



(51) International Patent Classification:

C22C 38/00 (2006.01)	C22C 38/20 (2006.01)
C22C 38/02 (2006.01)	C22C 38/22 (2006.01)
C22C 38/04 (2006.01)	C22C 38/24 (2006.01)
C22C 38/06 (2006.01)	C22C 38/28 (2006.01)
C22C 38/08 (2006.01)	C22C 38/32 (2006.01)
C22C 38/12 (2006.01)	C22C 38/34 (2006.01)
C22C 38/14 (2006.01)	C22C 38/38 (2006.01)
C22C 38/16 (2006.01)	

(72) Inventors: SCOTT, Colin; 70 McBay Road, Brantford, Ontario N3T 5LA (CA). REMY, Blandine; 7 rue des ronces, 57640 Sanry les Vigy (FR).

(74) Agent: PLAISANT, Sophie; ArcelorMittal France R&D Intellectual Property, 6, rue André Campra, Immeuble Le Cézanne, F-93200 Saint-Denis (FR).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(21) International Application Number:

PCT/IB2017/000597

(22) International Filing Date:

19 May 2017 (19.05.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

PCT/IB2016/000694

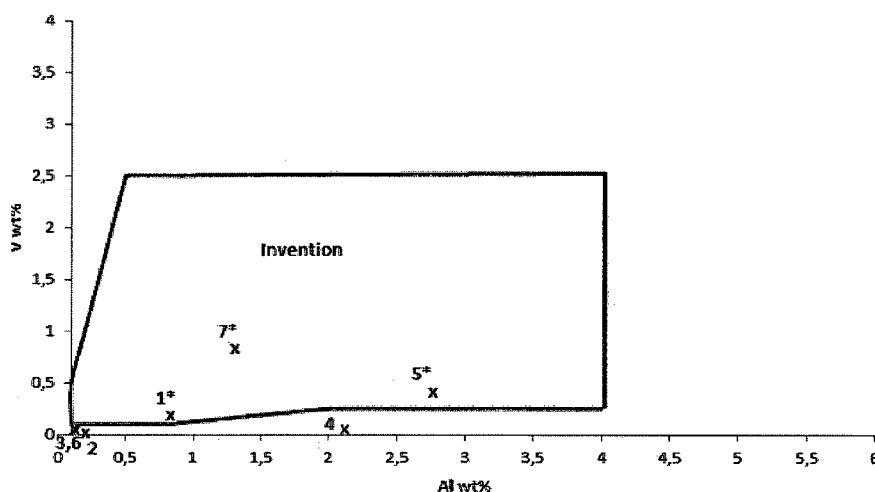
24 May 2016 (24.05.2016) IB

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,

(54) Title: TWIP STEEL SHEET HAVING AN AUSTENITIC MATRIX

Figure 1



(57) Abstract: The present invention relates to a TWIP steel sheet having an austenitic matrix and a method for the manufacture of this TWIP steel.

WO 2017/203342 A1

MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,  
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
KM, ML, MR, NE, SN, TD, TG).

**Published:**

— *with international search report (Art. 21(3))*

## **TWIP steel sheet having an austenitic matrix**

The present invention relates to a TWIP steel sheet having an austenitic matrix and a method for the manufacture of this TWIP steel. The invention is particularly well suited for the manufacture of automotive vehicles.

With a view of saving the weight of vehicles, it is known to use high strength steels for the manufacture of automobile vehicle. For example for the manufacture of structural parts, mechanical properties of such steels have to be improved. However, even if the strength of the steel is improved, the elongation and therefore the formability of high steels decreased. In order to overcome these problems, twinning induced plasticity steels (TWIP steels) having good formability have appeared. Even if these products show a very good formability, mechanical properties such as Ultimate tensile strength (UTS) and yield stress (YS) may not be high enough to fulfill automotive application.

To improve the strength of these steels while keeping good workability, it is known to induce a high density of twins by cold-rolling followed by a recovery treatment removing dislocations but keeping the twins. However, two processes are in competition, the recovery process and the recrystallization process. Indeed, it is difficult to control the recovery process since kinetics between both processes are quite closed. Consequently, there is a need to provide a way to control the recovery process in order to avoid the recrystallization.

The patent application KR20140013333 discloses a method of manufacturing a high-strength and high-manganese steel sheet with an excellent bendability and elongation, the method comprising the steps of:

- homogenization-processing, by heating to 1050 - 1300°C, a steel ingot or a continuous casting slab comprising, by weight%, carbon (C): 0.4~0.7%, manganese (Mn): 12~24%, aluminum (Al): 1.1~3.0%, silicon (Si): 0.3% or less, titanium (Ti): 0.005~0.10%, boron (B): 0.0005~0.0050%, phosphorus (P): 0.03% or less, sulfur (S): 0.03% or less, nitrogen(N): 0.04% or less, and the remainder being iron and other unavoidable impurities;
- hot-rolling the homogenization-processed steel ingot or the continuous casting slab at the finish hot rolling temperature of 850-1000°C;
- coiling the hot-rolled steel sheet at 400-700°C;

- cold-rolling the wound steel sheet;
- continuously annealing the cold-rolled steel sheet at 400-900°C;
- optionally, coating step by hot-dip galvanization or electro-galvanization,
- re-rolling the continuously annealed steel sheet at the reduction ratio of 10~50% and
- re-heat processing the rerolled steel sheet at 300-650°C during 20 seconds to 2hours.

