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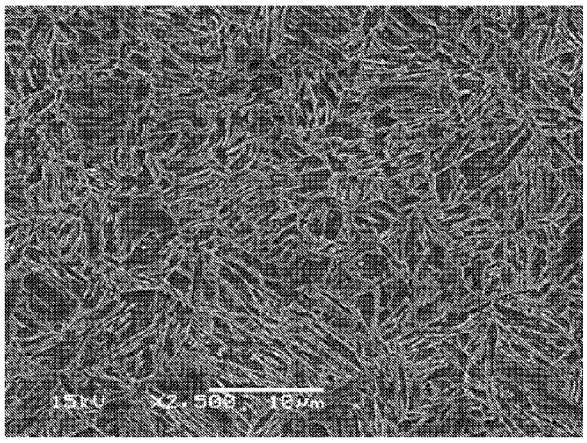
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(54) Title: METHOD FOR PRODUCING A HIGH STRENGTH STEEL SHEET HAVING IMPROVED STRENGTH, DUCTILITY AND FORMABILITY



(57) Abstract: A method for producing a high strength steel sheet having a yield strength YS of at least 850 MPa, a tensile strength TS of at least 1180 MPa, a total elongation of at least 14% and a hole expansion ratio HER of at least 30%. The chemical composition of the steel contains: 0.15% ≤ C ≤ 0.25%, 1.2% ≤ Si ≤ 1.8%, 2% ≤ Mn ≤ 2.4%, 0.1 % ≤ Cr ≤ 0.25%, Nb ≤ 0.05 %, Ti ≤ 0.05 %, Al < 0.50%, the remainder being Fe and unavoidable impurities. The sheet is annealed at an annealing temperature TA higher than 850 °C but less than 1000°C for more than 30 s, by cooling it to a quenching temperature QT between 275°C and 325°C, at a cooling speed suffioint to have, just after quenching, a structure consisting of austenite and at least 50% of martensite, the austenite content being such that the final structure can contain between 3% and 15% of residual austenite and between 85 and 97% of the sum of martensite and bainite, without ferrite, heated to a partitioning temperature PT between 420 °C and 470 °C and maintained at this temperature for time between 50 s and 150 s and cooled to the room temperature. Obtained steel sheet.

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METHOD FOR PRODUCING A HIGH STRENGTH STEEL SHEET HAVING IMPROVED STRENGTH, DUCTILITY AND FORMABILITY

The present invention relates to a method for producing a high strength steel sheet having improved strength, ductility and formability and to the sheets obtained with the method.

To manufacture various equipments such as parts of body structural members and body panels for automotive vehicles, it is usual to use sheets made of DP (dual phase) steels or TRIP (transformation induced plasticity) steels.

For example, such steels which include a martensitic structure and/or some retained austenite and which contains about 0.2% of C, about 2% of Mn, about 1.7% of Si have a yield strength of about 750 MPa, a tensile strength of about 980 MPa, a total elongation of more than 8%. These sheets are produced on continuous annealing line by quenching from an annealing temperature higher than Ac_3 transformation point, down to a quenching temperature higher than Ms transformations point followed by heating to an overaging temperature above the Ms point and maintaining the sheet at the temperature for a given time. Then the sheet is cooled to the room temperature.

Due to the wish to reduce the weight of the automotive in order to improve their fuel efficiency in view of the global environmental conservation it is desirable to have sheets having improved yield and tensile strength. But such sheets must also have a good ductility and a good formability and more specifically a good stretch flangeability.

In this respect, it is desirable to have sheets having a yield strength YS of at least 850 MPa, a tensile strength TS of about 1180 MPa, a total elongation of at least 14% and a hole expansion ratio HER measured according to the ISO standard 16630:2009 of at least 30%. It must be emphasized that, due to differences in the methods of measure, the values of hole expansion ration HER according to the ISO standard are very different and not comparable to the values of the hole expansion ratio λ according to the JFS T 1001 (Japan Iron and Steel Federation standard).

