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COLD-ROLLED STEEL PLATE COATED WITH ZINC OR A ZINC ALLOY, METHOD FOR MANUFACTURING SAME, AND USE OF SUCH A STEEL PLATE

The invention relates to the manufacture of cold-rolled coated steel plates having a "TRIP" (transformation induced plasticity) effect for manufacturing parts for pressing, more particularly intended for powered land vehicles.

The reduction of greenhouse gas emissions in the field of land transport is at the present time a challenge that involves reducing the weight of vehicles in order to reduce their fuel consumption. By combining this with the safety requirements of new-generation vehicles, motor manufacturers are more and more being led to use steels with improved mechanical strength in the bodywork in order to reduce the thickness of the parts and therefore the weight of the vehicles. The new-generation vehicle parts nevertheless have complex shapes that require sufficient ductility on the part of the steel sheets from which they are possibly made.

In this light, so-called TRIP steels have been greatly developed since they combine high strength with high shapability. This good compromise between mechanical strength and shapability results from its complex structure comprising ferrite, which is a ductile constituent, harder constituents such as martensite and austenite (MA) islets, mainly residual austenite, and finally the bainitic ferrite matrix having mechanical strength and ductility intermediate between ferrite and MA islets. The capacity for consolidation of TRIP effect steels is very great, which allows good distribution of deformations in the case of a collision or even when the automobile part is being formed. Thus it is possible to produce parts that are as complex as with conventional steels, but with superior mechanical properties, which allows a reduction in thickness to comply with an identical functional specification in terms of mechanical behaviour. In this way, these steels are an effective response to the requirements for lightening and safety of vehicles. In the field of hot-rolled or cold-rolled sheets, this type of steel finds in particular applications for structural and safety parts for motor vehicles.

Recent requirements for lightening and reducing energy consumption have led to a demand for certain TRIP steels, the mechanical strength Rm of which is between 780 and 900 MPa and the total elongation of which is greater than 19% with an ISO-type test piece. Apart from this strength and ductility level, these steels must have good weldability and good suitability for continuous hot galvanisation. These steels must also have good suitability for bending.

Thus the document JP 2001/254138 is known, which describes steels with the chemical composition: 0.05-0.3% C, 0.3-2.5% Si, 0.5-3.0% Mn and 0.001-2.0% Al, the remainder consisting of iron and unavoidable impurities. The structure comprises residual austenite, the carbon concentration by mass of which is greater than or equal to 1% and the volume fraction of which is between 3% and 50%, and ferrite, the shape factor of which is between 0.8 and 3 and the volume between 50% and 97%. This document refers to an uncoated steel, and the invention in the context of this patent does not make it possible to form a sheet requiring any particular mechanical strength associated with high ductility to form a complex coated automobile structure part.

The document WO 2002/101112 is also known, which moreover describes steels with the chemical composition: C: 0.0001-0.3%, Si: 0.001-2.5%, Mn: 0.001-3%, Al: 0.0001-4%, P: 0.0001-0.3%, S: 0.0001-0.1% and optionally one or more of the following elements: Nb, Ti, V, Zr, Hf and Ta to a total of between 0.001 and 1%, B: 0.0001 to 0.1%, Mo: 0.001 to 5%, Cr: 0.001 to 25%, Ni: 0.001 to 10%, Cu: 0.001 to 5%, Co: 0.001 to 5%, W: 0.001 to 5%, and Y, REM, Ca, Mg and Ce to a total of between 0.0001 and 1%, the remainder consisting of iron and unavoidable impurities. The microstructure claimed consists of 50% to 97% ferrite or of the ferrite + bainite assembly as the main structure and austenite as the second phase with a proportion of between 3% and 50% of the total volume. The teaching of this document does not make it possible to form a sheet requiring a particular mechanical strength associated with high ductility in order to form a complex coated part intended for a motor vehicle structure.

The document US 5,470,529 is also known, which describes the manufacture of steel sheets having a good combination of strength and hole expansion, with a composition containing 0.05-0.3% C, less than 1.0% Si, 0.05-4% Mn, 0.1-2% Al with Si + Al = 0.5-3%, 0-2.0% Cu, 0-1.0% Ni, with Ni $\geq$ Cu/3,0-5.0% Cr, 0-0.01% Ca, 0-0.10% Zr, 0-0.10% Nb, 0-0.10% Ti, 0-0.20% V, the structure containing at least 5% residual austenite. This document however does not give any information on the morphology of the M-A compounds necessary with a view to obtaining excellent resistance to crack propagation.

The document EP 1 865 085 is also known, which describes the manufacture of coated steel sheets containing 0.06-0.6% C, 0.1-2% Si, 0.01-3% Al, with Si + Al between 1 and 4%,1-6% Mn, with Si/Mn < 0.4, the surface of the sheet containing more than 10 composite oxides/mm^2 having an Mn/Si ratio > 0.5 and a maximum dimension of 0.01 to 5 µm, having a degree of surface oxide covering of less than 10% containing mainly silicon.

According to this document, the residual austenite must be present in the form of laths, that is to say with a high elongation factor.

The publication by A. Wasilkowska et al. "Microstructure and tensile behaviour of cold-rolled TRIP-aided steels", Journal of Materials Processing Technology, 157-158, 2004 is also known. This document relates however to uncoated TRIP steel sheets the mechanical strength of which is limited to 700 MPa.

The invention aims to produce a steel sheet coated with Zn or a Zn alloy with a combination of shapability, coatability and improved weldability criteria. Low sensitivity to weakening by the liquid zinc when the latter penetrates during welding improves the behaviour in service of the coated welded part. This weakening is explained by fusion of the coating based on zinc or zinc alloy due to the high temperatures imposed by the welding. In doing this, the liquid zinc penetrates the austenitic grain joints of the steel and weakens them, leading to a premature appearance of cracking in the region subjected to high external stresses during spot welding for example.

In this regard, the invention aims to make available "TRIP effect" steel sheets having a mechanical strength of between 780 and 900 MPa conjointly with a breaking elongation greater than 19%. Said sheet must be coatable with a Zn or Zn alloy coating, and be insensitive to the penetration of Zn into the austenitic grain joints.

The invention also aims to make available an economical manufacturing method avoiding the addition of expensive alloy elements.

