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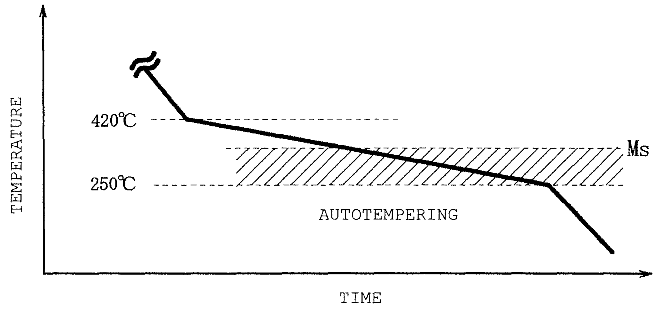
(54) HIGH-STRENGTH STEEL SHEET AND PROCESS FOR PRODUCTION THEREOF

(57) There is provided a high strength steel sheet having a tensile strength of 900 MPa or higher that can achieve both high strength and good formability. The high strength steel sheet has a composition including, on a mass basis, C: 0.1% or more and 0.3% or less; Si: 2.0% or less; Mn: 0.5% or more and 3.0% or less; P: 0.1% or less; S: 0.07% or less; Al: 1.0% or less; and N: 0.008% or less, with the balance Fe and incidental impurities. In the high strength steel sheet, a steel microstructure includes, on an area ratio basis, 5% or more and 80% or less of ferrite, 15% or more of autotempered martensite, 10% or less of bainite, 5% or less of retained austenite, and 40% or less of as-quenched martensite; the mean hardness of the autotempered martensite is HV ≤ 700; and the mean number of precipitated iron-based carbide grains each having a size of 5 nm or more and 0.5 μm or less and included in the autotempered martensite is 5 × 10^4 or more per 1 mm^2.

FIG.2



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Description

Technical Field

[0001] The present invention relates to a high strength steel sheet that is used in industrial fields such as an automobile industry and an electrical industry, has good formability, and has a tensile strength of 900 MPa or higher and a method for manufacturing the same. The high strength steel sheet of the present invention includes steel sheets whose surface is galvanized or galvannealed.

Background Art

[0002] In recent years, the improvement in the fuel efficiency of automobiles has been an important subject from the viewpoint of global environment conservation. Therefore, by employing a high strength automobile material, there has been an active move to reduce the thickness of components and thus to lighten the automobile body itself. However, since an increase in the strength of steel sheets reduces workability, the development of materials having both high strength and good workability has been demanded. To satisfy such a demand, various multiple-phase steel sheets such as a ferrite-martensite dual-phase steel (DP steel) and a TRIP steel that uses transformation-induced plasticity of retained austenite have been developed.

[0003] For example, the following Patent Documents disclose DP steels. Patent Document 1 discloses a high strength steel sheet with a low yield ratio that is excellent in surface quality and bendability and has a tensile strength of 588 to 882 MPa and a method for manufacturing the steel sheet, by specifying the composition and the hot-rolling and annealing conditions. Patent Document 2 discloses a high strength cold-rolled steel sheet with excellent bendability and a method for manufacturing the steel sheet, by specifying the hot-rolling, cold-rolling, and annealing conditions of steel having a certain composition. Patent Document 3 discloses a steel sheet that is excellent in collision safety and formability and a method for manufacturing the steel sheet, by specifying the volume fraction and grain diameter of martensite and the mechanical properties. Patent Document 4 discloses a high strength steel sheet, a high strength galvanized steel sheet, and a high strength galvannealed steel sheet that are excellent in stretch-flangeability and crashworthiness and a method for manufacturing the steel sheets, by specifying the composition and the volume fraction and grain diameter of martensite. Patent Document 5 discloses a high strength steel sheet, a high strength galvanized steel sheet, and a high strength galvannealed steel sheet that are excellent in stretch-flangeability, shape fixability, and crashworthiness and a method for manufacturing the steel sheets, by specifying the composition, the grain diameter and microstructure of ferrite, and the volume fraction of martensite. Patent Document 6 discloses a high strength steel sheet having excellent mechanical properties and a method for manufacturing the steel sheet, by specifying the composition, the amount of martensite, and the manufacturing method. Patent Documents 7 and 8 each disclose a high strength galvanized steel sheet that is excellent in stretch-flangeability and bendability and a method and facility for manufacturing the steel sheet, by specifying the composition and the manufacturing conditions in a galvanizing line.

