

(19)



(11)

EP 3 969 628 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
11.06.2025 Bulletin 2025/24

(21) Application number: **20716219.9**

(22) Date of filing: **30.03.2020**

(51) International Patent Classification (IPC):
C21D 8/02 (2006.01)

(52) Cooperative Patent Classification (CPC):
**C22C 38/42; C21D 1/19; C21D 1/26; C21D 8/041;
C21D 8/0426; C21D 8/0436; C21D 8/0463;
C21D 8/0473; C21D 9/48; C22C 38/001;
C22C 38/02; C22C 38/06; C22C 38/44;
C22C 38/46; C22C 38/48;**

(Cont.)

(86) International application number:
PCT/IB2020/052999

(87) International publication number:
WO 2020/229898 (19.11.2020 Gazette 2020/47)

(54) **A COLD ROLLED MARTENSITIC STEEL AND A METHOD FOR IT'S MANUFACTURE**

KALTGEWALZTER MARTENSITISCHER STAHL UND VERFAHREN ZU SEINER HERSTELLUNG

ACIER MARTENSITIQUE LAMINÉ À FROID ET PROCÉDÉ POUR SA FABRICATION

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Validation States:
MA

(30) Priority: **15.05.2019 PCT/IB2019/054022**

(43) Date of publication of application:
23.03.2022 Bulletin 2022/12

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EP 3 969 628 B1

(52) Cooperative Patent Classification (CPC): (Cont.)
C22C 38/50; C22C 38/54; C22C 38/58;
C21D 2211/002; C21D 2211/005; C21D 2211/008

Description

[0001] The present invention relates to a method of manufacturing of a cold rolled martensitic steel suitable for automotive industry and particularly to Martensitic steels having tensile strength 1280 MPa or more.

[0002] Automotive parts are required to satisfy two inconsistent necessities, viz. ease of forming and strength but in recent years a third requirement of improvement in fuel consumption is also bestowed upon automobiles in view of global environment concerns. Thus, now automotive parts must be made of material having high formability in order that to fit in the criteria of ease of fit in the intricate automobile assembly and at same time have to improve strength for vehicle crashworthiness and durability while reducing weight of vehicle to improve fuel efficiency.

[0003] Therefore, intense Research and development endeavors are put in to reduce the amount of material utilized in car by increasing the strength of material. Conversely, an increase in strength of steel sheets decreases formability, and thus development of materials having both high strength and high formability is necessitated.

[0004] Earlier research and developments in the field of high strength and high formability steel sheets have resulted in several methods for producing high strength and high formability steel sheets, some of which are enumerated herein for conclusive appreciation of the present invention:

EP3395993 is a cold-rolled steel sheet manufactured by a cold-rolled steel sheet manufacturing method comprising a continuous annealing step, which has a composition comprising, in percentage by weight: C: 0.1-0.15%; Si: 0.2% or less (including 0%); Mn: 2.3-3.0%; P: 0.001-0.10%; S: 0.010% or less (including 0%); Sol.Al: 0.01-0.10%; N: 0.010% or less (excluding 0%); Cr: 0.3-0.9%; B: 0.0010-0.0030%; Ti: 0.01-0.03%; Nb: 0.01-0.03%; the balance being Fe and other impurities, and satisfies following relational expression (1). [Relational expression 1] $1650 \leq 5541.4C + 239Mn + 169.1Cr + 0.74SS - 1.36RCS \leq 1688$ [wherein C, Mn and Cr are values representing the contents of the respective elements in weight%, SS represents a continuous annealing temperature (°C), and RCS represents a cooling end temperature (°C) in continuous annealing]. The present invention provides a high yield ratio type high strength cold-rolled steel sheet and the manufacturing method thereof, in which microstructure comprises, in area percentage, at least 90% of martensite and tempered martensite; and 10% or less of ferrite and bainite, in which the fraction of the tempered martensite in the martensite and the tempered martensite is 90% or more, in area percentage, and the ratio (b/a) of the C + Mn concentration (a) in the martensite to the C + Mn concentration (b) in the ferrite and the bainite is 0.65 or more.

[0005] The steel sheet of WO2017/065371 is manufactured through the steps of: rapidly heating a material steel sheet for 3 to 60 seconds to an Ac3 transformation point or higher and maintaining the material steel sheet, the material steel sheet containing 0.08 to 0.30 wt% of C, 0.01 to 2.0 wt% of Si, 0.30 to 3.0 wt% of Mn, 0.05 wt% or less of P and 0.05 wt% or less of S and the remainder being Fe and other unavoidable impurities; rapidly cooling the heated steel sheet to 100°C/s or higher with water or oil; and rapidly tempering to 500°C to A1 transformation point for 3 to 60 seconds including heating and maintaining time. But the steel of WO2017/065371 not able to surpass the tensile strength of 1300 MPa and do not mention about hole expansion ratio even having a tempered martensite single phase structure.

[0006] WO2010/036028 relates to a hot dip galvanized steel sheet and a manufacturing method thereof. The hot dip galvanize steel sheet includes a steel sheet including a martensitic structure as a matrix, and a hot dip galvanized layer formed on the steel sheet. The steel sheet includes C of 0.05 wt % to 0.30 wt %, Mn of 0.5 wt % to 3.5 wt %, Si of 0.1 wt % to 0.8 wt %, Al of 0.01 wt % to 1.5 wt %, Cr of 0.01 wt % to 1.5 wt %, Mo of 0.01 wt % to 1.5 wt %, Ti of 0.001 wt % to 0.10 wt %, N of 5 ppm to 120 ppm, B of 3 ppm to 80 ppm, an impurity, and the remainder of Fe. But the steel of WO2010/036028 does not mentions hole expansion ratio.

