(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 676 932 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.07.2006 Bulletin 2006/27

(51) Int Cl.:
C22C 38/02 *(2006.01)* *C22C 38/04* *(2006.01)*

(21) Application number: 05028444.7

(22) Date of filing: 23.12.2005

(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 LV MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK YU

(30) Priority: 28.12.2004 JP 2004381230
28.12.2004 JP 2004381231
28.12.2004 JP 2004381232
19.05.2005 JP 2005147238
19.05.2005 JP 2005147239
19.05.2005 JP 2005147240

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(54) High strength thin steel sheet having high hydrogen embrittlement resisting property

(57) The purpose of the present invention is to provide a high strength thin steel sheet that has high hydrogen embrittlement resisting property.

In order to achieve the above purpose, a high strength thin steel sheet having high hydrogen embrittlement resisting property comprises:

C: 0.10 to 0.25%; Si: 1.0 to 3.0%; Mn: 1.0 to 3.5%; P: 0.15% or less; S: 0.02% or less; and Al: 1.5% or less (higher than 0%) in terms of percentage by weight, with balance of iron and inevitable impurities;

and the metal structure comprises: residual austenite; 1% by area or more in proportion to the entire structure;
bainitic ferrite and martensite: 80% or more in total;
and ferrite and pearlite: 9% or less (may be 0%) in total,

while the mean axis ratio (major axis/minor axis) of said residual austenite grains is 5 or higher, and the steel has tensile strength of 1180 MPa or higher.

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a high strength thin steel sheet that has high hydrogen embrittlement resisting property (particularly the hydrogen embrittlement resisting property after being subjected to forming process) and high workability, especially to a high strength thin steel sheet that has high resistance against fractures due to hydrogen embrittlement such as season crack and delayed fracture that pose serious problems for steel sheets having tensile strength of 1180 MPa or higher, and has high workability.

[0002] There are increasing demands for the steel sheet, that is pressed or bent into a form of a high-strength component of automobile or industrial machine, to have both high strength and high ductility at the same time. In recent years, there are increasing needs for high strength steel sheets having strength of 1180 MPa or higher, as the automobiles are being designed with less weight. A type of steel sheet that is regarded as promising 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, undergoes considerable elongation due to induced transformation of the residual austenite (residual y) into martensite by the action of stress. Known examples of the TRIP steel 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 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 NISSIN STEEL TECHNICAL REPORT, No. 43, Dec. 1980, pp1-10), 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 high strength of 1180 MPa upward, however, the TRIP steel sheet is known to suffer a newly emerging problem of delayed fracture 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 grain boundary, and makes the steel brittle. This results in decreases in ductility and toughness of the metallic material.

[0005] It has been well known that the high strength steel that is widely used in the manufacture of PC steel wire and line pipe experiences hydrogen embrittlement (pickling embrittlement, plating embrittlement, delayed fracture, etc.) caused by the infiltration of hydrogen into the steel when tensile strength of the steel becomes 980 MPa or higher. Accordingly, most of technologies of improving hydrogen embrittlement resisting property have been developed aiming at steel members such as bolt. "New Development in Elucidation of Delayed Fracture" (published by The Iron and Steel Institute of Japan in January, 1997), for example, describes that it is effective in improving the resistance against delayed fracture to add element such as Cr, Mo or V that demonstrates resistance against temper softening to the metal structure that is based on tempered martensite as the major phase. This technology is intended to cause the delayed fracture to take place within grains instead of in the grain boundaries, thereby to constrain the fracture from occurring, by precipitating alloy carbide and making use thereof as the site for trapping hydrogen.

[0006] Thin steel sheets having strength higher than 780 MPa have rarely been used for the reason of workability and weldability. Also hydrogen embrittlement has rarely been regarded as a problem for thin steel sheets where hydrogen that has infiltrated therein is immediately released due to the small thickness. For these reasons, much efforts have not been dedicated to counter the hydrogen embrittlement. In recent years, however, higher strength is required of the reinforcement members such as bumper, impact beam and seat rail, etc., in order to meet the requirement of weight reduction of the automobile and to improve the collision _ safety. As a result, there have been increasing demands for high strength steel sheet having strength of 980 MPa or higher for the manufacture of these parts. This makes it necessary to improve hydrogen embrittlement resisting property of the high strength steel sheet.

[0007] Use of the technology addressed to the bolt steel described above may be considered for improving the hydrogen embrittlement resisting property of the high strength steel sheet. However, in the case of "New Development in Elucidation of Delayed Fracture" (published by The Iron and Steel Institute of Japan in January, 1997), for example, 0.4% or higher C content and much alloy elements are contained, and therefore application of this technology to a thin steel sheet compromises the workability required of the thin steel sheet. The technology also has a drawback related to the manufacturing process, since it takes several hours or longer period of heat treatment to cause the alloy carbide to precipitate. Therefore, improving the hydrogen-embrittlement resisting property of a thin steel sheet requires it to develop a novel technology.

[0008] Japanese Unexamined Patent Publication (Kokai) No. 11-293383 describes a technology to improve the hydrogen embrittlement resisting property of steel sheet, where hydrogen-induced defects can be suppressed by having oxides that include Ti and Mg exist as the main components in the structure. However, this technology is intended for thick steel sheets and, although consideration is given to delayed fracture after welding with a large input heat, no consideration is given to the environment (for example, corrosive environment, etc.) in which automobile parts manufactured by using thin steel sheets are used. Japanese Unexamined Patent Publication (Kokai) No. 2003-166035 describes that it is made possible to improve the ductility and delayed fracture resistance after being subjected to forming process, by controlling the mutual relationships between 1)the form (standard deviation and mean grain size) in which oxide, sulfide, composite crystallization product or composite precipitate of Mg is dispersed, 2)volumetric proportion of residual austenite and 3)strength of the steel sheet. However, it is difficult to improve the hydrogen embrittlement resisting property in such an environment as hydrogen is generated through corrosion of the steel sheet simply through the trapping effect achieved by controlling the form of precipitate.

[0009] Tomohiko HOJO et. al "Hydrogen Embrittlement of High Strength Low Alloy TRIP Steel (Part 1: Hydrogen Absorbing Characteristic and Ductility", The Society of Materials Science, Japan, proceedings of 51st academic lecture meeting, 2002, vol. 8, pp17-18 and Tomohiko HOJO et. al "Influence of Austempering Temperature on Hydrogen Embrittlement of High, for example, describe investigations into the hydrogen embrittlement resisting property of the TRIP steel. It is pointed out that, among the TRIP steels, TBF steel has particularly high hydrogen absorbing capacity, and observation of a fracture surface of the TBF steel shows the restriction of quasi cleavage fracture due to storage of hydrogen. However, the TBF steels reported in the documents described above show delayed fracture characteristic of about 1000 seconds at the most in terms of the time before crack occurrence measured in cathode charging test, indicating that these steels are not meant to endure the harsh operating environment such as that of automobile parts over a long period of time. Moreover, since the heat treatment conditions reported in the documents 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.

[0010] The present invention has been made with the background described above, and the object of the present invention is to make available a high strength thin steel sheet that shows high hydrogen embrittlement resisting property with workability improved under the tensile strength of 1180 MPa or higher.

[0011] Hydrogen-induced delayed fracture is believed to occur in such a steel that contains tempered martensite or martensite +ferrite, that has been commonly used as a high-strength steel ever before, because hydrogen is concentrated in grain boundaries of prior austenite thereby to form voids or other defects that become the starting points of the fracture. Common practice that has been employed to decrease the sensitivity to delayed fracture is to diffuse fine grains of carbide or the like uniformly as the site for trapping hydrogen, thereby to decrease the concentration of diffusive hydrogen. However, even when a large number of carbide grains or the like are diffused as the trap site for hydrogen, there is a limitation to the hydrogen trapping capability and delayed fracture attributable to hydrogen cannot be fully suppressed.

[0012] Thus, as a result of a hard study of the present inventors, they found that (a) decreasing the points of destroying grains and (b) neutralizing hydrogen by improving the ability of trapping hydrogen are satisfied in order to make it possible to show a satisfactory hydrogen embrittlement resisting property (delayed fracture resisting property) with its use environment sufficiently considered.

[0013] In order to achieve condition (a), it is desirable to form the matrix phase of the steel structure after processing from a binary phase structure of bainitic ferrite and martensite with the bainitic ferrite acting as the main phase, instead of the single phase structure of martensite that is generally used for high strength steels. Because in the case of the single phase structure of martensite, a carbide (for example, film-like cementite) is likely to precipitate in the grain boundaries, thus making intergranular fracture likely to occur. On the other hand, in the case of the binary structure of bainitic ferrite and martensite acting as the main phase, the bainitic ferrite is easy to increase the strength of the entire structure as in the case of the single phase of martensite, because a dislocation density of the bainitic ferrite is high as it is in the form of plates, differing from polygonal ferrite used commonly. The hydrogen embrittlement resisting property can also be improved as much hydrogen is trapped in the dislocations. It also has such an advantage that coexistence of the bainitic ferrite and the residual austenite which will be described later prevents the generation of carbide that acts as the intergranular fracture initiating points.

[0014] The bainitic ferrite is a hard phase and therefore it is easy to increase the strength of the entire structure. It can also absorb much hydrogen compared to the other TRIP steel as much hydrogen is trapped in the dislocations. It also has such an advantage that in the boundaries of the lath-shaped bainitic ferrite, it becomes easier to produce the lath-shaped residual austenite, thus providing an excellent elongation with it. Accordingly, it is found that it is required in the present invention that the binary structure of bainitic ferrite and martensite occupy 80% or more in order to effectively achieve the above action.

[0015] In order to achieve condition (b), it is desirable to form the lath-shaped residual austenite. In the past it has been thought that the residual austenite exerts a negative impact on its hydrogen embrittlement resisting property and fatigue. The present inventor has studied that although the residual austenite which is in the form of cluster in the submicron order exerts a negative impact on its hydrogen embrittlement resisting property and fatigue, if the residual austenite above described is controlled to be produced the lath-shaped residual austenite in the order of submicron, it can absorb and trap much hydrogen, thus improving the hydrogen embrittlement resisting property to a large degree due to the ability of absorbing hydrogen which the residual austenite naturally has. In particular, hydrogen embrittlement risk index sharply decreases when the mean axis ratio (major axis/minor axis) of the residual austenite grains increases beyond 5. This is supposedly because, when the mean axis ratio of the residual austenite grains becomes 5 or higher, intrinsic capability of the residual austenite to absorb hydrogen is put into full play, so that the residual austenite attains far higher capacity of trapping hydrogen than carbide and substantially neutralizes the hydrogen that infiltrates from the outside through atmospheric corrosion thereby to achieve remarkable achievement in hydrogen embrittlement resisting property.

[0016] The metal structure may include other structure such as ferrite (the term ferrite used herein refers to polygonal ferrite, that is a ferrite structure that includes no or very few dislocations) or pearlite to such an extent that the effect of the present invention is not compromised. The less the concentration of additional components is, more preferable it is. It is found that in particular, its concentration is preferably within 9%.

[0017] The present inventors conducted a research on a steel sheet to find that if it is controlled so that the below conditions are satisfied at a time, high hydrogen embrittlement resisting property is achieved even if too much alloys are not added and they brought to a completion of the present invention.

· bainitic ferrite and martensite: 80% or more in total;
· the mean axis ratio (major axis/minor axis) of said residual austenite grains is 5 or higher; and
· ferrite and pearlite: 9% or less (may be 0%) in total.

[0018] Thus, a first high strength thin steel sheet having high hydrogen embrittlement resisting property according to the present invention is constituted from 0.10 to 0.25% of C (contents of components given in terms of percentage in this patent application all refer to percentage by weight), 1.0 to 3.0% of Si, 1.0 to 3.5% of Mn, 0.15% or less P, 0.02% or less S and 1.5% or less (higher than 0%) of Al, with balance of iron and inevitable impurities, wherein the metallurgical structure comprises:

1% or more residual austenite;
80% or more in total of bainitic ferrite and martensite; and
9% or less (may be 0%) in total of ferrite and pearlite in the proportion of area to the entire structure, and wherein the mean axis ratio (major axis/minor axis) of the residual austenite grains is 5 or higher, and the steel has tensile strength of 1180 MPa or higher.

[0019] The present inventors also found that if its average length of minor axis of the lath-shaped grains in the residual austenite is 1 μm or less (submicrometer order), the surface area (interface) of the grains in the residual austenite becomes larger, thus improving the ability of trapping hydrogen and effectively improving high hydrogen embrittlement resisting property. And it has been found that hydrogen embrittlement resisting property can be improved further by controlling the minimum distance between adjacent residual austenite grains so that it is 1 μm or less. This is supposedly because propagation of cracks is suppressed so that the structure demonstrates higher resistance against fracture, when a large number of fine lath-shape grains of residual austenite are dispersed in proximity to each other.

[0020] Thus, a second high strength thin steel sheet having high hydrogen embrittlement resisting property according to the present invention is constituted from 0.10 to 0.25% of C, 1.0 to 3.0% of Si, 1.0 to 3.5% of Mn, 0.15% or less P, 0.02% or less S, 0.5% or less (higher than 0%) Al, with balance of iron and inevitable impurities, and wherein the metal structure comprises:

1% or more residual austenite;
the mean axis ratio (major axis/minor axis) of the residual austenite grains is 5 or higher;
mean length of minor axes of the residual austenite grains is 1 μm or less;
minimum distance between the residual austenite grains is 1 μm or less; and
tensile strength is 1180 MPa or higher.

[0021] Preferably, the high strength thin steel sheet according to the present invention may contain 0.5% or less (higher than 0%) by weight of Al. If the Al content increases over 0.5%, inclusions such as alumina increase and thus workability becomes poorer. With the content of Al to be restricted within 0.5% or less, it can prevent a steel sheet from having a poorer workability.

[0022] Preferably, the high strength thin steel sheets according to the present invention may further contain 0.003 to 0.5% of Cu and/or 0.003 to 1.0% of Ni in terms of percentage by weight. The effect of improving hydrogen embrittlement resisting property through control of the structure can be achieved further by containing 0.003 to 0.5% of Cu and/or 0.003 to 1.0% of Ni.

Further, it is preferred that the high strength thin steels sheet according to the present invention may further contain 0.003 to 1.0% of Ti and/or V. Ti and/or V has/have the effect of assisting in the generation of protective rust, the effect of rendering steel high corrosion resistance, and the effect of cleaning the steel. And V has the effect of increasing the strength of the steel sheet and decreasing the size of crystal grains, in addition to having the effect of improving hydrogen embrittlement resistance.

