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(71) Applicant (*for all designated States except US*): **TATA STEEL IJMUIDEN BV** [NL/NL]; P.O. Box 10000, NL-1970 CA Ijmuiden (NL).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **BERKHOUT, Basjan** [NL/NL]; Tafelbergstraat 28, NL-2021 SP Haarlem (NL). **CORNELISSEN, Marcus Cornelis Maria** [NL/NL]; Willen Alexandersingel 2, NL-1901 BZ Casstricum (NL). **PATEL, Jayesh Ramjibhai** [GB/GB]; 24 Rufford Rise, Sheffield, S20 2DW (GB).

(74) Agent: **BODIN, Andre**; Tata Steel Nederland Technology BV, Group Intellectual Property Services, P.O. Box 10000 - H3.18, NL-1970 CA Ijmuiden (NL).

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(54) Title: METHOD OF PRODUCING AN AUSTENITIC STEEL

(57) Abstract: This invention relates to a method of producing an austenitic steel sheet excellent in resistance to delayed cracking and a steel produced thereby.



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METHOD OF PRODUCING AN AUSTENITIC STEEL

The invention relates to a method of producing an austenitic steel sheet excellent in resistance to delayed cracking.

In view of fuel economy and safety in the case of collisions, high strength steels are used more and more in the automobile industry. This requires the use of structural materials that combine a high tensile strength with high ductility. Austenitic alloys comprising as main elements iron, carbon and high levels of manganese, which can be hot-rolled or cold-rolled and have a strength that may exceed 1000 MPa. The mode of deformation of these steels depends on the stacking fault energy: for a sufficiently high stacking fault energy, the observed mode of mechanical deformation is twinning, which results in a high work hardenability. By acting as an obstacle to the propagation of dislocations, the twins increase the flow stress. However, when the stacking fault energy exceeds a certain limit, slip of perfect dislocations becomes the main deformation mechanism and the work hardening is reduced. It is known that the sensitivity to delayed cracking increases with the mechanical strength, in particular after certain cold-forming operations since high residual tensile stresses are liable to remain after deformation. In combination with atomic hydrogen possibly present in the metal, these stresses are liable to result in delayed cracking, that is to say cracking that occurs a certain time after the deformation itself. Hydrogen may progressively build up by diffusion to crystal lattice defects, such as matrix/inclusion interfaces, twin boundaries and grain boundaries. It is in the latter areas that hydrogen may become harmful when it reaches a critical concentration after a certain time. For a constant grain size, the time required to attain a critical level depends on the initial concentration of mobile hydrogen, the intensity of the residual stress concentration field and the kinetics of hydrogen diffusion.

In particular circumstances, small amounts of hydrogen may be introduced at some stages of steel fabrication such as chemical or electrochemical pickling, annealing under special atmospheres, electroplating or hot dip galvanizing. Subsequent machining operations using lubricating oils and greases may also cause hydrogen production after decomposition of these substances at high temperatures.

It is an object of this invention to provide a method of producing an austenitic steel sheet excellent in resistance to delayed cracking.

It is also an object of this invention to provide a method of producing an austenitic steel sheet having an increased yield stress and excellent weldability.

It is a further object of this invention to provide a method of producing an austenitic steel sheet which is energy efficient and simple in comparison to the conventional route for this type of steel.

According to the invention one or more of these objects is reached by providing a method of producing an austenitic steel sheet excellent in resistance to delayed cracking comprising

- casting an ingot, or a continuously cast slab, or a continuously cast thin slab or a strip-cast strip, the composition thereof comprising, in weight:

- 0.50% - 0.80 %C
- 10 - 17% Mn
- at least 1.0 % Al
- at most 0.5% Si
- at most 0.020% S
- at most 0.050% P
- 50 - 200 ppm N
- 0.050 - 0.25 % V

the remainder being iron and unavoidable impurities inherent to fabrication;

- providing a hot-rolled strip by hot rolling the ingot, the continuously cast slab, the continuously cast thin slab or the strip-cast strip to the desired hot rolled thickness.

- cold-rolling the hot-rolled strip to the desired final thickness,
- continuous annealing of the cold-rolled strip in a process comprising heating up the strip at a heating rate V_h to an annealing temperature T_a for an annealing time t_a followed by cooling at a cooling rate V_c and wherein T_a is from 750 to 850°C.