[0004] The following Patent Documents disclose steel sheets having a microstructure including a phase other than martensite as a hard second phase. Patent Document 9 discloses a steel sheet that is excellent in fatigue properties, by employing martensite and/or bainite as a hard second phase and specifying the composition, the grain diameter, the hardness ratio, and the like. Patent Document 10 discloses a steel sheet that is excellent in stretch-flangeability, by mainly employing bainite or pearlite as a second phase and specifying the composition and the hardness ratio. Patent Document 11 discloses a high-strength and ductility galvanized steel sheet that is excellent in hole expandability and a method for manufacturing the steel sheet, by employing bainite and martensite as a hard second phase. Patent Document 12 discloses a multiple-phase steel sheet that is excellent in fatigue properties by employing bainite and martensite as a hard second phase and specifying the fraction of constituent phases, the grain diameter, the hardness, and the mean free path of the entire hard phase. Patent Document 13 discloses a high strength steel sheet that is excellent in ductility and hole expandability, by specifying the composition and the amount of retained austenite. Patent Document 14 discloses a high strength multiple-phase cold-rolled steel sheet that is excellent in workability, by employing a steel sheet including bainite and retained austenite and/or martensite and specifying the composition and the fraction of phases. Patent Document 15 discloses a high strength steel sheet that is excellent in workability and a method for manufacturing the steel sheet, by specifying the distribution state of the grains of a hard second phase in ferrite and the ratio of the grains of tempered martensite and bainite to the grains of ferrite. Patent Document 16 discloses an ultra-high strength cold-rolled steel sheet that is excellent in delayed fracture resistance and has a tensile strength of 1180 MPa or higher and a method for manufacturing the steel sheet, by specifying the composition and the manufacturing process. Patent Document 17 discloses an ultra-high strength cold-rolled steel sheet that is excellent in bendability and has a tensile strength of 980 MPa or higher and a method for manufacturing the steel sheet, by specifying the composition and the manufacturing method. Patent Document 18 discloses an ultra-high strength thin steel sheet that has a tensile strength of 980 MPa or higher and whose hydrogen embrittlement is prevented by limiting the number of iron-based carbide grains in tempered martensite to a certain number and a method for manufacturing the steel sheet.

[0005] However, the above-described inventions pose the problems below. Patent Documents 1 to 7, 9 to 10, and 12 to 14 disclose the inventions regarding steel sheets having a tensile strength of lower than 900 MPa, and the workability often cannot be maintained if the strength is further increased. Patent Document 1 describes that annealing is performed in a single phase region and the subsequent cooling is performed to 400°C at a cooling rate of 6 to 20 °C/s. However, in the case of a galvanized steel sheet, the adhesion of a coating needs to be taken into account and heating needs to be performed before coating because 400°C is lower than the temperature of a coating bath. Thus, the galvanized steel sheet cannot be manufactured in a continuous galvanizing and galvannealing line having no heating equipment before the coating bath. In Patent Documents 7 and 8, since tempered martensite needs to be formed during the heat treatment in a galvanizing line, there is required equipment for reheating the steel sheet after the cooling to Ms temperature or lower. In Patent Document 11, bainite and martensite are employed as a hard second phase and the fraction is specified. However, the characteristics significantly vary in the specified range, and the operating conditions need to be precisely controlled to suppress the variation. In Patent Document 15, since cooling is performed to Ms temperature or lower to form martensite before bainite transformation, equipment for reheating the steel sheet is required. Furthermore, the operating conditions need to be precisely controlled to achieve stable characteristics. Consequently, the costs for equipment and operation are increased. In Patent Documents 16 and 17, the steel sheet needs to be maintained in a bainite-formation temperature range after annealing to obtain a microstructure mainly composed of bainite, which makes it difficult to achieve ductility. In the case of a galvanized steel sheet, the steel sheet needs to be reheated to a temperature higher than the temperature of a coating bath. Patent Document 18 only describes the improvement in hydrogen embrittlement of a steel sheet, and there is little consideration for workability although bendability is considered to some extent.

[0006] In general, the ratio of a hard second phase to the entire microstructure needs to be increased to increase the strength of a steel sheet. However, when the ratio of a hard second phase is increased, the workability of a steel sheet is strongly affected by that of the hard second phase. The reason is as follows. When the ratio of the hard second phase is low, minimal workability is achieved by the deformation of ferrite itself that is a parent phase even if the workability of the hard second phase is insufficient. However, when the ratio of the hard second phase is high, the formability of a steel sheet is directly affected by the deformability of the hard second phase, not the deformation of ferrite. If the workability is insufficient, the formability is considerably degraded.