Preferably, the high strength thin steels sheet according to the present invention may further contain;
1.0% or less (higher than 0%) of Mo and 0.1% or less (higher than 0%) of Nb,
0.0002 to 0.01% of B, or
at least one kind selected from the group consisting of:

> 0.0005 to 0.005% of Ca;
> 0.0005 to 0.01% of Mg; and
> 0.0005 to 0.01% of REM
> in terms of percentage by weight.

[0023] According to the present invention, it is made possible to manufacture, with a high level of productivity, a high strength thin steel sheet having tensile strength of 1180 MPa or higher that neutralizes hydrogen that infiltrates from the outside after the steel sheet has been formed into a part thereby to maintain satisfactory hydrogen embrittlement resisting property, and demonstrates high workability during the forming process. Use of the high strength thin steel sheet makes it possible to manufacture high strength parts that hardly experience delayed fracture, such as bumper, impact beam and other reinforcement members and other automobile parts such as seat rail, pillar, etc.

[0024] Fig. 1 is a graph showing the relationship between the mean axis ratio of the residual austenite grains and hydrogen embrittlement risk index.

> Fig. 2 is a diagram schematically showing the minimum distance between residual austenite grains.
> Fig. 3 is a schematic perspective view of a part used in pressure collapse test in Example 1.
> Fig. 4 is a side view schematically showing the setup of pressure collapse test in Example 1.
> Fig. 5 is a schematic perspective view of a part used in impact resistance test in Example 1.
> Fig. 6 is a sectional view along A-A in Fig. 5.
> Fig. 7 is a side view schematically showing the setup of impact resistance test in Example 1.
> Fig. 8 is a photograph of TEM observation (magnification factor 15000) of No.101 (inventive steel) of Example 1.
> Fig. 9 is a photograph of TEM observation (magnification factor 15000) of No.120 (comparative steel) of Example 1.
> Fig. 10 is a photograph of TEM observation (magnification factor 15000) of No.201 (inventive steel) of Example 2.
> Fig. 11 is a photograph of TEM observation (magnification factor 15000) of No.220 (comparative steel) of Example 2.
> Fig. 12 is a photograph of TEM observation (magnification factor 15000) of No.301 (inventive steel) of Example 3.
> Fig. 13 is a photograph of TEM observation (magnification factor 60000) of No.301 (inventive steel) of Example 3.
> Fig. 14 is a photograph of TEM observation (magnification factor 15000) of No.313 (comparative steel) of Example 3.

[0025] The high strength thin steel sheet of non-limiting embodiment according to the present invention is explained in more detail below with reference to the drawing. The inventions can be made variable in the scope of the present invention.

(First Embodiment)

[0026] The first high strength thin steel sheet according to the present invention comprises higher than 0.10 and up to 0.25% of C (contents of components given in terms of percentage in this patent application all refer to percentage by weight), 1.0 to 3.0% of Si, 1.0 to 3.5% of Mn, 0.15% or less P, 0.02% or less S, 1.5% or less (higher than 0%) of Al, 1.0% or less (higher than 0%) of Mo and 0.1% or less (higher than 0%) of Nb, with balance of iron and inevitable impurities, and
the metal structure comprises:
1% or more residual austenite;
80% or more in total of bainitic ferrite and martensite; and
9% or less (may be 0%) in total of ferrite and pearlite in terms of the proportion of area to the entire structure, and
the mean axis ratio (major axis/minor axis) of the residual austenite grains is 5 or higher.

(1% or more residual austenite in the area proportion to the entire structure)

[0027] It is necessary that the metal contains 1% or more residual austenite in the area proportion to the entire structure, because residual austenite contributes not only to the improvement of hydrogen embrittlement resisting property, but also to the improvement of total elongation. Content of the residual austenite is preferably 3% or higher, and more preferably 5% or higher.

[0028] Since the desired level of high strength cannot be obtained when an excessive amount of residual austenite is contained, it is recommended to set an upper limit of 15% (more preferably 10%) to the residual austenite content.

[0029] It is recommended to increase the C content in the steel sheet as described above, thereby to maintain the concentration of C in the residual austenite ($C\gamma R$) of 0.8% or higher. Controlling the value of $C\gamma R$ to 0.8% or higher enables it to effectively improve the elongation property, which is preferably 1.0% or higher and more preferably 1.2% or higher. While it is preferable that $C\gamma R$ is as high as possible, it is considered that in practice there is an upper limit of around 1.6%.

[0030] The residual austenite refers to a region that is observed as FCC (face centered cubic lattice) by the FE-SEM/EBSP method which will be described later. Measurement by the EBSP may be done, for example, by measuring a measurement area (about 50 by 50 μm) at an arbitrarily chosen position in a surface parallel to the rolled surface at a position of one quarter of the thickness at measuring intervals of 0.1 μm. The measuring surface is prepared by electrolytic polishing in order to prevent the residual austenite from transforming. Then the test piece is set in the lens barrel of an FE-SEM equipped with the EBSP detector (of which details will be described later) and is irradiated with electron beam. An EBSP image projected onto a screen is captured by a high sensitivity camera (VE-1000-SIT manufactured by Dage-MTI Inc.) and is sent to a computer. The computer carries out image analysis and generates color mapping of the FCC phase through comparison with a structural pattern simulated with a known crystal system (FCC (face centered cubic lattice) phase in the case of residual austenite). Area proportion of the region that is mapped as described above is taken as the area proportion of the residual austenite. This analysis was carried out by means of hardware and software of OIM (Orientation Imaging Microscopy™) system of TexSEM Laboratories Inc.

(Mean axis ratio (major axis/minor axis) of the residual austenite grains: 5 or higher)

[0031] In the past it has been thought that the residual austenite exerts a negative impact on its hydrogen embrittlement resisting property and fatigue. The present inventor's studies show that although the residual austenite which is in the form of cluster in the order of submicron exerts a negative impact on its hydrogen embrittlement resisting property and fatigue, Lath-shaped grains of residual austenite have far higher capacity of trapping hydrogen than carbide, if the residual austenite above described is controlled to be produced the lath-shaped residual austenite.

[0032] Fig. 1 is a graph showing the relationship between the mean axis ratio of the residual austenite grains measured by a method to be described later and hydrogen embrittlement risk index (measured by a method to be described later in an example, lower value of this index means better hydrogen embrittlement resisting property). From Fig. 1, it can be seen that hydrogen embrittlement risk index sharply decreases when the mean axis ratio (major axis/minor axis) of the residual austenite grains increases beyond 5. This is supposedly because, when the mean axis ratio of the residual austenite grains becomes 5 or higher, intrinsic capability of the residual austenite to absorb hydrogen is put into full play, so that the residual austenite attains far higher capacity of trapping hydrogen than carbide and substantially neutralizes the hydrogen that infiltrates from the outside through atmospheric corrosion thereby to achieve remarkable achievement in hydrogen embrittlement resisting property. The mean axis ratio of the residual austenite grains is preferably 10 or higher, and more preferably 15 or higher.

[0033] While no upper limit of the mean axis ratio is specified for the consideration of improvement in hydrogen embrittlement resisting property, the residual austenite grains are required to have certain level of thickness in order to achieve the TRIP effect during processing. Thus it is preferable to set an upper limit to 30, more preferably to 20 or less. The mean axis ratio was determined by observing with TEM (magnification factor of 15000) in each of three arbitrarily chosen fields of view and averaging the distances measured in the three fields of view.

(80% or more in total of bainitic ferrite and martensite)

[0034] In the case of the binary structure of bainitic ferrite and martensite (with the bainitic ferrite acting as the main phase in the binary structure), the bainitic ferrite is a hard phase and therefore it is easy to increase the strength of the entire structure. The hydrogen embrittlement resisting property can also be improved as much hydrogen is trapped in the dislocations. It also has such an advantage that coexistence of the bainitic ferrite and the residual austenite which will be described later prevents the generation of carbide that acts as the intergranular fracture initiating points, and it becomes easier to create the lath-shaped residual austenite in the boundaries of lath-shaped bainitic ferrite.
Accordingly, it is required in the present invention that the binary structure of bainitic ferrite and martensite occupy 80% or more, preferably 85% or more and more preferably 90% or more. Upper limit of the proportion may be determined by the balance with other structure (residual austenite), and is set to 99% when the other structures (ferrite, etc.) than the residual austenite is not contained.

[0035] The bainitic ferrite referred to in the present invention is plate-shaped ferrite having a lower structure of high density of dislocations. It is clearly distinguished from polygonal ferrite that has lower structure including no or very low density of dislocations, by SEM observation as follows.

[0036] Area proportion of bainitic ferrite structure is determined as follows. A test piece is etched with Nital etchant. A measurement area (about 50 by 50 μm) at an arbitrarily chosen position in a surface parallel to the rolled surface at a position of one quarter of the thickness is observed with SEM (scanning electron microscope) (magnification factor of 1500) thereby to determine the area proportion.

[0037] Bainitic ferrite is shown with dark gray color in SEM photograph (bainitic ferrite, residual austenite and martensite may not be distinguishable in the case of SEM observation), while polygonal ferrite is shown black in SEM photograph and has polygonal shape that does not include residual austenite and martensite inside thereof.

[0038] The SEM used in the present invention is a high-resolution FE-SEM (Field Emission type Scanning Electron Microscope XL30S-FEG manufactured by Philips Inc.) equipped with an EBSP (Electron Back Scattering Pattern) detector, that has a merit of being capable of analyzing the area observed by the SEM at the same time by means of the EBSP detector. EBSP detection is carried out as follows. When the sample surface is irradiated with electron beam, the EBSP detector analyzes the Kikuchi pattern obtained from the reflected electrons, thereby to determine the crystal orientation at the point where the electron beam has hit upon. Distribution of orientations over the sample surface can be measured by scanning the electron beam two-dimensionally over the sample surface while measuring the crystal orientation at predetermined intervals. The EBSP detection method has such an advantage that different structures that are regarded as the same structure in the ordinary microscopic observation but have different crystal orientations can be distinguished by the difference in color tone.

(9% or less (may be 0%) in total of ferrite and pearlite)

[0039] The steel sheet after the processing may be constituted either from only the structures described above (namely, a mixed structure of bainitic ferrite + martensite and residual austenite), or may include other structure such as ferrite (the term ferrite used herein refers to polygonal ferrite, that is a ferrite structure that includes no or very few dislocations) or pearlite to such an extent that the effect of the present invention is not compromised. 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, within 9%, preferably less than 5% and more preferably less than 3% according to the present invention.

[0040] As described above, the present high strength steel is characterized in that the amount and form of residual austenite are controlled and the easy control of the amount and form of residual austenite can be achieved to provide the desired high strength steel according to the following composition.

<C: 0.10 to 0.25%>

[0041] C is an element required to achieve a high strength of 1180 MPa or higher. And C is an important element that can remain the desired austenite at room temperature by providing a sufficient amount of C into the phase of austenite. In the present invention, 0.10% or higher of C is contained, and 0.12% or more, preferably 0.15% or more C is contained. However, in order to ensure corrosion resistance and weldability, concentration of C is limited within 0.25%, preferably 0.23% or lower in the present invention.

<Si: 1.0 to 3.0%>

[0042] Si is an important element that effectively suppresses the residual austenite from decomposing and carbide from being generated, and is also effective in enhancing substitution solid solution for hardening the material. In order to make full use of these effects, it is necessary to include Si in a concentration of 1.0% or higher, preferably 1.2% or higher and more preferably 1.5% or higher. However, excessively high content of Si leads to conspicuous formation of scales due to hot rolling and makes it necessary to remove flaws, thus adding up to the manufacturing cost and resulting in economical disadvantage. Therefore Si content is controlled within 3.0%, preferably within 2.5% and more preferably within 2.0%.

<Mn: 1.0 to 3.5%>

[0043] 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 1.0% or higher, preferably 1.2% or higher, and more preferably 1.5% or higher. However, adding an excessive amount Mn leads to conspicuous segregation and poor workability. Therefore upper limit to the concentration of Mn is set to 3.5% and more preferably to 3.0% or less.

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

[0044] P intensifies intergranular fracture due to intergranular segregation, and the content thereof is therefore preferably as low as possible. Upper limit to the concentration of P is set to 0.15%, preferably 0.1% or less and more preferably to 0.05% or less.

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

[0045] S intensifies the absorption of hydrogen into the steel sheet in corrosive environment, and the content thereof is therefore preferably as low as possible. Upper limit to the concentration of S is set to 0.02%.

[0046] <A1: 1.5% or less (higher than 0%)> (In the case of inventive steel 1)
<A1: 0.5% or less (higher than 0%)> (In the case of inventive steel 2)
0.01% or higher content of Al may be included for the purpose of deoxidation. In addition to deoxidation, Al also has the effects of improving the corrosion resistance and improving hydrogen embrittlement resisting property.

[0047] The mechanism of improving the corrosion resistance is supposedly based on the improvement of corrosion resistance of the matrix phase per se and the effect of formation rust generated by atmospheric corrosion, while the effect of the formation rust presumably has greater contribution. This is supposedly because the formation rust is denser and better in protective capability than ordinary iron rust, and therefore checks the progress of atmospheric corrosion so as to decrease the amount of hydrogen generated by the atmospheric corrosion, thereby to effectively suppress the occurrence of hydrogen embrittlement, and hence the delayed fracture.

[0048] While details of the mechanism of improvement of the hydrogen embrittlement resistance by Al is not known, it is supposed that condensing of Al on the surface of the steel makes it difficult for hydrogen to infiltrate into the steel, and the decreasing diffusion rate of hydrogen in the steel makes it difficult for hydrogen to migrate so that hydrogen embrittlement becomes less likely to occur. In addition, stability of lath-shaped residual austenite improved by the addition of Al is believed to contribute to the improvement of hydrogen embrittlement resisting property.

[0049] In order to effectively achieve the effects of Al in improving the corrosion resistance and improving the hydrogen embrittlement resisting property, Al content is controlled to 0.2% or higher, preferably 0.5% or higher.

[0050] However, Al content must be controlled within 1.5% in order to keep inclusions such as alumina from increasing in number and size so as to ensure satisfactory workability, ensure the generation of fine residual austenite grains, suppress corrosion from proceeding from the inclusion containing Al as the starting point, and prevent the manufacturing cost from increasing. In view of the manufacturing process, it is preferable to control so that A3 point is not higher than 1000°C.

[0051] As the Al content increases, inclusions such as alumina increase and workability becomes poorer. In order to suppress the generation of the inclusions such as alumina and make a steel sheet having higher workability, Al content is restricted within 0.5%, preferably within 0.3% and more preferably within 0.1%.

[0052] While constituent elements (C, Si, Mn, P, S, Al, Mo, Nb) of the steel of this embodiment is as described above with the rest substantially being Fe, it may include inevitable impurities introduced into the steel depending on the stock material, production material, manufacturing facility and other circumstances, containing 0.001% or less N (nitrogen). In addition, other elements as described below may be intentionally added to such an extent that does not adversely affect the effects of the present invention.