By using a high aluminium content the SFE of the steel increases. Any adverse effects of the elements that lower the SFE, such as silicon, are counteracted by the addition of aluminium. Additionally, aluminium lowers the activity and the diffusivity of carbon in austenite, which reduces the driving force for forming carbides. The vanadium, which is added as an essential alloying addition, forms carbides. These vanadium-carbides act as hydrogen sinks if and when the size and distribution of the vanadium-carbides is correct. The increased aluminium content is therefore essential to control the vanadium-carbide precipitation

because it prevents the vanadium-carbides from coarsening due to the reduced carbon activity and diffusivity as a result of the presence of aluminium. The inventors found that at least 1.0 % Al and from 0.050 to 0.25 % V is required to achieve this. Lower aluminium contents led to too coarse vanadium-carbides, thereby rendering them ineffective as hydrogen sinks, and the amount of Vanadium needs to be controlled between the mentioned values to achieve a sufficient number of small precipitates. Higher V-values lead to early nucleation of the precipitates and thereby inevitably to coarse and fewer precipitates, whereas values below 0.050% V simply result in too few precipitates, even if they are fine enough. The annealing treatment is crucial in that it controls the precipitation of the vanadium-carbides and causes the recrystallisation of the cold-deformed microstructure caused by the cold-rolling to result in a fine grain structure. In a preferable embodiment the silicon content is very low, i.e. at impurity level. In principle the aluminium content is limited only by the fact that the steel according to the invention is an austenitic steel. In an embodiment the maximum aluminium content is 5%. Preferably the aluminium content is at least 1.25 and/or at most 3.5%, more preferably at least 1.5 and/or at most 2.5%.

In an embodiment the maximum annealing temperature T_a is 825°C or even 800°C. In an embodiment the cooling rate V_c is between 10 and 100 °C/s. A preferable cooling rate is between 20 and 80 °C/s. The heating rate is preferably between 3 and 60°C/s. The annealing time t_a is preferably between 15 and 300 seconds.

In a preferable embodiment, the maximum annealing temperature T_a is from 775 to 795 °C (i.e. $785 \pm 10^\circ\text{C}$).

Preferably, the steel strip material has been pickled before cold rolling. Pickling is (often) necessary before cold rolling to remove oxides, to prevent rolling in of oxides. Preferably, the cold rolled strip material is produced from a hot rolled strip material or a belt cast strip material.

In a preferred embodiment of the invention during the cooling at a cooling rate V_c after the continuous annealing the strip is led through a hot dip bath for providing a metallic coating by hot dipping the strip into a molten bath of the metal making up the metallic coating. This process leads to a very economical and quick process to produce a metallurgically coated steel strip. The metallic coating can be any known common coating such as zinc or zinc alloy, wherein the zinc may be alloyed with elements such as aluminium and/or magnesium.

In another embodiment of the invention the strip is pickled after continuous annealing and wherein the strip is provided with a metallic coating by pickling after annealing followed by heating to a temperature below the continuous annealing temperature before the strip is led through a hot dip bath for providing a metallic coating by hot dipping the strip into a molten bath of the metal making up the metallic coating. This alternative process is available if the economical process as described hereinabove is not preferred. There may be issues with adhesion with certain specific metallic coatings for which a pickling treatment may be necessary. After pickling, it is not necessary nor desirable to heat the strip above the T_a . It is preferable that the heating temperature remain below T_a .

With this method, the strip material is heated only to a temperature high enough to form a closed inhibition layer. This temperature is lower than the normal continuous annealing temperature necessary for metallurgical reasons (such as recrystallisation to influence mechanical properties). The forming of oxides on the surface of the steel strip material is thereby reduced.

Preferably, the temperature below the continuous annealing temperature is between 400 and 600 °C. In this temperature range the forming of oxides is considerably reduced and the strip material is heated sufficiently for the subsequent hot dip galvanizing.

According to a preferred embodiment, the Fe in the strip material is reduced during or after the heating to a temperature below the continuous annealing temperature and before the hot dip galvanizing. By reducing the strip material, the Fe-oxides that are formed are reduced, and in this way the amount of oxides present on the surface of the strip material before hot dip galvanizing is decreased considerably.

Preferably, the reduction is performed using H_2N_2 , more preferably using 5 – 30% H_2N_2 in the reducing atmosphere. It has been found that with the use of this atmosphere most oxides can be removed.

According to a preferred embodiment, an excess amount of O_2 is provided in the atmosphere during or after the heating of the strip material and before the reduction of the strip material. The providing of an excess amount of oxygen improves the quality of the surface of the steel strip material before the hot dip galvanizing, and thus the quality of the zinc layer coated on the AHSS strip material. It is supposed that the oxygen binds the alloying elements in the AHSS strip material both at the surface of the strip material and internally, and that in this way the oxides formed cannot migrate to the surface of the strip material.

The reducing atmosphere that follows after the oxidation will then reduce the oxides at the surface of the strip material, and in this way the amount of oxides at the surface of the strip material is considerably reduced or even almost absent, as experiments have shown. Preferably, the excess amount of O₂ is provided in an amount of 0,05 – 5 % O₂. This amount of oxygen has been found to suffice.