Therefore, the purpose of the present invention is to provide such sheet and a method to produce it.

For this purpose, the invention relates to a method for producing a high strength steel sheet having an improved ductility and an improved formability, the sheet having a yield strength YS of at least 850 MPa, a tensile strength TS of at least 1180 MPa, a total elongation of at least 14% and a hole expansion ratio HER according to the ISO standard of at least 30%, by heat treating a steel sheet whose the chemical composition of the steel contains, in weight %:

0.15% ≤ C ≤ 0.25%

1.2% ≤ Si ≤ 1.8%

2% ≤ Mn ≤ 2.4%

0.1% ≤ Cr ≤ 0.25%

Nb ≤ 0.05 %

Ti ≤ 0.05 %

Al ≤ 0.50%

the remainder being Fe and unavoidable impurities. The heat treatment comprises the following steps:

- annealing the sheet at an annealing temperature TA higher than 850°C but less than 1000°C for a time of more than 30 s,
- quenching the sheet by cooling it down to a quenching temperature QT between 275°C and 325°C, at a cooling speed sufficient to have, just after quenching, a structure consisting of austenite and at least 50% of martensite, the austenite content being such that the final structure i.e. after treatment and cooling to the room temperature, can contain between 3% and 15% of residual austenite and between 85 and 97% of the sum of martensite and bainite, without ferrite,
- heating the sheet up to a partitioning temperature PT between 420°C and 470°C and maintaining the sheet at this temperature for a partitioning time Pt between 50 s and 150 s and,
- cooling the sheet down to the room temperature.

In a particular embodiment, the chemical composition of the steel is such that Al ≤ 0.05%.

The invention relates also to a steel sheet whose chemical composition contains in weight %:

0.15% ≤ C ≤ 0.25%

1.2% ≤ Si ≤ 1.8%

2% ≤ Mn ≤ 2.4%

0.1 ≤ Cr ≤ 0.25%

Nb ≤ 0.05 %

Ti ≤ 0.05%

Al ≤ 0.5%

the remainder being Fe and unavoidable impurities, the sheet having a yield strength of at least 850 MPa, a tensile strength of at least 1180 MPa, a total elongation of at least 14% and a hole expansion ratio HER of at least 30% and the structure consists of 3% to 15% of retained austenite and 85% to 97% of martensite and bainite without ferrite.

The yield strength may even be greater than 950 MPa.

In a particular embodiment, the chemical composition of the steel is such that Al ≤ 0.05%.

The invention will now be described in details but without introducing limitations and illustrated by the only figure which is a scanning electron microscope micrograph corresponding to example 10.

According to the invention, the sheet is obtained by hot rolling and optionally cold rolling of a semi product which chemical composition contains, in weight %:

- 0.15% to 0.25%, and preferably more than 0.17% and preferably less than 0.21% of carbon for ensuring a satisfactory strength and improving the stability of the retained austenite which is necessary to obtain a sufficient elongation. If carbon content is too high, the hot rolled sheet is too hard to cold roll and the weldability is insufficient.

- 1.2% to 1.8% preferably more than 1.3% and less than 1.6% of silicon in order to stabilize the austenite, to provide a solid solution strengthening and to delay the formation of carbides during overaging.

- 2% to 2.4% and preferably more than 2.1% and preferably less than 2.3% of manganese to have a sufficient hardenability in order to obtain a structure containing at least 65% of martensite, tensile strength of more than 1180 MPa and to avoid having segregation issues which are detrimental for the ductility.

-0.1% to 0.25% of chromium to increase the hardenability and to stabilize the retained austenitic in order to delay the formation of bainite during overaging.

- up to 0.5% of aluminum which is usually added to liquid steel for the purpose of deoxidation, If the content of Al is above 0.5%, the annealing temperature will be too high to reach and the steel will become industrially difficult to process. Preferably, the Al content is limited to impurity levels i.e. a maximum of 0.05%.

