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(71) Applicant: **ARCELORMITTAL** [LU/LU]; 24-26, Boulevard d'Avranches, L-1160 Luxembourg (LU).

(72) Inventors: **XU, Wei**; Pres. J.F. Kennedylaan 3, B-9060 Zelzate (BE). **ARLAZAROV, Artem**; Voie Romaine BP 30320, F-57283 Maizieres-les-metz Cedex (FR).

(74) Agents: **DOMENEGO, Bertrand** et al.; Lavoix, 2, place d'Estienne d'Orves, F-75009 Paris (FR).

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(54) Title: METHOD FOR MANUFACTURING A HIGH STRENGTH STEEL SHEET HAVING IMPROVED FORMABILITY AND SHEET OBTAINED

(57) Abstract: A method for manufacturing a high-strength sheet having improved formability segregation accord which the chemical composition of the steel contains, in percent by weight: 0.1 %≤C≤0.4% 4.2%≤ Mn≤ 8.0% 1 %≤Si≤3% 0.2%≤ Mo≤ 0.5% the remainder being Fe and unavoidable impurities, the method comprising the steps of annealing a rolled sheet made of said steel by soaking it at an annealing temperature AT higher than the Ac3 transformation point of the steel, quenching the sheet by cooling it down to a quenching temperature QT between the Ms and Mf transformation points in order to obtain a final structure containing at least 65% of martensite and at least 20% of residual austenite, the sum of the ferrite and bainite contents being less than 10%, heating the sheet up to an overaging temperature PT between 300°C and 500°C and maintaining it at said temperature for a time Pt greater than 10s and cooling the sheet down to the ambient temperature. Sheet obtained.

METHOD FOR MANUFACTURING A HIGH STRENGTH STEEL SHEET HAVING IMPROVED FORMABILITY AND SHEET OBTAINED

The present invention relates to high-strength steel sheets excellent in formability and strength and to a method for producing the same.

To manufacture various equipments such as automotive parts, trailers, trucks and so on, high strength steel sheets, made of steels such as DP (dual phase) or TRIP (transformation induced plasticity) steels are used.

In order to reduce the weight of the equipments, which is very desirable in order to reduce the energy consumption, it is very desirable to have steels having better mechanical properties such as yield strength or tensile strength. But such steels should have a good formability.

For this purpose it was proposed to use steels containing about 0.2% C, 2.5% Mn, 1.5% Si and having a structure consisting of martensite and retained austenite. The sheets are produced on continuous annealing lines by a heat treatment consisting on an annealing, an interrupted quenching and an overaging. The purpose of the overaging is to generate a carbon enrichment of the retained austenite by transfer from the martensite in order to increase the stability of the retained austenite. In these steels, the Mn content remains always less than 3.5%. Although with such steels it is possible to obtain interesting properties, it remains desirable to obtain retained austenite having a better stability in order to obtain better characteristics. But the ductility which is necessary to have a good formability should remain good and, especially a good stretch flangeability is desirable.

For these reasons, it remains the need to have a steel and a process to manufacture easily high strength steel sheets on continuous heat treatment lines.

For this purpose, the invention relates to a method for easily manufacturing a high-strength sheet having an improved formability according to which the chemical composition of the steel contains, in percent by weight:

$$0.1\% \leq C \leq 0.4\%$$

$$4.2\% \leq Mn \leq 8.0\%$$

$$1\% \leq Si \leq 3\%$$

$$0.2\% \leq Mo \leq 0.5\%$$

the remainder being Fe and unavoidable impurities, the method comprising the steps of:

- annealing a rolled sheet made of said steel by soaking it at an annealing temperature AT higher than the Ac_3 transformation point of the steel,

- quenching the sheet by cooling it down to a quenching temperature QT between the Ms and Mf transformation points of the steel in order to obtain a structure containing at least 50% of martensite and at least 10% of residual austenite, the sum of ferrite and bainite being less than 10%,

- heating the sheet up to an overaging temperature PT between 300°C and 500°C and maintaining it at said temperature for a time Pt greater than 10 s and,

- cooling the sheet down to the room temperature.

Preferably, the chemical composition of the steel contains $4.5\% \leq Mn \leq 5.5\%$.