[0007] Therefore, in the case of a cold-rolled steel sheet, for example, martensite is formed through water quenching by adjusting the fraction of ferrite and a hard second phase using a continuous annealing furnace that can perform water quenching. Subsequently, the temperature is increased and held to temper martensite, whereby the workability of the hard second phase is improved.

[0008] However, in the case where equipment has no ability to temper the thus-formed martensite by increasing temperature and holding high temperature, the strength can be ensured, but it is difficult to ensure the workability of the hard second phase such as martensite.

[0009] To achieve stretch-flangeability using a hard phase other than martensite, the workability of a hard second phase is ensured by employing ferrite as a parent phase and bainite or pearlite containing carbides as a hard second phase. Unfortunately, in this case, sufficient ductility cannot be achieved.

[0010] When bainite is used, there is a problem in that the characteristics significantly vary due to the variation in a bainite-formation temperature range and the holding time. When martensite or retained austenite (including bainite containing retained austenite) is employed as a second phase, for example, a mixed microstructure of martensite and bainite is considered to be used as a second phase microstructure to ensure both ductility and stretch-flangeability.

[0011] However, to employ a mixed microstructure composed of various phases as a second phase and precisely control the fraction or the like, the heat treatment conditions need to be precisely controlled, which often poses a problem of manufacturing stability.

Patent Document 1: Japanese Patent No. 1853389
Patent Document 2: Japanese Patent No. 3610883
Patent Document 3: Japanese Unexamined Patent Application Publication No. 11-61327
Patent Document 4: Japanese Unexamined Patent Application Publication No. 2003-213369
Patent Document 5: Japanese Unexamined Patent Application Publication No. 2003-213370
Patent Document 6: Japanese Unexamined Patent Application Publication (Translation of PCT Application) No. 2003-505604
Patent Document 7: Japanese Unexamined Patent Application Publication No. 6-93340
Patent Document 8: Japanese Unexamined Patent Application Publication No. 6-108152
Patent Document 9: Japanese Unexamined Patent Application Publication No. 7-11383
Patent Document 10: Japanese Unexamined Patent Application Publication No. 10-60593
Patent Document 11: Japanese Unexamined Patent Application Publication No. 2005-281854

Patent Document 12: Japanese Patent No. 3231204
Patent Document 13: Japanese Unexamined Patent Application Publication No. 2001-207234
Patent Document 14: Japanese Unexamined Patent Application Publication No. 7-207413
Patent Document 15: Japanese Unexamined Patent Application Publication No. 2005-264328
Patent Document 16: Japanese Patent No. 2616350
Patent Document 17: Japanese Patent No. 2621744
Patent Document 18: Japanese Patent No. 2826058

Disclosure of Invention

[0012] The present invention advantageously solves the problems described above. An object of the present invention is to provide a high strength steel sheet having a tensile strength of 900 MPa or higher that can minimize the formation of bainite, which easily causes a variation in characteristics such as strength and formability, and can have both high strength and good formability and to provide an advantageous method for manufacturing the high strength steel sheet.

[0013] The formability is evaluated using TS × T. El and a λ value that represents stretch-flangeability. In the present invention, TS × T. El ≥ 14500 MPa·% and λ ≥ 15% are target characteristics.

[0014] To solve the problems described above, the inventors of the present invention have studied about the formation process of martensite, in particular, the effect of the cooling conditions of a steel sheet on martensite.

[0015] Consequently, the inventors have found that a high strength steel sheet having both good formability and high strength with a tensile strength of 900 MPa or higher that are targeted in the present invention can be obtained by the following method. By suitably controlling the heat treatment conditions after cold-rolling, martensite transformation is caused while at the same time the transformed martensite is tempered. The ratio of the thus-formed autotempered martensite is controlled to a certain ratio and also the distribution state of iron-based carbide grains included in the autotempered martensite is suitably controlled, whereby such a high strength steel sheet can be obtained.

[0016] The present invention has been completed through further investigation on the basis of the above-described findings. The gist of the invention is described below.