[0007] The purpose of the present invention is to solve these problems by making available cold-rolled martensitic steel sheets that simultaneously have:

- an ultimate tensile strength greater than or equal to 1280 MPa and preferably above 1300 MPa,
- a yield strength greater than or equal to 1100 MPa and preferably above 1150 MPa
- a hole expansion ratio of more the 40% and preferably above 50%. The solutions are given in the claims.

[0008] Preferably, such steel can also have a good suitability for forming, for rolling with good weldability and coatability.

[0009] Another object of the present invention is also to make available a method for the manufacturing of these sheets that is compatible with conventional industrial applications while being robust towards manufacturing parameters shifts.

[0010] The above object and other advantages of the present invention will become more apparent by describing in detail the preferred embodiment of the present invention.

[0011] The chemical composition of the cold rolled martensitic steel comprises of the following elements:

Carbon is present in the steel of present invention is between 0.1% and 0.2%. Carbon is an element necessary for increasing the strength of the Steel of present invention by producing a low-temperature transformation phases such as Martensite, Therefore, Carbon plays two pivotal roles, one is to increase the strength. But Carbon content less than 0.1% will not be able to impart the tensile strength to the steel of present invention. On the other hand, at a Carbon content exceeding 0.2%, the steel exhibits poor spot weldability which limits its application for the automotive parts. A preferable

content for the present invention may be kept between 0.11% and 0.19% and more preferably between 0.12% and 0.18%.

[0012] Manganese content of the steel of present invention is between 1.5 % and 2.5%. This element is gammagenous. Manganese provides solid solution strengthening and suppresses the ferritic transformation temperature and reduces ferritic transformation rate hence assist in the formation of martensite. An amount of at least 1.5% is required to impart strength as well as to assist the formation of Martensite. But when Manganese content is more than 2.5% it produces adverse effects such as it retards transformation of Austenite to Martensite during cooling after annealing. Manganese content of above 2.5% can get excessively segregated in the steel during solidification and homogeneity inside the material is impaired which can cause surface cracks during a hot working process. The preferred limit for the presence of Manganese is between 1.6% and 2.4% and more preferably between 1.6% and 2.2%.

[0013] Silicon content of the steel of present invention is between 0.1% and 0.25%. Silicon is an element that contributes to increasing the strength by solid solution strengthening. Silicon is a constituent that can retard the precipitation of carbides during cooling after annealing, therefore, Silicon promotes formation of Martensite. But Silicon is also a ferrite former and also increases the Ac3 transformation point which will push the annealing temperature to higher temperature ranges that is why the content of Silicon is kept at a maximum of 0.25%. Silicon content above 0.25% can also temper embrittlement and in addition silicon also impairs the coatability. The preferred limit for the presence of Silicon is between 0.16% and 0.24% and more preferably between 0.18% and 0.23%.

[0014] Chromium content of the composite coil of steel of present invention is between 0.1% and 1%. Chromium is an essential element that provide strength to the steel by solid solution strengthening and a minimum of 0.1% is required to impart the strength but when used above 1% impairs surface finish of steel. The preferred limit for the presence of Chromium is between 0.1% and 0.5%.

[0015] The content of the Aluminum is between 0.01% and 1%. in the present invention Aluminum removes Oxygen existing in molten steel to prevent Oxygen from forming a gas phase during solidification process. Aluminum also fixes Nitrogen in the steel to form Aluminum nitride to reduce the size of the grains. Higher content of Aluminum, above 1%, increases Ac3 point to a high temperature thereby lowering the productivity. The preferred limit for the presence of Aluminium is between 0.01% and 0.05%

[0016] Titanium is added to the Steel of present invention between 0.001 % to 0.1%. It forms Titanium-nitrides appearing during solidification of the cast product. The amount of Titanium is so limited to 0.1% to avoid the formation of coarse Titanium-nitrides detrimental for formability. In case the Titanium content below 0.001% does not impart any effect on the steel of present invention.

[0017] Sulfur is not an essential element but may be contained as an impurity in steel and from point of view of the present invention the Sulfur content is preferably as low as possible but 0.09% or less from the viewpoint of manufacturing cost. Further if higher Sulfur is present in steel it combines to form Sulfides especially with Manganese and reduces its beneficial impact on the present invention.

[0018] Phosphorus constituent of the Steel of present invention is between 0% and 0.09%, Phosphorus reduces the spot weldability and the hot ductility, particularly due to its tendency to segregate at the grain boundaries or co-segregate with Manganese. For these reasons, its content is limited to 0.09 % and preferably lower than 0.06%.

[0019] Nitrogen is limited to 0.09% to avoid ageing of material and to minimize the precipitation of Aluminum nitrides during solidification which are detrimental for mechanical properties of the steel.

[0020] Molybdenum is an optional element that constitutes 0% to 0.4% of the Steel of present invention; Molybdenum plays an effective role in improving hardenability and hardness, delays the appearance of Bainite hence promote the formation of Martensite, in particular when added in an amount of at least 0.001% or even of at least 0.002%. However, the addition of Molybdenum excessively increases the cost of the addition of alloy elements, so that for economic reasons its content is limited to 0.4%.

[0021] Niobium is present in the Steel of present invention between 0% and 0.1% and suitable for forming carbo-nitrides to impart strength of the Steel of present invention by precipitation hardening. Niobium will also impact the size of microstructural components through its precipitation as carbo-nitrides and by retarding the recrystallization during heating process. Thus, finer microstructure formed at the end of the holding temperature and as a consequence after the complete annealing will lead to the hardening of the product. However, Niobium content above 0.1% is not economically interesting as a saturation effect of its influence is observed this means that additional amount of Niobium does not result in any strength improvement of the product.

[0022] Vanadium is effective in enhancing the strength of steel by forming carbides or carbo-nitrides and the upper limit is 0.1% from economic points of view.

