

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 553 202 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

13.07.2005 Bulletin 2005/28

(51) Int Cl.7: **C22C 38/00**, C22C 38/02,
C22C 38/04, C22C 38/06,
C21D 8/02

(21) Application number: **05250049.3**

(22) Date of filing: **07.01.2005**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR**

Designated Extension States:

AL BA HR LV MK YU

- Ikeda, Sushi, c/o Kobe Corporate Research
Nishi-ku Kobe-shi Hyogo 651-2271 (JP)
- Makii, Koichi, c/o Kobe Corporate Research
Nishi-ku Kobe-shi Hyogo 651-2271 (JP)
- Mukai, Yoichi, c/o Kakogawa Works
Kakogawa-shi Hyogo 675-0137 (JP)
- Sugimoto, Koichi
Ueda-shi Nagano 386-0015 (JP)

(30) Priority: **09.01.2004 JP 2004004727**

(71) Applicants:

- Kabushiki Kaisha Kobe Seiko Sho (Kobe Steel,
Ltd.)
Kobe-shi, Hyogo 651-8585 (JP)
- Shinshu TLO Co. Ltd.
Nagano-386-8567 (JP)

(74) Representative: **Gillard, Richard Edward
Elkington and Fife LLP,
Prospect House
8 Pembroke Road
Sevenoaks, Kent TN13 1XR (GB)**

(72) Inventors:

- Akamizu, Hiroshi, c/o Kobe Corporate Research
Nishi-ku Kobe-shi Hyogo 651-2271 (JP)

(54) **Ultra-high strength steel sheet having excellent hydrogen embrittlement resistance, and method for manufacturing the same**

(57) The present invention provides an ultra-high strength steel sheet having excellent hydrogen embrittlement resistance, which includes:

0.06 to 0.6% of C;
0.5 to 3% of Si+Al;
0.5 to 3% of Mn;
0.15% or lower of P; and
0.02% or lower of S in terms of mass percentage,
and also includes 3% or higher of residual austenite structure,
30% or higher of bainitic ferrite structure, and preferably
50% or lower of polygonal ferrite in terms of an areal ratio to the entire structure,

wherein a mean grain size of bainite blocks is smaller than 20 μm as determined by comparing observations of the same region of the bainitic ferrite structure by EBSP (electron back scatter diffraction pattern) and SEM.

EP 1 553 202 A1

Description**BACKGROUND OF THE INVENTION**

5 [Technical Field]

[0001] The present invention relates to an ultra-high strength steel sheet having strength of at least 1180 MPa class and excellent hydrogen embrittlement resistance, and a method for efficiently manufacturing the ultra-high strength steel sheet.

10 [Background Art]

[0002] There are increasing demands for steel sheets, that are pressed into forms to be used in such applications as automobiles and industrial machines, to have both high strength and high ductility at the same time. Recently needs are increasing for ultra-high strength steel sheets having strength of at least 1180 MPa class. A type of steel sheet that is regarded as promising one to satisfy these needs is TRIP (transformation induced plasticity) steel sheet.

[0003] The TRIP steel sheet includes residual austenite structure and, when processed to deform at a temperature higher than the martensitic transformation start point (M_s point), undergoes considerable elongation due to induced transformation of the residual austenite (γ_R) into martensite by the action of stress. Known examples include TRIP type composite-structure steel (TPF steel) that consists of polygonal ferrite as the matrix phase and residual austenite; TRIP type tempered martensite steel (TAM steel) that consists of tempered martensite as the matrix phase and residual austenite; and TRIP type bainitic ferrite steel (TBF steel) that consists of bainitic ferrite as the matrix phase and residual austenite. Among these, the TBF steel has long been known (described, for example, in Nisshin Steel Technical Journal No. 43 published in 1980), and has such advantages as the capability to readily provide high strength due to the hard bainitic ferrite structure, and the capability to show outstanding elongation because fine residual austenite grains can be easily formed in the boundary of lath-shaped bainitic ferrite in the bainitic ferrite structure. The TBF steel also has such an advantage related to manufacturing, that it can be easily manufactured by a single heat treatment process (continuous annealing process or plating process).

[0004] In the realm of ultra-high strength of 1180 MPa upward, however, the TRIP steel sheet is known to suffer a newly emerging problem of delayed fracture (crack, etc.) caused by hydrogen embrittlement, similarly to the conventional high strength steel. Delayed fracture refers to the failure of high-strength steel under stress, that occurs as hydrogen originating in corrosive environment or the atmosphere infiltrates and diffuses in microstructural defects such as dislocation, void and boundary, and makes the steel brittle. This results in decrease in ductility and in toughness of the metallic material.

[0005] To counter such problems, researches have been recently conducted on hydrogen embrittlement of TRIP steel (Non-Patent Documents Nos. 1 and 2). According to reports of these researches, all of the types of TRIP steel mentioned above show high hydrogen embrittlement resistance, while the TBF steel has a particularly high hydrogen storage capacity. Observation of fracture surface of the TBF steel shows that quasi cleavage fracture due to hydrogen storage is suppressed. This fact suggests that the TBF steel has excellent resistance against delayed fracture. The mechanism behind this property is supposedly that the TBF steel consists of bainitic ferrite structure and therefore has a high density of dislocations in the matrix phase, so that much hydrogen is trapped on the dislocations, resulting in the storage of higher hydrogen than other types of TRIP steel.

[0006] However, the TBF steels reported in the literatures described above show delayed fracture characteristic of about 1000 seconds at the most in terms of crack occurrence time measured by cathode charging test, indicating the need for further improvement in the characteristic. Moreover, since the heat treatment conditions reported in the literatures described above involve heating temperature being set higher, there are such problems as low efficiency of practical manufacturing process. Thus it is strongly required to develop a new species of TBF steel that provides high production efficiency as well.

[0007] [Non-Patent Document 1] Tomohiko HOJO et. al, "Hydrogen Embrittlement of Ultra-High Strength Low Alloy TRIP Steel (Part 1: Hydrogen Storage Characteristic and Ductility)", Japan Materials Science Association, Proceedings of 51st Academic Lecture Meeting, 2002, Vol. 8, pp17-18.

[0008] [Non-Patent Document 2] Tomohiko HOJO et. al, "Influence of Austempering Temperature on Hydrogen Embrittlement of Ultra-high Strength Low Alloy TRIP steel", CAMP-ISIJ, 2003, Vol. 16, p568

SUMMARY OF THE INVENTION

[0009] The present invention has been made with the background described above, and has an object of providing a novel TRIP steel sheet having a bainitic ferrite structure as the matrix phase, that is an ultra-high strength steel sheet

having a tensile strength of 1180 MPa or higher and improved hydrogen embrittlement resistance, while maintaining the high ductility characteristic of the TRIP steel, and a method for manufacturing the same.

[0010] In order to achieve the object described above, the ultra-high strength steel sheet of the present invention (ultra-high strength steel sheet having tensile strength of 1180 MPa or higher, high capability to elongate and high hydrogen embrittlement resistance) has such a constitution as 0.06 to 0.6% of C, 0.5 to 3% of Si+Al, 0.5 to 3% of Mn, 0.15% or lower of P and 0.02% or lower of S are included in terms of mass percentage, residual austenite structure occupies 3% or higher and bainitic ferrite structure occupies 30% or higher in an areal ratio to the entire structure, wherein a mean grain size of bainite blocks is smaller than 20 μm as determined by comparing observations of the same region of the bainitic ferrite structure by EBSP (electron back scatter diffraction pattern) and SEM, and preferably area occupied by polygonal ferrite structure is in a range from 5% to 50% in terms of an areal ratio to the entire structure.

[0011] A variation of the steel sheet described above that further includes at least one of 1% or lower by mass (higher than 0%) of Mo, 0.5% or lower by mass (higher than 0%) of Ni, 0.5% or lower by mass (higher than 0%) of Cu and 1% or lower by mass (higher than 0%) of Cr; a variation that further includes at least one of 0.1% or lower by mass (higher than 0%) of Ti, 0.1% or lower by mass (higher than 0%) of Nb and 0.1% or lower by mass (higher than 0%) of V; and a variation that further includes 0.003% or lower by mass (higher than 0%) of Ca and/or 0.003% or lower by mass (higher than 0%) of REM are all preferred embodiments of the present invention.

[0012] The method of the present invention that solves the problems described above is a method of manufacturing the ultra-high strength steel sheet by applying continuous annealing or plating, including a heat treatment process wherein a steel that contains the components described above is kept at a temperature in a range from A3 point to (A3 point + 20°C) for 10 to 600 seconds, then cooled at a mean cooling rate of 3°C/s or more to a temperature not lower than Ms point and not higher than Bs point, and is kept in this temperature range for 1 to 1800 seconds.