However, since the coating is deposited before the second cold-rolling, there is a huge risk that the metallic coating is mechanically damaged. Moreover, since the re-heat step is realized after the coating deposition, the interdiffusion of steel and the coating will appear resulting in a significant modification of the coating and therefore of the coating desired properties. Additionally, the re-heat step can be performed in a wide range of temperature and time and none of these elements has been more specified in the specification, even in the examples. Then, by implementing this method, there is a risk that the productivity decreases and costs increase since a lot of steps are performed to obtain the TWIP steel. Finally, the patent application KR20140013333 is completely silent on the competition between the recrystallization and the recovery and therefore, do not disclose any way to control the recovery step in order to avoid the recrystallization.

Thus, the object of the invention is to solve the above drawbacks by providing a TWIP steel having a high strength, an excellent formability and elongation, such TWIP steel being recovered. It aims to make available, in particular, an easy to implement method in order to obtain this TWIP steel.

This object is achieved by providing a TWIP steel sheet according to claim 1. The steel sheet can also comprise characteristics of claims 2 to 12.

Another object of the present invention is a method for providing a TWIP steel sheet according to claim 13. The method can also comprise characteristics of claims 14 to 20.

Other characteristics and advantages of the invention will become apparent from the following detailed description of the invention.

To illustrate the invention, various embodiments and trials of non-limiting examples will be described, particularly with reference to the following Figure:

10 Figure 1 illustrates one embodiment according to the present invention.

3

The following terms will be defined:

- UTS: ultimate tensile strength (MPa),
- YS: yield strength (MPa),
- UE: uniform elongation and
- 5 - TE: total elongation (%).

The invention relates to a cold rolled and recovered TWIP steel sheet having an austenitic matrix comprising by weight :

- 10  $0.1 < C < 1.2\%$ ,
- $13.0 \leq Mn < 25.0\%$ ,
- $0.1 \leq Si \leq 3.0\%$ ,
- $0.1 \leq Cu \leq 5.0\%$ ,
- $S \leq 0.030\%$ ,
- $P \leq 0.080\%$ ,
- $N \leq 0.1\%$ ,
- 15  $0.1 \leq Al \leq 4.0\%$  and

$0.1 \leq V \leq 2.50\%$  in such way that:

- when the amount of Al < 2.0%, the weight ratio Al/V is between 0.2 and 8 or
- when the amount of Al  $\geq 2\%$ , the amount of V > 0.25%,

and on a purely optional basis, one or more elements such as

- 20  $Nb \leq 0.5 \%$ ,
- $B \leq 0.005\%$ ,
- $Cr \leq 1.0\%$ ,
- $Mo \leq 0.40\%$ ,
- $Ni \leq 1.0\%$ ,
- 25  $Ti \leq 0.5\%$ ,
- $0.06 \leq Sn \leq 0.2\%$ ,

the remainder of the composition making up of iron and inevitable impurities resulting from the elaboration.

Without willing to be bound by any theory it seems that the TWIP steel  
30 sheet according to the invention allows for an improvement of the mechanical properties such as the total elongation thanks to this specific microstructure, in particular with the combination of the amount of Al with respect to V as described

above. Indeed, outside the specific amount of Al with respect to V, there is a risk that the steel is not enough strengthened.

Regarding the chemical composition of the steel, C plays an important role in the formation of the microstructure and the mechanical properties. It increases the stacking fault energy and promotes stability of the austenitic phase. When combined with a Mn content ranging from 13.0 to 25.0 by weight, this stability is achieved for a carbon content of 0.1% or higher. In case there are vanadium carbides, a high Mn content may increase the solubility of vanadium carbide (VC) in austenite. However, for a C content above 1.2%, there is a risk that the ductility decreases due to for example an excessive precipitation of vanadium carbides or carbonitrides. Preferably, the carbon content is between 0.20 and 1.2%, more preferably between 0.5 and 1.0% and advantageously between 0.71 and 1.0% by weight so as to obtain sufficient strength combined optionally with optimum carbide or carbonitride precipitation.

Mn is also an essential element for increasing the strength, for increasing the stacking fault energy and for stabilizing the austenitic phase. If its content is less than 13.0%, there is a risk of martensitic phases forming, which very appreciably reduce the deformability. Moreover, when the manganese content is greater than 25.0%, formation of twins is suppressed, and accordingly, although the strength increases, the ductility at room temperature is degraded. Preferably, the manganese content is between 15.0 and 24.0 and more preferably between 17.0 and 24.0% so as to optimize the stacking fault energy and to prevent the formation of martensite under the effect of a deformation. Moreover, when the Mn content is greater than 24.0%, the mode of deformation by twinning is less favored than the mode of deformation by perfect dislocation glide.

Al is a particularly effective element for the deoxidation of steel. Like C, it increases the stacking fault energy which reduces the risk of forming deformation martensite, thereby improving ductility and delayed fracture resistance. However, Al is a drawback if it is present in excess in steels having a high Mn content, because Mn increases the solubility of nitrogen in liquid iron. If an excessively large amount of Al is present in the steel, the N, which combines with Al, precipitates in the form of aluminum nitrides (AlN) that impede the migration of grain boundaries during hot conversion and very appreciably increases the risk of

cracks appearing in continuous casting. In addition, as will be explained later, a sufficient amount of N must be available in order to form fine precipitates, essentially of carbonitrides. Preferably, the Al content is below or equal to 2%. When the Al content is greater than 4.0%, there is a risk that the formation of twins is suppressed decreasing the ductility.