[0053] The case in which 1.5% or less (higher than 0%) of Al is contained is referred to as an inventive steel 1. And the case in which 0.5% or less (higher than 0%) of A1 is contained is referred to as an inventive steel 2

(Cu: 0.003 to 0.5% and/or Ni: 0.003 to 1.0%)

[0054] It was found that by including 0.003 to 0.5% of Cu and/or 0.003 to 1.0% of Ni, the generation of hydrogen leading to the hydrogen embrittlement and the infiltration of hydrogen that has been generated can be sufficiently suppressed.

[0055] Specifically, presence of Cu and Ni improves the corrosion resistance of the steel, and effectively suppresses the generation of hydrogen due to corrosion of the steel sheet. These elements also have the effect of promoting the generation of iron oxide, α-FeOOH, that is believed to be particularly stable thermodynamically and have protective property among various forms of rust generated in the atmosphere. By assisting the generation of this rust, it is made possible to suppress hydrogen that has been generated from infiltrating into the spring steel thereby to sufficiently improve the hydrogen embrittlement resisting property to endure in harsh corrosive environment. This effect can be achieved particularly satisfactorily when Cu and Ni are contained at the same time.

[0056] In order to achieve the effects described above, concentration of Cu, if added, should be 0.003% or higher, preferably 0.05% or higher and more preferably 0.1% or higher. Concentration of Ni, if added, should be 0.003% or higher, preferably 0.05% or higher and more preferably 0.1% or higher.

[0057] Since excessively high concentration of either Cu or Ni is detrimental to workability, it is preferable to limit the Cu content to 0.5% or lower and limit the Ni content to 1.0% or lower.

<Ti and/or V: 0.003 to 1.0% in total>

[0058] Ti has the effect of assisting in the generation of protective rust, similarly to Cu and Ni. The protective rust has a very valuable effect of suppressing the generation of β-FeOOH that appears in chloride environment and has adverse effect on the corrosion resistance (and hence on the hydrogen embrittlement resisting property). Formation of such a protective rust is promoted particularly by adding Ti and V (or Zr). Ti renders the steel high corrosion resistance, and also has the effect of cleaning the steel.
V is effective in increasing the strength of the steel sheet and decreasing the size of crystal grains, in addition to having the effect of improving hydrogen embrittlement resistance through cooperation with Ti, as described previously.

[0059] In order to fully achieve the effect of Ti and/or V described above, it is preferable to add Ti and/or V in total concentration of 0.003% or higher (more preferably 0.01% or higher). For the purpose of improving hydrogen embrittlement resisting property, in particular, it is preferable to add more than 0.03% of Ti, more preferably 0.05% or more Ti. However, the effects described above reach saturation when an excessive amount of Ti is added, resulting in economical disadvantage. Excessive V content also increases the precipitation of much carbonitride and leads to poor workability and lower hydrogen embrittlement resisting property. Therefore, it is preferable to control the total concentration of Ti and/or V to within 1.0%, more preferably within 0.5%.

<Zr: 0.003 to 1.0%>

[0060] Zr is effective in increasing the strength of the steel sheet and decreasing the crystal grain size, and also has the effect of improving hydrogen embrittlement resisting property through cooperation with Ti. In order to sufficiently achieve these effects, it is preferable that 0.003% or more Zr is contained. However, excessive Zr content increases the precipitation of carbonitride and leads to poor workability and lower hydrogen embrittlement resisting property. Therefore, it is preferable to control the concentration of Zr to within 1.0%.

<Mo: 1.0% or less (higher than 0%)>

[0061] Mo has the effects of stabilizing austenite so as to retain the residual austenite, and suppress the infiltration of hydrogen thereby to improve hydrogen embrittlement resisting property. Mo also has the effect of improving the hardenability of the steel sheet. In addition, Mo strengthens the grain boundary so as to suppress hydrogen embrittlement from occurring. It is recommended to add 0.005% or more Mo in order to achieve these effects. More preferably 0.1% or more Mo is added. However, since the effects described above reach saturation when the Mo content exceeds 1.0%, resulting in economical disadvantage, Mo content is limited to 0.8% or less and more preferably to 0.5% or less.

<Nb: 0.1% or less (higher than 0%)>

[0062] Nb is very effective in increasing the strength of the steel sheet and decreasing the grain size of the structure. Nb achieves these effects particularly effectively in cooperation with Mo. In order to achieve these effects, it is recommended to include 0.005% or more Nb. More preferably 0.01% or more Nb is added. However, since the effects described above reach saturation when an excessive Nb content is included, resulting in economical disadvantage, Nb content is limited to 0.1% or less and more preferably to 0.08% or less.

<B: 0.0002 to 0.01%>

[0063] B is effective in increasing the strength of the steel sheet, and it is preferable that 0.0002% or more (more preferably 0.0005% or more) B is contained in order to achieve these effects. However, an excessive content of B leads to poor hot processing property. Therefore, it is preferable to control the concentration of B to within 0.01% (more preferably within 0.005%).

<At least one kind selected from among a group consisting of Ca: 0.0005% to 0.005%, Mg: 0.0005% to 0.01% and REM: 0.0005% to 0.01%)

[0064] Ca, Mg and REM (rare earth element) are effective in suppressing an increase in hydrogen ion concentration, that is, a decrease in pH in the atmosphere of the interface due to corrosion of the steel sheet surface, thereby to improve the corrosion resistance of the steel sheet. It is also effective in controlling the form of sulfide in the steel and improving the workability of the steel. In order to achieve the effects described above, it is recommended to add each of Ca, Mg and REM in concentration of 0.0005% or higher. However, since excessive contents of these elements leads to poor workability, it is preferable to keep the concentrations of Ca within 0.005%, Mg and REM each within 0.01%.

[0065] While the present invention does not specify the manufacturing conditions, it is recommended to apply heat treatment in the following procedure after hot rolling or cold rolling conducted thereafter, in order to form the structure described above that can be easily worked and has high strength and high hydrogen embrittlement resistance after the processing, by using the steel material of the composition described above.

[0066] The recommended procedure is to keep the steel the composition described above at a temperature (T1) in a range from A3 point to (A3 point + 50°C) for a period of 10 to 1800 seconds (t1), cool down the steel at a mean cooling rate of 3°C/s or higher to a temperature (T2) in a range from Ms point to Bs point and keep the material at this temperature for a period of 60 to 3600 seconds (t2).

[0067] It is not desirable that the temperature T1 becomes higher than (A3 point + 50°C) or the period t1 is longer than 1800 seconds, in which case austenite grains grow resulting in poor workability (elongation flanging property). When the temperature T1 is lower than A3 point, on the other hand, desirable bainitic ferrite structure cannot be obtained. When the period t1 is shorter than 10 seconds, austenitization does not proceed sufficiently and therefore cementite and other alloy carbides remain. The period t1 is preferably in a range from 30 to 600 seconds, more preferably from 60 to 400 seconds.

[0068] Then the steel sheet is cooled down. The steel is cooled at a mean cooling rate of 3°C/s or higher, for the purpose of preventing pearlite structure from being generated while avoiding the pearlite transformation region. The mean cooling rate should be as high as possible, and is preferably 5°C/s or higher, and more preferably 10°C/s or higher.

[0069] After quenching to the temperature between Ms point and Bs point at the rate described above, the steel is subjected to isothermal transformation so as to transform the matrix phase into binary phase structure of bainitic ferrite and martensite. When the heat retaining 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 amount of residual austenite decreases.

[0070] When the temperature holding period t2 is longer than 1800 seconds, density of dislocations in bainitic ferrite becomes low, the amount of trapped hydrogen decreases and the desired residual austenite cannot be obtained. When t2 is less than 60 second, on the other hand, desired bainitic ferrite structure cannot be obtained. The length of t2 is preferably from 90 to 1200 seconds, and more preferably from 120 to 600 seconds. There is no restriction on the method of cooling after maintaining the heating temperature, and air cooling, quenching or air-assisted water cooling may be employed.

[0071] 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 a 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. The plating may also be alloyed.

[0072] 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 Ar3 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 the hot rolled steel sheet has unsatisfactory 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 70%. Cold rolling beyond 70% leads to excessive rolling load that makes it difficult to carry out the cold rolling.

[0073] While the present invention is addressed to thin steel sheet, there is no limitation to the form of product, and may be applied, in addition to steel sheet made by hot rolling or steel sheet made by cold rolling, to those subjected to annealing after hot rolling or cold rolling, followed by chemical conversion treatment, hot-dip coating, electroplating, vapor deposition, painting, priming for painting, organic coating treatment or the like.

[0074] The plating process may be either galvanizing or aluminum plating. The method of plating may be either hot-dip coating or electroplating, and the plating process may also be followed by alloying heat treatment or multi-layer plating. A steel sheet, that is plated or not plated, may also be laminated with a film.

[0075] When the coating operation described above is carried out, chemical conversion treatment such as phosphating or electrodepositing coating may be applied in accordance to the application. The coating material may be a known resin that can be used in combination with a known hardening agent such as epoxy resin, fluorocarbon resin, silicone acrylic resin, polyurethane resin, acrylic resin, polyester resin, phenol resin, alkyd resin, or melamine resin. Among these, epoxy resin, fluorocarbon resin or silicone acrylic resin is preferably used in consideration of corrosion resistance. Known additives that are added to coating materials such as coloring agent, coupling agent, leveling agent, sensitization agent, antioxidant agent, anti-UV protection agent, flame retarding agent or the like may be used.

[0076] There is also no restriction on the coating and solvent-based coating, powder coating, water-based coating, water-dispersed coating, electrodeposition coating or like may be employed. Desired coating layer of the coating material described above can be formed on the steel by a known technique such as dipping, roll coater, spraying, or curtain flow coater. The coating layer may have any proper thickness.

[0077] The high strength thin steel sheet of the present invention may be applied to high-strength automotive components such as bumper, door impact beam, pillar and other reinforcement members and interior parts such as seat rail, etc. Automobile components that are manufactured by forming process also have sufficient properties (strength) and high hydrogen embrittlement resisting property.

(Second Embodiment)

[0078] The second high strength thin steel sheet according to the present invention comprises:

> C: higher than 0.10 up to 0.25%; Si: 1.0 to 3.0%; Mn: 1.0 to 3.5%; P: 0.15% or less; S: 0.02% or less; and Al: 1.5% or less (higher than 0%) in terms of percentage by weight, with balance of iron and inevitable impurities, wherein the metal structure comprises:
>
> > residual austenite; 1% by area or more in proportion to the entire structure;
> > while the mean axis ratio (major axis/minor axis) of said residual austenite grains is 5 or higher;
> > mean length of minor axes of said residual austenite grains is 1 μm or less; and
> > a minimum distance between said residual austenite grains is 1 μm or less; and the steel has tensile strength of 1180 MPa or higher. The structure may further contain 80% or more bainitic ferrite and martensite in total and/or 9% or less (may be 0%) ferrite and pearlite in total, and the structure may not contain them.

The reason why the above requirements are defined and a measuring method are explained in detail below. Requirements explained in the first embodiment are omitted below.

<Mean length of minor axes of the residual austenite grains is 1 μm or less>

[0079] According to the present invention, it has been found that hydrogen embrittlement resisting property can be effectively improved by dispersing fine grains of residual austenite of lath shape. Specifically, hydrogen embrittlement resisting property can be surely improved by dispersing the lath-shape grains of residual austenite having sizes of 1 μm or less (submicrometer order). This is supposedly because surface area of the residual austenite grains (interface) increases resulting in larger hydrogen trapping capability, when larger number of fine lath-shape grains of residual austenite having smaller mean length of minor axis are dispersed. Mean length of minor axes of the residual austenite grains is preferably 0.5 μm or less, more preferably 0.25 μm or less.

[0080] According to the present invention, hydrogen trapping capability of the fine lath-shape grains of residual austenite can be made far greater than that in the case of dispersing carbide, and thereby to substantially neutralize hydrogen that infiltrates from the outside through atmospheric corrosion, even when the same proportion by volume of residual austenite is contained, by controlling the mean axis ratio and mean length of minor axes of the residual austenite grains as described above.

<Minimum distance between residual austenite grains is 1 μm or less>

[0081] According to the present invention, it has been found that hydrogen embrittlement resisting property can be improved further by controlling the minimum distance between adjacent residual austenite grains, in addition to the above. Specifically, hydrogen embrittlement resistance can be surely improved when the minimum distance between residual austenite grains is 1 μm or less. This is supposedly because propagation of cracks is suppressed so that the structure demonstrates higher resistance against fracture, when a large number of fine lath-shape grains of residual austenite are dispersed in proximity to each other. Minimum distance between adjacent residual austenite grains is preferably 0.8 μm or less, and more preferably 0.5 μm or less.

[0082] The present invention will now be described below by way of examples, but the present invention is not limited to the examples. Various modifications may be conceived without departing from the technical scope of the present invention.

[Example 1]

[0083] Sample steels A-1 through Y-1 having the compositions described in Table 1 were melt-refined in vacuum to make test slabs. The slabs were processed in the following procedure (hot rolling → cold rolling →continuous annealing) thereby to obtain hot-rolled steel plates measuring 3.2 mm in thickness. The steel plates were pickled to remove scales from the surface and then cold rolled so as to reduce the thickness to 1.2 mm.

<Hot rolling>

[0084] Starting temperature (SRT): Held at a temperature between 1150 and 1250°C for 30 minutes.
Finishing temperature (FDT): 850°C
Cooling rate: 40°C/s
Winding-up temperature: 550°C
<Cold rolling>
Rolling ratio: 50%
<Continuous annealing>
Each steel specimen was kept at a temperature of A3 point + 30°C for 120 seconds, then cooled in air at a mean cooling rate of 20°C/s to temperature T0 shown in Table 2, and was kept at T0 for 240 seconds, followed by air-assisted water cooling to the room temperature.

[0085] No. 116 shown in Table 2 was made by heating a cold-rolled steel sheet to 830°C, keeping at this temperature for 5 minutes followed by quenching in water and tempering at 300°C for 10 minutes, thereby to form a martensite steel as a comparative example of the high-strength steel of the prior art. No. 120 was made by heating a cold-rolled steel sheet to 800°C, keeping at this temperature for 120 seconds, cooling down at a mean cooling rate of 20°C/s to 350°C and keeping at this temperature for 240 seconds.

[0086] The metal structures of steel sheets obtained as described above were observed, and their tensile strength (TS) and elongation (total elongation E1) and hydrogen embrittlement resisting property were measured by the following procedures.