[0013] According to the present invention, the ultra-high strength steel sheet having tensile strength of 1180 MPa or higher and improved hydrogen embrittlement resistance can be manufactured with high productivity.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Other objects and advantages of the invention will become apparent during the following discussion of the accompanying drawings, wherein:

Fig. 1 is a SEM photograph (magnification factor 1500) of No. 2 (example of the present invention) of Example 1, Fig. 2 is a photograph (magnification factor 1500) of the same region as shown in Fig. 1 using EBSP analysis, Fig. 3 is a photograph where residual austenite γ_R (FCC phase) is identified in the EBSP analysis photograph of Fig. 2, Fig. 4 is a schematic diagram showing a representative process according to the method of the present invention, and Fig. 5 shows EBSP photographs (magnification factor 5000) of the example (No. 1) of the present invention in Example 2 and the comparative example (No. 2). Fig. 6 is a schematic perspective view of a member for the crush resistance test in Example 1. Fig. 7 is a schematic side view showing the way in which the crush resistance test is conducted in Example 1. Fig. 8 is a schematic perspective view of a member for the impact resistance test in Example 1. Fig. 9 is a sectional view at A-A in Fig. 8. Fig. 10 is a schematic side view showing the way in which the impact resistance test is conducted in Example 1.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0015] For the purpose of further improving the hydrogen embrittlement resistance in ultra-high strength region of tensile strength above 1180 MPa, the present inventors took up TBF steel, that has bainitic ferrite structure as the matrix phase, from among various types of TRIP steel, and conducted a research. In particular, since the method described in Non-Patent Document 2 has such drawbacks as the high heating temperature results in a low efficiency of production in practical manufacturing process, high possibility of damaging the furnace and causing decarburization, the inventors focused their research on the heating temperature. It was found that growth of austenite grains can be prevented by controlling the temperature lower than that employed in the manufacture of the conventional TBF steel, thus making it possible to form fine bainite blocks that have been impossible to obtain in the conventional TBF steel, which lead to improved toughness and hydrogen embrittlement resistance of the steel, thereby completing the invention.

[0016] The present invention will now be described in detail.

[Structure]

[0017] Micro structure that characterizes the present invention most will be first described.

[0018] The ultra-high strength steel sheet of the present invention includes a residual austenite structure that occupies 3% or higher and a bainitic ferrite structure that occupies 30% or higher in an areal ratio to the entire structure and therefore may be constituted solely from the residual austenite and the bainitic ferrite, while 50% or lower (including 0%) of polygonal ferrite structure may be included where mean grain size of bainite blocks is smaller than 20 μm . as determined by comparing the observations of the same region of the bainitic ferrite structure by EBSP and SEM.

Bainitic ferrite structure

[0019] Bainitic ferrite structure is hard in nature, as mentioned previously, and can readily provide high strength. Also because the density of dislocations is high in the matrix phase, it has such an advantage that much hydrogen is trapped on the dislocations, resulting in the storage of higher hydrogen than other types of TRIP steel. Further, the bainitic ferrite structure has another advantage of high capability to elongate since fine residual austenite grains can be grown in the boundary of lath-shaped bainitic ferrite. In order to make full use of these advantages, it is controlled so that the bainitic ferrite structure occupies 30% or more preferably 40% or higher, and more preferably 50% or higher in terms of an areal ratio to the entire structure. While the upper limit of the proportion depends on balancing between the bainitic ferrite structure and other structures and cannot be definitely specified, it is recommended to set the upper limit to about 95% or lower, or preferably 93% or lower in case that the polygonal ferrite structure is not included. when polygonal ferrite structure is included, it is recommended to set the upper limit to about 92% or lower, more preferably 90% or lower.

[0020] The areal ratio of the bainitic ferrite structure is determined by etching the surface of a steel sheet with Nital etchant and observing an area (about 50 by 50 μm) with SEM (scanning electron microscope) photograph (magnification factor 1500) in a surface parallel to the surface on which it was rolled at a depth of one quarter of the thickness.

[0021] A high resolution FE-SEM equipped with an EBSP detector (Phillips' XL30S-FEG) was used for the SEM observation in the present invention. Use of this equipment has an advantage that an area observed with the SEM can be analyzed by the EBSP detector at the same time. Use of the FE-SEM also enables it to identify the bainite blocks in the bainitic ferrite (this subject will be taken up later).

Mean grain size of bainite blocks < 20 μm

[0022] The steel sheet or plate of the present invention satisfies the requirement that mean grain size of bainite blocks is smaller than 20 μm in the bainitic ferrite that is identified by the method to be described later in the bainitic ferrite structure. Thus the present invention is most distinctly characterized in that hydrogen embrittlement resistance of TBF steel is improved by forming particularly finer bainite blocks among the bainitic ferrite structure. The desired property cannot be achieved when such coarse grains are formed as mean grain size of bainite blocks is larger than 20 μm . It is preferable that mean grain size of bainite blocks is as small as possible, preferably 18 μm or lower, and more preferably 16 μm or lower.

[0023] The bainitic ferrite refers to plate-shaped ferrite in lower structure having higher density of dislocations (which may or may not have lath-shaped structure), and is clearly distinguished by SEM observation from polygonal ferrite that has a lower structure of extremely low density of dislocations, as described below.

[0024] Polygonal ferrite: black polygonal spots seen in SEM photograph, that do not include residual austenite or martensite therein.

[0025] Bainitic ferrite: dark gray spots that often cannot be distinguished from residual austenite or martensite in SEM photograph.

[0026] The method of identifying bainite block in bainitic ferrite will now be described below with reference to Fig. 1 and Fig. 2. These are the results of observing the same area of sample No. 2 of Example 1 with the FE-SEM equipped with an EBSP detector, of which Fig. 1 is an SEM photograph (magnification factor 1500) taken by the method described above, and Fig. 2 is a photograph of cross section (magnification factor 1500) in the direction of thickness subjected to EBSP analysis conducted at the same time in the area observed with SEM. Hardware and software used in the EBSP detection, measurement and analysis are those of OIM (Orientation Imaging Microscopy TM) system manufactured by TexSEM Laboratories Inc. The measuring interval is 0.1 μm .

[0027] As shown in Fig. 1, since polygonal ferrite and bainitic ferrite can be distinguished by SEM observation, the region (bainitic ferrite), from which polygonal ferrite identified by SEM is excluded, can be easily determined among the structure shown in Fig. 2 obtained by EBSP analysis upon comparison of the SEM photograph of Fig. 1 and EBSP photograph of Fig. 2.

[0028] In the bainitic ferrite that is determined as described above, regions having a difference in orientation not

lower than 15° in the inclination angle between adjacent structures (in the present invention, such regions are regarded as having the same crystal orientation) are color-identified in red, and grain boundaries (min. 15° , max. 180°) are added to the 001 inverse pole figure. The regions that are color-identified as described above (regions having a difference in orientation not lower than 15° in the inclination angle) are defined as bainite block in the present invention. In other words, bainite block is defined according to the present invention as a region that is determined by EBSD analysis to have the same crystal orientation (region having a difference in orientation not lower than 15° in the inclination angle) in the bainitic ferrite identified by SEM, when the same area is subjected to SEM observation and EBSD analysis.

[0029] The EBSD method will be briefly described here. EBSD is a method of determining the crystal orientation at the position where electron beam is incident, by analyzing Kikuchi pattern obtained from reflected electrons when the electron beam is directed toward the surface of specimen. Distribution of orientations over the specimen surface can be determined by measuring the crystal orientation at predetermined pitches while scanning the specimen surface with the electron beam. The EBSD observation has such an advantage that crystal structures of different orientations in the direction of thickness, that would be regarded as identical when observed with a conventional optical microscope, can be distinguished by the color difference. In case the bainite block defined on the basis of crystal orientation makes an essential factor as in the present invention, it is necessary to observe the structure by the EBSD method.

[0030] For the bainite blocks detected as described above, diameter of a circle that has the same area as the bainite block is determined. The diameter of the equivalent circle of bainite block is determined by using the photograph of EBSD analysis with magnification factor of 5000. Similarly, diameters of the equivalent circles of all bainite blocks in the measured area (about 50 μm by 50 μm) are measured and the mean value thereof is defined as the mean grain size of bainite blocks in the present invention.

Residual austenite structure (yR)

[0031] Residual austenite is effective in improving the elongation property. In order to make full use of this property, the areal ratio of residual austenite is controlled to be 3% or higher (preferably 5% or higher, and more preferably 7% or higher) of the entire structure. Since excessive content of residual austenite makes it difficult to maintain the ultra-high strength, it is recommended to keep the content within an upper limit of 30% (preferably 25%).

[0032] According to the present invention, the residual austenite structure preferably has the form of lath. The form of lath herein means a shape with mean axis ratio (major axis/minor axis) of 2 or more (preferably 4 or more, and more preferably 6 or more). Such a lath-shaped residual austenite not only has the TRIP effect similar to that of the conventional residual austenite, but also has an effect of greatly improving the delayed fracture characteristic, and is very useful. While there is no particular upper limit to the mean axis ratio, it is preferably within an upper limit of 30, and more preferably within 20, since the residual austenite is required to have a certain thickness in order to achieve the effect of TRIP.