The sheet can be manufactured by any suitable manufacturing method. It is however preferred to use a manufacturing method where small variations in parameters do not give rise to significant modifications to the microstructure or mechanical properties.

In a particularly preferred fashion, it is sought to make available a steel sheet that can easily be rolled cold, that is to say where the hardness after the hot-rolling step is limited so that the rolling forces remain moderate during the cold-rolling step.

To this end, the subject matter of the invention is a cold-rolled steel sheet, annealed and coated with zinc or zinc alloy, the composition of which comprises, the proportions being expressed by weight:

$0.17\% \leq C \leq 0.25\%$

$1.5\% \leq Mn \leq 2.0\%$

$0.50\% \leq Si \leq 1\%$

$0.50\% \leq Al \leq 1.2\%$

$B \leq 0.001\%$

P ≤ 0.030%

S ≤ 0.01%

Nb ≤ 0.030%

Ti ≤ 0.020%

V ≤ 0.015%

Cu ≤ 0.1%

Cr ≤ 0.150%

Ni ≤ 0.1%

0% ≤ Mo ≤ 0.150%,

it being understood that Si + Al ≥ 1.30%,

the rest of the composition consisting of iron and unavoidable impurities resulting from the production, the microstructure consisting, the proportions being expressed as a surface fraction, of 65% to 85% ferrite, said ferrite consisting of polygonal ferrite and bainitic ferrite, 15% to 35% martensite and residual austenite islets, said ferrite comprising less than 5% non-recrystallised ferrite, it being understood that the total proportion of residual austenite is between 10% and 25% and that the total proportion of martensite is less than or equal to 10%, the mean size of said martensite and residual austenite islets is less than 1.3 micrometres, their mean shape factor being less than 3, said shape factor being the ratio between the length and maximum width of said martensite and residual austenite islets, the mechanical strength Rm is between 780 and 900 MPa inclusive, and the breaking elongation A% is greater than or equal to 19%.

The sheet according to the invention may also have the following characteristics, taken in isolation or in combination:

- the composition comprises, the proportion being expressed by weight, 0.19% ≤ C ≤ 0.23%
- the composition comprises, the proportion being expressed by weight, 1.6% ≤ Mn ≤ 1.8%
- the composition comprises, the proportion being expressed by weight, 0.7% ≤ Si ≤ 0.9%
- the composition comprises, the proportion being expressed by weight, 0.6% ≤ Al ≤ 0.8%
- the composition comprises, the proportion being expressed by weight, 0% <B ≤ 0.0005%
- more than 90% as a surface proportion of the martensite and residual austenite islets have a size of less than or equal to two micrometres.

Another subject matter of the invention is a method for manufacturing a cold-rolled sheet, annealed and coated with zinc or zinc alloy, comprising the steps according to which:

- a steel with a composition according to the invention is procured, then
- said steel is cast in the form of a semi-finished product, then
- said semi-finished product is heated to a temperature of between 1150° and 1250°C, then
- said heated semi-finished product is hot-rolled, completing the rolling at an end-of-rolling temperature T_{FL} greater than or equal to Ar3 in order to obtain a sheet, then
- said hot-rolled sheet is coiled at a temperature Tbob of between 500° and 600°C, then
- said hot-rolled sheet is cooled to ambient temperature, then
- if necessary, said hot-rolled sheet is pickled, then
- said sheet is cold-rolled, then
- said cold-rolled sheet is heated at a rate Vc of between 1° and 30°C/s to a temperature Tr for a period tr greater than or equal to 15 seconds, said temperatures and durations being chosen so as to obtain a surface fraction of austenite of between 35% and 70%, the remainder being so-called polygonal ferrite, then
- -said cold-rolled sheet is cooled to a temperature Teq of between 475° and 440° at a sufficiently quick rate Vref to avoid the formation of perlite, then
- said cold-rolled sheet is maintained at the equalisation temperature T_{eq} for a period t_{eq} of between 20 and 120 seconds, then
- said cold-rolled sheet is coated by continuous hot immersion in a zinc or zinc alloy bath, then
- said cold-rolled and coated sheet is cooled to ambient temperature.

The method according to the invention may also have the following features, taken in isolation or in combination:

- the end-of-rolling temperature T_{FL} is greater than 900°C,
- the end-of-rolling temperature T_{FL} is greater than or equal to 920°C,
- the dew point during annealing at Tr during tr is between -20°C and -15°C,
- the annealing temperature Tr is between Ac1 + 50°C and Ac3 - 50°C,

- the annealing temperature Tr is between Ac1 + 50°C and Ac1 + 170°C,
- the period t_{eq} will preferably be between 30 and 80 seconds,
- the period t_{eq} will ideally be between 30 and 60 seconds.

The sheet according to the invention is suitable for resistance spot welding.

Another subject matter of the invention is the use of an annealed and coated cold-rolled sheet according to the invention or obtained by a method according to the invention for manufacturing structural or safety parts for powered land vehicles.

Other features and advantages of the invention will emerge during the following description given by way of example and made with reference to the accompanying figures, according to which:

- Figure 1 presents the dimensions of the traction test piece used for measuring the mechanical properties; these dimensions are set out in Table 4.
- Figure 2 presents an example of the microstructure of a steel sheet according to the invention with in white the MA islets and in black the matrix comprising polygonal ferrite, and bainite.
- Figure 3 presents an example of the distribution of the shape factors of the MA islets according to the invention according to their respective maximum lengths.

Thus, in the context of the invention, the influence of the fraction of austenite formed during the intercritical maintenance and its combination with the equalisation temperature on the final mechanical behaviour of the steel sheet has been revealed.

Carbon fulfils an important role in the formation of the microstructure and in the mechanical properties in terms of ductility and strength via the TRIP effect: below 0.17% by weight, the mechanical strength becomes insufficient, beyond 0.25%, weldability becomes more and more reduced whereas the TRIP effect will be improved. Preferentially, the carbon content will be between 0.19% and 0.23% inclusive.

Manganese is an element that hardens by substitutional solid solution that increases hardenability and slows down the precipitation of carbides. A minimum proportion of 1.5% by weight is necessary to obtain the desired mechanical properties. However, beyond 2%, its gammagenic character leads to the formation of an excessively pronounced band structure that may impair the shaping properties of the automobile structure part, and in addition the coatability will be reduced. Preferentially, the proportion of manganese will be between 1.6% and 1.8% inclusive.