[0023] Nickel may be added as an optional element in an amount of 0% to 1% to increase the strength of the steel present invention and to improve its toughness. A minimum of 0.01% is preferred to get such effects. However, when its content is above 1%, Nickel causes ductility deterioration.

[0024] Copper may be added as an optional element in an amount of 0% to 1% to increase the strength of the of Steel of present invention and to improve its corrosion resistance. A minimum of 0.01% is preferred to get such effects. However, when its content is above 1%, it can degrade the surface aspects.

[0025] Boron is an optional element for the steel of present invention and may be present between 0% and 0.05%. Boron forms boro-nitrides and impart additional strength to steel of present invention when added in an amount of at least 0.0001%.

[0026] Calcium can be added to the steel of present invention in an amount between 0.001% and 0.01%. Calcium is added to steel of present invention as an optional element especially during the inclusion treatment. Calcium contributes towards the refining of the Steel by binding the detrimental Sulfur content in globular form thereby retarding the harmful effect of Sulfur.

[0027] Other elements such as Sn, Pb or Sb can be added individually or in combination in the following proportions: Sn $\leq$ 0.1%, Pb $\leq$ 0.1% and Sb $\leq$ 0.1%. Up to the maximum content levels indicated, these elements make it possible to refine the grain during solidification. The remainder of the composition of the steel consists of iron and inevitable impurities resulting from processing.

[0028] The microstructure of the martensitic steel sheet will now be described in details, all percentages being in area fraction.

[0029] Martensite constitutes at least 95% of the microstructure by area fraction. The martensite of the present invention can comprise both fresh and tempered martensite. However, fresh martensite is an optional microconstituent which is limited in the steel at an amount of between 0% and 4%, preferably between 0 and 2% and even better equal to 0%. Fresh martensite may form during cooling after tempering. Tempered martensite is formed from the martensite which forms during the second step of cooling after annealing and particularly after below Ms temperature and more particularly between Ms-10°C and 20°C. Such martensite is then tempered during the holding at a tempering temperature T_{temper} between 150°C and 300°C. The martensite of the present invention imparts ductility and strength to such steel. Preferably, the content of martensite is between 96% and 99% and more preferably between 97% and 99%.

[0030] The cumulated amount of ferrite and bainite represents between 1% and 5% of the microstructure. The cumulative presence of bainite and ferrite does not affect adversely to the present invention till 5% but above 5% the mechanical properties may get impacted adversely. Hence the preferred limit for the cumulative presence ferrite and bainite is kept between 1% and 4% and more preferably between 1% and 3%.

[0031] Bainite forms during the reheating before tempering. In a preferred embodiment, the steel of present invention contains 1 to 3% of bainite. Bainite can impart formability to the steel but when present in a too big amount, it may adversely impact the tensile strength of the steel.

[0032] Ferrite may form during the first step of cooling after annealing but is not required as a microstructural constituent. Ferrite formation must be kept as low as possible and preferably less than 2% or even less than 1%.

[0033] Residual Austenite is an optional microstructure that can be present between 0% and 2% in the steel.

[0034] In addition to the above-mentioned microstructure, the microstructure of the cold rolled martensitic steel sheet is free from microstructural components such as pearlite and cementite.

[0035] The steel according to the invention can be manufactured by any suitable methods. It is however preferable to use the method according to the invention that will be detailed, as a non-limitative example.

[0036] Such preferred method consists in providing a semi-finished casting of steel with a chemical composition of the prime steel according to the invention. The casting can be done either into ingots or continuously in form of thin slabs or thin strips, i.e. with a thickness ranging from approximately 220mm for slabs up to several tens of millimeters for thin strip.

[0037] For example, a slab having the chemical composition according to the invention is manufactured by continuous casting wherein the slab optionally underwent a direct soft reduction during the continuous casting process to avoid central segregation and to ensure a ratio of local Carbon to nominal Carbon kept below 1.10. The slab provided by continuous casting process can be used directly at a high temperature after the continuous casting or may be first cooled to room temperature and then reheated for hot rolling.

[0038] The temperature of the slab, which is subjected to hot rolling, must be at least 1000°C and must be below 1280°C. In case the temperature of the slab is lower than 1280°C, excessive load is imposed on a rolling mill and, further, the temperature of the steel may decrease to a Ferrite transformation temperature during finishing rolling, whereby the steel will be rolled in a state in which transformed Ferrite contained in the structure. Therefore, the temperature of the slab must be high enough so that hot rolling should be completed in the temperature range of Ac₃ to Ac₃+100°C. Reheating at temperatures above 1280°C must be avoided because they are industrially expensive.

[0039] The sheet obtained in this manner is then cooled at a cooling rate of at least 20°C/s to the coiling temperature which must be below 650°C. Preferably, the cooling rate will be less than or equal to 200°C/s.

[0040] The hot rolled steel sheet is then coiled at a coiling temperature below 650°C to avoid ovalization and preferably between 475°C and 625°C to avoid scale formation, with an even preferred range for such coiling temperature between 500°C and 625°C. The coiled hot rolled steel sheet is then cooled down to room temperature before subjecting it to optional hot band annealing.

[0041] The hot rolled steel sheet may be subjected to an optional scale removal step to remove the scale formed during the hot rolling before optional hot band annealing. The hot rolled sheet may then have subjected to an optional hot band annealing. In a preferred embodiment, such hot band annealing is performed at temperatures between 400°C and 750°C,

preferably for at least 12 hours and not more than 96 hours, the temperature preferably remaining below 750°C to avoid transforming partially the hot-rolled microstructure and, therefore, possibly losing the microstructure homogeneity. Thereafter, an optional scale removal step of this hot rolled steel sheet may be performed through, for example, pickling of such sheet.