Vanadium also plays an important role within the context of the invention. According to the present invention, the amount of V is such that  $0.1 \leq V \leq 2.5\%$  and preferably  $0.1 \leq V \leq 1.0\%$ . Preferably, V forms precipitates. Without wishing to be bound by any theory, it seems that vanadium under the form of nitrides, carbides or carbonitrides precipitates increasingly delay the recrystallization so the recovery step can be performed without any risk of recrystallization. Preferably, the volumic fraction of such elements in steel is between 0.0001 and 0.05%. Preferably, vanadium elements are mostly localized in intragranular position. Advantageously, vanadium elements have a mean size below 7 nm, preferably between 0.2 and 5nm.

In addition to the above limits for aluminium and vanadium amounts, those elements have to respect the following conditions:

- if Al is strictly under 2.0%, the weight ratio Al/V has to be between 0.2 and 8 and

- if Al is  $\geq 2.0\%$ , the amount of V is strictly above 0.25%.

With these specific amounts of Al with respect to V, it is believed that Al is present in solid solution in the steel delaying the recrystallization in addition to Vanadium precipitates during the recovery step and therefore increasing the mechanical properties of the TWIP steel such as the total elongation.

The nitrogen content must be 0.1% or less so as to prevent excessive precipitation of AlN and the formation of volume defects (blisters) during solidification. In addition, when elements are capable of precipitating in the form of nitrides, such as vanadium, niobium, titanium, chromium, molybdenum and boron, the nitrogen content must not exceed 0.1%.

Silicon is also an effective element for deoxidizing steel and for solid-phase hardening. However, above a content of 3.0%, it reduces the elongation and tends to form undesirable oxides during certain assembly processes, and it must

therefore be kept below this limit. Preferably, the content of silicon is below or equal to 0.6%.

Likewise, copper with a content between 0.1 and 5.0% is one means of hardening the steel by precipitation of copper metal. Moreover, it is believed that the copper acts on the delay of the recrystallization. However, above this content, copper is responsible for the appearance of surface defects in hot-rolled sheet. Preferably, the amount of copper is below 2.0%.

Sulfur and phosphorus are impurities that embrittle the grain boundaries. Their respective contents must not exceed 0.030 and 0.080% so as to maintain sufficient hot ductility.

Some Boron may be added up to 0.005%, preferably up to 0.001%. This element segregates at the grain boundaries and increases their cohesion. Without intending to be bound to a theory, it is believed that this leads to a reduction in the residual stresses after shaping by pressing, and to better resistance to corrosion under stress of the thereby shaped parts. This element segregates at the austenitic grain boundaries and increases their cohesion. Boron precipitates for example in the form of borocarbides and boronitrides.

Nickel may be used optionally for increasing the strength of the steel by solution hardening. However, it is desirable, among others for cost reasons, to limit the nickel content to a maximum content of 1.0% or less and preferably between below 0.3%.

Titanium and Niobium are also elements that may optionally be used to achieve hardening and strengthening by forming precipitates. However, when the Nb or Ti content is greater than 0.50%, there is a risk that an excessive precipitation may cause a reduction in toughness, which has to be avoided. Preferably, the amount of Ti is between 0.040% and 0.50% by weight or between 0.030% and 0.130% by weight. Preferably, the titanium content is between 0.060% and 0.40% and for example between 0.060% and 0.110% by weight. Preferably, the amount of Nb is between 0.070% and 0.50% by weight or 0.040 and 0.220%. Preferably, the niobium content is between 0.090% and 0.40% and advantageously between 0.090% and 0.20% by weight.

Chromium and Molybdenum may be used as optional element for increasing the strength of the steel by solution hardening. However, since

chromium reduces the stacking fault energy, its content must not exceed 1.0% and preferably between 0.070% and 0.6%. Preferably, the chromium content is between 0.20% and 0.5%. Molybdenum may be added in an amount of 0.40% or less, preferably in an amount between 0.14% and 0.40%.

5 Furthermore, without willing to be bound by any theory, it seems that precipitates of Vanadium, Titanium, Niobium, Chromium and Molybdenum can reduce the sensitivity to delayed cracking, and do so without degrading the ductility and toughness properties. Thus, preferably, at least one element chosen from Titanium, Niobium, Chromium and Molybdenum under the form of carbides,  
10 nitrides and carbonitrides is present in an amount between 0.01 and 0.025%.

Optionally, tin (Sn) is added in an amount between 0.06 and 0.2% by weight. without willing to be bound by any theory, it is believed that since tin is a noble element and does not form a thin oxide film at high temperatures by itself, Sn is precipitated on a surface of a matrix in an annealing prior to a hot dip  
15 galvanizing to suppress a pro-oxidant element such as Al, Si, Mn, or the like from being diffused into the surface and forming an oxide, thereby improving galvanizability. However, when the added amount of Sn is less than 0.06%, the effect is not distinct and an increase in the added amount of Sn suppresses the formation of selective oxide, whereas when the added amount of Sn exceeds  
20 0.2%, the added Sn causes hot shortness to deteriorate the hot workability. Therefore, the upper limit of Sn is limited to 0.2% or less.

The steel can also comprise inevitable impurities resulting from the development. For example, inevitable impurities can include without any limitation: O, H, Pb, Co, As, Ge, Ga, Zn and W. For example, the content by weight of each  
25 impurity is inferior to 0.1% by weight.