[0033] In order to make full use of the effect of the lath-shaped residual austenite, the proportion of the lath-shaped residual austenite in the residual austenite is preferably as large as possible. Specific value of the proportion is determined in accordance to balancing with other structures (bainitic ferrite, polygonal ferrite, etc.) so as to obtain the desired property. For the purpose of increasing the strength, it is preferable to set the proportion of the lath-shaped residual austenite to 50% or higher, more preferably 60% or higher, still more preferably 70% or higher, further more preferably 80% or higher, and most preferably 85% or higher. The entire residual austenite may be lath-shaped residual austenite, but it is recommended to set an upper limit of about 95% to the proportion in practice, in consideration of the constraints imposed by the heating facility and cooling facility and other factors.

[0034] Concentration of C ($C_{\gamma R}$) in the residual austenite is preferably 0.8% or higher. The value of $C_{\gamma R}$ has great influence on the TRIP (strain-induced transformation processing) characteristics, and is effective in improving the elongation property when it is controlled to 0.8% or higher. The concentration is preferably 1% or higher, and more preferably 1.2% or higher. While the concentration of $C_{\gamma R}$ is preferably as high as possible, an upper limit of about 1.6% is supposedly imposed by the practical processing conditions.

[0035] The residual austenite in the present invention refers to a region that shows FCC phase (face-centered cubic lattice) when observed by FE-SEM/EBSD method described previously. Specifically, measurement is made on an area (about 50 by 50 μm , measurement pitch of 0.1 μm) in a surface parallel to the surface on which it was rolled at a depth of one quarter of the thickness. In case that the surface to be measured is exposed by grinding, electrolytic grinding is employed in order to prevent the residual austenite from transforming. Then the specimen placed in a lens barrel of the SEM is irradiated with electron beam by using the FE-SEM. EBSD image projected on a screen is captured by a high sensitivity camera (VE-1000-SIT manufactured by Dage-MIT Inc.) and is imported into a computer. The image is analyzed by the computer, and compared with a pattern generated by simulation using a known crystal system (FCC phase (face-centered cubic lattice) in the case of residual austenite) so as to color-identify the FCC phase. The areal ratio of the regions thus identified is defined as the areal ratio of residual austenite. Hardware and software used in the analysis described above are those of OIM (Orientation Imaging Microscopy TM) system manufactured by TexSEM

Laboratories Inc.

[0036] Fig. 3 shows the EBSD photograph of Fig. 2 wherein FCC phase is color-identified (magnification factor 1500). In Fig. 3, the region indicated by an arrow ($\leftarrow$) is the residual austenite (γ_R).

5 Polygonal ferrite

[0037] In the present invention, polygonal ferrite means a ferrite structure that includes no or very few dislocations.

[0038] In the present invention, polygonal ferrite may be optional structure and 0% of polygonal structure is included. In order to make full use of the effect of polygonal ferrite to improve the elongation property, the areal ratio of polygonal ferrite is preferably controlled to 5% or higher, and more preferably 10% or higher. In order to improve the elongation property, the content of polygonal ferrite is preferably as high as possible. However, since when the content of polygonal ferrite exceeds 50%, it becomes difficult to ensure the required level of strength, it is controlled within an upper limit of 50%, preferably 40% and more preferably 30%.

[0039] The areal ratio of polygonal ferrite is calculated by the following equation:

$$\begin{aligned} \text{Areal ratio of polygonal ferrite} = & 100 - [\text{Areal ratio of} \\ & \text{bainitic ferrite (\%)}] - [\text{Areal ratio of residual austenite} \\ & \text{(\%)}] \end{aligned}$$

Note: The areal ratio of bainitic ferrite and the areal ratio of residual austenite are measured by the method described previously.

25 Others

[0040] The steel sheet of the present invention may be constituted either from only the structures described above (namely, a composite structure of bainitic ferrite and residual austenite or a composite structure of bainitic ferrite, polygonal ferrite and residual austenite), or may include other structure (for example, martensite, etc.) to such an extent that the effect of the present invention is not disturbed. Such additional components are structures that can inevitably remain in the manufacturing process of the present invention, of which concentration is preferably as low as possible (for example, total areal ratio is within an upper limit of 10% at the most).

[0041] Now the essential components of the steel sheet of the present invention will be described. Hereinafter concentrations of components are all given in terms of mass percentage.

C: 0.06 to 0.6%

[0042] C is an essential element for ensuring high strength and maintaining residual austenite. Particularly it is important to contain a sufficient content of C in the austenite phase, so as to maintain the desired austenite phase to remain even at the room temperature, and C content is useful in achieving better compromise between the strength and the elongation property. Adding 0.25% or higher of C increases the amount of the residual austenite and also increases the concentration of C in the residual austenite, thus enabling it to obtain very high strength and elongation.

[0043] However, the concentration of C higher than 0.6% does not increase the effect beyond saturation and may also result in defects due to segregation. The concentration of C higher than 0.25% leads to poor weldability.

[0044] Therefore, when emphasis is placed on weldability, it is preferable to control the concentration of C in a range from 0.06% to 0.25% (more preferably within 0.2%, and further more preferably within 0.15%). For such applications that require high elongation but does not involve point welding, it is recommended to control the concentration of C in a range from 0.25% to 0.6% (more preferably 0.3% or higher).

Si+Al: 0.5 to 3%

[0045] Si and Al have an effect of suppressing residual austenite from decomposing and producing carbide. Si, in particular, is also effective in enhancing solid solution. In order to make full use of this effect, it is necessary to add Si and Al in total concentration of 0.5% or more preferably 0.7% or higher, and more preferably 1% or higher. However, adding Si and Al in total concentration of higher than 3% does not increase the effect beyond saturation and cannot be justified economically. Further, too much content leads to hot rolling brittleness. Therefore, the concentration is controlled within an upper limit of 3%, preferably within 2.5% and more preferably within 2%.

Mn: 0.5 to 3%

[0046] Mn is an element required to stabilize austenite and obtain desired residual austenite. In order to make full use of this effect, it is necessary to add Mn in concentration of 0.5% or more preferably 0.7% or higher, and more preferably 1% or higher. However, adding Mn in concentration higher than 3% causes adverse effects. The concentration is preferably within 2.5% and more preferably within 2%.

P: 0.15% or lower (higher than 0%)

[0047] P is an element that is effective in obtaining desired residual austenite. In order to make full use of this effect, it is recommended to add P in concentration of 0.03% or higher (preferably 0.05% or higher). However, adding P in concentration higher than 0.15% adversely affects the ease of secondary processing. Thus the concentration is more preferably within 0.1%.

S: 0.02% or lower (higher than 0%)

[0048] S forms sulfide inclusion such as MnS that initiates crack and adversely affects the workability of the steel. Concentration of S is preferably within 0.02% and more preferably within 0.015%. Effect of decreasing the S content in suppressing the deterioration of the workability does not hold when the concentration of S decreases below 0.003%. Decreasing the S content below this level is expensive without providing benefit. Therefore, it is recommended to set the lower limit of S content to over 0.003%, or preferably to 0.005% or higher.

[0049] While the steel of the present invention includes the elements described above as the fundamental components with the rest substantially consisting of iron and impurities, the following elements may be added to such an extent that does not disturb or compromise the effect of the present invention.

At least one of Mo: 1% or lower (higher than 0%), Ni: 0.5% or lower (higher than 0%), Cu: 0.5% or lower (higher than 0%) and Cr: 1% or lower (higher than 0%)

[0050] These elements are effective in strengthening the steel and stabilizing and ensuring the predetermined amount of residual austenite. In order to make full use of this effect, it is recommended to add Mo in concentration of 0.05% or higher (preferably 0.1% or higher), Ni in concentration of 0.05% or higher (preferably 0.1% or higher), Cu in concentration of 0.05% or higher (preferably 0.1% or higher) and Cr in concentration of 0.05% or higher (preferably 0.1% or higher). However, the effects described above reach saturation when higher than 1% of Mo and Cr, and higher than 0.5% of Ni and Cu are added, resulting in economical disadvantage. It is more preferable to add 0.8% or lower Mo, 0.4% or lower Ni, 0.4% or lower Cu and 0.8% or lower Cr.

At least one of Ti: 0.1% or lower (higher than 0%), Nb: 0.1% or lower (higher than 0%) and V: 0.1% or lower (higher than 0%)

[0051] These elements have the effects of enhancing precipitation and making the structure finer, and are effective in strengthening the steel. In order to make full use of these effects, it is recommended to add Ti in concentration of 0.01% or higher (preferably 0.02% or higher), Nb in concentration of 0.01% or higher (preferably 0.02% or higher) and V in concentration of 0.01% or higher (preferably 0.02% or higher). However, the effects described above reach saturation when the concentration of any of these elements exceeds 0.1%, resulting in economical disadvantage. It is more preferable to add 0.08% or lower Ti, 0.08% or lower Nb and 0.08% or lower V.

Ca: 0.003% or lower and/or REM: 0.003% or lower (higher than 0%)

[0052] Ca and REM (rare earth element) are effective in controlling the form of sulfide in the steel and improve the workability of the steel. Sc, Y, La and the like may be used as the rare earth element in the present invention. In order to achieve the effect described above, it is recommended to add each of these elements in concentration of 0.0003% or higher (preferably 0.0005% or higher). However, the effects described above reach saturation when the concentration exceeds 0.003%, resulting in economical disadvantage. It is more preferable to keep the concentration within 0.0025%.