Observation of metal structure

[0087] Metal structures of the test pieces were observed before and after the processing as follows. A measurement area (about 50 by 50 μm) at an arbitrarily chosen position in a surface parallel to the rolled surface at a position of one quarter of the thickness was photographed at measuring intervals of 0.1 μm, and area proportions of bainitic ferrite (BF), martensite (M) and residual austenite (residual γ) were measured by the method described previously. Then similar measurements were made in two fields of view that were arbitrarily selected, and the measured values were averaged. Area proportions of other structures (ferrite, pearlite, etc.) were subtracted from the entire structure. Mean axis ratio of the residual austenite grains of the steel sheet before and after the processing were measured by the method described previously. Test pieces having mean axis ratio of 5 or higher were regarded to satisfy the requirements of the present invention (o), and those having mean axis ratio of lower than 5 were regarded to fail to satisfy the requirements of the present invention (x).

Measurement of tensile strength (TS) and elongation (E1)

[0088] Tensile test was conducted on the JIS No. 5 test piece before processing, so as to measure the tensile strength (TS) and elongation (E1). Stretching speed of the tensile test was set to 1 mm/sec. Among the steel sheets having tensile strength of 1180 MPa as measured by the method described previously, those which showed elongation of 10% or more were evaluated as high in elongation property.

Evaluation of hydrogen embrittlement resisting property

[0089] In order to evaluate hydrogen embrittlement resisting property, the JIS No. 5 test piece was stretched. Then after bending with a radius of curvature of 15 mm, load of 1000 MPa was applied and the test piece was immersed in 5% solution of hydrochloric acid, and the time before crack occurred was measured.

[0090] Hydrogen-charged 4-point bending test was also conducted for some steel species. Specifically, a rectangular test piece measuring 65 mm by 10 mm made of each steel sheet elongated by 3% was immersed in a solution of 0.5 mol of H_2SO_4 and 0.01 mol of KSCN and was subjected to cathode hydrogen charging. Maximum stress endured without breaking for 3 hours was determined as the critical fracture stress (DFL).

[0091] Results of these tests are shown in Table 2.

Evaluation of weldability

[0092] Test of weldability was conducted on No.101 and No.114 which are representative steel species.
The test on weldability was conducted on the test pieces made according to the procedures of JIS Z 3136 and JIS Z

3137. And then spot welding was conducted on these pieces under the following conditions. Then tensile shear test (in which ultimate load was measured in the tensile velocity of 20mm/min) and cross tension test (in which ultimate load was measured in the tensile velocity of 20mm/min) was conducted on these pieces, so as to measure the tensile shear strength (TSS) and cross tension strength (CTS). And if the ductibility ratio(CTS/TSS) of cross tension strength (CTS) to the tensile shear strength (TSS) is 0.2 or higher, it was evaluated that the test piece has a better weldability. As a result, it was found that No.101(present invention) is better than No.114(prior art) in reference to weldability because the ratio of ductibility in sample No.114 is 0.19 while that in sample No.101 is 0.22.

[0093] [Conditions of spot welding]

- Initial pressurization time:60 cycles/60Hz,
  Pressurized force 450 kgf (4.4kN)
- Power distribution time: 1 cycle/60Hz
- Power current for welding: 8.5kA.

[0094]

Table 1

Steel species Symbol	Chemical composition (mass%)*									Ac3 (℃)	Bs (℃)	Ms (℃)
	C	Si	Mn	P	S	Al	Nb	Mo	Others			
A-1	0.20	2.01	2.01	0.012	0.002	0.033	0.05	0.2	—	876.7	578.5	395.7
B-1	0.17	1.50	2.50	0.011	0.002	0.032	0.05	0.2	—	845.2	542.5	393.7
C-1	0.13	2.01	2.54	0.011	0.002	0.031	0.06	0.2	—	876.9	549.7	411.4
D-1	0.20	2.52	2.51	0.011	0.002	0.030	0.05	0.2	—	882.6	533.5	379.2
E-1	0.23	2.02	1.43	0.011	0.002	0.031	0.04	0.2	—	886.4	622.6	400.6
F-1	0.19	2.00	3.20	0.011	0.002	0.030	0.05	0.2	—	840.9	474.1	361.1
G-1	0.20	2.02	2.50	0.011	0.002	0.031	0.08	0.2	—	860.9	534.4	379.5
H-1	0.22	1.98	2.48	0.011	0.002	0.033	0.05	0.8	—	875.0	481.0	358.1
I-1	0.22	2.02	2.50	0.011	0.002	0.031	0.05	0.2	B:0.0005	856.5	529.0	370.0
J-1	0.20	1.98	2.53	0.011	0.002	0.033	0.05	0.2	Ca:0.004	859.0	531.7	378.5
K-1	0.20	1.49	2.48	0.012	0.002	0.033	0.04	0.2	Mg:0.005	839.3	536.2	380.2
L-1	0.23	1.50	2.50	0.011	0.002	0.032	0.06	0.2	REM:0.005	831.5	526.3	365.3
M-1	0.20	1.50	2.50	0.011	0.002	0.033	0.05	0.2	Ca:0.004, Mg:0.005, B:0.0005	838.5	534.4	379.5
N-1	0.30	2.00	2.00	0.014	0.005	0.031	0.06	0.2	—	856.7	552.4	348.6
O-1	0.25	2.50	0.90	0.014	0.005	0.031	0.05	0.2	—	921.8	664.9	408.6
P-1	0.20	0.16	1.98	0.014	0.002	0.043	0.05	0.2	—	800.3	581.2	396.7
Q-1	0.05	2.01	2.01	0.012	0.002	0.033	0.06	0.2	—	922.1	619.0	466.8
R-1	0.21	2.02	1.60	0.012	0.002	0.033	0.2	0.2	—	887.2	612.7	404.5
S-1	0.20	2.00	1.20	0.012	0.002	0.031	0.05	1.5	—	940.7	543.5	395.1
T-1	0.17	1.50	2.50	0.011	0.002	0.051	0.05	0.2	—	852.8	542.5	393.7
U-1	0.18	1.49	2.50	0.012	0.002	0.320	0.05	0.2	—	958.2	539.8	389.0
V-1	0.17	1.50	2.51	0.011	0.002	0.415	0.05	0.2	Ca : 0.004	998.1	541.6	393.4
W-1	0.17	1.50	2.51	0.011	0.002	0.550	0.05	0.2	Ca : 0.004	1052.1	541.6	393.4
X-1	0.17	1.49	2.55	0.012	0.002	0.730	0.05	0.2	Mg:0.005, B:0.0005	1123.1	538.0	392.1
Y-1	0.18	1.50	2.60	0.011	0.002	1.65	0.05	0.2	—	1486.9	530.8	385.7

* The balance consists of iron and inevitable impurities.

[0095]

Table 2

Test No.	Steel species Symbol	To ℃	Residual γ %	Mean axis ratio of residual γ	BF+M %	Others %	TS MPa	El %	Hydrogen embrittlement h	DFL MPa
101	A-1	320	8	○	92	0	1476	11	Over 24	-
102	B-1	300	3	○	97	0	1495	11	Over 24	405
103	C-1	300	6	○	92	2	1193	15	Over 24	-
104	D-1	320	7	○	93	0	1376	12	Over 24	-
105	E-1	350	8	○	92	0	1356	12	Over 24	-
106	F-1	300	7	○	92	1	1487	11	Over 24	-
107	G-1	300	6	○	91	3	1531	11	Over 24	-
108	H-1	300	8	○	91	1	1540	10	Over 24	-
109	I-1	300	8	○	91	1	1522	11	Over 24	-
110	J-1	320	7	○	93	0	1487	12	Over 24	-
111	K-1	320	7	○	93	0	1454	11	Over 24	-
112	L-1	320	8	○	92	0	1551	11	Over 24	-
113	M-1	320	7	○	93	0	1491	11	Over 24	-
114	N-1	320	12	○	88	0	1543	10	12	-
115	O-1	320	<1	×	99	<1	1279	7	8	-
116	P-1	-	<1	×	99	<1	1511	5	3	-
117	Q-1	370	2	○	98	0	891	19	Over 24	-
118	R-1	350	3	○	97	0	1370	1	-	-
119	S-1	350	4	○	96	0	1341	2	-	-
120	A-1	350	12	×	20	68	960	13	Over 24	-
121	T-1	300	3	○	97	0	1507	11	Over 24	505
122	U-1	300	4	○	96	0	1511	12	Over 24	630
123	V-1	320	6	○	94	0	1493	12	Over 24	660
124	W-1	320	6	○	94	0	1505	11	Over 24	680
125	X-1	320	8	○	92	0	1513	11	Over 24	700
126	Y-1	320	9	×	60	31	1210	15	12	300

[0096] The results shown in Tables 1 and 2 can be interpreted as follows (numbers in the following description are test Nos. in Table 2).

[0097] Test pieces Nos. 101 through 113 (inventive steel sheets 2) and test pieces Nos. 121 through 125 (inventive steel sheets 1) that satisfy the requirements of the present invention have high strength of 1180 MPa or higher, and high hydrogen embrittlement resisting property in harsh environment after the forming process. They also have high elongation property required of the TRIP steel sheet, thus providing steel sheets best suited for reinforcement parts of automobiles that are exposed to corrosive atmosphere. Test pieces Nos. 121 through 125, in particular, show even better hydrogen embrittlement resisting property.

[0098] Test pieces Nos. 114 through 120 and 126 that do not satisfy the requirements of the present invention, in contrast, have the following drawbacks.

[0099] No. 114 made of steel species N-1 that includes excessive amounts of C content does not have good weldability.

[0100] No. 115 made of steel species O-1 that includes insufficient Mn content does not retain sufficient residual austenite and is inferior in hydrogen embrittlement resisting property after the processing.

[0101] No. 116, martensite steel that is a conventional high strength steel made of steel species P-1 that includes insufficient Si content, hardly contains residual austenite and is inferior in hydrogen embrittlement resisting property. It also does not show the elongation property required of a thin steel sheet.

[0102] No. 117 made of steel species Q-1 that includes excessive C content has precipitation of carbide and is inferior in both forming workability and hydrogen embrittlement resisting property after processing.

[0103] No. 118 made of steel species R-1 that includes excessive Mo content and No. 119 made of steel species S-1 that includes excessive Nb content are inferior in forming workability. Nos. 118 and 119 could not undergo the processing, making it impossible to investigate the property after the processing.

[0104] No. 120, that was made of a steel that has the composition specified in the present invention but was not manufactured under the recommended conditions, resulted in the conventional TRIP steel. As a result, the residual austenite does not have the mean axis ratio specified in the present invention, while the matrix phase is not formed in binary phase structure of bainitic ferrite and martensite, and therefore sufficient level of hydrogen embrittlement resisting property is not achieved.

[0105] No. 126 includes Al content higher than that specified for the inventive steel sheet 1. As a result, although the predetermined amount of residual austenite is retained, the residual austenite does not have the mean axis ratio specified in the present invention, the desired matrix phase is not obtained and inclusions such as AlN are generated thus resulting in poor hydrogen embrittlement resisting property.

[0106] Then parts were made by using steel species A-1, J-1 shown in Table 1 and comparative steel sheet (590 MPa class high strength steel sheet of the prior art). Performance (pressure collapse resistance and impact resistance) of the formed test piece were studied by conducting pressure collapse test and impact resistance test as follows.

Pressure collapse test

[0107] The part 1 (hat channel as test piece) shown in Fig. 1. was made by using steel species A-1, J-1 shown in Table 1 and the comparative steel sheet, and was subjected to pressure collapse test. The part was spot welded at the positions 2 of the part shown in Fig. 1 at 35 mm intervals as shown in Fig. 1 by supplying electric current of a magnitude less than the expulsion generating current by 0.5 kA from an electrode measuring 6 mm in diameter at the distal end. Then a die 3 was pressed against the part 1 from above the mid portion thereof in the longitudinal direction as shown in Fig. 2, and the maximum tolerable load was determined. Absorbed energy was determined from the area under the load-deformation curve. The results are shown in Table 3.

[0108]

Table 3

Steel sheet used				Evaluation of test piece	
Steel species Symbol	TS	EL	Residual Y	Maximum load	Energy absorbed
	(MPa)	(%)	(Area %)	(kN)	(kJ)
A-1	1470	11	8	13.8	0.66
H-1	1540	10	8	14.3	0.7
Comparative steel sheet	613	22	0	5.7	0.33

[0109] From Table 3, it can be seen that the part (test piece) made from the steel sheet of the present invention has higher load bearing capability and absorbs greater energy than a part made of the conventional steel sheet having lower strength, thus showing high pressure collapse resistance.

Impact resistance test

[0110] The parts 4 (hat channel as test piece) shown in Fig. 3 were made by using steel species A-1, J-1 shown in Table 1 and the comparative steel sheet, and were subjected to impact resistance test. Fig. 4 is a sectional view along A-A of the part 4 shown in Fig. 3. In the impact resistance test, after the part was spot welded at the positions 5 of the part 4 similarly to the pressure collapse test, the part 4 was placed on a base 7 as schematically shown in Fig. 5. A weight 6 (weighing 10kg) was dropped onto the part 4 from a height of 11 meters, and the energy absorbed before the part 4 underwent deformation of 40 mm in the direction of height. The results are shown in Table 4.

[0111]

Table 4

Steel sheet used				Evaluation of test piece
Steel species Symbol	TS	EL	Residual γ	Energy absorbed
	(MPa)	(%)	(Area %)	(kJ)
A-1	1476	11	8	6.58
J-1	1540	10	8	6.87
Comparative steel sheet	613	22	0	3.56

[0112] From Table 4, it can be seen that the part (test piece) made from the steel sheet of the present invention absorbs greater energy than a part made of the conventional steel sheet that has lower strength, thus showing higher impact resistance.

[0113] TEM photograph of the test piece made in this example is shown as reference. Fig. 6 is a photograph of TEM observation of No. 101 of the present invention. From Fig. 6, it can be seen that the high strength thin steel sheet of the present invention contains lath-shaped residual austenite (black portion of bar shape in Fig. 6) specified in the present invention dispersed therein. Fig. 7 is a photograph of TEM observation of No. 120 of a comparative example. From Fig. 7, it can be seen that the high strength thin steel sheet of No. 120 contains residual austenite (black portion of somewhat round shape in Fig. 7), although the residual austenite has a block shape that does not satisfy the requirements of the present invention.

[Example 2]

[0114] By using sample steels A-2 through Y-2 having the compositions described in Table 5, test slabs were produced under the same requirements as that in Example 1(hot rolling, cold rolling and continuous annealing). In addition, No. 217 in Table 6 was prepared by the procedure of No.116 in Table 2 according to Example 1 to produce a known high strength martensite steel as a comparative example. No. 220 was prepared by the procedure of No.120 in Table 2 according to Example 1.