Preferably, the chemical composition of the steel is such that:

$$0.15\% \leq C \leq 0.25\%$$

$$1.4\% \leq Si \leq 1.8\%$$

$$0.2\% \leq Mo \leq 0.35\%.$$

Preferably, the chemical composition of the steel contains:

$$0.15\% \leq C \leq 0.25\%$$

$$4.5\% \leq Mn \leq 5.5\%.$$

$$1.4\% \leq Si \leq 1.8\%$$

$$0.2\% \leq Mo \leq 0.35\%,$$

and the annealing temperature AT is greater than 780°C and less than 950°C, the quenching temperature is between 130°C and 180°C and the overaging time is between 100 s and 600 s.

Optionally, the sheet can be furthered coated for example by hot dip coating with or without alloying, the coating being possibly made before cooling the sheet down to the room temperature.

The invention also relates to a high-tensile steel sheet made of steel which chemical composition contains in percent by weight:

$$0.1\% \leq C \leq 0.4\ \%$$

$$4.2\ \% \leq Mn \leq 8\ \%$$

$$1\% \leq Si \leq 3\%$$

$$0.2\ \% \leq Mo \leq 0.5\ \%$$

the remainder being Fe and unavoidable impurities, the steel having a structure containing at least 50% of martensite, at least 10% of retained austenite, less than 10% of the sum ferrite and bainite and there is no central segregation when observed with optical microscope.

In particular, the chemical composition of the steel is such that $4.2\ \% \leq Mn \leq 8.0\%$.

Preferably, the chemical composition of the steel is such that $4.5\% \leq Mn \leq 5.5\ \%$.

Preferably, the chemical composition of the steel contains:

$0.15\% \leq C \leq 0.25\ \%$

$4.5\% \leq Mn \leq 5.5\ \%$

$1.4\% \leq Si \leq 1.8\ \%$

$0.2\ \% \leq Mo \leq 0.35\ \%$.

The yield strength YS can be greater than or equal to 1000 MPa, the tensile strength greater than or equal to 1300 MPa, the uniform elongation UE greater than or equal to 10%, the total elongation greater than or equal to 13%, and the hole expansion ratio HER measured according to the standard ISO 16630:2009 greater than or equal to 15%.

Optionally, at least one face of the sheet is coated, for example by metallic hot dip coating.

The invention will now be described in details and illustrated by examples without introducing limitations.

The composition of the steel according to the invention comprises, in percent in weight:

- $0.1\% \leq C \leq 0.4\%$ and preferably $0.15\% \leq C$ and/or $C \leq 0.25\%$ in order to obtain a satisfactory strength and to improve the stability of the retained austenite. If the carbon content is too high, the weldability is reduced.
- $4.2\% \leq Mn \leq 8.0\ \%$. The Mn content is higher than 4.2% in order to improve the stability of the retained austenite by a higher enrichment of the austenite in Mn and by decreasing the austenite grain size. The decrease of the austenite grain size has the advantage of decreasing the diffusion distance which is necessary for transferring carbon and manganese from martensite to austenite and therefore fastening the diffusion of these elements during the overaging step. Moreover, a manganese content higher than 4.2% decreases the Ms, Ac_1 and Ac_3 transformation points which makes easier the achievement of the heat treatment. Preferably Mn content is above 4.5%. But, the manganese content must remain less than 8%, and preferably less than 5.5% in order not to reduce too much the ductility.
- $Si \geq 1\%$ and preferably $Si \geq 1.4\ \%$, and $Si \leq 3\%$ and preferably $Si \leq 1.8\%$**.** Silicon is useful to stabilize the austenite, to provide solid solution strengthening and to retard the formation of carbides during carbon redistribution from martensite to austenite. But at a too high silicon content, silicon oxides will form at the surface of the sheet which is detrimental to coatability and ductility.
- $0.2\% \leq Mo \leq 0.5\%$ Mo should be above 0.2% in order to reduce the central segregation which can result from the high manganese content and which is detrimental to the stretch flangeability. Above 0.5%, molybdenum may form too much carbides which may be detrimental for the ductility. Preferably, Mo content is below or equal 0.35%

The remainder is Fe and impurities resulting from the melting. Such impurities include N, S, P and residual elements such as Cr, Ni, B and Al.