[0053] The method for manufacturing the steel sheet of the present invention will now be described.

[0054] The method of the present invention is characterized in that the steel that has the composition described above is kept at a temperature in a range from A3 point to (A3 point + 20°C) for 10 to 600 seconds, then cooled at a mean cooling rate of 3°C/s or more to a temperature not lower than Ms point and not higher than Bs point, and is kept in this temperature range for 1 to 1800 seconds. Each stage of this process will be described below with reference to

Fig. 4 that schematically illustrates the method of the invention.

[0055] First, the steel that has the composition described above is heated to a temperature in a range from A3 point to (A3 point + 20°C) (T1 in Fig. 4) and is kept at this temperature for 10 to 600 seconds (t1 in Fig. 4). T1 (soaking temperature) and t1 (soaking time) are very important for obtaining the desired bainite blocks. Austenite grains will grow to produce coarse bainite blocks, when T1 is higher than (A3 point + 20°C) or t1 is longer than 600 seconds.

[0056] When T1 is lower than the temperature of A3 point, on the other hand, predetermined bainitic ferrite structure cannot be obtained. When t1 is lower than 10 seconds, austenizing process does not proceed sufficiently, leaving cementite and other carbides to remain.

[0057] Based on these considerations, it is preferable to set T1 (soaking temperature) in a range from 650 to 900°C and t1 (soaking time) in a range from 30 to 300 seconds, and more preferably in a range from 60 to 240 seconds.

[0058] Then the steel is cooled at a mean cooling rate of 3°C/s (CR1 in Fig. 4) or higher to a temperature (T2 in Fig. 1) not lower than Ms point and not higher than Bs point, and is kept in this temperature range for 1 to 1800 seconds (t2 in Fig. 4).

[0059] This process is designed for the purpose of forming the desired bainitic ferrite structure (which may include polygonal ferrite structure) and avoiding the formation of pearlite structure that is not desirable for the present invention (to suppress the areal ratio of pearlite within 10% at the most).

[0060] The purpose of cooling the heated steel at the mean cooling rate of 3°C/s (CR1) or more is to avoid the pearlite transformation zone so as to prevent the generation of pearlite structure. The mean cooling rate is desired to be as fast as possible, preferably 10°C per second or more (more preferably 20°C per second or more). While the steel may be cooled quickly to the predetermined temperature T2 (1-stage cooling) as shown in Fig. 1, it is difficult to form the polygonal ferrite structure in 1-stage cooling process. Therefore, when it is desired to form the polygonal ferrite structure as well, it is recommended to employ multi-stage cooling process by dividing the cooling process into several stages. In this case, too, it is recommended to set the mean cooling rate in each cooling stage to 3°C per second or higher (preferably 10°C per second or higher and more preferably 20°C per second or higher).

[0061] After quenching to the temperature (T2) that is not lower than Ms point and not higher than Bs point, the steel is kept at this temperature so as to undergo isothermal transformation in which the desired bainitic ferrite structure is formed. When the temperature T2 is higher than Bs, much pearlite that is not desirable for the present invention is formed, thus hampering the formation of the predetermined bainitic ferrite structure. When T2 is below Ms, on the other hand, the areal ratio of austenite decreases.

[0062] When the temperature holding period t2 is longer than 1800 seconds, density of dislocations in bainitic ferrite becomes low and the desired residual austenite cannot be obtained. When t2 is lower than 1 second, on the other hand, desired bainitic ferrite cannot be obtained. Length of t2 is preferably from 30 to 1200 seconds, and more preferably from 60 to 600 seconds.

[0063] In the practical manufacturing process, the annealing process described above can be carried out easily by employing a continuous annealing facility or a batch annealing facility. In case that cold rolled sheet is plated with zinc by hot dipping, the heat treatment process may be replaced by the plating process by setting the plating conditions so as to satisfy the heat treatment conditions. Further, the plating may also be alloyed.

[0064] There is no restriction on the hot rolling process (or cold rolling process as required) that precedes the continuous annealing process described above, and commonly employed process conditions may be used. Specifically, the hot rolling process may be carried out in such a procedure as, after hot rolling at a temperature above A3 point, the steel sheet is cooled at a mean cooling rate of about 30°C/s and is wound up at a temperature from about 500 to 600°C. In case that the hot rolled steel sheet has poor appearance, cold rolling may be applied in order to rectify the appearance. It is recommended to set the cold rolling ratio in a range from 1 to 30%. Cold rolling beyond 30% leads to excessive rolling load that makes it difficult to carry out the cold rolling.

[0065] A steel sheet according to the present invention has not only a high capability to elongate and a high hydrogen embrittlement resistance, but also excellent properties for safety in collision. Therefore, the steel sheet is used, for example, for construction members of a vehicle and industrial machinery. Especially, the steel sheet is suitable for automobile members such as crush members, for example, side members of the front portion and the back portion and crush boxes, construction members, for example, pillar members (such as center pillar reinforce), roof rail reinforces, side sills, floor members and kick portions, and impact absorbing members, for example, bumper reinforces and door impact beams.

[0066] Now the present invention will be described in detail below by way of examples. It is understood, however, that the present invention is not limited by these examples, and various modifications that do not deviate from the spirit of the present invention described herein are all within the scope of the present invention.

[Examples]

Example 1: Investigation on composition

[0067] In this example, steel specimens A through P having the compositions shown in Table 1 (rest of the composition consists of iron and impurities, and the concentrations in the table being given in mass percentage) was made by vacuum melting to obtain an experimental slab that was subjected to the process described below (hot rolling → cold rolling → continuous annealing) to turn into a hot rolled steel sheet having thickness of 3.2 mm (thickness: 2.5 mm in No. Q to T), that was then pickled to remove scales from the surface and was cold rolled to a thickness of 1.2 mm.

[0068] Hot rolling process: Starting temperature (SRT) 1150°C, finishing temperature (FDT) 850°C, cooling rate of 40°C/s and take-up temperature 550°C.

[0069] Cold rolling process: Rolling ratio 50%.

[0070] Continuous annealing process: Each steel specimen was kept at a temperature (A3 point + 15°C) (T1 in Table 1) for 120 seconds (t1 in Table 1), then cooled (water cooling) at a mean cooling rate of 25°C/s (CR1 in Table 1) to 420°C (T2 in Table 1), and was then kept at 420°C for 120 seconds (t2 in Table 1).

[0071] Tensile strength (TS), elongation (total elongation E1) and hydrogen embrittlement resistance (cathode CH life) were measured on each of the steel sheets obtained as described above. The areal ratio of structure and mean grain size of bainite blocks in each steel sheet were measured by the methods described previously.

[Measurement of tensile strength (TS) and elongation]

[0072] Tensile test was conducted by using JIS No. 5 test piece to measure tensile strength (TS) and elongation (E1). Speed of elongation in the tensile test was set to 1 mm/sec. in the present invention. The steel sheet of the present invention is one that shows tensile strength of 1180 MPa or higher in the test described above, and those that show 13% or higher elongation are evaluated as excellent in elongation property in the present invention.

[Measurement of hydrogen embrittlement resistance]

[0073] Hydrogen embrittlement resistance was measured by using rectangular test pieces of the steel sheets described above having a size of 15 mm by 65 mm. The rectangular test piece was loaded with a pressure of 980 MPa by 4-point bending and was subjected to a potential of -80 mV, a potential baser than the natural potential, using a potentiostat in a solution of 0.5 mol of sulfuric acid and 0.01 mol of KSCN, and the elapsed time before crack occurred was measured thereby to evaluate the hydrogen embrittlement resistance (cathode CH life). In the present invention, those that survived for 1000 seconds or more without crack are evaluated as excellent in hydrogen embrittlement resistance.

[0074] The test results are shown in Table 2.

[Table 1]

	C	Si	Al	Si+Al	Mn	P	S	Others	A3 transformation point
A	0.03	1.5	0.03	1.53	1.5	0.02	0.005	-	871
B	0.3	1.5	0.03	1.53	1.5	0.02	0.005	-	795
C	0.5	1.5	0.03	1.53	1.5	0.02	0.005	-	763
D	0.3	0.5	0.5	1.00	1.5	0.02	0.005	-	652
E	0.3	0.1	0.03	0.13	1.5	0.02	0.005	-	732
F	0.3	1.5	0.03	1.53	0.3	0.02	0.005	-	831
G	0.3	1.5	0.03	1.53	5.0	0.02	0.005	-	690
H	0.3	1.5	0.03	1.53	1.5	0.02	0.005	Mo: 0.2	801
I	0.3	1.5	0.03	1.53	1.5	0.02	0.005	Ni: 0.2	792
J	0.3	1.5	0.03	1.53	1.5	0.02	0.005	Cu: 0.2	799
K	0.3	1.5	0.03	1.53	1.5	0.02	0.005	Cr: 0.2	780
L	0.3	1.5	0.03	1.53	1.5	0.02	0.005	Ti: 0.03	783

EP 1 553 202 A1

[Table 1] (continued)