In a preferred embodiment, the TWIP steel comprising Al, V, C, Mn, Si, Cu and Nb so as to ensure that the following equation is satisfied:

$$105.1 * Al\% - 358.1 * V\% \leq 279.67 * C\% - 11 * Mn\% + 30 * Si\% - 69.02 * Cu\% + 78.3 * Nb\% + 144$$

30 Indeed, without willing to be bound by any theory it seems that when the above equation is satisfied, the mechanical properties of the TWIP steel are further improved.

Preferably, the mean size of grain of steel is up to 5 $\mu$ m, preferably between 0.5 and 3 $\mu$ m.

According to the invention, the steel sheet is recovered, meaning that it is not yet recrystallized. In a preferred embodiment, the recovered fraction of the steel is above 75% and preferably above 90%. Preferably, the recovered fraction is determined with Transmission Electron Microscope (TEM) or Scanning Electron Microscopy (SEM).

In a preferred embodiment, the steel sheet is covered by a metallic coating. The metallic coating can be an aluminum-based coating or a zinc-based coating.

Preferably, the aluminium-based coated comprises less than 15% Si, less than 5.0% Fe, optionally 0.1% to 8.0% Mg and optionally 0.1% to 30.0% Zn, the remainder being Al.

Advantageously, the zinc-based coating comprises 0.01-8.0% Al, optionally 0.2-8.0% Mg, the remainder being Zn.

For example, the coated steel sheet is a galvanized steel sheet obtained after an annealing step performed after the coating deposition.

In a preferred embodiment, the steel sheet has a thickness between 0.4 and 1 mm.

The method according to the present invention for producing a TWIP steel sheet comprises the following steps:

- A. The feeding of a slab having the above mentioned composition,
- B. Reheating such slab and hot rolling it,
- C. A coiling step,
- D. A first cold-rolling,
- E. A recrystallization annealing,
- F. The second cold-rolling and
- G. A recovery heat treatment.

According to the present invention, the method comprises the feeding step A) of a semi product, such as slabs, thin slabs, or strip made of steel having the composition described above, such slab is cast. Preferably, the cast input stock is heated to a temperature above 1000°C, more preferably above 1050°C and advantageously between 1100 and 1300°C or used directly at such a temperature after casting, without intermediate cooling.

The hot-rolling is then performed at a temperature preferably above 890°C, or more preferably above 1000°C to obtain for example a hot-rolled strip usually having a thickness of 2 to 5 mm, or even 1 to 5 mm. To avoid any cracking problem through lack of ductility, the end-of-rolling temperature is preferably above  
5 or equal to 850° C.

After the hot-rolling, the strip has to be coiled at a temperature such that no significant precipitation of carbides (essentially cementite (Fe,Mn)<sub>3</sub>C)) occurs, something which would result in a reduction in certain mechanical properties. The coiling step C) is realized at a temperature below or equal to 580°C, preferably  
10 below or equal to 400°C.

A subsequent cold-rolling operation followed by a recrystallization annealing is carried out. These additional steps result in a grain size smaller than that obtained on a hot-rolled strip and therefore results in higher strength properties. Of course, it must be carried out if it is desired to obtain products of smaller thickness,  
15 ranging for example from 0.2 mm to a few mm in thickness and preferably from 0.4 to 4mm. A hot-rolled product obtained by the process described above is cold-rolled after a possible prior pickling operation has been performed in the usual manner.

The first cold-rolling step D) is performed with a reduction rate between 30  
20 and 70%, preferably between 40 and 60%.

After this rolling step, the grains are highly work-hardened and it is necessary to carry out a recrystallization annealing operation. This treatment has the effect of restoring the ductility and simultaneously reducing the strength. Preferably, this annealing is carried out continuously. Advantageously, the  
25 recrystallization annealing E) is realized between 700 and 900°C, preferably between 750 and 850°C, for example during 10 to 500 seconds, preferably between 60 and 180 seconds. Preferably, during this annealing, at least one vanadium element under the form of nitrides, carbides or carbonitrides can precipitate delaying thus the recrystallization.

30 Then, a second cold-rolling step F) is realized with a reduction rate between 1 to 50%, preferably between 10 and 40% and more preferably between 20 and 40%. It allows for the reduction of the steel thickness. Moreover, the steel sheet manufactured according to the aforesaid method, may have increased strength

through strain hardening by undergoing a re-rolling step. Additionally, this step induces a high density of twins improving thus the mechanical properties of the steel sheet.

After the second cold-rolling, a recovery step G) is realized in order to additionally secure high elongation and bendability of the re-rolled steel sheet. Recovery is characterized by the removal or rearrangement of dislocations in the steel microstructure while keeping the deformation twins. Both deformation twins and dislocations are introduced by plastic deformation of the material, such as rolling step.

In a preferred embodiment, a recovery step G) is performed by heating the steel sheet at a temperature between 410 and 700°C in a batch annealing or a continuous annealing furnace. In this case, it can be followed by a hot-dip coating step G), i.e. by preparing the surface of the steel sheet for the coating deposition in a continuous annealing followed by the dipping the steel sheet in a molten metallic bath having a temperature between 410 and 700°C depending on the nature of the molten bath.

In another preferred embodiment, the recovery step G) is performed by hot-dip coating. In this case, the recovery step and the hot-dip coating are realized in the same time allowing cost saving and the increase of the productivity in contrary to the patent application KR201413333 wherein the hot-dip plating is realized after the recrystallization annealing.

In this embodiment, it seems that the recovery process in the steel microstructure begins during the preparation of steel surface in a continuous annealing and is achieved during the dipping into a molten bath.