Usually, the N content remains less than 0.01%, the S content less than 0.01%, the P content less than 0.02%, the Cr content less than 0.1% the Ni content less than 0.1% the Cu content less than 0.2%, the B content less than 0.0005% and the Al content less than 0.001%. However, it must be noted that Al may be added in order to deoxidize the steel. In this case, its content can reach 0.04%. Moreover, Al can form small precipitates of AlN which can be used to limit the austenitic grain growth during annealing.

No micro-alloying, such as Ti, V, and Nb, is targeted in the steel according to the invention. Such elements contents are limited individually to 0.050%, preferably, the sum of Nb, Ti, V is limited to 0.1 %.

Hot rolled sheet having a thickness between 2 and 5 mm can be produced in a known manner with this steel. After hot rolling, the sheet can be batch annealed at a temperature between 400°C and 600°C for 300 seconds to 10 hours. The hot rolled sheet can be pickled and cold rolled to obtain a cold rolled sheet having a thickness between 0.5 mm and 2 mm.

Then, the sheet is heat treated on a continuous annealing line.

Before the heat treatment, an optimum quenching temperature QTop is determined. This optimum quenching temperature is the temperature at which the quenching has to be stopped in order to obtain an optimum content of retained austenite. This optimum quenching temperature can be calculated using the Andrews and Koistinen Marburger relationships:

$$Ms = 539 - 423 \times C - 30.4 \times Mn - 12.1 \times Cr - 7.5 \times Mo - 7.5 \times Si$$

and

$$f\alpha' = 1 - \exp\{-0.011 \times (Ms-T)\}$$

$f\alpha'$ being the proportion of martensite at the temperature T during quenching,

and by assuming that, after quenching down to a temperature QT the steel is overaged at a temperature higher than QT and that due to the overaging, the partitioning of carbon between the martensite and the remaining austenite is completely realized.

Those which are skilled in the art know how to make this calculation.

The purpose of the heat treatment is to obtain a structure consisting of at least 50% and preferably at least 65% of martensite and at least 10% and preferably at least 20% of retained austenite with as little as possible of ferrite or bainite. The sum of ferrite and bainite surface fraction is less than 10% and preferably less than 5%.

It is clear for those who are skilled in the art that this structure is the final structure, i.e. after the complete treatment. Just after quenching, the structure contains only martensite and austenite.

The proportions of martensite, ferrite and bainite are area fractions of these constituents. The proportion of residual austenite is measured by RX diffraction. Those which are skilled in the art know how to determine these proportions.

For this, the sheet is annealed at an annealing temperature AT higher than the Ac_3 transformation point of the steel but preferably less than 950°C in order not to coarsen too much the austenite grains.

Then, the sheet is quenched by cooling at a cooling speed greater than 0.1°C/s down to a quenching temperature QT less than the Ms transformation point of the steel and preferably between QT_{OP} - 20°C and QT_{OP} + 20°C. This is an important feature of the invention since the hardenability is high in the steel according to the invention. As a consequence, ferrite does not form upon cooling even at low cooling rates such as 3°C/s, it is therefore not necessary to have an accelerated cooling. Preferably, the cooling rate is between 0.1°C/s and 70°C/s.

After quenching, the sheet is heated to an overaging temperature between 300°C and 500°C and maintained at this temperature or around this temperature for a time of at least 10 s and preferably between 100 s and 600 s in order to transfer carbon from the martensite to the austenite without forming carbides.

For a steel which composition comprises 0.15% to 0.25%C, 4.5% to 5.5% Mn, 1.4% to 1.8% Si and 0.2% to 0.35% Mo, the annealing temperature can be between 780°C and 950°C and the quenching temperature between 130°C and 180°C.

After overaging, the sheet is cooled down to the room temperature. With this steel and this process it is possible to obtain a sheet having a yield strength YS of more than 1000 MPa, a tensile strength TS of more than 1300 MPa, a uniform elongation UE greater or equal to 10% and a total elongation TE greater or equal to 13%, without central segregation when observed with optical microscope.