	C	Si	Al	Si+Al	Mn	P	S	Others	A3 transformation point
M	0.3	1.5	0.03	1.53	1.5	0.02	0.005	Nb: 0.03	795
N	0.3	1.5	0.03	1.53	1.5	0.02	0.005	V: 0.03	798
O	0.3	1.5	0.03	1.53	1.5	0.02	0.005	Ca: 0.001	794
P	0.08	1.5	0.03	1.53	1.5	0.02	0.005	Mo: 0.2 Ti: 0.03	843
Q	0.2	1.5	0.03	1.53	2.5	0.01	0.005	Nb: 0.05 Mo: 0.2	798
R	0.2	1.5	0.03	1.53	3.0	0.01	0.004	Nb: 0.05 Mo: 0.2	783
S	0.17	1.5	0.03	1.53	2.5	0.01	0.005	Nb: 0.05 Mo: 0.2 Ti: 0.05 Cu: 0.3 Ni: 0.2	788
T	0.17	1.35	0.04	1.37	2.0	0.01	0.005	-	810

[Table 2]

No.	Type	Continuous annealing process					Structure				Bainite block (μm)	Properties			
		T1 (°C)	t1 (s)	CR1 (°C/s)	T2 (°C)	t2 (s)	Bainite	Areal ratio (%)		Residual γ		TS (MPa)	EL (%)	Cathode CH life (Seconds)	
								Ferrite							
1	A	886	120	25	420	120	16	79		5		10	690	30	-
2	B	810	120	25	420	120	82	10		8		11	1198	15	1519
3	C	778	120	25	420	120	80	10		10		12	1230	15	1424
4	D	667	120	25	420	120	77	15		8		13	1220	15	1529
5	E	747	120	25	420	120	90	10		0		12	1200	10	1374
6	F	846	120	25	420	120	88	11		1		11	1180	12	1477
7	G	705	Process interrupted by hot rolling crack.				-	-		-		-	-	-	-
8	H	816	120	25	420	120	82	10		8		9	1230	15	1552
9	I	807	120	25	420	120	82	10		8		9	1232	15	1647
10	J	814	120	25	420	120	82	10		8		8	1234	15	1641
11	K	795	120	25	420	120	82	10		8		8	1236	15	1599
12	L	798	120	25	420	120	82	10		8		10	1238	15	1629
13	M	810	120	25	420	120	82	10		8		10	1240	14	1619
14	N	813	120	25	420	120	82	10		8		10	1242	14	1613
15	O	809	120	25	420	120	82	10		8		11	1241	14	1587
16	P	858	120	25	420	120	82	10		8		9	1190	15	1525
17	Q	815	120	20	400	120	92	2		6		6	1510	10	1215
18	R	800	120	20	400	120	90	2		8		5	1530	10	1220
19	S	805	120	20	300	120	89	4		7		8	1410	12	1310
20	T	880	120	WQ	200	120	0	35		1		-	1045	16	-

Residual γ : Residual austenite

Residual γ : Residual austenite

[0075] These results can be interpreted as follows (all the numbers in the following discussion are the experiment numbers shown in Table 2).

[0076] Nos. 2 through 4 and 8 through 16 are all examples of the present invention manufactured in accordance to the method of the present invention using the steel of types that satisfy the conditions of the present invention (B through D and H through P in Table 1), and show excellent performance in both elongation property and hydrogen embrittlement resistance in the realm of ultra-high strength of 1180 MPa upward.

[0077] The steel of types that do not satisfy the conditions of the present invention (A and E through G in Table 1), on the other hand, have such drawbacks as described below.

[0078] No. 1 is an example made of a steel of type A having lower C content, where the predetermined amount of the bainitic ferrite structure (hard structure) could not be formed while excessive ferrite structure was observed, showing lower strength. Hydrogen embrittlement resistance was not measured because of such a low strength that load could not be applied in 4-point bending test.

[0079] No. 5 is an example made of a steel of type E that has a low total concentration of Si and Al, where the desired residual austenite is not obtained and elongation is low.

[0080] No. 6 is an example made of a steel of type F that has a low concentration of Mn, where the desired residual austenite is not obtained and, as a result, elongation property is low.

[0081] No. 7 is an example made of a steel of type G that has a high concentration of Mn, where excessively high strength caused rolling crack during hot rolling, thus making it impossible to carry out the subsequent annealing process.

[0082] No. 20 is a conventional dual-phase steel sheet, and has a lower strength because it does not contain bainite. Hydrogen embrittlement resistance was not measured because it did not have a sufficient strength.

[0083] Next, formed products made of steel sheet No. 17 or No. 20 were evaluated in crush resistance, impact resistance and hydrogen embrittlement resistance in order to examine the properties as formed product.

<Crush Resistance Test>

[0084] A member 1 as shown in Fig. 6 (hat channel member) was made of No. 17 or No. 19. A crush resistance test for the member was conducted in the following way. Spot welding was performed in 35 mm pitch for the spot welding positions 2 in the member 1, as shown in Fig. 6, wherein an electrode of 6 mm diameter was used and a current 0.5 kA lower than the splash current was applied. Then, as shown in Fig. 7, a metal mold was pushed from above onto the center of the member 1 in the longitudinal direction and the maximum load was obtained. At the same time, absorbed energy was obtained according to the area in load-displacement diagram. The results are shown in Table 4.

Table 3

No.	Used Steel Sheet				Test Results	
	Steel Composition	TS (MPa)	EL (%)	Retained γ (areal ratio %)	Maximum Load (kN)	Absorbed Energy (kJ)
17	Q	1510	10	6	13.6	0.61
20	T	1045	16	0.2	10.2	0.48

[0085] Table 3 shows that the member made of No. 17 steel sheet has a higher load and higher energy absorption property than one made of a conventional low strength steel sheet and that it has an excellent crush resistance.

<Impact Resistance Test>

[0086] A member 4 as shown in Fig. 8 (hat channel member) was made of No. 17 or No. 19. An impact resistance test for the member was conducted in the following way. Fig. 9 is a sectional view of the member 4 at A-A in Fig. 8. Spot welding was performed for the spot welding positions 5 in the member 4. Then, as schematically shown in Fig. 10, the member 4 was installed on a base 7 and a hammer 6 (110 kg mass) was dropped from the position 11 m high above the member 4. Absorbed energy until the member was deformed (in the height direction) by 40 mm was obtained. The results are shown in Table 4.

Table 4

No.	Used Steel Sheet				Test Results
	Steel Composition	TS (MPa)	EL (%)	Retained γ (areal ratio%)	Absorbed Energy (kJ)
17	Q	1510	10	6	6.23
20	T	1045	16	0.2	4.38

[0087] Table 4 shows that the member made of No. 17 steel sheet has an energy absorption property higher than one made of a conventional low strength steel sheet and that it has excellent impact resistance.

<Evaluation of Hydrogen Embrittlement Resistance>

[0088] Members for real use were formed using Nos. 17 and 19 steel sheets. Hydrogen embrittlement resistance was evaluated in the state of formed products. Specifically, Nos. 17 and 19 steel sheets were press-worked into center pillar reinforces, door impact beams and roof rail reinforces and then dipped into 5% hydrochloric acid. It was examined whether cracks generated in the test members or not. The results are shown in Table 5.

Table 5

No.	Steel Composition	Formed Member	Crack generation in 24 hours after dipping into acid solution
17	Q	center pillar	No
		door impact beam	No
		roof rail	No
20	T	center pillar	No
		door impact beam	No
		roof rail	No

[0089] Table 5 shows that the member made of No. 17 steel sheet suffers no crack generation and an excellent hydrogen embrittlement resistance in spite of its high strength.

Example 2: Investigation of manufacturing conditions

[0090] In this example, an experimental slab made by using the steel of type B shown in Table 1 (steel that satisfies the conditions of the present invention) was subjected to hot rolling and cold rolling under the same conditions as those of the Example 1, followed by continuous annealing under various conditions shown in Table 6, thereby to obtain the cold rolled steel sheets Nos.1 through 11, all 1.2 mm in thickness.

[0091] Then structures and various properties of these steel sheets were investigated similarly to the Example 1. The results are shown in Table 6.

(Table 6)

No.	Continuous annealing or plating process						Structure				Properties		
	T1 (°C)	t1 (s)	CR1 (°C/s)	T2 (°C)	t2 (s)	Zn-GA (°C)	Areal ratio (%)			Bainite block (µm)	TS (MPa)	EL (%)	Cathode CH life (Seconds)
							Bainite	Ferrite	Residual γ				
1	810	120	25	420	120	-	82	10	8	0	1198	15	1519
2	930	120	25	420	120	-	82	10	8	0	1198	15	1119
3	760	120	25	420	120	-	10	75	15	0	980	18	-
4	810	300	25	420	120	-	82	10	8	0	1198	22	1185
5	810	1	25	420	120	-	89	10	1	0	1198	11	1165
6	810	120	1	420	120	-	0	40	0	P(60)	1010	11	819
7	810	120	25	600	120	-	20	10	1	P(69)	1200	11	898
8	810	120	25	200	120	-	89	10	1	0	1220	10	1165
9	810	120	25	420	0.5	-	0	10	8	M(82)	1250	8	780
10	810	120	25	420	3600	-	89	10	1	0	1182	11	919
11	810	120	25	420	120	550	82	10	8	0	1199	15	1519

P: Pearlite

M: Martensite

Residual γ: Residual austenite

[0092] No. 1 is an example of the present invention manufactured in accordance to the method of the present invention. No. 11 is an example of the present invention that was subjected, after the process described above, to alloying treatment (dipped in molten zinc and then heat-treated at 500°C for alloying). Both specimens have ultra-high strength above 1180 MPa, and are excellent in both elongation and hydrogen embrittlement resistance.