The preparation of the steel surface is preferably performed by heating the steel sheet from ambient temperature to the temperature of molten bath, i.e. between 410 to 700°C. In preferred embodiments, the thermal cycle can comprise at least one heating step wherein the steel is heated at a temperature above the temperature of the molten bath. For example, the preparation of the steel sheet surface can be performed at 650°C during few seconds followed by the dipping into a zinc bath during 5 seconds, the bath temperature being at a temperature of 450°C.

Preferably, the temperature of the molten bath is between 410 and 700°C depending on the nature of the molten bath.

Advantageously, the steel sheet is dipped into an aluminum-based bath or a zinc-based bath. Preferably, the dipping into a molten bath is performed during 1 to 60 seconds, more preferably between 1 and 20 seconds and advantageously, between 1 to 10 seconds.

In a preferred embodiment, the aluminum-based bath comprises less than 15% Si, less than 5.0% Fe, optionally 0.1 to 8.0% Mg and optionally 0.1 to 30.0% Zn, the remainder being Al. Preferably, the temperature of this bath is between 550 and 700°C, preferably between 600 and 680°C.

In another preferred embodiment, the zinc-based bath comprises 0.01-8.0% Al, optionally 0.2-8.0% Mg, the remainder being Zn. Preferably, the temperature of this bath is between 410 and 550°C, preferably between 410 and 460°C.

The molten bath can also comprise unavoidable impurities and residuals elements from feeding ingots or from the passage of the steel sheet in the molten bath. For example, the optionally impurities are chosen from Sr, Sb, Pb, Ti, Ca, Mn, Sn, La, Ce, Cr, Zr or Bi, the content by weight of each additional element being inferior to 0.3% by weight. The residual elements from feeding ingots or from the passage of the steel sheet in the molten bath can be iron with a content up to 5.0%, preferably 3.0%, by weight.

Advantageously, the recovery step G) is performed during 1 second to 30minutes, preferably between 30 seconds and 10 minutes.

For example, an annealing step can be performed after the coating deposition in order to obtain a galvanized steel sheet.

A TWIP steel sheet comprising an austenitic matrix having a high strength, an excellent formability and elongation is thus obtainable from the method according to the invention.

With the method according to the present invention, such TWIP steel sheet is achieved by inducing a high number of twins thanks to the two cold-rolling steps followed by a recovery step during which dislocations are removed but twins are kept.

Example

In this example, TWIP steel sheets having the following weight composition were used:

Samples	C%	Si%	Mn%	P%	Cr%	Cu%	Ti%	%N	S%	%Al	%V	Al/V
1*	0.595	0.2	18.3	0.034	-	1.68	-	0.01	≤ 0.03	0.785	0.18	4.36
2	0.635	-	21.79	≤0.08	-	-	-	<0.001	≤ 0.03	-	0.16	-
3	0.894	0.513	18.64	0.02	0.109	0.156	-	0.0032	≤ 0.03	0.003	0.002	1.5
4	0.88	0.508	17.96	0.03	0.109	0.15	-	0.0044	≤ 0.03	2.11	0.093	-
5*	0.876	0.502	17.63	0.032	0.108	0.149	-	0.0061	≤ 0.03	2.78	0.384	-
6	0.579	0.208	22.87	0.02	0.114	0.162	0.005	0.0037	≤ 0.03	0.002	0.007	0.28
7*	0.856	0.21	21.94	0.027	0.114	0.155	0.04	0.008	≤ 0.03	1.35	0.891	1.52

\*examples according to the present invention.

5 Firstly, samples were heated and hot-rolled at a temperature of 1200°C. The finishing temperature of hot-rolling was set to 890°C and the coiling was performed at 400°C after the hot-rolling. Then, a 1<sup>st</sup> cold-rolling was realized with a cold-rolling reduction ratio of 50%. Thereafter, a recrystallization annealing was performed at 750°C during 180seconds. Afterwards, the 2<sup>nd</sup> cold-rolling was  
10 realized with a cold-rolling reduction ratio of 30%.

Finally, for sample 1, a recovery heat step was performed during 40 seconds in total. The steel sheet was first prepared through heating in a furnace up to 675°C, the time spent between 400 and 675°C being 37 seconds and then dipped into a molten bath comprising 9% by weight of Silicon, up to 3% of iron, the  
15 rest being aluminum, during 3 seconds. The molten bath temperature was of 675°C.

For sample 2, a recovery heat treatment was performed during 40 seconds in total. The steel sheet was first prepared through heating in a furnace up to 675°C, the time spent between 400 and 675°C being 34 seconds and then dipped  
20 into a molten bath comprising 9% by weight of Silicon, up to 3% of iron, the rest being aluminum during 6 seconds. The molten bath temperature was of 675°C.

For samples 3 to 5, a recovery heat treatment was performed during 90 seconds in total. The steel sheet was first prepared through heating in a furnace up to 650°C, the time spent between 460 and 650°C being 84 seconds and then  
25 dipped into a zinc bath during respectively 6s seconds. The molten bath temperature was of 460°C.