[0042] This hot rolled steel sheet is then subjected to cold rolling to obtain a cold rolled steel sheet with a thickness reduction between 35 to 90%.

[0043] Thereafter the cold rolled steel sheet is being heat treated which will impart the steel of present invention with requisite mechanical properties and microstructure.

[0044] The cold rolled steel sheet is heated at a heating rate which is of at least 2°C/s and preferably greater than 3°C/s, to a soaking temperature Tsoak between Ac3 and Ac3+100° C and preferably between Ac3+10°C and Ac3+100°C, wherein Ac3 for the steel sheet is calculated by using the following formula:

$$Ac3 = 910 - 203[C]^{(1/2)} - 15.2[Ni] + 44.7[Si] + 104[V] + 31.5[Mo] + 13.1[W] - 30[Mn] - 11[Cr] - 20[Cu] + 700[P] + 400[Al] + 120[As] + 400[Ti]$$

wherein the elements contents are expressed in weight percentage of the cold rolled steel sheet.

[0045] The cold rolled steel sheet is held at Tsoak during 10 seconds to 500 seconds to ensure a complete recrystallization and full transformation to austenite of the strongly work hardened initial structure.

[0046] The cold rolled steel sheet is then cooled in a two steps cooling process wherein the first step of cooling starts from Tsoak, the cold rolled steel sheet being cooled down, at a cooling rate CR1 between 15°C/s and 150°C/s, to a temperature T1 which is in a range between 650°C and 750°C. In a preferred embodiment, the cooling rate CR1 for such first step of cooling is between 20°C/s and 120°C/s. The preferred T1 temperature for such first step is between 660°C and 725°C.

[0047] In the second step of cooling, the cold rolled steel sheet is cooled down from T1 to a temperature T2 which is between Ms-10°C and 20°C, at a cooling rate CR2 of at least 50°C/s. In a preferred embodiment, the cooling rate CR2 for the second step of cooling is at least 100°C/s and more preferably at least 150°C/s. The preferred T2 temperature for such second step is between Ms-50°C and 20°C.

[0048] Ms for the steel sheet is calculated by using the following formula:

$$Ms = 545 - 601.2 * (1 - EXP(-0.868[C])) - 34.4[Mn] - 13.7[Si] - 9.2[Cr] - 17.3[Ni] - 15.4[Mo] + 10.8[V] + 4.7[Co] - 1.4[Al] - 16.3[Cu] - 361[Nb] - 2.44[Ti] - 3448[B]$$

[0049] Thereafter the cold rolled steel sheet is reheated to a tempering temperature Ttemper between 150°C and 300°C with a heating rate of at least 1°C/s and preferably of at least 2°C/s and more of at least 10°C/s during 100 s and 600 s. The preferred temperature range for tempering is between 200°C and 300°C and the preferred duration for holding at Ttemper is between 200 s and 500 s.

[0050] Then, the cold rolled steel sheet is cooled down to room temperature to obtain a cold rolled martensitic steel.

[0051] The cold rolled martensitic steel sheet of the present invention may optionally be coated with zinc or zinc alloys, or with aluminum or aluminum alloys to improve its corrosion resistance.

EXAMPLES

[0052] The following tests, examples, figurative exemplification and tables which are presented herein are non-restricting in nature and must be considered for purposes of illustration only and will display the advantageous features of the present invention.

[0053] Steel sheets made of steels with different compositions are gathered in Table 1, where the steel sheets are produced according to process parameters as stipulated in Table 2, respectively. Thereafter Table 3 gathers the microstructures of the steel sheets obtained during the trials and table 4 gathers the result of evaluations of obtained properties.

Table 1

Steels	C	Mn	Si	Al	Cr	Nb	S	P	N	Mo	Cu	Ni	V	B	Ti
A	0.148	1.884	0.204	0.028	0.176	0.0005	0.019	0.0183	0.0041	0.0022	0.012	0.015	0.0022	0.0001	0.0235
B	0.153	1.882	0.202	0.025	0.182	0.0012	0.002	0.0116	0.0047	0.0026	0.016	0.016	0.0018	0.0001	0.0206
C	0.141	1.888	0.203	0.024	0.184	0.0005	0.008	0.0139	0.0043	0.0027	0.027	0.016	0.0018	0.0001	0.0227
according to the invention; R = reference; underlined values: not according to the invention.															

Table 2

Table 2 gathers the hot rolling and annealing process parameters implemented on cold rolled steel sheets to impart the steels of table 1 with requisite mechanical properties to become a cold rolled martensitic steel.

The table 2 is as follows:

Trials	Steel	Reheat ing (°C)	Hot rolling			CR Reduction (%)	Annealing			Step 1 Cooling		Step 2 Cooling	
			FRT (°C)	Cooling rate to coiling (°C/s)	Coiling (°C)		Heating rate to Tsoak (°C/s)	Tsoak (°C)	Annealing time(s)	T1 (°C)	CR1 (°C/s)	T2 (°C)	CR2 (°C/s)
I1	A	1245	895	30	530	40	6.5	888	290	692	36	25	690
I2	B	1245	895	30	530	60	10	890	165	690	72	25	1030
I3	C	1245	895	30	530	50	7	890	245	675	48	25	750
R1	A	1245	895	30	530	40	6.5	880	290	<u>600</u>	34	25	600
R2	A	1245	895	30	530	40	6.5	882	290	<u>643</u>	35	25	636

Trials	Steel	Tempering			Ms (°C)	Ac3 (°C)
		Heating rate to Temper (°C/s)	Temper (°C)	Holding time (s)		
I1	A	12	230	290	403	816
I2	B	20	230	165	400	808
I3	C	15	230	245	405	812
R1	A	12	230	290	403	816
R2	A	12	230	290	403	816

I = according to the invention; R = reference; underlined values: not according to the invention.