In a preferred embodiment of the invention V-alloyed TWIP steel strip material according to the invention was hot rolled, pickled and cold rolled, and continuously annealed to a temperature according to the invention and pickled again. Then the strip material is heated to a temperature of 527 °C in an annealing line, and thereafter hot dip galvanised in a galvanising bath at approximately 450°C.

During the heating of the strip material to the temperature of 527 °C, an excess amount of 1% O₂ is provided. The oxygen is provided at such a high temperature so that not only forms oxides at the surface of the strip material, but also at some depth under the surface binds the alloying elements. After the providing of the oxygen, the strip material is reduced using approximately 5% H₂N₂. The reduction of the strip material removes the oxides from the surface, but the oxides formed under the surface remain where they are and cannot migrate to the surface.

Thus, by reducing the surface the oxides are effectively removed and no new oxides can be formed at the surface. These oxides, when not removed, cause a bad adhesion of the zinc layer to the substrate, resulting in bare spots, flaking and the forming of cracks in the zinc layer when the material is bent. It is presumed that by normal reduction, the alloying elements migrate to the surface very fast at the alloying temperature and thus form oxides at the surface again before the hot dip galvanising takes place. Whatever the exact mechanism may be, it has been found that the use of this method diminishes or almost eliminates the amount of oxides found in a hot dip galvanised zinc layer on a V-alloyed TWIP steel.

In an embodiment of the invention the cold-rolling reduction is between 10 to 90%, more preferably between 30 and 85, even more preferably between 45 and 80%.

In an embodiment of the invention the annealed strip is temper rolled with a reduction of from 0.5 to 10% prior to or after the metallic coating has been provided to the strip.

In an embodiment of the invention the Vanadium content is between 0.06 and 0.22%.

In a second aspect of the invention a strip or sheet is provided produced by a method according to any one of claims 1 to 6, wherein the steel preferably is provided with a metallic coating. In a preferred embodiment of the invention the strip or sheet is used for the production of automotive inner or outer parts or wheels or for hydroforming applications.

The invention will now be further explained by means of the following, non-limitative examples:

The chemical compositions of the materials used in this study are shown in Table 1.

Table 1 Chemical composition of the materials studied (incl. typical semi-industrial Si-free reference material) (all in wt%, Balance: Fe and impurities)

Code	C	Si	Mn	Al	V	S	N	P
8V-1	0.74	0.36	13.8	2.2	0.080	0.011	0.011	Low*
8V-2	0.74	0.36	13.8	2.3	0.086	0.011	0.009	Low
8V-3	0.74	0.31	13.7	2.3	0.084	0.011	0.007	Low
10V	0.71	0.22	13.4	2.4	0.106	0.010	0.011	Low
16V	0.72	0.25	14.5	2.3	0.160	0.001	0.006	0.008
21V	0.69	0.21	14.9	2.6	0.213	0.010	-	0.005
Si-free	0.70	<0.20	14.5	2.5	impurity	0.004	0.007	0.030

* Low = impurity level

The finish rolling temperature (FRT) was chosen to ensure recrystallisation of the deformed microstructure and the coiling temperature was kept below 500°C to avoid carbide precipitation. Recrystallisation does not solely depend on the FRT but also depends on the time, on the rolling strain accumulated since the last recrystallisation event during hot rolling and on the strain rate.

All hot rolled materials were 50% cold rolled and subsequently recrystallisation annealed. Different annealing cycles were applied to determine the optimal annealing parameters. Note that the elongations were between 45% and 50% for all samples, except for those that were not recrystallised (36-45%) and the material annealed 920°C (65%). Since the strength is considered more important, the following discussion will focus on that.

For annealing temperatures up to 750°C, the material softens due to an increased fraction of recrystallised material and probably some grain growth. At these temperatures, the effect of precipitation is limited. The difference between the (fully recrystallised) materials annealed at 775°C and 800°C is small because the

precipitation is considered optimal in this temperature region for minimising grain growth. Based on these observations, the recommended annealing temperature is $785^{\circ}\text{C} \pm 10^{\circ}\text{C}$.

5 **Table 1 Mechanical properties of the materials after 50% cold rolling and annealing.**

Grade	Heating rate ($^{\circ}\text{C/s}$)	T_a ($^{\circ}\text{C}$)	t_a (s)	R_p (MPa)	R_m (MPa)	A_g (%)	A_{tot} (%)
Si-free	5	700	270	580	920		43
Si-free	5	750	270	546	900		46
Si-free	5	800	270	490	875		47
Si-free	5	850	270	450	850		48
Si-free	5	920	270	410	870		65
8V-1	5	785	270	584	962	44	46
8V-2	5	785	270	595	970	45	49
8V-3	5	785	270	585	964	46	50
10V	5	785	270	575	939	45	49
16V	5	700	270	764	1072	32	36
16V	5	725	270	687	1012	37	41
16V	5	750	270	636	977	41	45
16V	5	775	270	614	964	42	46
16V	5	800	270	590	946	43	48
16V	5	750	60	670	1004	39	43
16V	5	775	60	626	973	41	45
16V	5	800	60	597	955	44	48
21V	30	700	60	655	985		45
21V	30	750	60	600	950		43
21V	30	920	60	425	835		53

10 The delayed cracking and stress corrosion cracking results on the V-alloyed grades show a lower susceptibility to crack formation as the material is annealed at a higher temperature. For the stress corrosion cracking sensitivity, V addition is clearly beneficial at an annealing temperature of 750°C , but also at higher annealing temperatures.