For samples 6 and 7, a recovery heat treatment was performed during 30 seconds in total. The steel sheet was first prepared through heating in a furnace

up to 625°C, the time spent between 460 and 625°C being 24seconds and then dipped into a zinc bath during respectively 6s seconds. The molten bath temperature was of 460°C. Microstructures of samples 1 to 7 were analyzed with a SEM to confirm that no recrystallization did occur during the recovery step. The

5 mechanical properties were determined. Results are in the following Table:

Samples	Recovery time (s)	Recovered samples	YS (MPa)	UTS (MPa)	UE (%)	TE (%)	Hardness (HV)
1*	40	Yes	-	1181	-	-	378
2	40	No	-	1149	-	-	367
3	60	No	729	1338	39.25	42.55	ND
4	60	No	1175.5	1410	21.55	25.95	ND
5*	60	Yes	1326	1472	13.65	17	ND
6	30	No	1101	1418.5	21.5	27.95	ND
7*	30	Yes	1480	1653.5	9.35	11.1	ND

\*examples according to the present invention; ND: not done

Results show that sample 1 having the weight ratio Al/V according to the present invention was recovered. On the contrary, Trial 2 was recrystallized.

10 The mechanical properties of Sample 1 are better than the mechanical properties of Sample 2.

Sample 5 according to the present invention was recovered after the recovery heat treatment. On the contrary, Samples 3 and 4 were recrystallized. In addition, the mechanical properties, in particular UTS and YS, of sample 5 was higher than the mechanical properties of Samples 3 and 4.

15 Sample 7 according to the present invention was recovered after the recovery heat treatment. On the contrary, Sample 6 was recrystallized. In addition, the mechanical properties, in particular UTS and YS, of sample 7 were higher than the mechanical properties of Sample 6.

Figure 1 shows the amount of Al and V in the Samples 1 to 7.

**CLAIMS**

1. A cold rolled and recovered TWIP steel sheet having an austenitic matrix comprising by weight :

$$0.1 < C < 1.2\%,$$

5

$$13.0 \leq Mn < 25.0\%,$$

$$0.1 \leq Si \leq 3.0\%,$$

$$0.1 \leq Cu \leq 5.0\%,$$

$$S \leq 0.030\%,$$

$$P \leq 0.080\%,$$

10

$$N \leq 0.1\%,$$

$$0.1 \leq Al \leq 4.0\% \text{ and}$$

$$0.1 \leq V \leq 2.50\% \text{ in such way that:}$$

- when the amount of Al < 2.0%, the weight ratio Al/V is between 0.2 and 8 or

- when the amount of Al  $\geq$  2.0%, the amount of V > 0.25%,

15

and on a purely optional basis, one or more elements such as

$$Nb \leq 0.5 \%,$$

$$B \leq 0.005\%,$$

$$Cr \leq 1.0\%,$$

$$Mo \leq 0.40\%,$$

20

$$Ni \leq 1.0\%,$$

$$Ti \leq 0.5\%,$$

$$0.06 \leq Sn \leq 0.2\%,$$

the remainder of the composition being made of iron and inevitable impurities resulting from the elaboration.

25

2. A steel sheet according to claim 1, wherein the amount of V is between 0.1 and 1.0%.

3. A steel sheet according to anyone of claims 1 to 2, wherein the amount of Al is

30

between is below or equal to 2.0%.

15.

4. A steel sheet according to anyone of claims 1 to 3, wherein at least one vanadium element under the form of nitrides, carbides or carbonitrides is present in the steel.

5. A steel sheet according to anyone of claims 1 to 4, wherein the amount of Cu is below 2.0%.

6. A steel sheet according to anyone of claims 1 to 5, wherein the amount of Nb is between 0.070 and 0.50% by weight.

10

7. A steel sheet according to anyone of claims 1 to 6, wherein the amount of Si is below or equal to 0.6% by weight.

8. A steel sheet according to anyone of claims 1 to 7, wherein the amount of Al, V, C, Mn, Si, Cu and Nb satisfies the following equation:

$$105.1 * Al\% - 358.1 * V\% \leq 279.67 * C\% - 11 * Mn\% + 30 * Si\% - 69.02 * Cu\% + 78.3 * Nb\% + 144$$

9. A steel sheet according to anyone of claims 1 to 8, wherein the steel sheet is covered by a metallic coating.

20

10. A steel sheet according to anyone of claims 1 to 9, wherein the steel sheet is covered by an aluminum-based coating or a zinc-based coating.

11. A steel sheet according to claim 10, wherein the aluminium-based coated comprises less than 15% Si, less than 5.0% Fe, optionally 0.1 to 8.0% Mg and optionally 0.1 to 30.0% Zn, the remainder being Al.

25

12. A steel sheet according to claim 11, wherein the zinc-based coating comprises 0.01-8.0% Al, optionally 0.2-8.0% Mg, the remainder being Zn.