As an example (Ex) and a comparison (Comp), steels whose compositions in weight %, transformation points and optimal quenching temperature QTop are given in Table 1, were produced. For the chemical composition, only C, Si, Mn and Mo contents are given, the remainder being Fe and impurities. The Ac_1 and Ac_3 values were measured. The Ms and Mf values were calculated using the Andrews and Koistinen Marburger relationships.

Table 1

	C %	Si %	Mn %	Mo %	AC_1 °C	AC_3 °C	Ms °C	Mf °C	QTop °C
Ex	0.2	1.6	5	0.3	557	752	282	97	177
Comp	0.2	1.6	5	-	562	742	284	104	160

Hot rolled sheets having a thickness of 2.4 mm were produced. The sheets were batch annealed at 600°C for 5 hours, then picked, then cold rolled to obtain cold rolled sheets having a thickness of 1.2 mm. Three samples of the cold rolled sheets were heat treated by varying the quenching temperature QT.

The heat treatment conditions and the mechanical properties resulting from the heat treatments are reported in table 2.

Table 2

EX	AT °C	QT °C	PT °C	Pt s	YS MPa	TS MPa	UE %	TE %	HER %	α (°)	RA %
Ex 1	800	135	400	500	1109	1408	11	14	16	65	19
Ex 2	800	155	400	500	1136	1407	11	14	15	80	21
Ex 3	820	135	400	500	1218	1367	10.7	14.6	19	-	21
Ex 4	820	155	400	500	1143	1399	12.2	15.1	18	-	23
Ex 5	820	175	400	500	1002	1436	11.6	13.9	15	-	21
Ex 6	820	20	400	500	1374	1497	1.8	5.7	-	-	3
Ex 7	780	120	400	500	1234	1390	9.0	11.3	-	-	8
Ex 8	820	230	400	500	702	1557	4.1	4.1	-	-	6
Comp	800	140	400	500	1154	1428	11	15	9	68	23

In this table 2, AT is the annealing temperature, QT the quenching temperature, PT the overaging temperature, Pt the overaging time, YS is the Yield strength, TS the tensile strength, UE the uniform elongation, TE the total elongation, HER the hole expansion ratio, α the folding angle measured by the bendability test and RA the amount of retained austenite in the microstructure. The hole expansion ratio which is a measure of the stretch flangeability is measured using the method according to the standard ISO 16630: 2009. Due to the differences between the methods of measure, the value of ratio HER according to the ISO standard is very different and not comparable to the value of the ratio λ

according to the JFS T 1001 standard (Japan Iron and Steel Federation standard). The folding angle is measured using any method known by those who are skilled in the art.

It can be seen that, with the steel according to the invention, it is possible to obtain simultaneously high yield strength, high tensile strength, very good elongations and significantly better hole expansion ratio than with the steel "comp" which does not contain molybdenum, for similar QT temperatures.

The comparison of examples 1 and 2 with examples 3 and 4 illustrate that when the annealing temperature AT, being higher than the Ac_3 transformation point of the steel, is increased, the austenitic grain size is increased, which leads to generally better elongation properties.

The comparison of examples 4 and 5 show that when the quenching temperature is increased, the yield strength decreases whereas the tensile strength increases, owing to the presence of a lower content of tempered martensite in the microstructure.

The steel of examples 6 is quenched at a quenching temperature below Mf, which leads to a structure containing a too low content of retained austenite, and therefore having unsatisfactory elongation properties.

The quenching temperatures of examples 7 and 8 are comprised between the Ms and Mf transformation points of the steel points of the steel, but not such that a final structure containing at least 10% of residual austenite is obtained. In particular, the quenching temperature of example 7 is too low to ensure a residual austenite content of at least 10%. The quenching temperature of example 8 is too high, so that when the steel reaches the quenching temperature, the amount of martensite is too low to ensure a sufficient stabilization of austenite when the sheet is maintained at the overaging temperature. Therefore, the uniform and total elongations of examples 6, 7 and 8 are insufficient.

Moreover, a micrographical examination showed that in the steels according to the invention there was no central segregation when the steel microstructure is observed with an optical microscope. It is why formability is improved because central segregation is detrimental to the in-use-properties.