Stabilisation of the residual austenite is made possible by the addition of silicon and aluminium, which considerably slow down the precipitation of the carbides during the annealing cycle and more particularly during the bainitic transformation. This will allow enrichment of the austenite with carbon, leading to its stabilisation at ambient temperature on the annealed steel sheet. Subsequently, the application of an external stress, of shaping for example, will lead to the transformation of this austenite into martensite. This transformation is the cause of the good compromise between the mechanical strength and the ductility of TRIP steels.

Silicon is an element that hardens in substitutional solid solution. This element also plays an important role in the formation of the microstructure by slowing down the precipitation of the
carbides during the equalisation stage after primary cooling; this makes it possible to concentrate the carbon in the residual austenite for stabilisation thereof. Silicon fulfils an effective role combined with that of aluminium, the best result of which is obtained, with regard to the properties sought, beyond 0.50%. However, an addition of silicon in a quantity greater than 1% risks impairing the suitability for dip coating by promoting the formation of oxides adhering to the surface of the products: its content must be limited to 1% by weight in order to facilitate dip coatability. Preferentially, the silicon content will be between 0.7% and 0.9% inclusive. Furthermore, silicon reduces weldability: a proportion of less than or equal to 1% makes it possible to simultaneously ensure very good suitability for welding as well as good coatability.

Aluminium plays an important role in the invention by greatly slowing down the precipitation of carbides; its effect is combined with that of silicon, since the proportions by weight of silicon and aluminium are such that: Si + Al $\geq$ 1.30% in order to sufficiently delay the precipitation of carbides and to stabilise the residual austenite. This effect is obtained when the aluminium content is greater than 0.50% and when it is less than 1.2%. Preferentially, it will be less than or equal to 0.8% and greater than or equal to 0.6%. It is normally considered in fact that high proportions of Al increase the erosion of refractories and the risk of blocking of spouts during the pouring of the steel upstream of the rolling. In addition, aluminium segregates negatively and it may lead to macrosegregations. In excessive quantities, the aluminium reduces hot ductility and increases the risk of the appearance of defects in continuous casting. Without a thorough check on the casting conditions, defects of the micro- and macrosegregation type give, ultimately, a central segregation on the annealed steel sheet.

This central band will be harder than its surrounding matrix and will impair the shapability of the material.

Beyond a sulphur content of 0.01%, ductility is reduced because of the excessive presence of sulphides such as MnS (manganese sulphides), which reduce suitability for the shaping; this is in fact a source of the initiation of cracks. Furthermore, it is a residual element the proportion of which it is wished to limit.

Phosphorus is an element that hardens in solid solution but considerably reduces spot weldability and hot ductility, in particular because of its capacity for segregation at the grain joints or its tendency towards co-segregation with manganese. For these reasons, its content must be limited to 0.03% in order to obtain good suitability for spot welding and good hot ductility. Furthermore, it is a residual element the proportion of which it is wished to limit.

Molybdenum fulfils an effective role in hardenability and hardness and delays the appearance of bainite. However, addition thereof excessively increases the cost of the additions of alloy elements and thus for economic reasons its content is limited to 0.150% or even 0.100%.

Chromium, through its role in hardenability, also contributes to delaying the formation of proeutectoid ferrite. Furthermore, this element is a hardener by substitutional solid solution; however, for economic reasons, its content is limited to 0.150% or even to 0.100% since it is an expensive alloy.

Nickel, which is a powerful stabiliser of austenite, will promote the stabilisation of the latter. However, beyond 0.1%, the cost of the addition of alloy elements is financially unviable. The proportion of nickel is therefore limited to 0.1% for economic reasons.

Copper, which is also a stabiliser of austenite, will promote the stabilisation of the latter. However, beyond 0.1%, the cost of the addition of alloy elements becomes financially prohibitive. The proportion of copper is therefore limited to 0.1% for economic reasons.

Boron acts strongly on the hardenability of steel. It limits the activity of carbon and limits diffusive phase transformations (ferritic or bainitic transformation during cooling), thus leading to the formation of hardening phases such as martensite. This effect is not desirable in the invention since it is wished to promote bainitic transformation in order to stabilise the austenite and prevent the formation of an excessive high surface proportion of martensite. Thus the boron content is limited to 0.001%.

Microalloy elements such as niobium, titanium and vanadium are respectively limited to the maximum proportions of 0.030%, 0.020% and 0.015% since these elements have the particularity of forming hardening precipitates with carbon and/or nitrogen, which also tend to reduce the ductility of the product. Furthermore, they delay recrystallisation during the heating step and maintain annealing and therefore refine the microstructure, which also hardens the material.

The rest of the composition consists of iron and unavoidable impurities resulting from the production.

So-called TRIP effect steels have a microstructure comprising islets of residual austenite and of martensite referred to as "MA islets" as well as ferrite. This ferrite can be divided into two categories: so-called intercritical ferrite that is the polygonal ferrite formed during maintenance after heating during annealing at Tr, and so-called bainitic ferrite, free from carbides, formed, after the maintenance, during the primary cooling and during the equalisation step at the time of annealing. The term "ferrite" will encompass these two subcategories hereinafter. Martensite, present in the microstructure, is not desired but its presence is difficult to avoid.

In the context of the invention, forming more than 5% of non-recrystallised ferrite will be avoided. This proportion of non-recrystallised ferrite is assessed in the following way: after having identified the ferritic phase in the microstructure, the surface percentage of non-recrystallised ferrite compared with the whole of the ferritic phase is quantified. This non-recrystallised ferrite has very little ductility and is the source of the initiation of cracks during the final shaping and does not make it possible to obtain the characteristics sought by the invention.

According to the invention, the microstructure consists, the proportions being expressed as a surface fraction, of 65% to 85% ferrite and 15% to 35% islets of martensite and residual austenite, it being understood that the total proportion of residual austenite is between 10% and 25% and that the total proportion of martensite is less than or equal to 10% as a surface proportion.