- Nb content is limited to 0.05% because above such value large precipitates will form and formability will decrease, making the 14% of total elongation more difficult to reach.

- Ti content is limited to 0.05% because above such value large precipitates will form and formability will decrease, making the 14% of total elongation more difficult to reach.

The remainder is iron and residual elements resulting from the steelmaking. In this respect, Ni, Mo, Cu, V, B, S, P and N at least are considered as residual elements which are unavoidable impurities. Therefore, their contents are less than 0.05% for Ni, 0.02% for Mo, 0.03% for Cu, 0.007% for V, 0.0010% for B, 0.007 % for S, 0.02% for P and 0.010% for N.

The sheet is prepared by hot rolling and optionally cold rolling according to the methods known by those who are skilled in the art.

After rolling the sheets are pickled or cleaned then heat treated.

The heat treatment which is made preferably on a combined continuous annealing line comprise the steps of:

- annealing the sheet at an annealing temperature TA higher than the Ac_3 transformation point of the steel, and preferably higher than Ac_3 + 15°C i.e. higher than 850°C for the steel according to the invention, in order to be sure that the structure is completely austenitic, but less than 1000°C in order not to coarsen too much the austenitic grains. The sheet is maintained at the annealing temperature i.e. maintained between TA - 5°C and TA + 10°C, for a time sufficient to homogenize the chemical composition. This time is preferably of more than 30 s but does not need to be of more than 300 s.
- quenching the sheet by cooling down to a quenching temperature QT lower than the Ms transformation point at a cooling rate enough to avoid ferrite and bainite formation, The quenching temperature is between 275°C and 325°C in order to have, just after quenching, a structure consisting of austenite and at least 50% of martensite, the austenite content being such that the final structure i.e. after treatment and cooling to the room temperature, can contain between 3% and 15% of residual austenite and between 85 and 97% of the sum of martensite and bainite, without ferrite. A cooling rate of at least 30°C/s is required to avoid the ferrite formation during cooling from the annealing temperature.
- reheating the sheet up to a partitioning temperature PT between 420°C and 470°C. The reheating rate can be high when the reheating is made by induction heater, but that reheating rate had no apparent effect on the final properties of the sheet.
- maintaining the sheet at the partitioning temperature PT for a time between 50 s and 150 s. Maintaining the sheet at the partitioning temperature means that during partitioning the temperature of the sheet remains between PT - 10°C and PT + 10°C.
- cooling the sheet down to room temperature with a cooling rate preferably of more than 1°C/s in order not to form ferrite or bainite. Currently, this cooling speed is between 2°C/s and 4°C/s.

With such treatment, sheets have a structure consisting of 3% to 15% of retained austenite and 85% to 97% of martensite and bainite, without ferrite. Indeed, due to the quenching under the Ms point, the structure contains martensite and at least 50%. But for such steels, martensite and bainite are very difficult to distinguish. It is why only the sum

of the contents of martensite and bainite are considered. With such structure, the sheet having a yield strength YS of at least 850 MPa, a tensile strength of at least 1180 MPa, a total elongation of at least 14% and a hole expansion ratio (HER) according to the ISO standard 16630:2009 of at least 30% can be obtained.

As an example a sheet of 1.2 mm in thickness having the following composition: C = 0.19%, Si = 1.5% Mn = 2.2%, Cr = 0.2%, the remainder being Fe and impurities, was manufactured by hot and cold rolling. The theoretical Ms transformation point of this steel is 375°C and the Ac_3 point is 835°C.

Samples of the sheet were heat treated by annealing, quenching and partitioning, i.e; heating to a partitioning temperature and maintaining at this temperature, and the mechanical properties were measured.

The conditions of treatment and the obtained properties are reported at table I where the annealing type (Ann. type) column specifies if the annealing is intercritical (IA) or fully austenitic (full γ).