The sheet which is described above is not coated. But it is clear that the sheet may be coated by any means i.e. by hot dip coating, by electro-coating, by vacuum coating such as JVD or PVD and so on. When the sheet is hot dip coated, the coating can be galvanizing with or without alloying (galvannealing). In these cases, the heat treatment corresponding to the hot dip and eventually to the alloying which are made before cooling the sheet down to the ambient temperature have to be considered. Those who are skilled in the art know how to do that, for example by tests, in order to optimize the overaging

temperature and time. In this case, at least one face of the sheet can be coated and more specifically metallic coated.

CLAIMS

1.- A method for manufacturing a high-strength sheet having improved formability according to which the chemical composition of the steel contains, in percent by weight:

$$0.1\% \leq C \leq 0.4\%$$

$$4.2\% \leq Mn \leq 8.0\%$$

$$1\% \leq Si \leq 3\%$$

$$0.2\% \leq Mo \leq 0.5\%$$

the remainder being Fe and unavoidable impurities,

the method comprising the steps of:

- annealing a rolled sheet made of said steel by soaking it at an annealing temperature AT higher than the Ac_3 transformation point of the steel,
- quenching the sheet by cooling it down to a quenching temperature QT between the Ms and Mf transformation points of the steel in order to obtain a final structure containing at least 50% of martensite and at least 10% of residual austenite, the sum of ferrite and bainite being less than 10 %,
- heating the sheet up to an overaging temperature PT between 300°C and 500°C and maintaining it at said temperature for a time Pt greater than 10 s and,
- cooling the sheet down to ambient temperature.

2.- The method according to claim 1, characterized in that the chemical composition of the steel contains:

$$4.5\% \leq Mn \leq 5.5\%.$$

3.- The method according to any one of claims 1 or 2, characterized in that the chemical composition of the steel is such that:

$$0.15\% \leq C \leq 0.25\%$$

$$1.4\% \leq Si \leq 1.8\%$$

$$0.2\% \leq Mo \leq 0.35\%$$

and in that the annealing temperature AT is greater than 780°C and less than 950°C, the quenching temperature is between 130°C and 180°C and the overaging time is between 100 s and 600 s.

4 – The method according to any one of claims 1 to 3, characterized in that the sheet is cooled to the quenching temperature QT so that the final structure satisfies one or more of the following conditions:

- the content of martensite is at least 65%,
- the content of retained austenite is at least 20%,
- the sum of ferrite and bainite is less than 5%.

5.- The method according to any one of claims 1 to 4, characterized in that the sheet is further coated.

6.- The method according to claim 5, characterized in that the sheet is coated by hot dip coating with or without alloying, the coating being made before cooling the sheet down to ambient temperature.

7.- A high-tensile steel sheet made of steel whose chemical composition contains in percent by weight:

$$0.1\% \leq C \leq 0.4\%$$
$$4.2\% \leq Mn \leq 8.0\%$$
$$1\% \leq Si \leq 3\%$$
$$0.2\% \leq Mo \leq 0.5\%$$

the remainder being Fe and unavoidable impurities, the steel having a structure containing more than 50% of martensite, more than 10% of retained austenite, less than 10% of the sum of ferrite and bainite and there is no central segregation when observed with optical microscope.

8.- The high-tensile steel sheet according to claim 7, characterized in that the chemical composition of the steel contains $4.5\% \leq Mn \leq 5.5\%$.

9.- The high-tensile steel sheet according to claim any one of claims 7 or 8, characterized in that the chemical composition of the steel is such that:

$$0.15\% \leq C \leq 0.25\ \%,$$
$$1.4\% \leq Si \leq 1.8\%,$$
$$0.2\% \leq Mo \leq 0.35\%.$$

10.- The high-tensile steel sheet according to claims 8 and 9, characterized in that the yield strength YS is greater than or equal to 1000 MPa, the tensile strength is greater than or equal to 1300 MPa, the uniform elongation UE is greater than or equal to 10%, the total elongation is greater than or equal to 13% and the hole expansion ratio HER is greater than or equal to 15%.

11 - The high-tensile steel sheet according to any one of claims 7 to 10, characterized in that the structure satisfies one or more of the following conditions:

- the content of martensite is at least 65%,
- the content of retained austenite is at least 20%,
- the sum of ferrite and bainite is less than 5%.

12.- The high-tensile steel sheet according to any one of claims 7 to 11, characterized in that at least one face of the sheet is coated.