A quantity of MA islets of less than 15% does not make it possible to significantly increase the resistance to damage. Thus the total elongation of 19% would not be achieved. In addition, since the MA islets are hard, if their proportion is less than 15%, there is a risk of not achieving the 780 MPa sought. Beyond 35%, a high carbon content will be necessary to stabilise it sufficiently and this would impair the weldability of the steel. Preferentially, the proportion by mass of carbon in the residual

austenite is greater than 0.8% in order to obtain sufficient MA islets stable at ambient temperature. Ferrite makes it possible, in the context of the invention, to improve ductility, the presence of this ductile structure being necessary in order to achieve the 19% total elongation sought. Bainitic ferrite stabilises the residual austenite.

Figure 2 illustrates a microstructure according to the invention with an image issuing from an optical microscope. The MA islets appear in white and the ferrite is in black. At this stage the polygonal ferrite of the bainitic ferrite cannot be distinguished since the magnification is too low and in both cases there is a cubic structure centred from the crystallographic point of view. The main difference being that the bainitic ferrite has a density of dislocations and a carbon content greater than polygonal intercritical ferrite.

For example, the method according to the invention may comprise the following successive steps:

A steel with a composition according to the invention is procured, and then a semi-finished product is cast from this steel. This casting can be carried out in ingots or continuously in the form of slabs.

- The cast semi-finished products are first of all raised to a temperature T_{rech} above 1150°C and below 1250°C in order at every point to achieve a temperature favourable to the high deformations that the steel will undergo during rolling. This temperature range makes it possible to be in the austenitic domain.

However, if the temperature T_{rech} is above 1275°C, the austenitic grains increase undesirably and will lead to a coarser final structure.

- The semi-finished product is hot rolled in a temperature range where the structure of the steel is therefore totally austenitic: if the end-of-rolling temperature T_{fL} is lower than the temperature of the start of transformation of the austenite into ferrite on cooling Ar3, the ferrite grains are work-hardened by the rolling and ductility is considerably reduced. Preferentially, an end-of-rolling temperature T_{fL} above 900°C will be chosen. More preferentially, the end-of-rolling temperature T_{fL} will be greater than or equal to 920°C.

- Next the hot-rolled product is coiled at a temperature T_{bob} of between 500° and 600°C. This temperature range makes it possible to obtain a complete bainitic transformation during the quasi-isothermal maintenance associated with the coiling followed by slow cooling. A coiling temperature greater than 600°C leads to the formation of undesired oxides.

When the coiling temperature is too low, the hardness of the product is increased, which increases the forces necessary during the subsequent cold rolling.

- It is then possible, if necessary, to pickle the hot-rolled product in accordance with a process known per se, and then cold rolling is carried out with a degree of reduction preferentially between 30% and 80%.

- The cold-rolled product is next heated, preferentially in a continuous annealing installation, with a mean heating rate V_c of between 1° and 30°C/s. In relation to the annealing temperature T_r below, this heating rate range makes it possible to obtain a non-recrystallised ferrite fraction of less than 5%.

The heating is carried out to an annealing temperature T_r, preferably between the temperature Ac1 (temperature of the start of allotropic transformation on heating) + 50°C, and Ac3 (the temperature of the end of allotropic transformation on heating) -50°C, and for a time t_r chosen so that between 35% and 70% intercritical austenite is obtained. This can in particular be obtained by choosing, for reasons of energy saving, the temperature T_r between Ac1 + 50°C and Ac1 + 170°C. When T_r is less than (Ac1 + 50°C), the structure may still comprise non-recrystallised ferrite regions, the surface fraction of which may be as much as 5%. An annealing temperature Tr according to the invention makes it possible to obtain a quantity of intercritical austenite sufficient to subsequently form on cooling ferrite in a quantity such that the residual austenite will be sufficiently stabilised and the desired mechanical characteristics will be achieved.

When the proportion of intercritical austenite is greater than 70%, at the temperature Tr, its carbon concentration is low, and this leads to an excessively rapid and excessively copious subsequent transformation into polygonal and bainitic ferrite respectively during the cooling and the equalisation stage between 440° and 475°C. The ferrite is a fairly soft phase, and its presence in an excessively large quantity will not make it possible to achieve the target of 780 MPa and to have a total elongation ≥ 19%.

The maintenance period t_{mm} is between 15 and 300 seconds. A minimum maintenance period t_r greater than or equal to 15 seconds at the temperature Tr enables the carbides to be dissolved, and in particular allows a sufficient transformation into austenite. The effect is saturated beyond a period of 300 seconds. A maintenance time greater than 300 seconds

is also not compatible with the productivity requirements of continuous annealing installations, in particular the speed of travel of the coil.

At the end of the annealing maintenance, the sheet is cooled until it reaches a temperature close to the temperature T_{eg}, the rate of cooling V_{ref} being sufficiently rapid to avoid any transformation on cooling and particularly the formation of perlite hungry for carbon. To this end, the cooling rate V_{ref} is preferentially greater than 5°C/s. A partial transformation of the austenite into ferrite occurs at this stage. This makes it possible, when carbon is expelled towards the austenite, the latter being little soluble in ferrite, to stabilise the latter in order to promote the TRIP effect.

The maintenance in the temperature range 440° to 475°C must be greater than 20 seconds in order to allow stabilisation of the austenite by enrichment of said austenite with carbon, and less than 120 seconds so as to limit the surface proportion of ferrite and to limit the precipitation of carbides to the maximum extent. This is because, beyond 120 seconds, cementite Fe_3C precipitates and thereby reduces the proportion of carbon available for the TRIP effect from the residual austenite. Thus there is obtained both a low mechanical strength because of an austenite that decomposes and has a low carbon content and low elongation because of a TRIP effect with an austenite that is less stable since it is less rich in carbon. This austenite will have islets that will transform into martensite prematurely during mechanical stressing. Since martensite is not very ductile, the total elongation of the steel will be reduced.

Preferentially, the period t_{eg} for maintaining at the temperature T_{eg} will be between 30 and 80 seconds, ideally, it will be between 30 and 60 seconds in order to have an optimum effect on the microstructure and the mechanical properties.

Next, hot galvanisation is carried out by immersion in a zinc or zinc alloy bath, the temperature T_{Zn} of which may be between 440° and 475°C.

For example, the composition of the zinc or zinc alloy bath may be such that:

Al(%) + Fe(%) + 10 (Pb + Cd) < 0.55%, the remainder to 100% consisting of zinc.