[0115] The metal structures of steel sheets obtained as described above, their tensile strength (TS) and elongation (total elongation E1) and hydrogen embrittlement resisting property were measured by the procedures in Example 1 and the following procedures.

Evaluation of hydrogen embrittlement resisting property

[0116] In order to evaluate hydrogen embrittlement resisting property, test pieces were produced by the same procedures as in Example 1. Then the test pieces were immersed in the same solution of hydrochloric acid as that in Example 1, and the time before crack occurred was measured.

The bent test pieces prepared as described in Example 1 were subjected to accelerated exposure test in which 3% solution of NaCl was sprayed once every day for 30 days simulating the actual operating environment, and the number of days before crack occurred was determined. In addition, hydrogen-charged 4-point bending test was also conducted for some steel species as is the case with Example 1. Maximum stress endured without breaking for 3 hours was determined as the critical fracture stress (DFL). Then the ratio (DFL ratio) of this value to the value of DFL of test No. 203 (steel species C-2) shown in Table 6 was determined.

Results of these tests are shown in Table 6.

Evaluation of weldability

[0117] Test of weldability was conducted on No.201 and No.215 which are representative steel species. As a result, it was found that No.201(present invention) is better than No.215(prior art) in reference to weldability because the ratio of ductibility in sample No.215 is 0.19 while that in sample No.201 is 0.22.

[0118]

Table 5

Steel species Symbol	Chemical composition (mass%)*													Ac3 (℃)	Bs (℃)	Ms (℃)
	C	Si	Mn	P	S	Al	Cuu	Ni	Ti	V	Nb	Mo	Others			
A-2	0.24	2.04	2.01	0.012	0.002	0.033	0.3	-	-	-	—	—	—	857.0	584.3	380.9
B-2	0.13	2.01	2.48	0.011	0.002	0.031	-	0.3	-	-	—	—	—	867.8	560.6	412.4
C-2	0.21	2.54	2.51	0.011	0.002	0.030	-	0.3	-	-	—	—	—	870.4	536.3	373.5
D-2	0.22	2.02	1.20	0.011	0.002	0.031	-	0.3	-	-	—	—	—	884.6	651.5	412.0
E-2	0.20	2.00	3.20	0.011	0.002	0.030	-	0.3	-	-	—	—	—	827.8	476.9	355.5
F-2	0.20	1.98	2.53	0.011	0.002	0.033	0.3	0.05	-	-	—	—	—	846.0	546.5	381.9
G-2	0.19	2.02	2.50	0.011	0.002	0.031	0.3	0.2	0.05	-	—	—	—	867.9	546.3	385.0
H-2	0.22	1.98	2.48	0.011	0.002	0.033	0.3	0.2	-	0.05	—	—	—	846.0	540.0	371.5
I-2	0.22	2.02	2.50	0.011	0.002	0.031	0.3	0.2	0.05	0.05	—	—	—	866.3	538.2	370.8
J-2	0.20	1.49	2.48	0.012	0.002	0.032	0.3	0.2	0.035	-	—	—	Zr:0.02	837.6	545.4	381.0
K-2	0.19	2.00	2.50	0.011	0.002	0.032	0.3	0.2	0.05	-	0.05	0.2	—	873.7	529.7	380.8
L-2	0.21	2.01	2.50	0.011	0.002	0.033	0.3	0.2	0.05	-	0.06	0.2	—	870.0	524.3	371.4
M-2	0.17	1.98	2.50	0.011	0.002	0.032	0.3	0.2	0.05	-	0.05	0.2	B:0.0005	877.6	535.1	390.3
N-2	0.20	2.01	2.50	0.011	0.002	0.033	0.3	0.2	0.05	-	0.05	0.2	Ca:0.004, Mg:0.005	872.2	527.0	376.1
O-2	0.30	2.00	2.00	0.014	0.005	0.031	-	0.3	-	-	—	—	—	845.9	557.9	347.7
P-2	0.25	2.50	0.90	0.014	0.005	0.031	-	0.3	-	-	—	—	—	910.9	670.4	407.7
Q-2	0.20	0.16	1.42	0.014	0.002	0.043	-	0.3	-	-	—	—	—	806.2	637.1	414.2
R-2	0.05	2.01	2.01	0.012	0.002	0.033	-	0.3	-	-	—	—	—	911.2	624.5	465.9
S-2	0.21	2.02	1.20	0.012	0.002	0.033	-	-	-	-	—	—	—	892.9	665.3	421.9
T-2	0.24	2.04	2.01	0.011	0.002	0.052	0.3	-	-	-	—	—	—	863.9	584.3	380.9
U-2	0.23	2.01	2.00	0.012	0.002	0.276	0.3	0.2	-	-	—	—	—	952.3	580.5	382.6
V-2	0.25	1.99	2.02	0.011	0.002	0.355	0.3	0.3	0.05	-	—	—	—	996.0	569.6	370.7
W-2	0.23	2.02	1.99	0.011	0.002	0.751	0.3	0.2	0.05	-	0.05	0.2	—	1168.6	564.8	378.7
X-2	0.23	2.00	2.02	0.012	0.002	1.02	0.3	0.2	0.05	-	0.05	0.2	Ca:0.004 Mg:0.005	1275.1	562.1	377.7
Y-2	0.24	1.98	2.00	0.011	0.002	1.66	0.3	0.2	0.05	-	0.05	0.2	—	1528.0	561.2	373.6

* The balance consists of iron and inevitable impurities.

[0119]

Table 6

Test No.	Steel species Symbol	To	Residual γ	Mean axis ratio of residual γ	BF+M	other	TS	El	Hydrochloric acid immersion	Exposure test	DFL ratio
		℃	%		%	%	MPa	%	h	day	–
201	A-2	320	8	○	92	0	1492	12	Over 24	Over 30	–
202	B-2	320	3	○	97	0	1210	14	Over 24	Over 30	1.00
203	C-2	300	7	○	92	1	1234	14	Over 24	Over 30	–
204	D-2	320	7	○	93	0	1533	11	Over 24	Over 30	–
205	E-2	350	8	○	92	0	1467	12	Over 24	Over 30	–
206	F-2	320	7	○	93	0	1511	11	Over 24	Over 30	–
207	G-2	320	8	○	92	0	1492	11	Over 24	Over 30	–
208	H-2	320	8	○	92	0	1532	12	Over 24	Over 30	–
209	I-2	320	8	○	92	0	1567	11	Over 24	Over 30	–
210	J-2	320	7	○	93	0	1461	12	Over 24	Over 30	–
211	K-2	320	7	○	93	0	1519	11	Over 24	Over 30	–
212	L-2	320	7	○	93	0	1495	11	Over 24	Over 30	–
213	M-2	320	6	○	94	0	1490	12	Over 24	Over 30	–
214	N-2	320	7	○	93	0	1503	11	Over 24	Over 30	–
215	O-2	300	8	○	92	0	1562	11	12	15	–
216	P-2	320	<1	×	99	<1	1313	8	8	9	–
217	Q-2	–	<1	×	99	<1	1488	3	3	5	–
218	R-2	370	<1	×	99	<1	992	17	Over 24	Over 30	–
219	S-2	320	5	○	94	1	1448	10	Over 24	17	–
220	A-2	350	12	×	20	68	961	14	Over 24	Over 30	–
221	T-2	300	7	○	93	0	1495	11	Over 24	Over 30	1.24
222	U-2	300	8	○	92	0	1509	12	Over 24	Over 30	1.56
223	V-2	320	8	○	92	0	1512	11	Over 24	Over 30	1.66
224	W-2	320	8	○	92	0	1513	12	Over 24	Over 30	1.71
225	X-2	320	9	○	91	0	1504	11	Over 24	Over 30	1.78
226	Y-2	320	10	×	61	29	1230	14	13	16	0.73

[0120] The results shown in Tables 5 and 6 can be interpreted as follows (numbers in the following description are test Nos. in Table 6).

Test pieces Nos. 201 through 214 (inventive steel sheets 2) and test pieces Nos. 221 through 225 (inventive steel sheets 1) that satisfy the requirements of the present invention have high strength of 1180 MPa or higher, and high hydrogen embrittlement resisting property in harsh environment after the forming process. They also have high elongation property required of the TRIP steel sheet, thus providing steel sheets best suited for reinforcement parts of automobiles that are exposed to corrosive atmosphere. Test pieces Nos. 221 through 225, in particular, show even better hydrogen embrittlement resisting property.

[0121] Test pieces Nos. 215 through 220 and 226 that do not satisfy the requirements of the present invention, in contrast, have the following drawbacks.

[0122] No. 215 made of steel species O-2 that includes insufficient C content has the amount of residual austenite significantly decreased after the processing, and fails to show the required level of hydrogen embrittlement resisting property of the present invention.

[0123] No. 216 made of steel species P-2 that includes insufficient Mn content does not retain sufficient residual austenite and is inferior in hydrogen embrittlement resisting property after the processing.

[0124] No. 217, martensite steel that is a conventional high strength steel made of steel species Q-2 that includes insufficient Si content, hardly contains residual austenite and is inferior in hydrogen embrittlement resisting property. It also does not show the elongation property required of a thin steel sheet.

[0125] No. 218 made of steel species R-2 that includes excessive C content has precipitation of carbide and is inferior in both the forming workability and the hydrogen embrittlement resisting property after processing. No. 219 made of steel species S-2 that does not include Cu and/or Ni shows insufficient corrosion resistance and fails to show the required level of hydrogen embrittlement resisting property of the present invention.

[0126] No. 220, that was made of a steel that has the composition specified in the present invention but was not manufactured under the recommended conditions, resulted in the conventional TRIP steel. As a result, the residual austenite does not have the mean axis ratio specified in the present invention, while the matrix phase is not formed in binary phase structure of bainitic ferrite and martensite, and therefore sufficient level of hydrogen embrittlement resisting property is not achieved.

[0127] No. 226 includes Al content higher than that specified for the inventive steel sheet 1. As a result, although the predetermined amount of residual austenite is retained, the residual austenite does not have the mean axis ratio specified in the present invention, the desired matrix phase is not obtained and inclusions such as AlN are generated thus resulting in poor hydrogen embrittlement resisting property.

[0128] Then parts were made by using steel species A-2, I-2 shown in Table 5 and comparative steel sheet (590 MPa class high strength steel sheet of the prior art). Performance (pressure collapse resistance and impact resistance) of the formed test piece were studied by conducting pressure collapse test and impact resistance test as follows.

Pressure collapse test

[0129] Maximum tolerable load was determined similarly to Example 1 by using steel species A-2, K-2 shown in Table 5 and the comparative steel sheet. Absorbed energy was determined from the area lying under the load-deformation curve. The results are shown in Table 7.

[0130]

Table 7

Steel sheet used				Evaluation of test piece	
Steel species Symbol	TS	EL	Residual γ	Maximum load	Energy absorbed
	(Mpa)	(%)	(Area%)	(kN)	(kJ)
A-2	1492	12	8	13.9	0.68
I-2	1567	11	8	14.6	0.71
Comparative steel sheet	613	22	0	5.7	0.33

[0131] From Table 7, it can be seen that the part (test piece) made from the steel sheet of the present invention has higher load bearing capability and absorbs greater energy than a part made of the conventional steel sheet that has lower strength, thus showing higher pressure collapse resistance.

Impact resistance test

[0132] The impact resistance test was conducted similarly to Example 1 on the steel sheets made of steel species A-2, K-2 shown in Table 5 and the comparative steel sheet. The results are shown in Table 8.

[0133]

Table 8

Steel sheet used			Evaluation of test piece	
Steel species Synbol	TS	EL	Residual γ	Energy absorbed
	(MPa)	(%)	(Area %)	(Kj)
A-2	1492	12	8	6.65
I-2	1567	11	8	6.99
Comparative steel sheet	613	22	0	3.56

[0134] From Table 8, it can be seen that the part (test piece) made from the steel sheet of the present invention absorbs greater energy than a part made of the conventional steel sheet having lower strength, thus showing higher impact resistance.

[0135] TEM photograph of the test piece made in this example is shown as reference. Fig. 8 is a photograph of TEM observation of No. 201 of the present invention. From Fig. 8, it can be seen that the high strength thin steel sheet of the present invention contains lath-shaped residual austenite (black portion of bar shape in Fig. 8) specified in the present invention dispersed therein. Fig. 9 is a photograph of TEM observation of No. 220 of a comparative example. From Fig. 9, it can be seen that the high strength thin steel sheet of No. 220 contains residual austenite (black portion of somewhat round shape in Fig. 9), although the residual austenite has a block shape that does not satisfy the requirements of the present invention.

[Example 3]

[0136] By using sample steels A-3 through R-3 having the compositions described in Table 9, test slabs were produced under the same conditions as that in Example 1(hot rolling, cold rolling and continuous annealing). In addition, No.312 in Table 10 was prepared by the procedure of No.116 in Table 2 according to Example 1 to produce a known high strength martensite steel as a comparative example. No. 313 was prepared by the procedure of No.120 in Table 2 according to Example 1.

[0137] The metal structures of steel sheets obtained as described above, their tensile strength (TS) and elongation (total elongation E1) and hydrogen embrittlement resisting property were measured by the procedures in Example 1 and the following procedures.

Evaluation of hydrogen embrittlement resisting property

[0138] In order to evaluate the hydrogen embrittlement resisting property, flat test piece 1.2 mm in thickness was subjected to slow stretching rate test (SSRT) with a stretching speed of 1×10^{-4}/sec, to determine hydrogen embrittlement risk index (%) defined by the equation shown below.

$$\text{Hydrogen embrittlement risk index (\%)} = 100 \times (1-E1/E0)$$

[0139] E0 represents the elongation before rupture of a steel test piece that does not substantially contain hydrogen, E1 represents the elongation before rupture of a steel test piece that has been charged with hydrogen electrochemically in sulfuric acid. Hydrogen charging was carried out by immersing the steel test piece in a mixed solution of H_2SO_4 (0.5 mol/L) and KSCN (0.01 mol/L) and supplying constant current (100A/m^2) at room temperature.

[0140] A steel sheet having hydrogen embrittlement risk index higher than 50% is likely to undergo hydrogen embrittlement during use. In the present invention, steel sheets having hydrogen embrittlement risk index not higher than 50% were evaluated to have high hydrogen embrittlement resisting property. Results of the test are shown in Table 10.

Evaluation of weldability

[0141] Test of weldability was conducted on No.201 and No.215 which are representative steel species. As a result, it was found that No. 301 (present invention) is better than No.311 (prior art) in reference to weldability because the ratio of ductibility in sample No.311 is 0.19 while that in sample No.301 is 0.22.

