions.

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