Table I

Sample	TA °C	Ann. type	QT °C	PT °C	Pt s	YS MPa	TS MPa	UE %	TE %	HER %	γ %
1	825	IA	250	400	99	990	1200	7	11.7	24	
2	825	IA	250	450	99	980	1180	9	14		
3	825	IA	300	400	99	865	1180	8.2	13.2	-	
4	825	IA	300	450	99	740	1171	10.2	15.4	13	12.6
5	825	IA	350	400	99	780	1190	10.1	15.4		
6	825	IA	350	450	99	650	1215	11	15.5	8	
7	875	Full γ	250	400	99	1190	1320	3.5	8		
8	875	Full γ	250	450	99	1170	1250	6.1	10.5		
9	875	Full γ	300	400	99	1066	1243	7.2	12.8	31	12.3
10	875	Full γ	300	450	99	1073	1205	9.3	14.4	37	12
11	875	Full γ	350	400	99	840	1245	7.5	11		
12	875	Full γ	350	450	99	760	1220	9.5	13.2	9	
13	825	IA	400	400	99	756	1232		15.2	13	
14	825	IA	450	450	99	669	1285		13.5	-	
15	875	Full γ	400	400	99	870	1301		11.7	24	
16	875	Full γ	450	450	99	784	1345		10.7	-	

In this table, TA is the annealing temperature, QT the quenching temperature, PT temperature of partitioning, Pt the time of partitioning, YS the yield strength, TS the tensile strength, UE the uniform elongation, TE the total elongation, HER the hole expansion

ration according to the ISO standard and γ is the proportion of retained austenite in the structure.

In table I, example 10 is according to the invention and all properties are better than the minimal required properties. As shown in the figure its structure contains 11.2% of retained austenite and 88.8% of the sum of martensite and bainite.

Examples 1 to 6 which are related to samples annealed at an intercritical temperature show that even if the total elongation is greater than 14%, which is the case only for samples 4, 5 and 6, the hole expansion ratio is too low.

Examples 13 to 16 which are related to prior art i.e. to sheets that were not quenched under the Ms point (QT is above the Ms point and PT is equal to QT), show that with such heat treatment, even if the tensile strength is very good (above 1220 MPa), the yield strength is not very high (below 780) when the annealing is intercritical and the formability (hole expansion ratio) is not sufficient (below 30%) in all cases.

Examples 7 to 12 which are all related to samples which were annealed at a temperature higher than Ac_3 i.e. the structure was completely austenitic, show that the only way to reach the targeted properties is a quenching temperature 300°C (+/-10) and a partitioning temperature 450°C (+/-10). With such conditions, it is possible to obtain a yield strength greater than 850 MPa and even greater than 950 MPa, a tensile strength greater than 1180 MPa, a total elongation greater than 14% and a hole expansion ratio greater than 30%.

CLAIMS

1.- A method for producing a high strength steel sheet having an improved ductility and an improved formability, the sheet having a yield strength YS of at least 850 MPa, a tensile strength TS of at least 1180 MPa, a total elongation of at least 14% and a hole expansion ratio HER of at least 30%, by heat treating a steel sheet wherein the chemical composition of the steel contains:

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

$1.2\% \leq Si \leq 1.8\%$

$2\% \leq Mn \leq 2.4\%$

$0.1\% \leq Cr \leq 0.25\%$

$Nb \leq 0.05\%$

$Ti \leq 0.05\%$

$Al \leq 0.50\%$

the remainder being Fe and unavoidable impurities,

and wherein the heat treatment comprises the following steps:

- annealing the sheet at an annealing temperature TA higher than 850°C but less than 1000°C for a time of more than 30 s,
- quenching the sheet by cooling it down to a quenching temperature QT between 275°C and 325°C, at a cooling speed sufficient to have, just after quenching, a structure consisting of austenite and at least 50% of martensite, the austenite content being such that the final structure i.e. after treatment and cooling to the room temperature, can contain between 3% and 15% of residual austenite and between 85 and 97% of the sum of martensite and bainite, without ferrite,
- heating the sheet up to a partitioning temperature PT between 420°C and 470°C and maintaining the sheet at this temperature for a partitioning time Pt between 50 s and 150 s and,
- cooling the sheet down to the room temperature.