[0142]

Table 9

Steel species Symbol	Chemical composition (mass%)*													Ac3 (℃)	Bs (℃)	Ms (℃)
	C	Si	Mn	P	S	Al	Cu	Ni	Ti	V	Nb	Mo	Other			
A-3	0.21	2.02	2.50	0.011	0.002	0.031	-	-	-	-	—	—	—	852.4	548.3	379.0
B-3	0.22	1.98	2.52	0.011	0.002	0.033	-	0.2	-	-	—	—	—	845.6	536.4	370.2
C-3	0.24	2.04	2.01	0.012	0.002	0.033	0.3	0.2	0.035	-	—	—	—	868.0	576.9	377.5
D-3	0.19	1.98	2.53	0.011	0.002	0.033	0.3	0.2	0.05	0.05	—	—	—	871.2	543.6	384.1
E-3	0.21	2.02	2.51	0.011	0.002	0.030	-	-	0.05	0.05	—	—	—	876.9	547.4	378.6
F-3	0.22	1.98	2.48	0.011	0.002	0.031	-	-	-	-	0.05	0.2	—	855.3	530.8	370.7
G-3	0.20	2.00	2.53	0.011	0.002	0.030	-	-	-	-	—	—	B:0.0005	852.4	548.3	382.7
H-3	0.18	1.98	2.50	0.011	0.002	0.032	-	-	-	0.05	0.05	0.2	B:0.0005	869.4	539.8	389.0
I-3	0.21	2.01	2.50	0.011	0.002	0.033	0.3	0.3	0.05		0.05	0.2	Ca:0.004, Mg:0.005	868.5	520.6	369.7
J-3	0.22	1.98	2.48	0.011	0.002	0.033	-	-	-	-	—	—	REM:0.005	849.8	547.4	374.9
K-3	0.40	2.00	2.00	0.014	0.005	0.031	-	-	-	-	—	—	—	833.2	542.0	305.4
L-3	0.20	0.16	1.42	0.014	0.002	0.043	-	-	-	-	—	—	—	810.8	648.2	419.3
M-3	0.21	2.00	2.48	0.011	0.002	0.051	-	-	-	-	—	—	—	860.1	550.1	379.6
N-3	0.20	2.02	2.50	0.012	0.002	0.251	0.3	0.2	-	-	—	—	—	934.3	543.6	380.3
O-3	0.22	1.99	2.51	0.012	0.002	0.374	0.3	0.2	0.05	0.05	—	—	—	997.4	537.3	370.5
P-3	0.21	2.01	2.51	0.012	0.002	0.750	0.3	0.3	0.05	0.05	—	—	—	1149.4	536.3	373.5
Q-3	0.21	2.02	2.55	0.012	0.002	1.03	0.3	0.3	0.05	0.05	0.05	0.2	Ca:0.004, Mg:0.005	1266.9	516.1	368.0
R-3	0.21	2.00	2.60	0.011	0.002	1.68	-	-	-	-	-	-	-	1508.1	539.3	375.7

* The balance consists of iron and inevitable impurities.

[0143]

Table 10

Test No.	Steel species Symbol	To	Residual γ	Mean axis of residual γ (nm)	Minimum distance between residual γ grains (nm)	Mean axis ratio of residual γ	BF+M	Other	TS	El	Hydrogen embrittlement risk index (%)
		℃	%				%	%	MPa	%	
301	A-3	350	8	160	320	10	92	0	1280	14	28
302	B-3	350	9	170	340	7	91	0	1310	14	30
303	C-3	320	8	140	280	15	92	0	1480	12	25
304	D-3	320	8	130	260	20	92	0	1495	11	23
305	E-3	320	8	120	240	25	92	0	1460	11	18
306	F-3	320	8	140	280	15	92	0	1490	11	30
307	G-3	320	7	120	240	25	93	0	1470	10	20
308	H-3	320	7	110	220	30	93	0	1480	11	18
309	I-3	300	6	90	180	40	93	1	1470	10	15
310	J-3	300	6	80	160	50	93	1	1470	10	12
311	K-3	350	15	270	520	20	85	0	1520	10	40
312	L-3	350	<1	-	-	-	99	<1	1400	8	90
313	A-3	350	11	1300	1200	1.5	20	69	960	15	85
314	M-3	350	8	190	380	10	92	0	1290	14	28
315	N-3	320	7	140	280	13	93	0	1410	13	22
316	O-3	320	7	130	260	12	93	0	1480	12	19
317	P-3	320	7	130	260	12	93	0	1509	11	19
318	Q-3	320	7	120	240	11	93	0	1513	11	14
319	R-3	350	12	1000	1200	3	59	29	1295	14	75

[0144] The results shown in Tables 9 and 10 can be interpreted as follows (numbers in the following description are test Nos. in Table 10).

[0145] Test pieces Nos. 301 through 310 (inventive steel sheets 2) and test pieces Nos. 314 through 318 (inventive steel sheets 1) that satisfy the requirements of the present invention have high strength of 1180 MPa or higher, and show high hydrogen embrittlement resisting property in harsh environment after the forming process. They also have high elongation property required of the TRIP steel sheet, thus providing steel sheets best suited for reinforcement parts of automobiles that are exposed to corrosive atmosphere.

[0146] Test pieces Nos. 311 through 313 and 319 that do not satisfy the requirements of the present invention, in contrast, have the following drawbacks.

[0147] No. 311 made of steel species K-3 that includes excessive C content has carbide precipitated and residual austenite of longer mean length of minor axis, thus resulting poor performance in both workability and hydrogen embrittlement resisting property after processing.

[0148] No. 312, martensite steel that is a conventional high strength steel made of steel species L-3 that includes insufficient Si content, hardly contains residual austenite and is inferior in hydrogen embrittlement resisting property. It also does not show the elongation property required of a thin steel sheet.

[0149] No. 313, that was made of a steel that has the composition specified in the present invention but was not manufactured under the recommended conditions, resulted in the conventional TRIP steel. As a result, the residual austenite does not have the mean axis ratio and the mean length of minor axis specified in the present invention, while the matrix phase is not formed in binary phase structure of bainitic ferrite and martensite, thus resulting in low strength and poor hydrogen embrittlement resisting property.

[0150] No. 319 includes Al content higher than that specified for the inventive steel sheet 1. As a result, although the predetermined amount of residual austenite is retained, the residual austenite does not have the mean axis ratio specified in the present invention, the desired matrix phase is not obtained and inclusions such as AlN are generated thus resulting in poor hydrogen embrittlement resisting property.

[0151] Then parts were made by using steel species A-3, D-3 shown in Table 9 and comparative steel sheet (590 MPa class high strength steel sheet of the prior art). Performance (pressure collapse resistance and impact resistance) of the formed test piece were studied by conducting pressure collapse test and impact resistance test as follows.

Pressure collapse test

[0152] Maximum tolerable load was determined similarly to Example 1 by using steel species A-3, D-3 shown in Table 9 and the comparative steel sheet. Absorbed energy was determined from the area under the load-deformation curve. The results are shown in Table 11.

[0153]

Table 11

Steel sheet used				Evaluation of test piece	
Steel species Symbol	TS	EL	Residual ϒ	Maximum load	Energy absorbed
	(MPa)	(%)	(Area %)	(kN)	(kJ)
A-3	1280	14	8	12	0.6
D-3	1495	11	8	13.9	0.67
Comparative steel sheet	613	22	0	5.7	0.33

[0154] From Table 11, it can be seen that the part (test piece) made from the steel sheet of the present invention has higher load bearing capability and absorbs greater energy than a part made of the conventional steel sheet having lower strength, thus showing high pressure collapse resistance.

Impact resistance test

[0155] The impact resistance test was conducted similarly to Example 1 on the steel sheets made of steel species A-3, D-3 shown in Table 9 and the comparative steel sheet. The results are shown in Table 12.

[0156]

Table 12

Steel sheet used				Evaluation of test piece
Steel species Symbol	TS	EL	Residual ϒ	Energy absorbed
	(MPa)	(%)	(Area %)	(kJ)
A-3	1280	14	8	5.95
D-3	1495	11	8	6.77

Table continued

Steel sheet used				Evaluation of test piece
Steel species Symbol	TS	EL	Residual ϒ	Energy absorbed
	(MPa)	(%)	(Area %)	(kJ)
Comparative steel sheet	613	22	0	3.56

[0157] From Table 12, it can be seen that the part (test piece) made from the steel sheet of the present invention absorbs greater energy than a part made of the conventional steel sheet that has lower strength, thus showing high impact resistance.

[0158] TEM photographs of the test pieces made in this example are shown as reference. Fig. 12 is a photograph of TEM observation (magnification factor 15000) of No. 301 of the present invention. Fig. 13 is a photograph of TEM observation (magnification factor 60,000) of a portion shown in the photograph of Fig. 12. From Figs. 12, 13, it can be seen that the high strength thin steel sheet of the present invention contains fine residual austenite grains (black portion of bar shape in Figs. 12, 13) specified in the present invention dispersed therein, and that the residual austenite has the lath shape specified in the present invention. Fig. 14 is a photograph of TEM observation of No. 313 of a comparative example. From Fig. 14, it can be seen that the high strength thin steel sheet of No. 313 contains residual austenite (black portion of somewhat round shape in Fig. 14), although the residual austenite has a block shape that does not satisfy the requirements of the present invention.

Claims

1. A high strength thin steel sheet having high hydrogen embrittlement resisting property, which comprises:

C: 0.10 to 0.25%;
Si: 1.0 to 3.0%;
Mn: 1.0 to 3.5%;
P: 0.15% or less;
S: 0.02% or less; and
Al: 1.5% or less (higher than 0%) in terms of percentage by weight, with balance of iron and inevitable impurities;

wherein the metal structure comprises:

residual austenite: 1% by area or more in proportion to the entire structure;
bainitic ferrite and martensite: 80% or more in total; and
ferrite and pearlite: 9% or less (may be 0%) in total,
while the mean axis ratio (major axis/minor axis) of said residual austenite grains is 5 or higher, and
the steel has tensile strength of 1180 MPa or higher.

2. The high strength thin steel sheet according to claim 1,
wherein the metal structure further satisfies the requirements that:

mean length of minor axes of said residual austenite grains is 1 μm or less; and
minimum distance between said residual austenite grains is 1 μm or less.

3. A high strength thin steel sheet having high hydrogen embrittlement resisting property, which comprises:

C: 0.10 to 0.25%;
Si: 1.0 to 3.0%;
Mn: 1.0 to 3.5%;
P: 0.15% or less;
S: 0.02% or less; and
Al: 1.5% or less (higher than 0%) in terms of percentage by weight,
with balance of iron and inevitable impurities,
wherein the metal structure comprises:

residual austenite of 1% by area or more in proportion to the entire structure,
while the mean axis ratio (major axis/minor axis) of said residual austenite grains is 5 or higher; mean length of minor axes of said residual austenite grains is 1 μm or less; and
minimum distance between said residual austenite grains is 1 μm or less; and
the steel has tensile strength of 1180 MPa or higher.

4. The high strength thin steel sheet according to any one of claims 1 to 3, wherein 0.5% or less (higher than 0%) by weight of Al is contained.

5. The high strength thin steel sheet according to any one of claims 1 to 4, wherein
0.003 to 0.5% of Cu and/or
0.003 to 1.0% of Ni
in terms of percentage by weight are further contained.

6. The high strength thin steel sheet according to any one of claims 1 to 5, wherein
0.003 to 1.0% of Ti and/or V
in terms of percentage by weight are further contained.

7. The high strength thin steel sheet according to any one of claims 1 to 6, wherein
1.0% or less (higher than 0%) of Mo and
0.1% or less (higher than 0%) of Nb
in terms of percentage by weight are further contained.

8. The high strength thin steel sheet according to any one of claims 1 to 7, wherein 0.0002 to 0.01% of B in terms of percentage by weight is further contained.

9. The high strength thin steel sheet according to any one of claims 1 to 8, wherein at least one element selected from the group consisting of:
0.0005 to 0.005% of Ca;
0.0005 to 0.01% of Mg; and
0.0005 to 0.01% of REM
in terms of percentage by weight is further contained.

Fig. 1

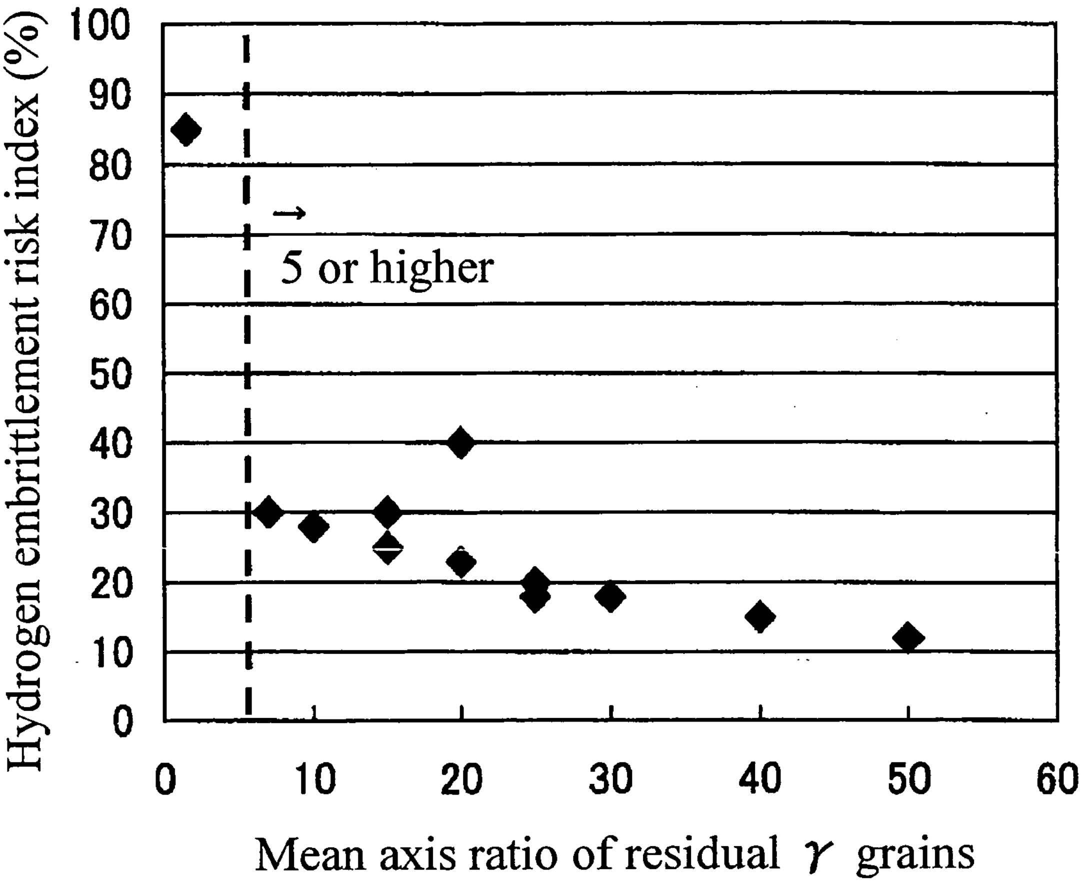

Hydrogen embrittlement risk index (%)
100
90
80
70
60
50
40
30
20
10
0
→
5 or higher
0
10
20
30
40
50
60
Mean axis ratio of residual γ grains