[0054] Table 3 exemplifies the results of the tests conducted in accordance with the standards on different microscopes such as Scanning Electron Microscope for determining the microstructures of both the inventive and reference steels in terms of area fraction. The results are stipulated herein:

Table 3 :

Trials	Steel	Tempered Martensite	Fresh Martensite	Ferrite + Bainite	Residual Austenite
I1	A	98%	0	2%	0
I2	B	98%	0	2%	0
I3	C	98%	0	2%	0
R1	A	<u>89%</u>	<u>0</u>	<u>11%</u>	0
R2	A	<u>93.5%</u>	<u>0</u>	<u>6.5%</u>	0
I = according to the invention; R = reference; underlined values: not according to the invention.					

Table 4

The results of the various mechanical tests conducted in accordance to the standards are gathered. For testing the ultimate tensile strength and yield strength are tested in accordance of JIS-Z2241. To estimate hole expansion, a test called hole expansion is applied, in this test sample is subjected to punch a hole of 10mm and deformed after deformation we measure the hole diameter and calculate $HER\% = 100 \cdot (D_f - D_i) / D_i$

Trials	Steels	Tensile Strength (MPa)	Yield Strength (MPa)	HER (%)
I1	A	1321	1160	68
I2	B	1344	1207	70

(continued)

The results of the various mechanical tests conducted in accordance to the standards are gathered. For testing the ultimate tensile strength and yield strength are tested in accordance of JIS-Z2241. To estimate hole expansion, a test called hole expansion is applied, in this test sample is subjected to punch a hole of 10mm and deformed after deformation we measure the hole diameter and calculate $HER\% = 100 \cdot (D_f - D_i) / D_i$

Trials	Steels	Tensile Strength (MPa)	Yield Strength (MPa)	HER (%)
I3	C	1334	1208	50
R1	A	<u>1190</u>	<u>983</u>	<u>20</u>
R2	A	<u>1262</u>	<u>1071</u>	<u>35</u>

I = according to the invention; R = reference; underlined values: not according to the invention.

Claims

1. A cold rolled martensitic steel sheet comprising of the following elements, expressed in percentage by weight:

$$0.1 \% \leq C \leq 0.2 \%;$$

$$1.5 \% \leq Mn \leq 2.5 \%;$$

$$0.1\% \leq Si \leq 0.25 \%;$$

$$0.1\% \leq Cr \leq 1 \%;$$

$$0.01\% \leq Al \leq 0.1 \%;$$

$$0.001\% \leq Ti \leq 0.1\%;$$

$$0\% \leq S \leq 0.09\%;$$

$$0\% \leq P \leq 0.09\%;$$

$$0\% \leq N \leq 0.09\%;$$

and can contain one or more of the following optional elements

$$0\% \leq Ni \leq 1\%;$$

$$0\% \leq Cu \leq 1\%;$$

$$0\% \leq Mo \leq 0.4\%;$$

$$0\% \leq Nb \leq 0.1\%;$$

$$0\% \leq V \leq 0.1\%;$$

$$0\% \leq B \leq 0.05\%;$$

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$$0\% \leq \text{Sn} \leq 0.1\%;$$

$$0\% \leq \text{Pb} \leq 0.1\%;$$

$$0\% \leq \text{Sb} \leq 0.1\%;$$

$$0.001\% \leq \text{Ca} \leq 0.01\%;$$

the remainder composition being composed of iron and unavoidable impurities caused by processing, the microstructure of said steel comprising, by area percentage, at least 95% of martensite consisting of tempered martensite and of optionally fresh martensite in an amount of between 0% and 4% in the steel,

a cumulated amount of ferrite and bainite between 1 % and 5%, and an optional amount of residual austenite between 0% and 2%.

2. The cold rolled martensitic steel sheet according to claim 1, wherein the composition includes 0.16% to 0.24% of Silicon.

3. The cold rolled martensitic steel sheet according to claim 1 or 2, wherein the composition includes 0.11% to 0.19% of Carbon.

4. The cold rolled martensitic steel sheet according to anyone of claims 1 to claim 3, wherein the composition includes 0.01 % to 0.05% of Aluminum.

5. The cold rolled martensitic steel sheet according to anyone of claims 1 to 4, wherein the composition includes 1.6% to 2.4% of Manganese.

6. The cold rolled martensitic steel sheet according to anyone of claims 1 to 5, wherein the composition includes 0.1% to 0.5% of Chromium.

7. The cold rolled martensitic steel sheet according to anyone of claims 1 to 6, wherein, the amount of martensite is between 96% and 99%.

8. The cold rolled martensitic steel sheet according to anyone of claims 1 to 7, wherein the cumulated amount of ferrite and bainite is between 1% and 4%.

9. The cold rolled martensitic steel sheet according to anyone of claims 1 to 8, wherein said sheet has an ultimate tensile strength of 1280 MPa or more, and a yield strength of 1100 MPa or more.