The galvanised product is next cooled at a rate V_{ref2} greater than 2°C/s to ambient temperature. In this way a cold-rolled steel sheet, annealed and galvanised, is obtained, comprising a surface proportion of 65% to 85% ferrite and 15% to 35% islets of martensite and residual austenite, it being understood that the residual austenite content is between 10% and 25%.

In order to promote the phenomenon of internal oxidation of the easily oxidisable elements such as manganese, aluminium and silicon and thus to facilitate the deposition of the zinc-based coating on the sheet, the annealing in the furnace after cold rolling is carried out with a high dew point, that is to say with an increase of the oxygen flow in the metal.

This is because, when the annealing is carried out in an atmosphere having a dew point of -40°C or less, the product has unacceptable wettability and the zinc deposited does not entirely cover the surface of the sheet. In addition, poor adhesion of the zinc-based coating has been shown with this dew point at -40C.

On the other hand, with a dew point of between -20°C and -15°C, wettability and the adhesion of the zinc-based coating will be considerably improved.

The methods for coating by zinc plating or PVD (physical vapour deposition) are also suitable.

The present invention will now be illustrated using the following examples given non-limitatively:

Steels were produced, the composition of which appears in the following table, expressed as percentages by weight. Steels IX1, IX2, IX3 and IX4 having been used for manufacturing the sheets according to the invention, the composition of steels R1 to R6 that were used for manufacturing reference sheets have been indicated by way of comparison.

Steel	C (%)	Mn (%)	Si (%)	Al (%)	Si + Al (%)	B (%)	P (%)	S (%)	Nb (%)	Ti (%)	Co (%)	Cr (%)	Ni (%)	Mo (%)	N (%)
IX1	0.215	1.670	0.805	0.695	1.500	0.0004	0.0006	0.0018	0.0006	0.0051	0.020	0.038	0.0174	0.0020	0.0045
IX2	0.170	1.750	0.775	0.605	1.380	0.0002	0.023	0.0024	0.001	0.002	0.006	0.012	0.020	0.015	0.0007
IX3	0.205	1.780	0.775	0.705	1.480	0.0003	0.025	0.0028	0.001	0.002	0.005	0.012	0.016	0.003	0.0007
IX4	0.170	1.622	0.727	0.840	1.567	0.0002	0.018	0.0021	0.030	0.0045	0.024	0.025	0.021	0.002	0.0004
R1	0.175	1.615	0.326	1.225	1.551	0.00038	0.08	0.0020	0.0003	0.0120	0.017	0.020	0.021	0.0019	0.0042
R2	0.200	1.847	1.599	0.035	1.834	0.0003	0.010	0.004	0.001	0.0020	0.008	0.015	0.019	0.0020	0.0043
R3	0.180	1.720	0.775	0.605	1.380	0.0002	0.025	0.0021	0.003	0.002	0.006	0.012	0.018	0.015	0.0004
R4	0.155	1.611	0.793	0.797	1.590	0.0003	0.019	0.0011	0.001	0.012	0.001	0.003	0.001	0.001	0.00011
R5	0.159	1.593	0.806	0.785	1.591	0.0001	0.023	0.0015	0.003	0.044	0.001	0.009	0.001	0.009	0.0003
R6	0.166	1.605	0.722	0.835	1.557	0.0004	0.017	0.001	0.041	0.0045	0.024	0.025	0.020	0.005	0.0004

Table 1: Compositions of steels (% weight). R_i = References No i

Underlined values: Not in accordance with the invention

Semi-finished cast products corresponding to the above compositions were cast, heated to 1230°C and then hot rolled in a range where the structure is entirely austenitic. The manufacturing conditions for these hot-rolled products (end-of-rolling temperature T_{FL} and coiling temperature T_{bob}) are indicated in Table 2.

Steel	T_{FL} (°C)	Ar3 (°C)	T_{bob} (°C)
IX1	920	713	580
IX2	> 920	716	550
IX3	> 920	702	550
IX4	> 920	726	535
R1	910	726	550
R2	915	715	540
R3	922	721	560
R4	> 920	774	540
R5	> 920	690	540
R6	> 920	687	540

Table 2: Manufacturing conditions for hot-rolled products

The hot-rolled products were all next pickled and then cold-rolled with a degree of reduction of between 30% and 80%. From the same composition, some steels were subjected to different manufacturing conditions.
Table 3 indicates the manufacturing conditions for sheets annealed after cold rolling:

- Heating rate Vc
- The initial austenite content at the end of the (intercritical) maintenance γ_{init}
- Annealing temperature Tr
- Annealing maintenance time t_r
- Cooling rate after annealing Vref
- Cooling rate after galvanisation V'ref
- Equalisation temperature T_{eq}
- Duration on equalisation stage t_{eq}

The transformation temperatures Ac1 and Ac3 have also been entered in Table 3.
The microstructure of the TRIP steels was also determined, with quantification of the residual austenite content. The surface fractions of

MA islets were quantified after attack of the metabisulphite, Klemm or Lepera type, followed by an image analysis using Aphelion™ software.
The sheets were all coated with Zn.
The end-of-rolling temperatures were estimated in some cases but these remain between 900° and 1000°C where it is mentioned that they are above 920°C.
The inscription "n.e" means "not evaluated".

Test	Composition of steel	Vc (°C/s)	Ac1-Ac3 (°C)	Tr (°C)	t_c (s)	γ_{limit} (%)	V_{ref} (°C/s)	T_{eq} (°C)	t_{eq} (s)	V'ref (°C/s)
1	IX1	4	729-920	815	45	37	35	460	45	5
2	IX1	4	729-920	850	45	62	35	460	45	5
3	IX1	5	729-920	770	45	25	35	460	45	5
4	IX1	4.4	729-920	840	55	60	55.5	430	180	8.7
5	IX2	4.4	727-1059	800	67	30	34	460	43	5
6	IX2	4.4	727-1059	830	67	35	34	480	43	5
7	IX3	4.4	729-1090	800	67	35	34	460	43	5
8	IX3	4.4	729-1090	830	67	40	34	460	43	5
9	IX4	4.4	727-1154	780	67	30	34	460	43	5
10	IX4	4.4	727-1154	820	67	35	34	460	43	5
11	IX4	4.4	727-1154	850	67	40	34	460	43	5
12	IX4	3	727-1154	800	128	32	21	460	314	6
13	R1	6	729-1115	850	39	40	47	460	33	7
14	R1	5	729-1115	770	39	24	44	460	33	6
15	R2	4	752-875	830	46	50 to 65	32	460	45	4.4
16	R2	3	752-875	830	116	50 to 65	37	400	270	87
17	R3	5.5	726-1050	830	37	40 to 55	40	460	36	6