Fig.2

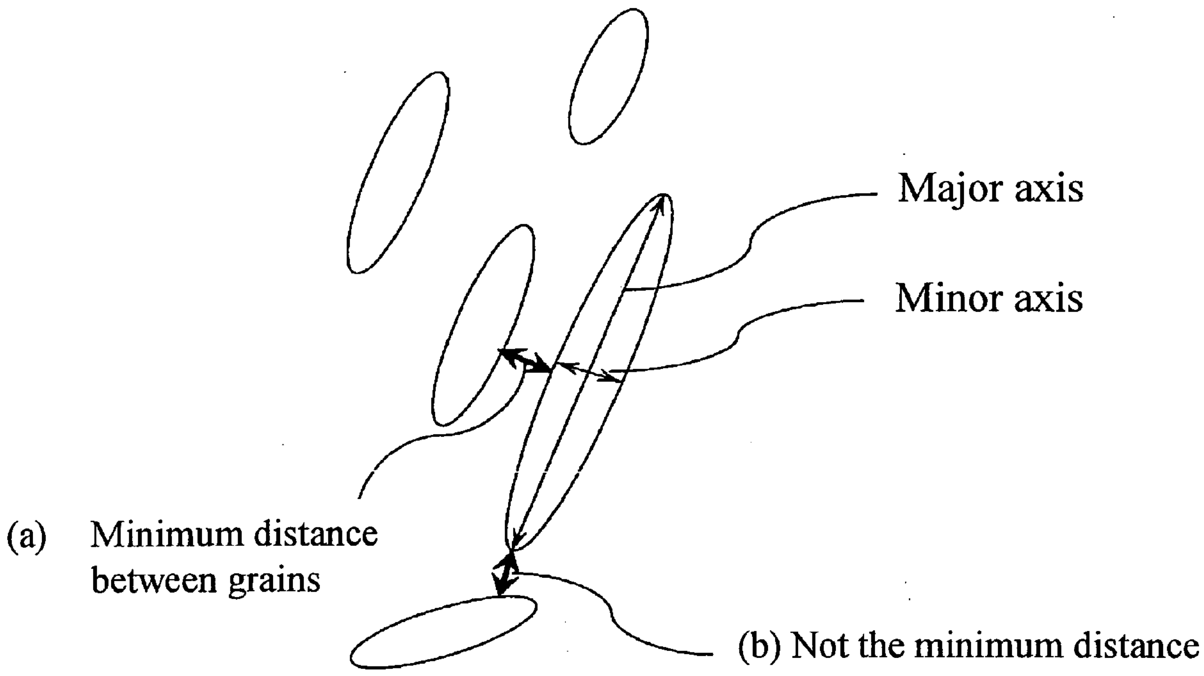

Major axis
Minor axis
(a) Minimum distance between grains
(b) Not the minimum distance