10. A method of production of a cold rolled martensitic steel sheet according to anyone of claims 1 to 9 comprising the following successive steps:

- providing a steel composition according to anyone of claims 1 to 6;
- reheating said semi-finished product to a temperature between 1000°C and 1280°C;
- rolling the said semi-finished product in the austenitic range wherein the hot rolling finishing temperature is between Ac_3 and $\text{Ac}_3 + 100^\circ\text{C}$ to obtain a hot rolled steel sheet;
- cooling the sheet at a cooling rate of at least 20°C/s to a coiling temperature which is below 650°C; and coiling the said hot rolled sheet;
- cooling the said hot rolled sheet to room temperature;
- optionally performing scale removal process on said hot rolled steel sheet;
- optionally annealing may be performed on hot rolled steel sheet;
- optionally performing scale removal process on said hot rolled steel sheet;
- cold rolling the said hot rolled steel sheet with a reduction rate between 35 and 90% to obtain a cold rolled steel sheet;
- then heating the said cold rolled steel sheet at a rate of at least 2°C/s to a soaking temperature T_{soak} between Ac_3 and $\text{Ac}_3 + 100^\circ\text{C}$ where it is held during 10 to 500 seconds;

- then cooling the said cold rolled steel sheet in a two step cooling wherein:

- the first step of cooling the cold rolled steel sheet starts from Tsoak down to a temperature T1 between 650°C and 750°C, with a cooling rate CR1 between 15°C/s and 150°C/s;
- the second step of cooling starts from T1 down to a temperature T2 between Ms-10°C and 20°C, with a cooling rate CR2 of at least 50°C/s,

- then reheating the said cold rolled steel sheet at a rate of at least 1°C/s to a tempering temperature Ttemper between 150°C and 300°C where it is held during 100 to 600 seconds;
 - then cooling to room temperature with a cooling rate of at least 1°C/s to obtain a cold rolled martensitic steel sheet.

11. A method according to claim 10, wherein said coiling temperature is between 475°C and 625°C.

12. A method according to claim 10 or 11, wherein Tsoak is between Ac3+10°C and Ac3+100°C.

13. A method according to anyone of claims 10 to 12, wherein CR1 is between 20°C/s and 120°C/s.

14. A method according to anyone of claim 10 to 13, wherein T1 is between 660°C and 725°C

15. A method according to anyone of claims 10 to 14, wherein CR2 is greater than 100°C/s.

16. A method according to anyone of claims 10 to 15, wherein T2 is between Ms-50°C and 20°C.

17. A method according to anyone of claims 10 to 16, wherein Ttemper is between 200°C and 300°C

18. Use of a steel sheet obtainable according to anyone of claims 1 to 9 for manufacturing a structural part of a vehicle.

Patentansprüche

1. Kaltgewalztes Stahlblech, umfassend die folgenden Elemente, ausgedrückt in Gewichtsprozent:

$$0,1 \% \leq C \leq 0,2 \%;$$

$$1,5 \% \leq Mn \leq 2,5 \%;$$

$$0,1 \% \leq Si \leq 0,25 \%;$$

$$0,1 \% \leq Cr \leq 1 \%;$$

$$0,01 \% \leq Al \leq 0,1 \%;$$

$$0,001 \% \leq Ti \leq 0,1 \%;$$

$$0 \% \leq S \leq 0,09 \%;$$

$$0 \% \leq P \leq 0,09 \%;$$

$$0 \% \leq N \leq 0,09 \%;$$

und das eines oder mehrere der folgenden optionalen Elemente enthalten kann

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$$0 \% \leq \text{Ni} \leq 1 \%;$$

$$0 \% \leq \text{Cu} \leq 1 \%;$$

$$0 \% \leq \text{Mo} \leq 0,4 \%;$$

$$0 \% \leq \text{Nb} \leq 0,1 \%;$$

$$0 \% \leq \text{V} \leq 0,1 \%;$$

$$0 \% \leq \text{B} \leq 0,05 \%;$$

$$0 \% \leq \text{Sn} \leq 0,1 \%;$$

$$0 \% \leq \text{Pb} \leq 0,1 \%;$$

$$0 \% \leq \text{Sb} \leq 0,1 \%;$$

$$0,001 \% \leq \text{Ca} \leq 0,01 \%;$$

wobei die restliche Zusammensetzung aus Eisen und unvermeidlichen, durch die Verarbeitung verursachten Verunreinigungen besteht, die Mikrostruktur des Stahls, bezogen auf den Flächenprozentsatz, umfassend mindestens 95 % Martensit bestehend aus angelassenem Martensit und optional aus frischem Martensit in einer Menge zwischen 0 % und 4 % im Stahl, eine kumulierte Menge an Ferrit und Bainit zwischen 1 % und 5 % und optional eine Menge an Restaustenit zwischen 0 % und 2 %.

2. Kaltgewalztes martensitisches Stahlblech nach Anspruch 1, wobei die Zusammensetzung 0,16 % bis 0,24 % Silizium beinhaltet.
3. Kaltgewalztes martensitisches Stahlblech nach Anspruch 1 oder 2, wobei die Zusammensetzung 0,11 % bis 0,19 % Kohlenstoff beinhaltet.
4. Kaltgewalztes martensitisches Stahlblech nach einem der Ansprüche 1 bis Anspruch 3, wobei die Zusammensetzung 0,01 % bis 0,05 % Aluminium beinhaltet.
5. Kaltgewalztes martensitisches Stahlblech nach einem von Anspruch 1 bis 4, wobei die Zusammensetzung 1,6 % bis 2,4 % Mangan beinhaltet.
6. Kaltgewalztes martensitisches Stahlblech nach einem der Ansprüche 1 bis 5, wobei die Zusammensetzung 0,1 % bis 0,5 % Chrom beinhaltet.
7. Kaltgewalztes martensitisches Stahlblech nach einem der Ansprüche 1 bis 6, wobei die Menge an Martensit zwischen 96 % und 99 % ist.
8. Kaltgewalztes martensitisches Stahlblech nach einem der Ansprüche 1 bis 7, wobei die kumulierte Menge an Ferrit und Bainit zwischen 1 % und 4 % ist.
9. Kaltgewalztes martensitisches Stahlblech nach einem der Ansprüche 1 bis 8, wobei das Blech eine Zugfestigkeit von 1280 MPa oder mehr und eine Streckgrenze von 1100 MPa oder mehr aufweist.
10. Verfahren zur Herstellung eines kaltgewalzten martensitisches Stahlblechs nach einem der Ansprüche 1 bis 9, umfassend die folgenden aufeinanderfolgenden Schritte:

- Bereitstellen einer Zusammensetzung nach einem der Ansprüche 1 bis 6;
- Wiedererhitzen des Halbfertigprodukts auf eine Temperatur zwischen 1000 °C und 1280 °C;
- Walzen des Halbfertigprodukts in dem austenitischen Bereich, wobei die Warmwalzabschlusstemperatur zwischen Ac3 und Ac3 + 100 °C sein muss, um ein warmgewalztes Stahlblech zu erlangen;
- Abkühlen des Blechs mit einer Abkühlgeschwindigkeit von mindestens 20 °C/s auf eine Aufwickeltemperatur, die unter 650 °C ist; und Aufwickeln des warmgewalzten Blechs;
- Abkühlen des warmgewalzten Blechs auf Raumtemperatur;
- optional Ausführen von Zunderentfernungsverfahren an dem warmgewalzten Stahlblech;
- optional kann ein Glühen an warmgewalztem Stahlblech ausgeführt werden;
- optional Ausführen eines Zunderentfernungsprozesses an dem warmgewalzten Stahlblech;
- Kaltwalzen des warmgewalzten Stahlblechs mit einem Reduktionsgrad zwischen 35 und 90 %, um ein kaltgewalztes Stahlblech zu erlangen;
- dann Erhitzen des kaltgewalzten Stahlblechs mit einer Geschwindigkeit von mindestens 2 °C/s auf eine Haltezeittemperatur Thalten zwischen Ac3 und Ac3+100 °C, wo es während 10 bis 500 Sekunden gehalten wird;
- anschließend Abkühlen des kaltgewalzten Stahlblechs in einem zweistufigen Abkühlen, wobei:

- die erste Stufe eines Abkühlens des kaltgewalzten Stahlblechs mit Thalten bis zu einer Temperatur T1 zwischen 650 °C und 750 °C, mit einer Abkühlgeschwindigkeit CR1 zwischen 15 °C/s und 150 °C/s beginnt;
- die zweite Stufe eines Abkühlens bei T1 bis zu einer Temperatur T2 zwischen Ms-10 °C und 20 °C mit einer Abkühlgeschwindigkeit CR2 von mindestens 50 °C/s beginnt,

- dann Wiedererhitzen des kaltgewalzten Stahlblechs mit einer Geschwindigkeit von mindestens 1 °C/s auf eine Anlasstemperatur Ttemper zwischen 150 °C und 300 °C, bei der es 100 bis 600 Sekunden gehalten wird;
- dann Abkühlen auf Raumtemperatur mit einer Abkühlgeschwindigkeit von mindestens 1 °C/s, um ein kaltgewalztes martensitisches Stahlblech zu erlangen.

11. Verfahren nach Anspruch 10, wobei die Aufwickeltemperatur zwischen 475 °C und 625 °C ist.

12. Verfahren nach Anspruch 10 oder 11, wobei Thalten zwischen Ac3+10 °C und Ac3+100 °C ist.

13. Verfahren nach einem der Ansprüche 10 bis 12, wobei CR1 zwischen 20 °C/s und 120 °C/s ist.

14. Verfahren nach einem der Ansprüche 10 bis 13, wobei T1 zwischen 660 °C und 725 °C ist.

15. Verfahren nach einem der Ansprüche 10 bis 14, wobei CR2 größer als 100 °C/s ist.

16. Verfahren nach einem der Ansprüche 10 bis 15, wobei T2 zwischen Ms-50 °C und 20 °C ist.

17. Verfahren nach einem der Ansprüche 10 bis 16, wobei Ttemper zwischen 200 °C und 300 °C ist.

18. Verwendung eines Stahlblechs, das gemäß einem der Ansprüche 1 bis 9 erlangt werden kann, zum Herstellen eines Strukturteils eines Fahrzeugs.

Revendications

1. Tôle d'acier martensitique laminée à froid comprenant les éléments suivants, exprimés en pourcentage en poids :

$$0,1 \% \leq C \leq 0,2 \% ;$$

$$1,5 \% \leq Mn \leq 2,5 \% ;$$

$$0,1 \% \leq Si \leq 0,25 \% ;$$

$$0,1 \% \leq Cr \leq 1 \% ;$$

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$$0,01 \% \leq \text{Al} \leq 0,1 \% ;$$

$$0,001 \% \leq \text{Ti} \leq 0,1 \% ;$$

$$0 \% \leq \text{S} \leq 0,09 \% ;$$

$$0 \% \leq \text{P} \leq 0,09 \% ;$$

$$0 \% \leq \text{N} \leq 0,09 \% ;$$

et pouvant contenir un ou plusieurs des éléments facultatifs suivants

$$0 \% \leq \text{Ni} \leq 1 \% ;$$

$$0 \% \leq \text{Cu} \leq 1 \% ;$$

$$0 \% \leq \text{Mo} \leq 0,4 \% ;$$

$$0 \% \leq \text{Nb} \leq 0,1 \% ;$$

$$0 \% \leq \text{V} \leq 0,1 \% ;$$

$$0 \% \leq \text{B} \leq 0,05 \% ;$$

$$0 \% \leq \text{Sn} \leq 0,1 \% ;$$

$$0 \% \leq \text{Pb} \leq 0,1 \% ;$$

$$0 \% \leq \text{Sb} \leq 0,1 \% ;$$

$$0,001 \% \leq \text{Ca} \leq 0,01 \% ;$$

la composition restante étant composée de fer et d'impuretés inévitables causées par le traitement, la micro-structure dudit acier comprenant, en pourcentage de surface, au moins 95 % de martensite consistant en de la martensite revenue et optionnellement en de la martensite fraîche en une quantité entre 0% et 4% dans l'acier, une quantité cumulée de ferrite et de bainite comprise entre 1 % et 5 %, et une quantité facultative d'austénite résiduelle comprise entre 0 % et 2 %.