18	R3	4.4	726-1050	830	37	40 to 55	56	420	180	6

Table 3: Manufacturing conditions for sheets cold rolled and annealed

Underlined values: Not in accordance with the invention

Test	Composition of steel	Vc (°C/s)	γ_{inert} (%)	Tr	A_{c3} - A_{c1} (°C)	t_x (s)	V_{ref} (°C/s)	T_{eq} (°C)	T_{eq} (s)	V'ref (°C/s)
19	R4	5.5	20	780	729-1149	36	43	460	34	5.5
20	R4	5.5	25	850	729-1149	36	43	460	34	5.5
21	R5	5.5	20	780	717-1138	36	43	460	34	5.5
22	R5	5.5	25	850	717-1138	36	43	460	34	5.5
23	R6	5.5	20	780	714-1147	36	43	460	34	5.5
24	R6	5.5	25	850	714-1147	36	43	460	34	5.5

Table 3 (Continuation): Manufacturing conditions for sheets cold rolled and annealed

Underlined values: Not in accordance with the invention

The mechanical tensile properties obtained (elasticity limit Re, strength Rm and breaking elongation A have been set out in Table 5 below. These are obtained using a test piece of the ISO 20 x 80 type with the dimensions in Table 4 illustrated in Figure 1. Uniaxial tractions make it possible to obtain these mechanical properties being done in the direction perpendicular to that of the cold rolling.

Table 4: Dimensions of the traction test pieces, the units being expressed in mm (Figure 1 illustrates the lengths mentioned)

Type	b	Lo	Lc	R	T	Lt	Dimensions of blank
ISO 20 x 80	20	80	100	20	30	260	260 x 32

The suitability for coating was quantified as follows: a sheet is bent in a block at 180°, then, a scotch is applied to the bent external surface; when the scotch is removed, if the coating is adherent, the coating is not

pulled away. If the coating is not adherent, the coating is pulled away with the scotch.

Likewise, the sensitivity to weakening by penetration of liquid Zn is assessed by a welding test on a piece coated with Zn. The test consisting of observing the cracks under the microscope and their depth according to the material and method used, and the classification is then done relatively.

For these two tests, the quotation is expressed from 1 (poor coatability/sensitive to liquid Zn) to 5 (very good suitability for coating/insensitive to liquid Zn). Results quoted 1-2 are considered to be unsatisfactory.

Steel sheet	Fraction (MA %)	Re (MPa)	Rm (MPa)	A (%)	Sensitivity to liquid Zn	Coatability with liquid Zn	Mean length of MA islets (µm)
1	19	444	796	27	3	5	1.06
2	22	445	787	27	3	5	1.06
3	≤ 15	425	735	28	3	5	n.e
4	≤ 15	460	730	32	3	5	n.e
5	15<X< 21	376	802	22	4	5	< 1.3
6	15<X< 21	389	805	22	4	5	<1.3
7	15<X< 21	389	844.5	19	3	5	1.04
8	15<X< 21	386	829	20	3	5	1.04
9	15<X< 21	560	889	20	4	5	< 1.1
10	15<X< 21	568	860	19	4	5	< 1.1
11	15<X< 21	557	861	19	4	5	< 1.1
12	15<X< 21	577	857	15.3	4	5	< 1.1
13	15	475	735	27	4	5	n.e
14	13	429	684	29	4	5	n.e
15	> 22	437	933	21.6	2	2	1.6
16	20	540	820	31	2	2	1.74
17	≤ 15	474	735	24	3	5	n.e
18	≤ 15	450	705	25.4	3	5	n.e
19	≤ 15	411	737	27	4	5	n.e
20	≤ 15	426	729	28	4	5	n.e
21	≤ 15	700	963	15	4	5	n.e
22	≤ 15	640	875	17	4	5	n.e
23	≤ 15	555	869	14	4	5	n.e
24	≤ 15	557	880	18	4	5	n.e

Table 5: Results obtained on cold-rolled and annealed sheets

Underlined values: Not in accordance with the invention

The steel sheets according to the invention have a set of microstructural and mechanical characteristics allowing the advantageous manufacture of parts, in particular for applications involving structural parts: strengths of between 780 and 900 MPa, breaking elongation greater than 19% with a test piece of the ISO 20 x 80 type as described by Table 4, good

suitability for coating and insensitive to weakening through the penetration of liquid zinc. Figure 2 illustrates the morphology of the steel sheet 1 with the MA islets in white.

The sheets IX1, IX2, IX3 and IX4 are in accordance with the invention from the point of view of chemical composition. The tests associated with these compositions ranging from 1 to 12 show the stability of the properties obtained and demonstrate the limits of the manufacturing method for obtaining the sheet of the invention.

The chemical compositions IX1, IX2, IX3 and IX4 associated with the tests according to the invention (1, 2 and 5 to 11 inclusive) are insensitive to the penetration of liquid zinc, in particular during resistance spot welding. They have good coatability and MA islets which, surprisingly, have an average of 1.06 micrometres, and therefore fine grains. Furthermore, their mechanical strength is between 780 and 900 MPa and their total elongation is much greater than 19%. Figure 2 illustrates the microstructure of the sheet of test 1. Each martensite/austenite islet, referred to as "MA islet", is characterised by its maximum length and its maximum width. On the basis of a representative sample of more than 100 islets characterised, the mean of the length of the islets is astonishingly low and equal to 1.06 micrometres. The confidence range is 95% for having a mean situated between 0.97 and 1.15 micrometres. The smallest islet measured 0.38 micrometres and the longest 3.32 micrometres. The first quartile, that is to say the largest islet of the 25% of smallest islets, was measured at 0.72 micrometres; while the third quartile, that is to say the smallest of the 25% of longest islets, measured 1.29 micrometres. The median was calculated at 0.94 micrometres. The proximity between the median and the mean is a good indicator that the data have a distribution centred on a length of 1 micrometre to within 0.1 µm. The MA islets are also characterised by their shape factor, that is to say the ratio between their length and their maximum width $\frac{L_{max}}{L_{min}}$. The MA islets of test 1 have a shape-factor distribution shown by Figure 3. The mean of the shape factors is 2.15. The confidence range is 95% for having a shape-factor mean situated between 1.95 and 2.34.