1. A high strength steel sheet having a tensile strength of 900 MPa or higher, includes a composition including, on a mass basis:

   C: 0.1% or more and 0.3% or less;
   Si: 2.0% or less;
   Mn: 0.5% or more and 3.0% or less;
   P: 0.1% or less;
   S: 0.07% or less;
   Al: 1.0% or less; and
   N: 0.008% or less, with the balance Fe and incidental impurities, wherein a steel microstructure includes, on an area ratio basis, 5% or more and 80% or less of ferrite, 15% or more of autotempered martensite, 10% or less of bainite, 5% or less of retained austenite, and 40% or less of as-quenched martensite; a mean hardness of the autotempered martensite is HV ≤ 700; and the mean number of precipitated iron-based carbide grains each having a size of 5 nm or more and 0.5 μm or less and included in the autotempered martensite is 5×10^4 or more per 1 mm^2.

2. The high strength steel sheet according to the above-described 1, further includes, on a mass basis, at least one element selected from:

   Cr: 0.05% or more and 5.0% or less;
   V: 0.005% or more and 1.0% or less; and
   Mo: 0.005% or more and 0.5% or less.

3. The high strength steel sheet according to the above-described 1 or 2, further includes, on a mass basis, at least one element selected from:

   Ti: 0.01% or more and 0.1% or less;
   Nb: 0.01% or more and 0.1% or less;
   B: 0.0003% or more and 0.0050% or less;
   Ni: 0.05% or more and 2.0% or less; and
   Cu: 0.05% or more and 2.0% or less.

4. The high strength steel sheet according to any one of the above-described 1 to 3, further includes, on a mass basis, at least one element selected from:

Ca: 0.001% or more and 0.005% or less; and
REM: 0.001% or more and 0.005% or less.

5. The high strength steel sheet according to any one of the above-described 1 to 4, wherein the area ratio of autotempered martensite in which the number of precipitated iron-based carbide grains each having a size of 0.1 μm or more and 0.5 μm or less is 5×10^2 or less per 1 mm^2 to the entire autotempered martensite is 3% or more.
6. The high strength steel sheet according to any one of the above-described 1 to 5, wherein a galvanized layer is disposed on a surface of the steel sheet.
7. The high strength steel sheet according to any one of the above-described 1 to 5, wherein a galvannealed layer is disposed on a surface of the steel sheet.
8. A method for manufacturing a high strength steel sheet, includes the steps of hot-rolling and then cold-rolling a slab to be formed into a steel sheet having the composition according to any one of the above-described 1 to 4 to form a cold-rolled steel sheet; annealing the cold-rolled steel sheet in a first temperature range of 700°C or higher and 950°C or lower for 15 seconds or longer and 600 seconds or shorter; in a second temperature range, which is a temperature range from the first temperature range to 420°C, cooling the steel sheet from the first temperature range to 550°C at an average cooling rate of 3 °C/s or higher and cooling the steel sheet from 550°C to 420°C within 600 seconds; and cooling the steel sheet at a cooling rate of 50 °C/s or lower in a third temperature range of 250°C or higher and 420°C or lower to perform, in the third temperature range, autotempering treatment in which martensite transformation is caused while at the same time the transformed martensite is tempered.
9. The method for manufacturing a high strength steel sheet according to the above-described 8, wherein when the steel sheet is cooled at a cooling rate of 50 °C/s or lower in the third temperature range of 250°C or higher and 420°C or lower, the steel sheet is cooled at a cooling rate of 1.0 °C/s or higher and 50 °C/s or lower in a temperature range of at least (Ms temperature - 50)°C or lower to perform, in the third temperature range, autotempering treatment in which martensite transformation is caused while at the same time the transformed martensite is tempered.
10. The method for manufacturing a high strength steel sheet according to the above-described 8 or 9, wherein martensite start temperature Ms of the slab is approximated by M represented by Formula (1) below, and the M is 300°C or higher:

$$M\ (^\circ C) = 540 - 361 \times \{[C\%]/(1 - [\alpha\%]/100)\} - 6 \times [Si\%] - 40 \times [Mn\%] + 30 \times [Al\%] - 20 \times [Cr\%] - 35 \times [V\%] - 10 \times [Mo\%] - 17 \times [Ni\%] - 10 \times [Cu\%] \cdots (1)$$

where [X%] is mass% of a constituent element X of the slab and [α%] is an area ratio (%) of polygonal ferrite.