2. Tôle d'acier martensitique laminée à froid selon la revendication 1, dans laquelle la composition inclut de 0,16 % à 0,24 % de silicium.
3. Tôle d'acier martensitique laminée à froid selon la revendication 1 ou 2, dans laquelle la composition inclut de 0,11 % à 0,19 % de carbone.
4. Tôle d'acier martensitique laminée à froid selon l'une quelconque des revendications 1 à 3, dans laquelle la composition inclut de 0,01 % à 0,05 % d'aluminium.
5. Tôle d'acier martensitique laminée à froid selon l'une quelconque des revendications 1 à 4, dans laquelle la composition inclut de 1,6 % à 2,4 % de manganèse.

6. Tôle d'acier martensitique laminée à froid selon l'une quelconque des revendications 1 à 5, dans laquelle la composition inclut de 0,1 % à 0,5 % de chrome.
- 5 7. Tôle d'acier martensitique laminée à froid selon l'une quelconque des revendications 1 à 6, dans laquelle la quantité de martensite est comprise entre 96 % et 99 %.
8. Tôle d'acier martensitique laminée à froid selon l'une quelconque des revendications 1 à 7, dans laquelle la quantité cumulée de ferrite et de bainite est comprise entre 1 % et 4 %.
- 10 9. Tôle d'acier martensitique laminée à froid selon l'une quelconque des revendications 1 à 8, dans laquelle ladite tôle d'acier présente une résistance à la traction ultime de 1280 MPa ou plus, et une limite d'élasticité de 1100 MPa ou plus.
- 10 10. Procédé de production d'une tôle d'acier martensitique laminée à froid selon l'une quelconque des revendications 1 à 9 comprenant les étapes successives suivantes :
 - 15 - fournir une composition d'acier selon l'une quelconque des revendications 1 à 6 ;
 - réchauffer ledit produit semi-fini à une température comprise entre 1000 °C et 1280 °C ;
 - laminer ledit produit semi-fini dans le domaine austénitique, dans lequel la température de finition du laminage à chaud est comprise entre Ac3 et Ac3 + 100 °C, afin d'obtenir une tôle d'acier laminée à chaud ;
 - 20 - refroidir la tôle à une vitesse de refroidissement supérieure à 20 °C/s jusqu'à une température de bobinage inférieure à 650 °C ; et bobiner ladite tôle laminée à chaud ;
 - refroidir ladite tôle laminée à chaud jusqu'à la température ambiante ;
 - effectuer facultativement un processus d'élimination de la calamine sur ladite tôle d'acier laminée à chaud ;
 - éventuellement, le recuit peut être effectué sur la tôle d'acier laminée à chaud ;
 - 25 - effectuer facultativement un processus d'élimination de la calamine sur ladite tôle d'acier laminée à chaud ;
 - laminer à froid ladite tôle d'acier laminée à chaud avec un taux de réduction compris entre 35 et 90 %, de manière à obtenir une tôle d'acier laminée à froid ;
 - chauffer ensuite ladite tôle d'acier laminée à froid à une vitesse d'au moins 2 °C/s jusqu'à une température de trempage Tsoak comprise entre Ac3 et Ac3+100 °C où elle est maintenue pendant 10 à 500 secondes ;
 - 30 - puis, refroidir ladite tôle d'acier laminée à froid lors d'un refroidissement en deux étapes dans lequel :
 - la première étape du refroidissement de la tôle d'acier laminée à froid commence à partir de Tsoak jusqu'à une température T1 comprise entre 650 °C et 750 °C, avec une vitesse de refroidissement CR1 comprise entre 15 °C/s et 150 °C/s ;
 - 35 ◦ la deuxième étape de refroidissement commence à partir de T1 jusqu'à une température T2 comprise entre Ms-10 °C et 20 °C, avec une vitesse de refroidissement CR2 d'au moins 50 °C/s,
 - puis réchauffer ladite tôle d'acier laminée à froid à une vitesse d'au moins 1 °C/s jusqu'à une température de trempage Tsoak comprise entre 150 °C et 300 °C, où elle est maintenue pendant 100 à 600 secondes ;
 - 40 - puis refroidir à la température ambiante avec une vitesse de refroidissement d'au moins 1 °C/s pour obtenir une tôle d'acier martensitique laminée à froid.
11. Procédé selon la revendication 10, dans lequel ladite température de bobinage est comprise entre 475 °C et 625 °C.
- 45 12. Procédé selon la revendication 10 ou 11, dans lequel Tsoak est comprise entre Ac3 +10 °C et Ac3 +100 °C.
13. Procédé selon l'une quelconque des revendications 10 à 12, dans lequel CR1 est comprise entre 20 °C/s et 120 °C/s.
14. Procédé selon l'une quelconque des revendications 10 à 13, dans lequel T1 est comprise entre 660 °C et 725 °C.
- 50 15. Procédé selon l'une quelconque des revendications 10 à 14, dans lequel CR2 est supérieure à 100 °C/s.
16. Procédé selon l'une quelconque des revendications 10 à 15, dans lequel T2 est comprise entre Ms-50 °C et 20 °C.
- 55 17. Procédé selon l'une quelconque des revendications 10 à 16, dans lequel Ttemper est comprise entre 200 °C et 300 °C
18. Utilisation d'une tôle d'acier pouvant être obtenue selon l'une quelconque des revendications 1 à 9 pour la fabrication de pièces structurales d'un véhicule.

REFERENCES CITED IN THE DESCRIPTION

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