30

13. A method for producing a TWIP steel sheet comprising the following steps :

A. The feeding of a slab having a composition according to anyone of claims 1 to 8,

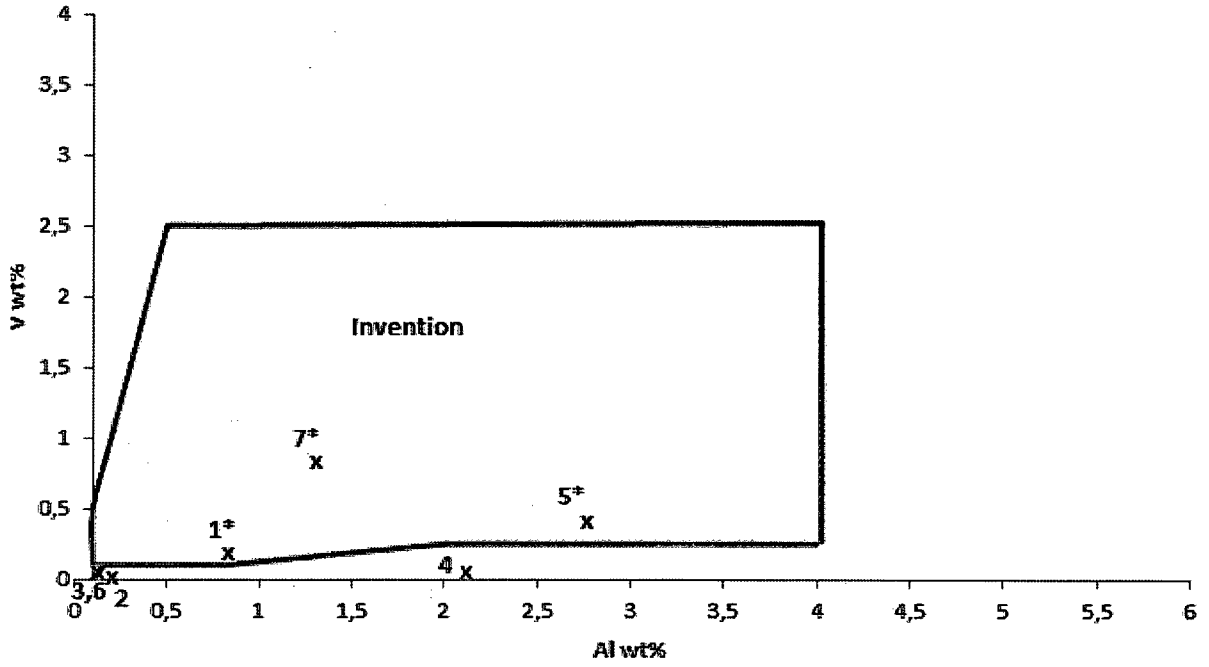
- B. The reheating such slab at a temperature above 1000°C and hot rolling it with a final rolling temperature of at least 850°C,
  - C. A coiling step at a temperature below or equal to 580°C,
  - D. A first cold-rolling with a reduction rate between 30 and 70%,
  - 5 E. A recrystallization annealing between 700 and 900°C,
  - F. A second cold-rolling with a reduction rate between 1 to 50% and
  - G. A recovery heat treatment.
- 10 14. Method according to claim 13, wherein the recovery step G) is performed by heating the steel sheet at a temperature between 410 and 700°C in a batch annealing or a continuous annealing furnace.
- 15 15. Method according to claim 13, wherein the recovery step G) is performed by hot-dip coating, i.e. by preparing the surface of the steel sheet for the coating deposition in a continuous annealing followed by the dipping the steel sheet in a molten metallic bath having a temperature between 410 and 700°C depending on the nature of the molten bath.
- 20 16. Method according to anyone of claim 15, wherein during the preparation of steel surface, the steel sheet is heated from ambient temperature to the temperature of the molten bath.
- 25 17. Method according to anyone of claims 15 to 16, wherein the bath is aluminum-based and comprises less than 15% Si, less than 5.0% Fe, optionally 0.1 to 8.0% Mg and optionally 0.1 to 30.0% Zn, the remainder being Al.
- 30 18. Method according to anyone of claims 15 to 16, wherein the bath is zinc-based and comprises 0.01-8.0% Al, optionally 0.2-8.0% Mg, the remainder being Zn.
- 35 19. Method according to anyone of claims 13 to 18, wherein the recovery step G) is performed during 1 second to 30minutes.

20. Method according to claim 19, wherein the recovery step H) is performed during 30 seconds to 10 minutes.

1 / 1

Figure 1

5



10

INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2017/000597

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C22C38/00	C22C38/02	C22C38/04	C22C38/06	C22C38/08
	C22C38/12	C22C38/14	C22C38/16	C22C38/20	C22C38/22
	C22C38/24	C22C38/28	C22C38/32	C22C38/34	C22C38/38

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) C22C C21D C23C

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 practicable, search terms used) EPO-Internal, WPI Data
--

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/209833 A1 (SCOTT COLIN [FR] ET AL) 15 August 2013 (2013-08-15) paragraphs [0004] - [0006], [0021] - [0055], [0062], [0067] - [0075], [0099] table 1	1-20
X	US 2006/179638 A1 (ENGL BERNHARD [DE] ET AL) 17 August 2006 (2006-08-17) paragraphs [0008] - [0010], [0013] - [0021], [0031], [0033] claim 1	1,2,4-6, 8-20
X	US 2009/010793 A1 (BECKER JENS-ULRIK [DE] ET AL) 8 January 2009 (2009-01-08) paragraphs [0001], [0011] - [0027], [0057] - [0060] claim 1	1,2,5-8
	----- -/--	

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
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"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	

Date of the actual completion of the international search 1 September 2017	Date of mailing of the international search report 11/09/2017
---	--

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Martinavicius, A
--	--

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2017/000597

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2016/010173 A1 (SCOTT COLIN [FR] ET AL) 14 January 2016 (2016-01-14) paragraphs [0008], [0016], [0020], [0111] - [0117] -----	1-20
A	US 2008/083477 A1 (DRILLET PASCAL [FR] ET AL) 10 April 2008 (2008-04-10) paragraphs [0001], [0014], [0043] - [0049] -----	1-20
A	WO 2009/084792 A1 (POSCO [KR]; KIM GYO SUNG [KR]; KANG SOO CHANG [KR]; HAN TAE KYO [KR];) 9 July 2009 (2009-07-09) paragraphs [0013], [0014], [0065] -----	1-20