Fig. 3

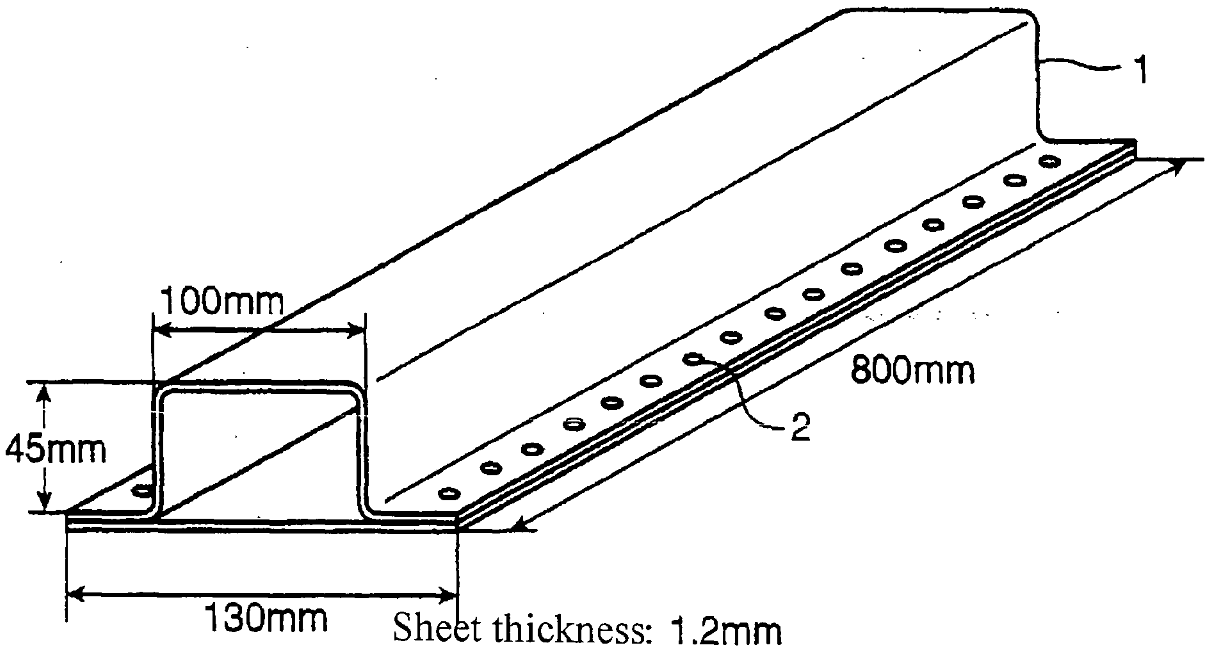


Fig. 4

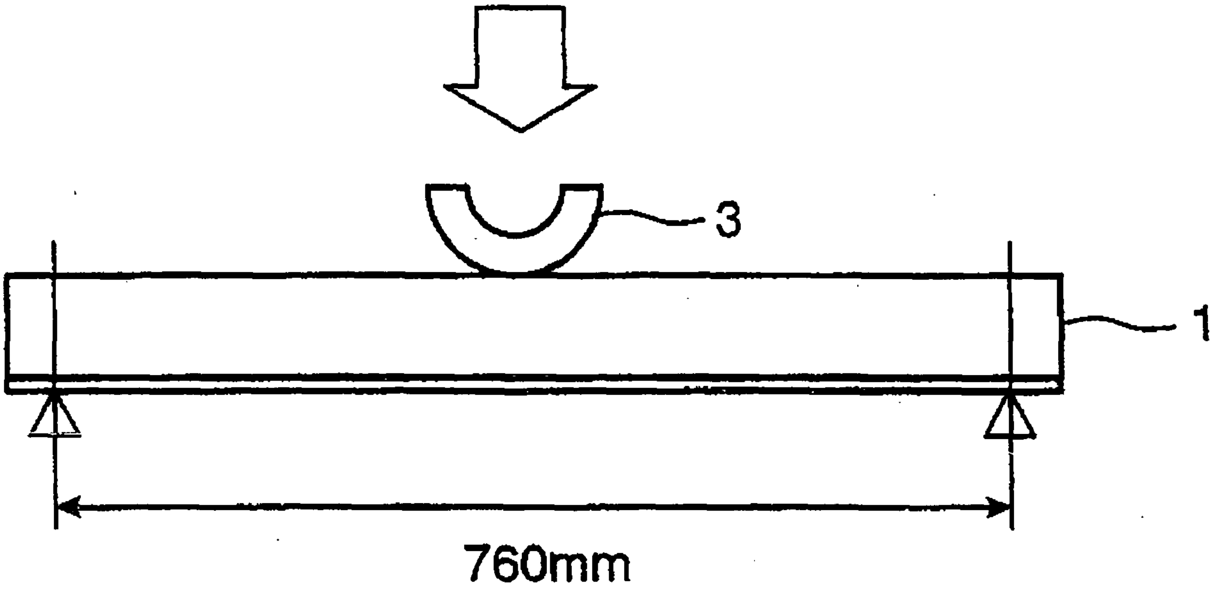


Fig. 5

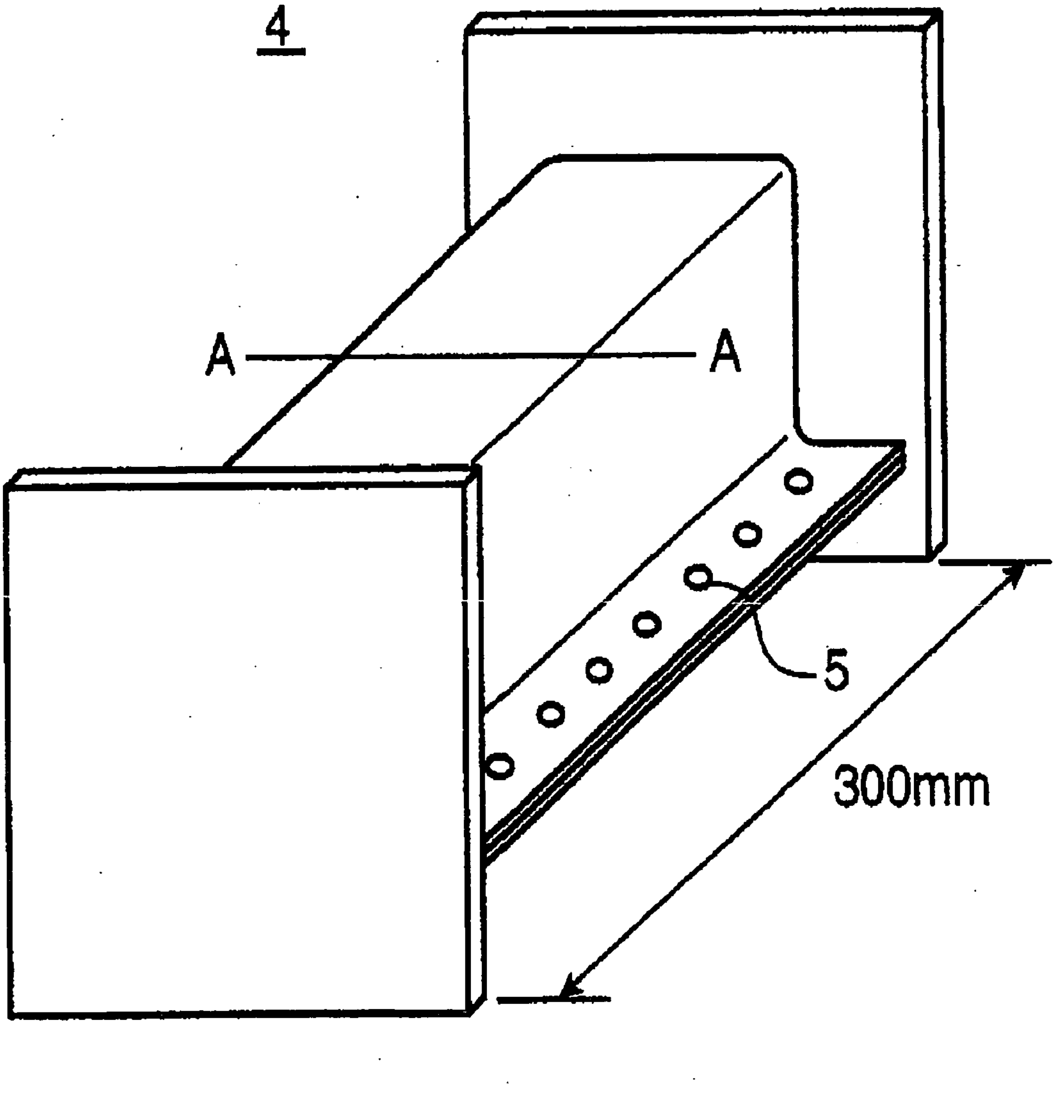


Fig. 6

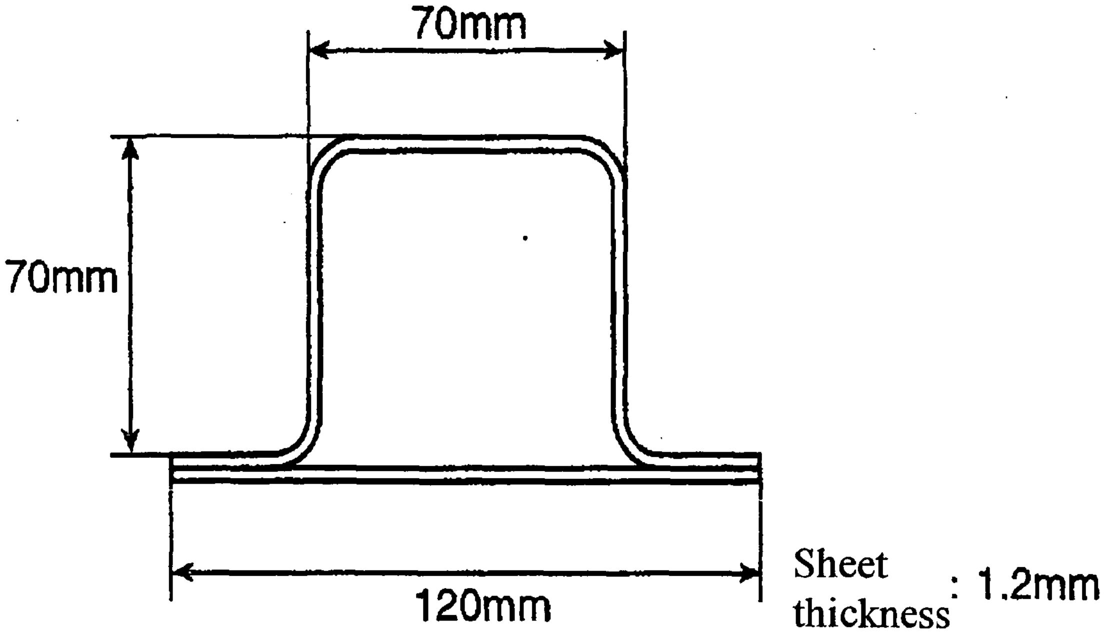


Fig. 7

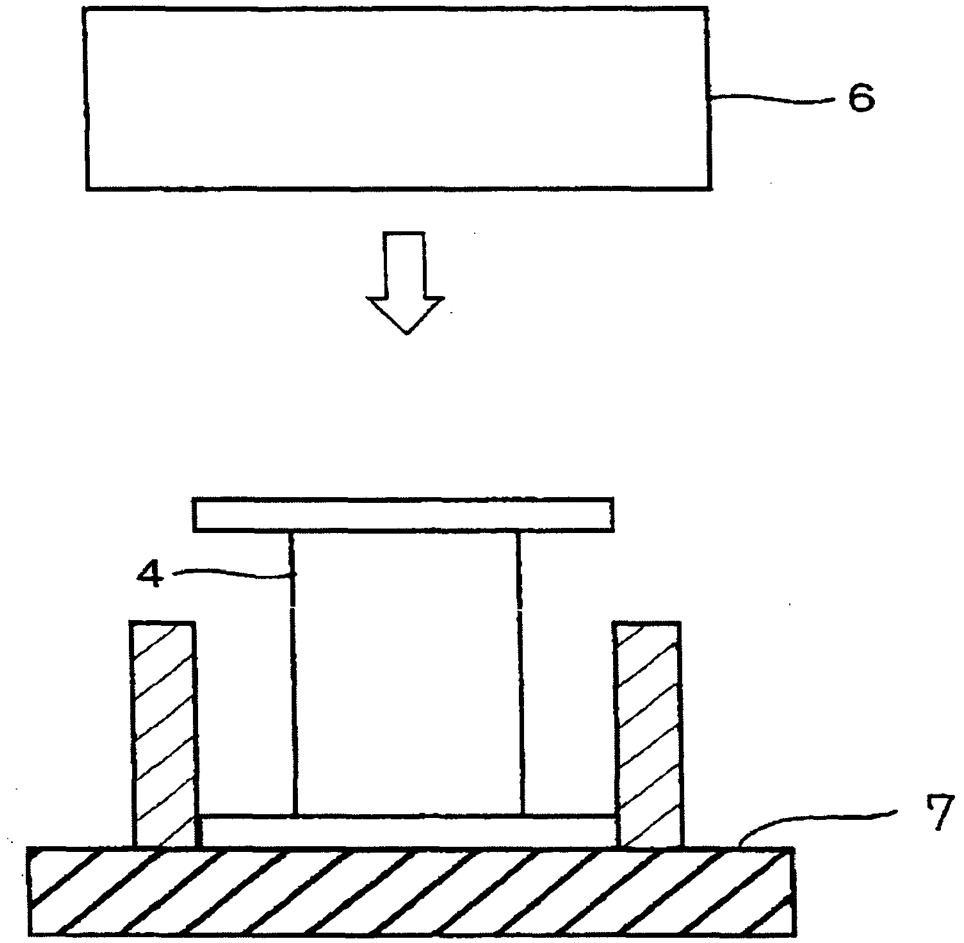


Fig. 8

Fig. 9

Fig. 10

Fig. 11

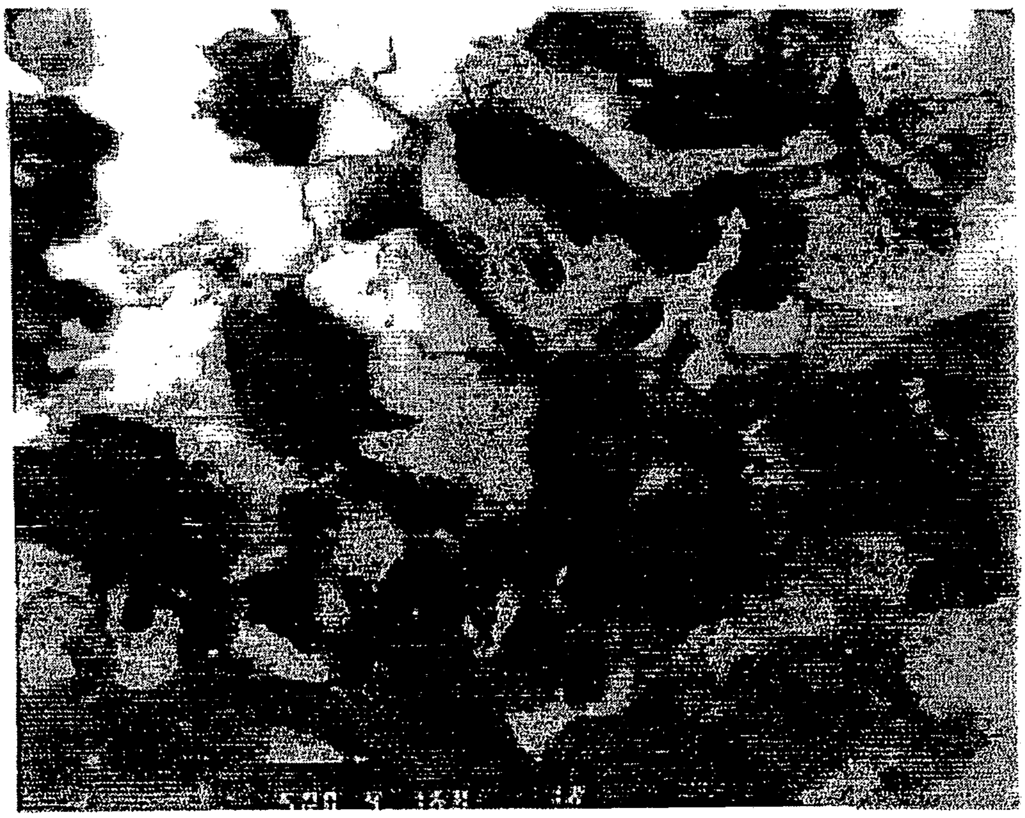


Fig. 12

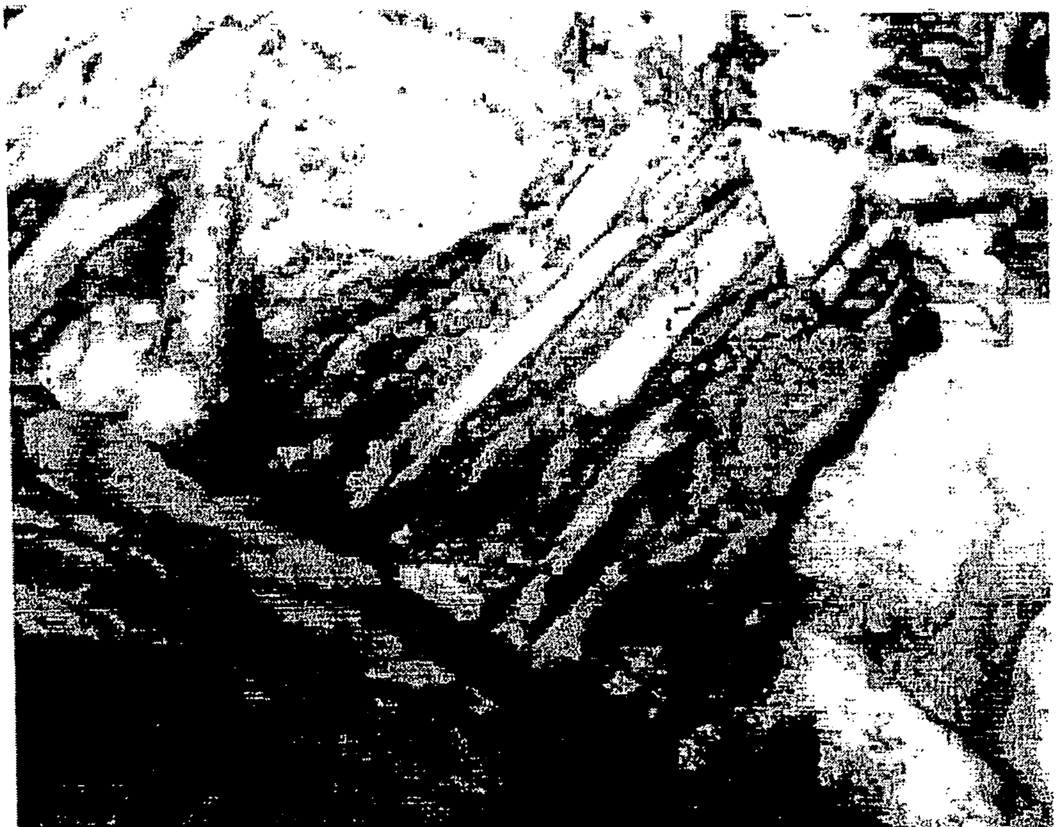


Fig. 13

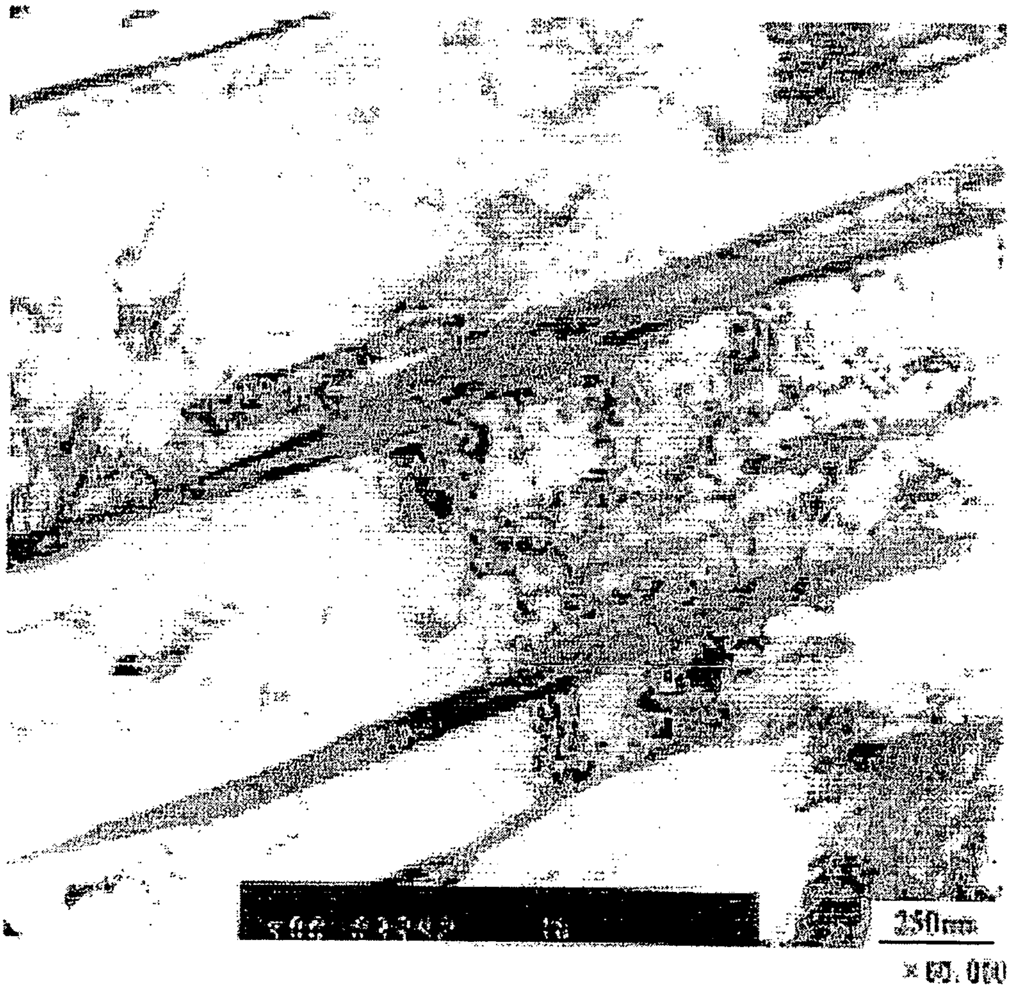
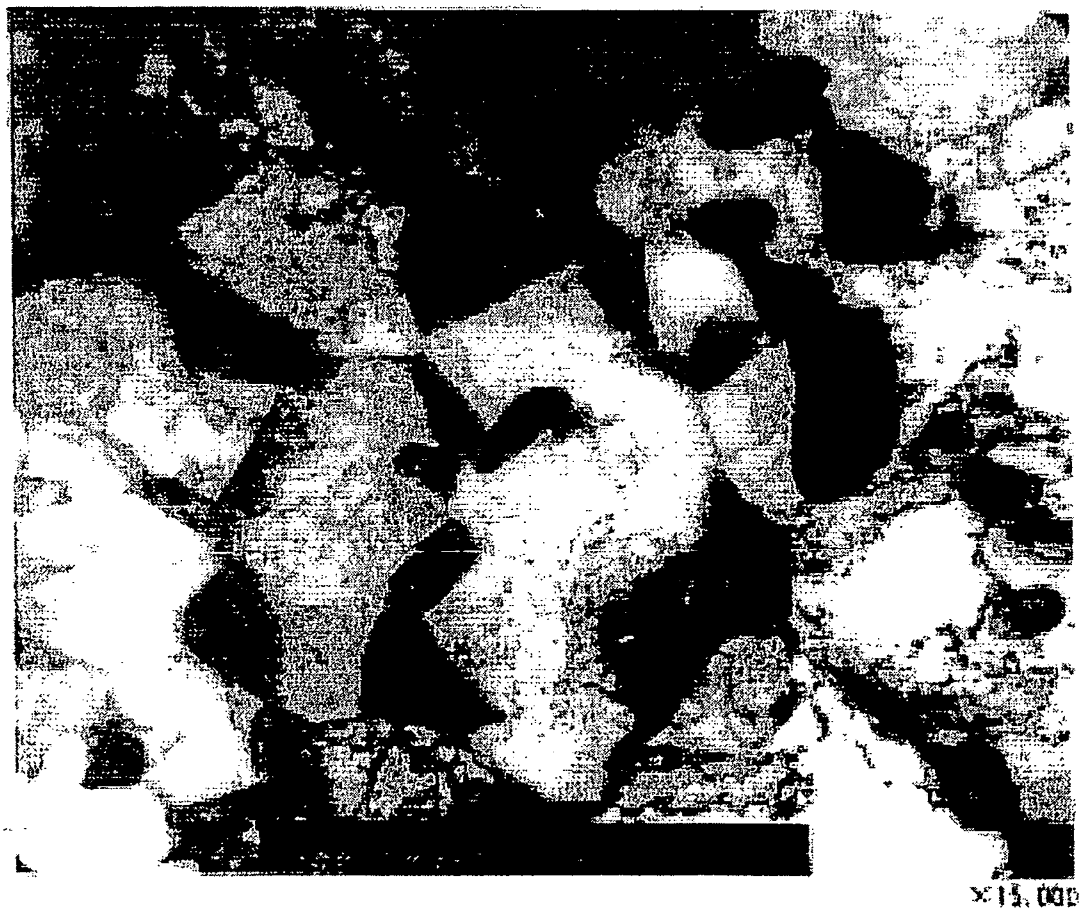


Fig. 14



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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	24 February 2006	Lilimpakis, E

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EUROPEAN SEARCH REPORT

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