2.- The method according to claim 1, wherein the chemical composition of the steel is such that $Al \leq 0.05\%$.

3.- A steel sheet wherein the chemical composition of the steel contains in weight %:

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

1.2% ≤ Si ≤ 1.8%

2% ≤ Mn ≤ 2.4%

1.1 ≤ Cr ≤ 0.25%

Nb ≤ 0.05 %

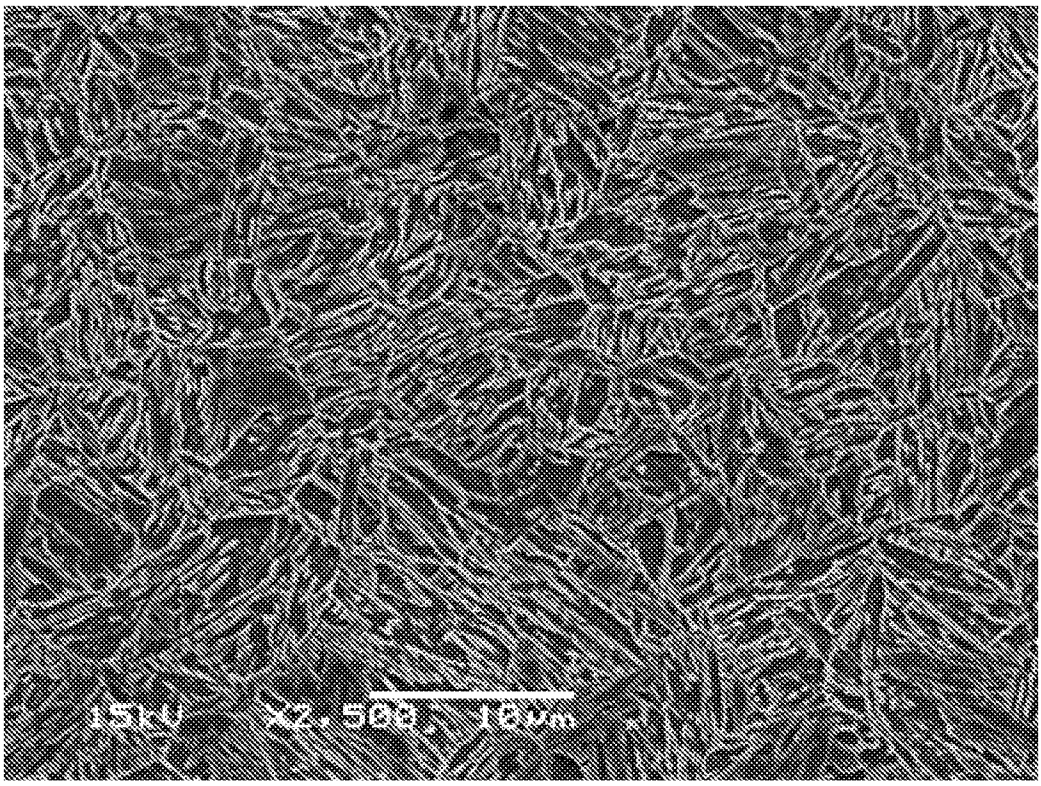
Ti ≤ 0.05%

Al ≤ 0.5%

the remainder being Fe and unavoidable impurities, the sheet having a yield strength of at least 850 MPa, a tensile strength of at least 1180 MPa, a total elongation of at least 14% and a hole expansion ratio HER of at least 30% and the structure consists of 3% to 15% of retained austenite and 85% to 97% of martensite and bainite without ferrite.

4.- The sheet according to claim 3, wherein the yield strength is greater than 950 MPa.

5. - The sheet according to claim 3 or 4, wherein the chemical composition of the steel is such that Al $\leq$ 0.05%.