15 The V-alloys were subjected to a resistance spot welding tests. Hot cracking in the weld was largely reduced compared to the Si-free non V-alloyed material.

CLAIMS

1. A method of producing an austenitic steel sheet excellent in resistance to delayed cracking, comprising
- 5 - casting an ingot, or a continuously cast slab, or a continuously cast thin slab or a strip-cast strip, the composition thereof comprising, in weight:
- 0.50% - 0.80 %C
- 10 - 17% Mn
- at least 1.0 % Al
- at most 0.5% Si
- 10 - at most 0.020% S
- at most 0.050% P
- 50 - 200 ppm N
- 0.050 - 0.25 % V
- the remainder being iron and unavoidable impurities inherent to fabrication;
- 15 - providing a hot-rolled strip by hot rolling the ingot, the continuously cast slab, the continuously cast thin slab or the strip-cast strip to the desired hot rolled thickness.
- cold-rolling the hot-rolled strip to the desired final thickness,
- continuous annealing of the cold-rolled strip in a process comprising
- 20 heating up the strip at a heating rate V_h to an annealing temperature T_a for an annealing time t_a followed by cooling at a cooling rate V_c and wherein T_a is from 750 to 850°C.
2. Process according to claim 1 wherein the aluminium content is at least 1.25 and/or at most 3.5%.
- 25 3. Process according to claim 1 wherein during the cooling at a cooling rate V_c after the continuous annealing the strip is led through a hot dip bath for providing a metallic coating by hot dipping the strip into a molten bath of the metal making up the metallic coating.
- 30 4. Process according to claim 1 wherein the strip is pickled after continuous annealing and wherein the strip is provided with a metallic coating by pickling after annealing followed by heating to a temperature below the continuous annealing temperature before the strip is led through a hot dip bath for

- providing a metallic coating by hot dipping the strip into a molten bath of the metal making up the metallic coating.
5. Process according to any one of the preceding claims wherein the cold-rolling reduction is between 10 to 90%, more preferably between 30 and 85, even more preferably between 45 and 80%.
6. Process according to any one of the preceding claims wherein the annealed strip is temper rolled with a reduction of from 0.5 to 10% prior to or after the metallic coating has been provided to the strip.
7. Process according to any one of the preceding claims wherein the Vanadium content is between 0.06 and 0.22%.
8. Process according to any one of the preceding claims wherein:
- the cooling rate V_c is between 10 and 100°C/s, and/or wherein
 - the heating rate V_h is preferably between 3 and 60°C/s, and/or wherein
 - the annealing time t_a is preferably between 15 and 300 seconds.
9. Process according to any one of the claims 1, 2 or 4 to 8 wherein the strip is pickled after continuous annealing and wherein the strip is provided with a metallic coating, by pickling after continuous annealing followed by heating to a temperature between 400 and 600 °C before the strip is led through a hot dip bath for providing a metallic coating by hot dipping the strip into a molten bath of the metal making up the metallic coating.
10. Process according to claim 9 wherein the Fe in the strip material is reduced during or after the heating to a temperature below the continuous annealing temperature and before the hot dip galvanising, preferably wherein the reduction is performed using H_2N_2 , more preferably using 5 – 30% H_2N_2 in the reducing atmosphere.
11. Process according to claim 10 wherein an excess amount of O_2 is provided in the atmosphere during or after the heating of the strip material and before the reduction of the strip material, preferably wherein the excess amount of O_2 is provided in an amount of 0,05 – 5 % O_2 .
12. Process according to any one of the preceding claims wherein the coiling temperature after hot rolling is kept below 500°C and/or wherein the annealing temperature T_a is 785°C ± 10°C.

13. Strip or sheet produced by a method according to any one of claims 1 to 12, wherein the steel preferably is provided with a metallic coating.
14. Use of a strip or sheet according to claim 13 for the production of automotive inner or outer parts or wheels.
- 5 15. Use of a strip or sheet according to claim 13 for hydroforming applications.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
 INV. C21D1/70 C21D6/00 C21D8/04 C21D9/34 C21D9/48
 C22C38/00 C22C38/04 C22C38/06 C22C38/12
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C21D C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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