[0093] Specimens Nos.2 through 10 that do not satisfy some of the conditions of the present invention, on the other

hand, have such drawbacks as described below.

[0094] No. 2, that was heated at temperature T1 of 930°C, higher than the upper limit of the present invention (815°C since A3 point of steel type B is 795°C), included coarse bainite blocks and showed lower hydrogen embrittlement resistance.

[0095] No. 3, that was heated at temperature T1 of 760°C, lower than the lower limit of the present invention (A3 point of steel type B = 795°C), did not include predetermined amount of bainitic ferrite structure, showing lower strength. Hydrogen embrittlement resistance was not measured because of such a low strength that load could not be applied in 4-point bending test.

[0096] No. 4, that was heated for a long heating time t1, resulted in the growth of austenite grains and coarse bainite blocks, with lower hydrogen embrittlement resistance.

[0097] In No. 5, that was heated for a short heating time t1, austenizing did not proceed sufficiently thus leaving cementite to remain, with such a result that the desired residual austenite was not obtained and elongation was low, while hydrogen embrittlement resistance decreased.

[0098] In No. 6, that was cooled at a slow cooling rate CR1, much pearlite structure was formed and the predetermined amount of bainitic ferrite was not obtained, thus desired elongation and hydrogen embrittlement resistance could not be achieved. In addition, predetermined amount of residual austenite was not obtained and elongation was low.

[0099] In No. 7, that was heated to beyond Ms point at heating temperature T2 of 600°C after cooling, much pearlite structure was formed and the predetermined amount of bainitic ferrite was not obtained, thus desired strength could not be achieved and hydrogen embrittlement resistance deteriorated. In addition, predetermined amount of residual austenite was not obtained and elongation was low.

[0100] In No. 8, that was heated to below Bs point at heating temperature T2 of 200°C after cooling, the predetermined amount of residual austenite was not obtained, with elongation and hydrogen embrittlement resistance becoming lower.

[0101] In No. 9, that was heated for a short heating time t2 after cooling, predetermined bainitic ferrite was not obtained, resulting in low hydrogen embrittlement resistance. In addition, martensite was formed and elongation became lower.

[0102] In No. 10, that was heated for a long heating time t2 after cooling, decomposition of residual austenite proceeded, thus predetermined amount of residual austenite was not obtained and elongation was low.

[0103] Fig. 5 shows EBSP photographs (color-identified with magnification factor 5000) of the example (NO. 1) of the present invention and the comparative example (No. 2) for reference. From Fig. 5, it can be seen that No. 1 made by the method of the present invention shows the desired fine bainite blocks formed therein, while the comparative example No. 2 that does not fall in the scope of the present invention shows coarse bainite blocks formed therein.

Claims

1. An ultra-high strength steel sheet having excellent hydrogen embrittlement resistance, which includes:

0.06 to 0.6% of C;
0.5 to 3% of Si+Al;
0.5 to 3% of Mn;
0.15% or lower of P; and
0.02% or lower of S in terms of mass percentage,
and also includes 3% or higher of residual austenite structure and
30% or higher of bainitic ferrite structure in terms of an areal ratio to the entire structure,

wherein a mean grain size of bainite blocks is smaller than 20 μm as determined by comparing observations of the same region of the bainitic ferrite structure by EBSP (electron back scatter diffraction pattern) and SEM.

2. The ultra-high strength steel sheet according to claim 1, wherein 5% to 50% of polygonal ferrite structure is included in terms of an areal ratio to the entire structure.

3. The ultra-high strength steel sheet according to claim 1 or 2 wherein 40% or higher of bainitic ferrite structure is included in terms of an areal ratio to the entire structure.

4. The ultra-high strength steel sheet according to any one of claims 1 to 3, wherein 50% or higher of bainitic ferrite structure is included in terms of an areal ratio to the entire structure.

5. The ultra-high strength steel sheet according to any one of claims 1 to 4, further comprising at least one of:

1% or lower (higher than 0%) of Mo;
 0.5% or lower (higher than 0%) of Ni;
 0.5% or lower (higher than 0%) of Cu; and
 1% or lower (higher than 0%) of Cr in mass percentage.

6. The ultra-high strength steel sheet according to any one of claims 1 to 5, further comprising at least one of:

0.1% or lower (higher than 0%) of Ti;
 0.1% or lower (higher than 0%) of Nb; and
 0.1% or lower (higher than 0%) of V in mass percentage.

7. The ultra-high strength steel sheet according to any one of claims 1 to 6, further comprising:

0.003% or lower (higher than 0%) of Ca; and/or
 0.003% or lower (higher than 0%) of REM (rare earth element) in mass percentage.

8. The ultra-high strength steel sheet according to any one of claims 1 to 7, that has a strength of 1180 MPa class or higher.

9. A method for manufacturing the ultra-high strength steel sheet according to any one of claims 1 to 8, which comprises a heat treatment process of:

heating a steel that contains the components described in any one of claims 1 to 8 at a temperature in a range from A3 point to (A3 point + 20°C) for 10 to 600 seconds after rolling the steel, then cooling the steel at a mean cooling rate of 3°C/s or more to a temperature not lower than Ms point and not higher than Bs point, and keeping the steel in this temperature range for 1 to 1800 seconds.