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IB2017/000597

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 3(completely); 1, 2, 4-20(partially)

A cold rolled and recovered TWIP steel sheet having an austenitic matrix comprising by weight:  $0.1 < C < 1.2\%$ ,  $13.0 \leq Mn < 25.0\%$ ,  $0.1 \leq Si \leq 3.0\%$ ,  $0.1 \leq Cu \leq 5.0\%$ ,  $S \leq 0.030\%$ ,  $P \leq 0.080\%$ ,  $N \leq 0.1\%$ ,  $0.1 \leq Al < 2.0\%$  and  $0.1 \leq V \leq 2.50\%$  in such way that the weight ratio Al/V is between 0.2 and 8 and on a purely optional basis, one or more elements such as  $Nb \leq 0.5 \%$ ,  $B \leq 0.005\%$ ,  $Cr \leq 1.0\%$ ,  $Mo \leq 0.40\%$ ,  $Ni \leq 1.0\%$ ,  $Ti \leq 0.5\%$ , the remainder of the composition being made of iron and inevitable impurities resulting from the elaboration.

---

2. claims: 1, 2, 4-20(all partially)

A cold rolled and recovered TWIP steel sheet having an austenitic matrix comprising by weight:  $0.1 < C < 1.2\%$ ,  $13.0 \leq Mn < 25.0\%$ ,  $0.1 \leq Si \leq 3.0\%$ ,  $0.1 \leq Cu \leq 5.0\%$ ,  $S \leq 0.030\%$ ,  $P \leq 0.080\%$ ,  $N \leq 0.1\%$ ,  $2.0 \geq Al \leq 4.0\%$  and  $0.25 < V \leq 2.50\%$ , and on a purely optional basis, one or more elements such as  $Nb \leq 0.5 \%$ ,  $B \leq 0.005\%$ ,  $Cr \leq 1.0\%$ ,  $Mo \leq 0.40\%$ ,  $Ni \leq 1.0\%$ ,  $Ti \leq 0.5\%$ , the remainder of the composition being made of iron and inevitable impurities resulting from the elaboration.

---

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No

PCT/IB2017/000597

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 2013209833	A1	15-08-2013	BR 112013009694 A2	19-07-2016
			CA 2815018 A1	26-04-2012
			CN 103261464 A	21-08-2013
			EP 2630269 A1	28-08-2013
			ES 2544607 T3	02-09-2015
			HU E027094 T2	29-08-2016
			JP 2013544968 A	19-12-2013
			KR 20130126612 A	20-11-2013
			MA 34613 B1	02-10-2013
			MX 346491 B	22-03-2017
			RU 2013123061 A	27-11-2014
			UA 107519 C2	12-01-2015
			US 2013209833 A1	15-08-2013
			WO 2012052626 A1	26-04-2012
WO 2012052689 A1	26-04-2012			
US 2006179638	A1	17-08-2006	AT 448331 T	15-11-2009
			AU 2003273899 A1	09-07-2004
			CA 2510754 A1	01-07-2004
			CN 1732275 A	08-02-2006
			DE 10259230 A1	15-07-2004
			EP 1573075 A1	14-09-2005
			ES 2336095 T3	08-04-2010
			JP 4500688 B2	14-07-2010
			JP 2006509912 A	23-03-2006
			KR 20050084429 A	26-08-2005
			KR 20110091009 A	10-08-2011
			MX PA05006411 A	19-08-2005
			RU 2329308 C2	20-07-2008
			US 2006179638 A1	17-08-2006
WO 2004055223 A1	01-07-2004			
US 2009010793	A1	08-01-2009	BR PI0419185 A	18-12-2007
			CN 101065503 A	31-10-2007
			EP 1807542 A1	18-07-2007
			JP 2008519160 A	05-06-2008
			US 2009010793 A1	08-01-2009
			WO 2006048034 A1	11-05-2006
US 2016010173	A1	14-01-2016	AU 2007273982 A1	17-01-2008
			BR PI0715458 A2	05-03-2013
			CA 2657508 A1	17-01-2008
			CA 2787998 A1	17-01-2008
			CN 101506402 A	12-08-2009
			EP 1878811 A1	16-01-2008
			EP 2041330 A2	01-04-2009
			JP 5697125 B2	08-04-2015
			JP 2009542920 A	03-12-2009
			KR 20090043508 A	06-05-2009
			MA 30583 B1	01-07-2009
			RU 2009104474 A	20-08-2010
			UA 95642 C2	25-08-2011
			US 2009308499 A1	17-12-2009
			US 2016010173 A1	14-01-2016
			US 2016010187 A1	14-01-2016
			WO 2008007192 A2	17-01-2008
ZA 200900177 B	25-11-2009			

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2017/000597

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008083477	A1	10-04-2008	AT 394517 T 15-05-2008
			BR PI0516997 A 30-09-2008
			CA 2584449 A1 27-04-2006
			CN 101072892 A 14-11-2007
			EP 1805341 A1 11-07-2007
			ES 2306247 T3 01-11-2008
			FR 2876711 A1 21-04-2006
			JP 4828544 B2 30-11-2011
			JP 2008517157 A 22-05-2008
			KR 20070064373 A 20-06-2007
			RU 2363756 C2 10-08-2009
			US 2008083477 A1 10-04-2008
			WO 2006042930 A1 27-04-2006
			ZA 200703345 B 30-04-2008
WO 2009084792	A1	09-07-2009	KR 20090072118 A 02-07-2009
			WO 2009084792 A1 09-07-2009