Test 3 associated with the chemical composition IX1 has an austenite content at the end of the maintenance γ_{maint} that is too low since the maintenance temperature is below Ac1 + 50°C, and consequently the final surface fraction of MA islets is too small and this microstructural characteristic is associated with a reduction in the mechanical strength in the context of the invention. Test 4 associated with chemical composition

IX1 saw an annealing at a temperature making it possible to obtain 60% of γ_{max} and is therefore situated in the range claimed by the invention. However, the galvanisation temperature Teg is 430°C and is therefore too low and the equalisation temperature t_{eq} is 180 seconds, which is too long. Thus the surface fraction of said islets is too small and the consequence is a mechanical strength below 780 MPa.

Test 12, associated with chemical composition IX4, saw an equalisation level stage t_{eq} of 314 seconds, which is above the specification in the context of the invention, which is 120 seconds, and thus the total elongation is too small at 15.3%.

R1 presents a chemical composition departing from the target of the invention. This is because R1 has an Si content that is too small and a phosphorus content that is too high. Thus tests 13 and 14 present mechanical-strength properties that are unsatisfactory with respect to the targets of the invention since they are below 780 MPa despite compliance with the manufacturing conditions for test 13. Test 14 also has an annealing temperature T_r of below Ac1 + 50°C.

Chemical compositions R3 and R4 are not in accordance with the invention since the proportions by mass of carbon are below 0.17%. Tests 17, 18, 19 and 20 associated with R3 (17 and 18) and R4 (19 and 20) do not make it possible to achieve 780 MPa. The fractions of MA islets obtained at the end of said annealing are too small since there is not enough carbon to stabilise the austenite and form a sufficient number of MA islets. The proportion of the latter is therefore too small and consequently the mechanical strength is below 780 MPa for these tests.

Chemical composition R2 is not in accordance with the invention since the Si content is above 1% and that of aluminium below 0.5%. Two tests issued from this chemical composition, tests 15 and 16. Test 15 does not correspond to the invention despite an annealing cycle corresponding to the claim. The fraction of MA islets at the end of said annealing is too high because of the double hardening effect of silicon and its ferritising capacity less than that of aluminium. Ferrite is a soft structure compared with MA islets and the use of ferritising elements softens the steel sheet whereas aluminium would have served here to rebalance the hardnesses in order to obtain a sheet with a mechanical strength below 900 MPa. Thus the mechanical strength of the steel sheet 15 is greater than 900 MPa and the mean size of the MA islets is appreciably greater than 1.3 micrometres. Such a grain size will facilitate connectivity between the grains and accelerate the propagation of a crack already formed. Furthermore, the

sensitivity to the penetration of liquid zinc (2/5) of this reference is below the minimum sought for the invention (3/5).

Test 16 does not correspond to the invention, the mean size of the islets MA is greatly above 1.3 micrometres. Furthermore, the silicon content will lead to the formation of silicon oxides on the surface during annealing before hot galvanisation. Thus the coatability of this product will be below the minimum mark sought of 3/5. Its sensitivity to the penetration of liquid zinc is also less than 3/5.

The chemical composition R5 does not correspond to the invention. The carbon content is less than 0.17% and the Ti content is greater than 0.020%. The result, as shown by tests 21 and 22, is that the elongation target of 19% is not achieved.

The chemical composition R6 does not correspond to the invention since the niobium content is greater than 0.030%. Examples 23 and 24 show that the elongation target of 19% is not achieved.

The steel sheets according to the invention will be used advantageously for the manufacture of structural or safety parts in powered land vehicles. The following examples are given non-limitatively: cross-members, longitudinal members and centre pillars.

Hidegen hengerelt acéllemez, cink vagy cink ötvözet borítással és eljárás előállítására, valamint az acéllemez alkalmazása

SZABADALMI IGÉNYPONTOK

1. Hidegen hengerelt acéllemez, cink vagy cink ötvözet borítással, aminek súlyszázalékos összetétele az alábbi:

$0{,}17\% \leq C \leq 0{,}25\%$

$1{,}5\% \leq Mn \leq 2{,}0\%$

$0{,}50\% \leq Si \leq 1\%$

$0{,}50\% \leq Al \leq 1{,}2\%$

$B \leq 0{,}001\%$

$P \leq 0{,}030\%$

$S \leq 0{,}01\%$

$Nb \leq 0{,}030\%$

$Ti \leq 0{,}020\%$

$V \leq 0{,}015\%$

$Cu \leq 0{,}1\%$

$Cr \leq 0{,}150\%$

$Ni \leq 0{,}1\%$

$0\% \leq Mo \leq 0{,}150\%$,

és a Si + Al ≥ 1.30 %,

a maradékban pedig vas és a gyártásból szükségszerűen adódó szennyeződések,

a mikro-szerkezet a felületek arányában:

- 65% - 85% ferrit, ami poligonális ferritből és bainites ferritből áll, és
- 15% - 35% martenzit visszamaradó ausztenit zárványokkal,

ahol a ferrit 5%-nál kevesebb nem-rekristallizált ferritet tartalmaz, és a maradék ausztenit teljes részaránya 10% - 25%, és a martenzit teljes részaránya 10% vagy kevesebb annál, a martenzit és a maradék ausztenit zárványok átlagos mérete kisebb, mint 1.3 µm, átlagos alak tényezőjük kevesebb, mint 3, ahol az alak tényező a martenzit és a maradék ausztenit zárványok hossza és maximális szélessége közötti arány,

a lemez Pm mechanikai szilárdsága 780 - 900 MPa, és A% szakadási nyúlása 19% vagy annál nagyobb.