10. The method according to claim 9, wherein the heat treatment process is included in a molten zinc plating process.

Fig. 1

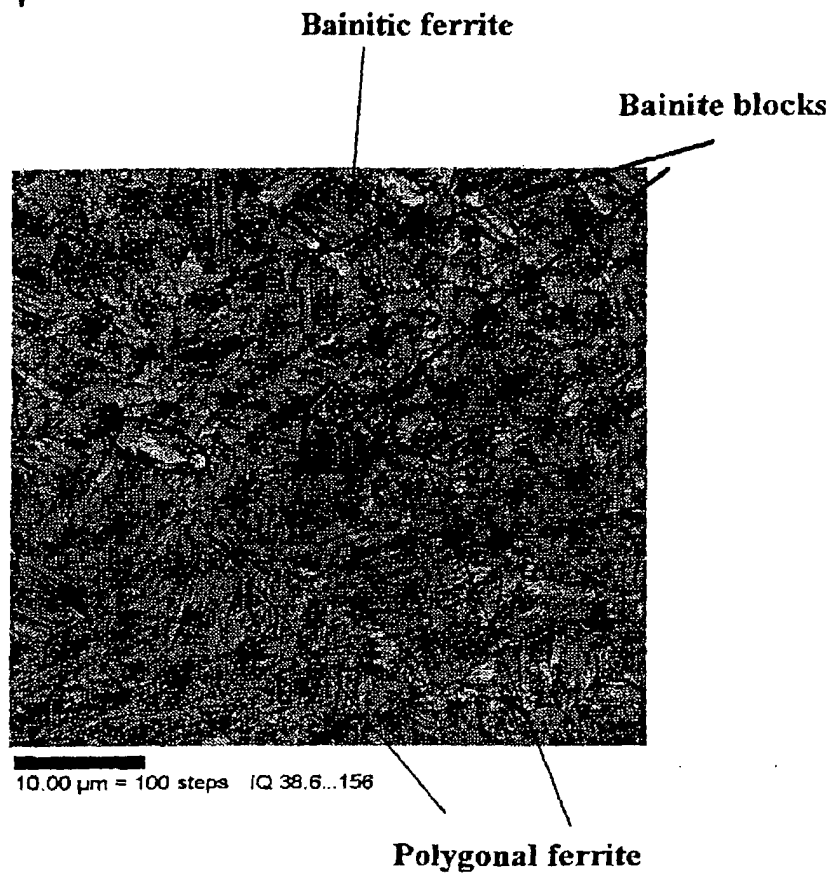


Fig. 2

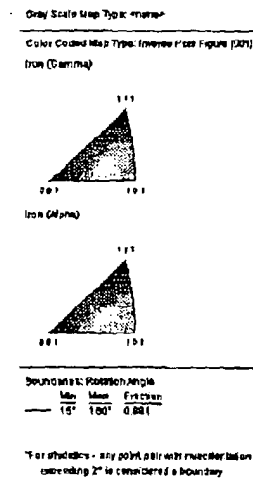
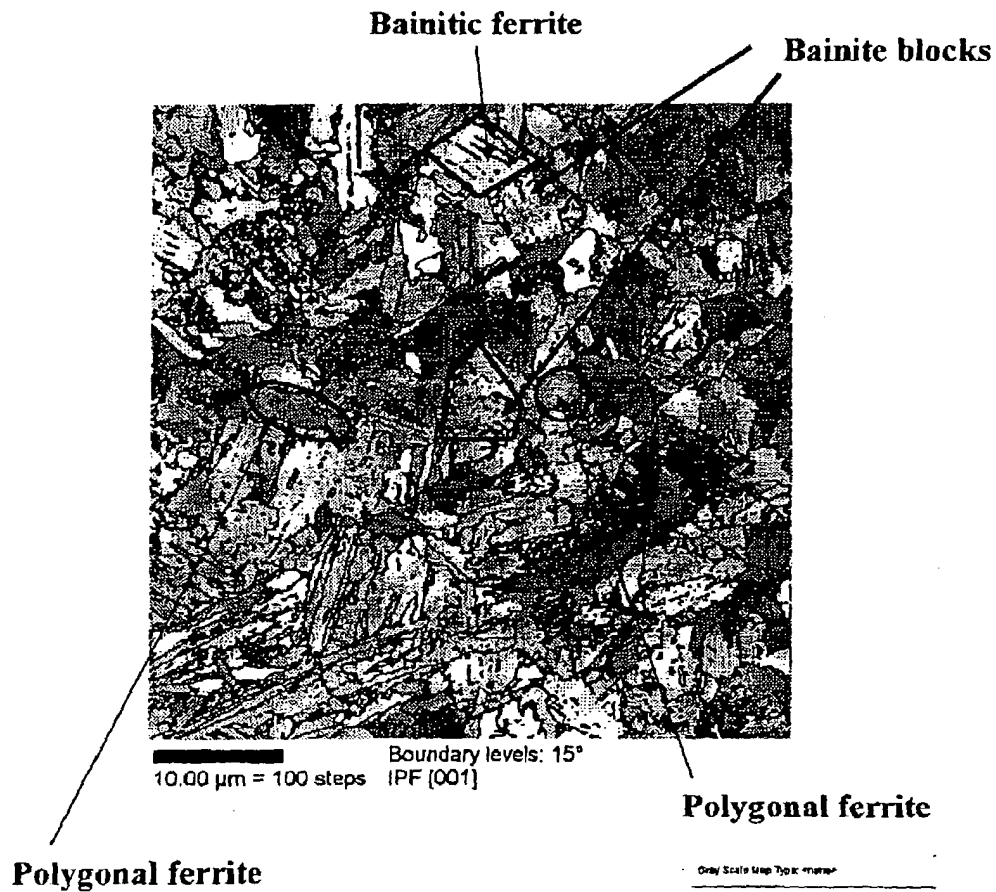


Fig. 3

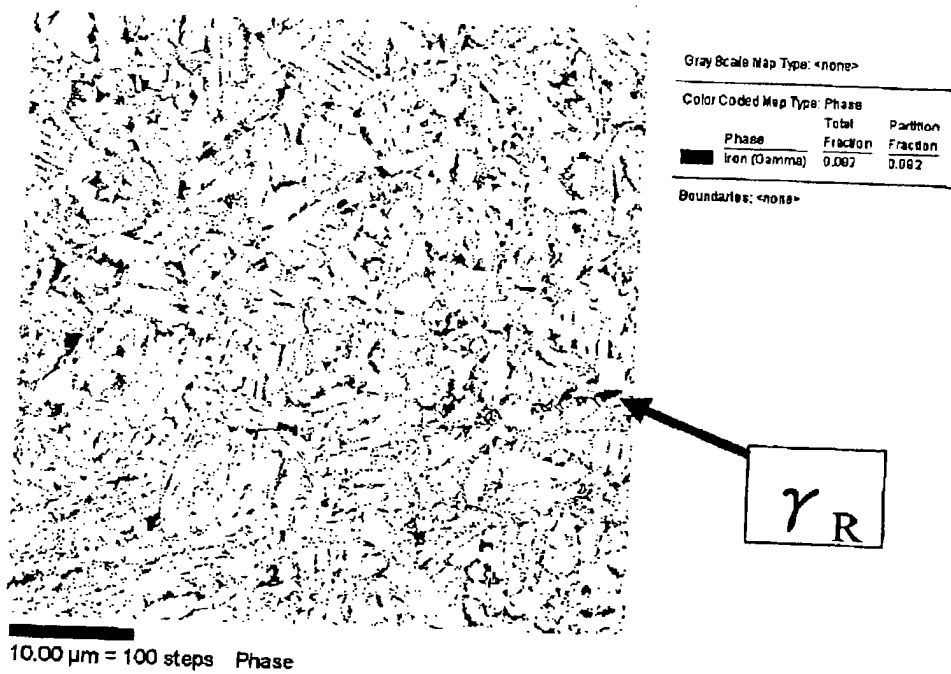


Fig. 4

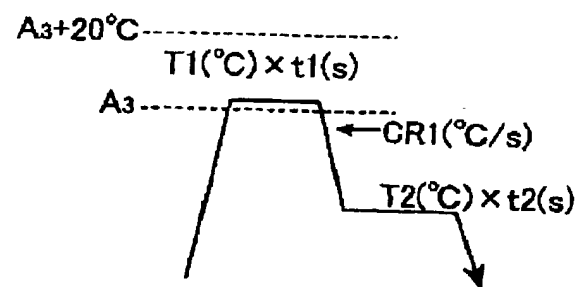
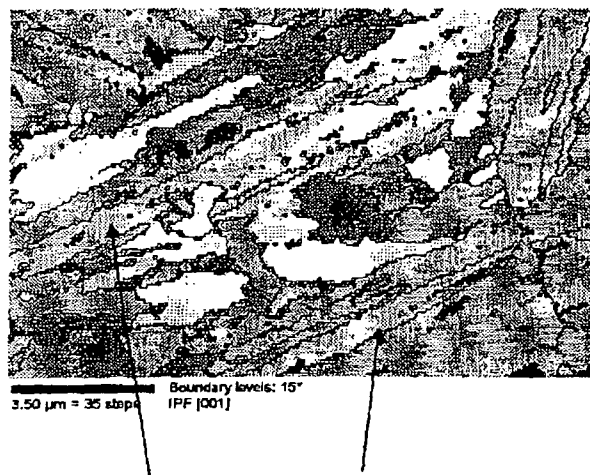