15kV X2,500 10μm

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2014/002256

A. CLASSIFICATION OF SUBJECT MATTER
INV. C21D8/02 C21D9/46 C21D9/48 C21D1/18 C22C38/02
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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 practicable, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data, COMPENDEX, METADEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006/011274 A1 (SPEER JOHN G [US] ET AL) 19 January 2006 (2006-01-19) paragraphs [0001], [0010], [0011], [0013], [0014], [0016], [0018]-[0021]; claim 1; figures 2, 3	1-5
Y	US 2008/251161 A1 (KASHIMA TAKAHIRO [JP] ET AL) 16 October 2008 (2008-10-16) paragraphs [0001] and [0040]; tables 2, 4	1-5
Y	JP 2007 197819 A (KOBE STEEL LTD; SHINSHU TLO KK) 9 August 2007 (2007-08-09) abstract; tables 1, 2	1-5

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 February 2015	25/02/2015

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

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/221138 A1 (NAKAYA MICHIHARU [JP] ET AL) 2 September 2010 (2010-09-02) paragraphs [0015] and [0052]; tables 1, 3	1-5
A	EP 2 524 970 A1 (THYSSENKRUPP STEEL EUROPE AG [DE]) 21 November 2012 (2012-11-21) the whole document	1-5
A	EP 2 325 346 A1 (JFE STEEL CORP [JP]) 25 May 2011 (2011-05-25) the whole document	1-5
A	EP 2 683 839 A1 (TATA STEEL NEDERLAND TECH BV [NL]) 15 January 2014 (2014-01-15) the whole document	1-5
T	EDMONDS D V ET AL: "Quenching and partitioning martensite-A novel steel heat treatment", MATERIALS SCIENCE AND ENGINEERING A: STRUCTURAL MATERIALS:PROPERTIES, MICROSTRUCTURE & PROCESSING, LAUSANNE, CH, vol. 438-440, 25 November 2006 (2006-11-25), pages 25-34, XP027953091, ISSN: 0921-5093 [retrieved on 2006-11-25] the whole document	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2014/002256

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006011274 A1	19-01-2006	AU 2003270334 A1	29-03-2004
		US 2006011274 A1	19-01-2006
		WO 2004022794 A1	18-03-2004
US 2008251161 A1	16-10-2008	CN 101155940 A	02-04-2008
		JP 4716358 B2	06-07-2011
		JP 2006274417 A	12-10-2006
		KR 20070105375 A	30-10-2007
		US 2008251161 A1	16-10-2008
		WO 2006106733 A1	12-10-2006
JP 2007197819 A	09-08-2007	JP 4174592 B2	05-11-2008
		JP 2007197819 A	09-08-2007
US 2010221138 A1	02-09-2010	CN 101460646 A	17-06-2009
		GB 2452230 A	04-03-2009
		JP 4974341 B2	11-07-2012
		JP 2007321237 A	13-12-2007
		KR 20090016500 A	13-02-2009
		US 2010221138 A1	02-09-2010
		WO 2007142197 A1	13-12-2007
EP 2524970 A1	21-11-2012	CN 103597100 A	19-02-2014
		EP 2524970 A1	21-11-2012
		EP 2710158 A1	26-03-2014
		JP 2014518945 A	07-08-2014
		KR 20140024903 A	03-03-2014
		US 2014322559 A1	30-10-2014
		WO 2012156428 A1	22-11-2012
EP 2325346 A1	25-05-2011	CA 2734976 A1	18-03-2010
		CN 102149840 A	10-08-2011
		EP 2325346 A1	25-05-2011
		JP 5418047 B2	19-02-2014
		JP 2010090475 A	22-04-2010
		KR 20110039395 A	15-04-2011
		TW 201016862 A	01-05-2010
		US 2011146852 A1	23-06-2011
		WO 2010029983 A1	18-03-2010
EP 2683839 A1	15-01-2014	EP 2683839 A1	15-01-2014
		WO 2012120020 A1	13-09-2012