2. Az 1. igénypont szerinti acéllemez, ami tartalmaz:
   0.19 s% ≤ C ≤ 0.23 s%
3. Az 1. vagy 2. igénypont szerinti acéllemez, ami tartalmaz:
   1.6 s% ≤ Mn ≤ 1.8 s%
4. Az 1 - 3. igénypontok bármelyike szerinti acéllemez, ami tartalmaz:
   0.7 s% ≤ Si ≤ 0.9 s%
5. Az 1 - 4. igénypontok bármelyike szerinti acéllemez, ami tartalmaz:
   0.6 s% ≤ Al ≤ 0.8 s%
6. Az 1 - 5. igénypontok bármelyike szerinti acéllemez, ami tartalmaz:
   0 s% ≤ B ≤ 0.0005 s%
7. Az 1 - 6. igénypontok bármelyike szerinti acéllemez, ahol a martenzit és a maradék ausztenit zárványok felületi arányának több, mint 90%-a két µm méretű vagy annál kisebb.
8. Eljárás cink vagy cink ötvözet bevonattal ellátott hidegen hengerelt lemez előállítására, amelynek során:
   - gondoskodunk az 1 - 7. igénypontok bármelyike szerinti összetételű acélról, majd

- az acélból félterméket öntünk, majd
- a félterméket 1150 és 1250°C hőmérsékletre hevítjük, majd
- a felmelegített félterméket melegen lemezzé hengereljük úgy, hogy a hengerlést Ar3 hőmérsékleten vagy annál magasabb T_{FL} hőmérsékleten fejezzük be, majd
- a melegen hengerelt lemezt 500 és 600°C közötti Tbob hőmérsékleten feltekercseljük, majd
- a melegen hengerelt lemezt szobahőmérsékletre hűtjük, majd
- adott esetben a melegen hengerelt lemezt maratjuk, majd
- a lemezt hidegen hengereljük, majd
- a hidegen hengerelt lemezt 1°C/sec - 30°C/sec Vc sebességgel Tr hőmérsékletre melegítjük 15 másodpercre vagy annál hosszabb időre, amikor is a hőmérsékleteket és időtartamokat úgy választjuk meg, hogy az ausztenites felületi frakció arány 35% és 70% között legyen, majd
- a hidegen hengerelt lemezt lehűtjük 475°C és 440°C Teg hőmérsékletre eléggé nagy Vref sebességgel ahhoz, hogy elkerüljük a perlit képződést, majd
- a hidegen hengerelt lemezt a Teg kiegyenlítődési hőmérsékleten tartjuk 20 és 120 másodperc közötti t_{eq} időre, majd
- a hidegen hengerelt lemezt bevonattal látjuk el cink vagy cink ötvözet fürdőn történő folyamatos átvezetéssel, majd
- a hidegen hengerelt és bevonattal ellátott lemezt környezeti hőmérsékletre hűtjük.

9. A 8. igénypont szerinti eljárás, ahol a T_{FL} hőmérséklet magasabb, mint 900°C.

10. A 8. igénypont szerinti eljárás, ahol a T_{FL} hőmérséklet 920°C vagy annál magasabb.

11. A 8 - 10. igénypontok bármelyike szerinti eljárás, ahol a Tr hőmérsékleten tr ideig végzett izzítás során a harmatpont -20 és -15°C között van.

12. A 8 - 11. igénypontok bármelyike szerinti eljárás, ahol a Tr hőmérséklet Ac1 + 50°C és Ac3 - 50°C között van.

13. A 8 - 11. igénypontok bármelyike szerinti eljárás, ahol a Tr hőmérséklet Ac1 + 50°C és Ac1 + 170°C között van.

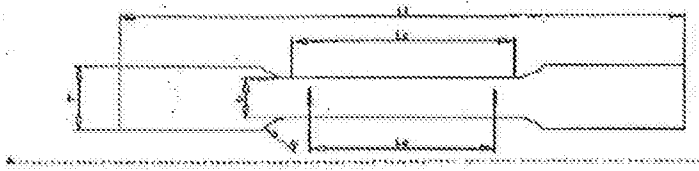
14. A 8 - 13. igénypontok bármelyike szerinti eljárás, ahol a t_{eq} időtartam 30 és 60 másodperc között van.

15. A 8 - 13. igénypontok bármelyike szerinti eljárás, ahol a t_{eq} időtartam 30 és 60 másodperc között van.

16. Eljárás munkadarabok előállítására az 1 – 7. igénypontok bármelyike szerinti borítással ellátott hidegen hengerelt vagy a 8 – 15. igénypontok bármelyike szerint előállított lemez hegesztésével, ahol a hegesztést ellenállás ponthegesztéssel végezzük.

17. Az 1 – 7. igénypontok bármelyike szerinti borítással ellátott hidegen hengerelt vagy a 8 – 16. igénypontok bármelyike szerint előállított lemez alkalmazása szerkezeti vagy biztonsági elemek gyártására mezőgazdasági erőgépekhez.

Figure 1



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Modified field code

Figure 2

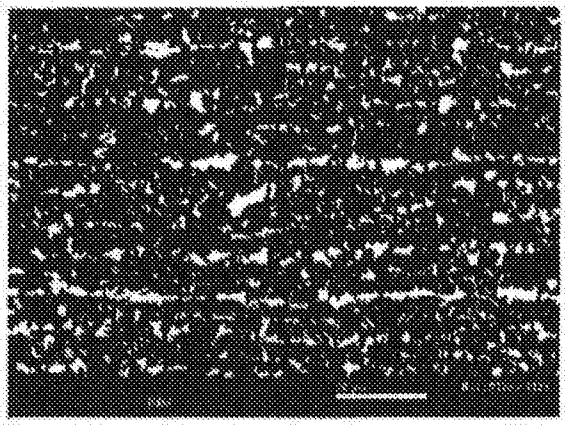
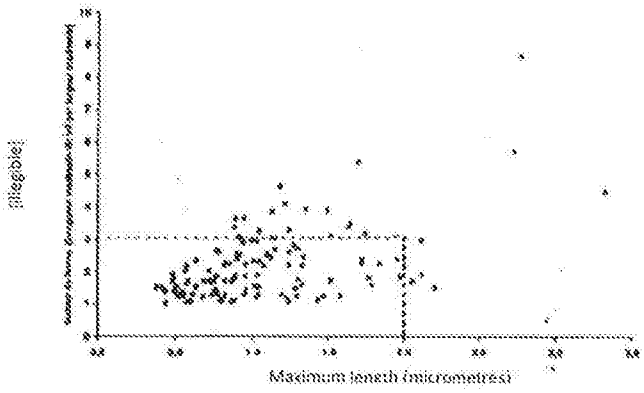


Figure 3



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