Fig. 5

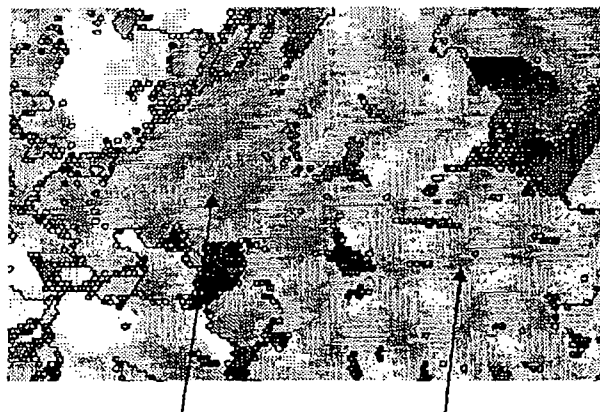
No. 1



Bainitic ferrite

Bainitic ferrite

No. 2



Bainite block

Bainite block

Fig. 6

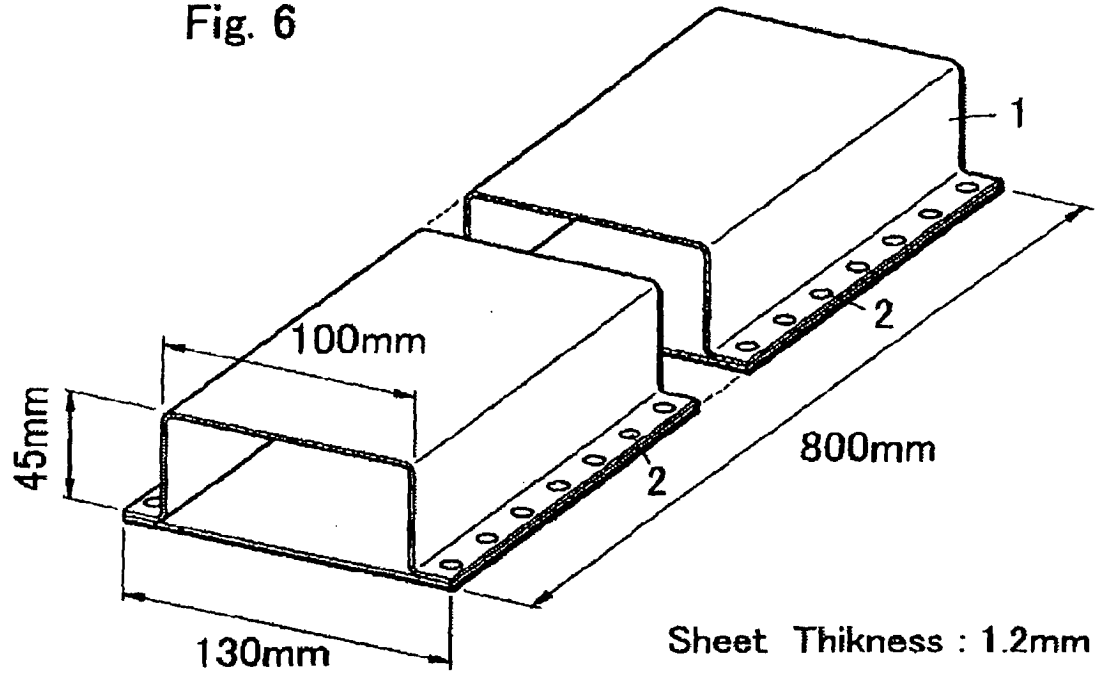


Fig. 7

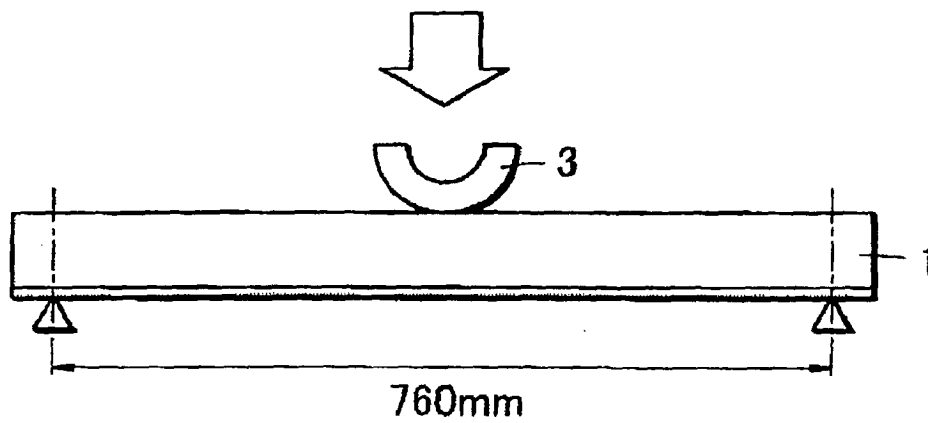


Fig. 8

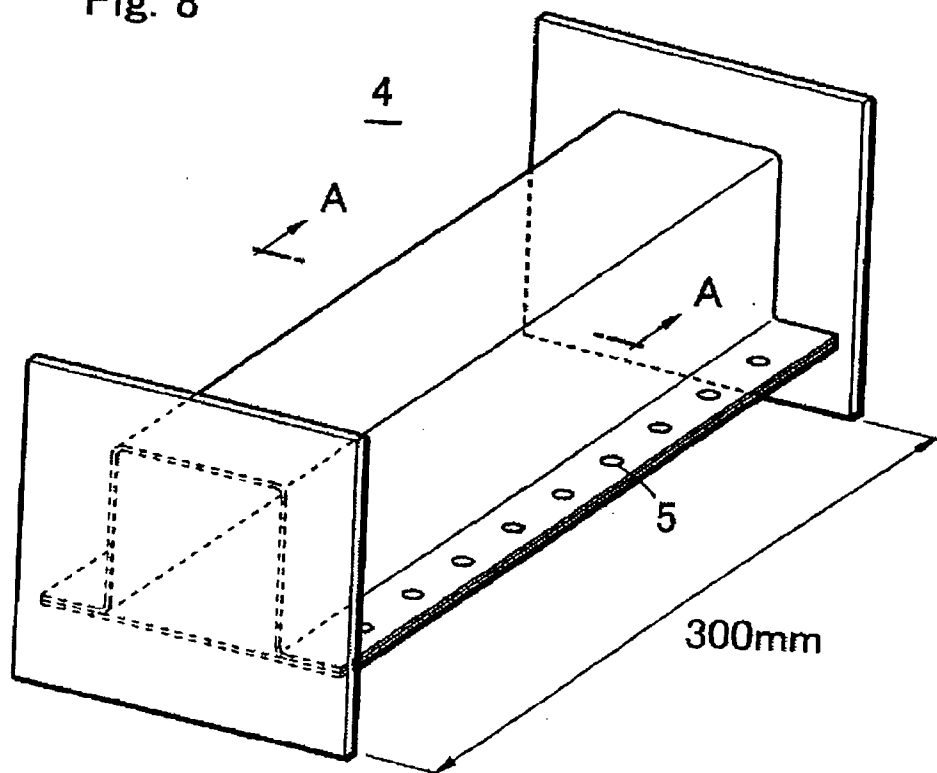
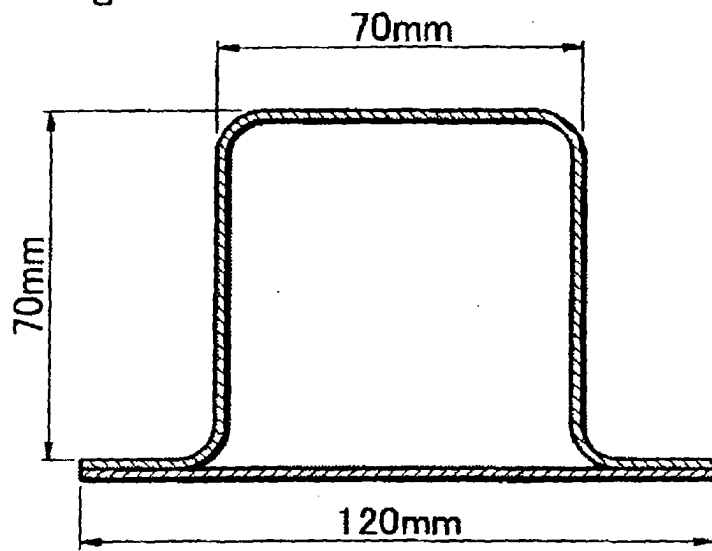
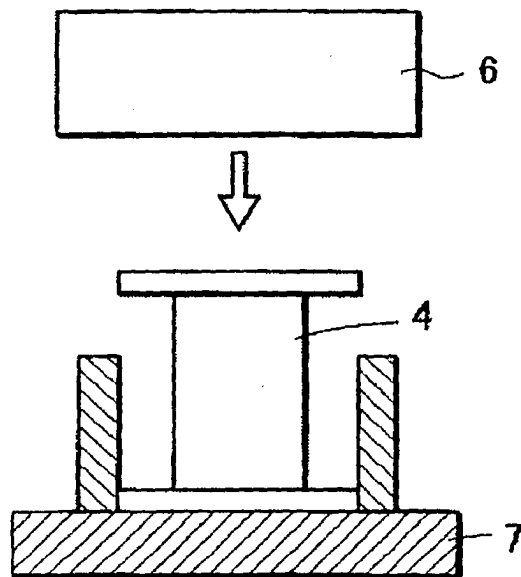


Fig. 9



Sheet Thikness : 1.2mm

Fig. 10





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 25 0049

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 14, 22 December 1999 (1999-12-22) -& JP 11 256273 A (KOBEL STEEL LTD), 21 September 1999 (1999-09-21) * abstract * * examples 2-8; table 1 * * examples 1-22; table 2 *	1-10	C22C38/00 C22C38/02 C22C38/04 C22C38/06 C21D8/02
P,A	EP 1 391 526 A (KABUSHIKI KAISHA KOBEL SEIKO SHO) 25 February 2004 (2004-02-25) * paragraph [020] - paragraph [0027] * * paragraphs [0044] - [0049], [0058], [0064], [0065] * * page 9; examples 2-14; table 1 * * page 10; examples 1-18; table 2 * * claims 1,4-6 *	1-10	
A	EP 1 207 213 A (JFE STEEL CORPORATION; KAWASAKI STEEL CORPORATION) 22 May 2002 (2002-05-22) * paragraph [0066] - paragraph [0070]; examples A-L; table 1 * * page 12 - page 13; examples 1-20; table 2 * * claims 1,2,4 *	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C21D C22C
A	EP 1 201 780 A (NIPPON STEEL CORPORATION) 2 May 2002 (2002-05-02) * page 4, line 40 - line 52 * * paragraph [0067] - paragraph [0068] * * page 12 - page 13; examples C,G-0; tables 1,2 * * page 15 - page 17; examples A,E-0; tables 3,4 * * claims 1-3,5-8 *	1-10	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 7 March 2005	Examiner Gavriliu, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

2
EPO FORM 1503 03.92 (P04C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 25 0049

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 12, 29 October 1999 (1999-10-29) -& JP 11 193439 A (NIPPON STEEL CORP), 21 July 1999 (1999-07-21) * abstract * * examples 1-15; tables 1-4 * * examples 16-40; tables 5-8 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 7 March 2005	Examiner Gavriliu, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

2
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 05 25 0049

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-03-2005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 11256273 A	21-09-1999	JP 3401427 B2	28-04-2003
EP 1391526 A	25-02-2004	JP 2004076114 A	11-03-2004
		EP 1391526 A2	25-02-2004
		US 2004035500 A1	26-02-2004
EP 1207213 A	22-05-2002	JP 2001303185 A	31-10-2001
		CA 2377701 A1	08-11-2001
		EP 1207213 A1	22-05-2002
		US 2003047258 A1	13-03-2003
		CN 1383458 A	04-12-2002
		WO 0183839 A1	08-11-2001
EP 1201780 A	02-05-2002	JP 2001303186 A	31-10-2001
		JP 2001303187 A	31-10-2001
		EP 1201780 A1	02-05-2002
		US 2002179193 A1	05-12-2002
		WO 0181640 A1	01-11-2001
JP 11193439 A	21-07-1999	JP 3492176 B2	03-02-2004