[0017] According to the present invention, a high strength steel sheet having a tensile strength of 900 MPa or higher that can achieve high strength, good workability, and good ductility can be obtained by forming an appropriate amount of autotempered martensite in a steel sheet and suitably controlling the distribution state of carbide grains included in the autotempered martensite. Therefore, the present invention significantly contributes to the weight reduction of automobile bodies.
[0018] In the method for manufacturing a high strength steel sheet according to the present invention, since the reheating of a steel sheet after quenching is not needed, special manufacturing equipment is not required and the method can be easily applied to a galvanizing or galvannealing process. Therefore, the present invention contributes to decreases in the number of steps and in the cost.

Brief Description of Drawings

[0019]

[Fig. 1] Fig. 1 is a schematic view showing quenching and tempering steps performed to obtain typical tempered martensite.
[Fig. 2] Fig. 2 is a schematic view showing an autotempering treatment step performed to obtain autotempered

martensite in accordance with the present invention.

Best Mode for Carrying Out the Invention

[0020] The present invention will now be specifically described.

[0021] The reason for the above-described limitation of the microstructure of a steel sheet according to the present invention will be described below.

Area ratio of ferrite : 5% or more and 80% or less

[0022] To achieve both workability and a tensile strength of 900 MPa or higher, the ratio between ferrite and a hard phase described below is important and thus the area ratio of ferrite needs to be 5% or more and 80% or less. If the area ratio of ferrite is less than 5%, ductility is not ensured. If the area ratio of ferrite is more than 80%, the area ratio of the hard phase becomes insufficient and thus the strength becomes insufficient. The area ratio of ferrite is preferably set in the range of 10% or more and 65% or less.

Area ratio of autotempered martensite: 15% or more

[0023] In the present invention, autotempered martensite is a microstructure obtained by simultaneously causing martensite transformation and the tempering of the martensite through autotempering treatment, and not so-called tempered martensite obtained through quenching and tempering treatments as in the related art. The microstructure is not a uniformly tempered microstructure formed by completing martensite transformation through quenching and then performing tempering through a temperature increase as in typical quenching and tempering treatments, but is a microstructure including martensites in different tempered states obtained by performing martensite transformation and the tempering of the martensite in stages through the control of a cooling process in a temperature range of Ms temperature or lower.

[0024] This autotempered martensite is a hard phase for increasing strength. If the area ratio of autotempered martensite is less than 15%, sufficient strength cannot be achieved and work hardening of ferrite cannot be facilitated. Thus, the area ratio of autotempered martensite needs to be 15% or more and is preferably 30% or more.

[0025] In the present invention, the microstructure of a steel sheet is preferably composed of ferrite and autotempered martensite within the above-described range. When such phases are formed, other phases such as bainite, retained austenite, and as-quenched martensite are sometimes formed. These phases may be formed as long as some parameters are within the tolerable ranges described below. The tolerable ranges will now be described.

Area ratio of bainite: 10% or less (including 0%)

[0026] Bainite is a hard phase that contributes to an increase in strength, but the characteristics significantly vary in accordance with the formation temperature range and the variation in the quality of material is sometimes increased. Therefore, the area ratio of bainite in a steel microstructure is desirably as low as possible, but up to 10% of bainite is tolerable. The area ratio of bainite is preferably 5% or less.

Area ratio of retained austenite: 5% or less (including 0%)

[0027] Retained austenite is transformed into hard martensite when processed, which decreases stretch-flangeability. Thus, the area ratio of retained austenite in a steel microstructure is desirably as low as possible, but up to 5% of retained austenite is tolerable. The area ratio of retained austenite is preferably 3% or less.

Area ratio of as-quenched martensite: 40% or less (including 0%)

[0028] Since as-quenched martensite has considerably poor workability, the area ratio of as-quenched martensite in a steel microstructure is desirably as low as possible, but up to 40% of as-quenched martensite is tolerable. The area ratio of as-quenched martensite is preferably 30% or less. Herein, as-quenched martensite can be differentiated from autotempered martensite in that carbides of as-quenched martensite are not observed with a scanning electron microscope (SEM) or a transmission electron microscope (TEM).

Mean hardness of autotempered martensite: $HV \leq 700$

[0029] If the mean hardness of autotempered martensite is $700 < HV$, stretch-flangeability is considerably degraded.

Thus, HV ≤ 700 needs to be satisfied and HV ≤ 630 is preferably satisfied.

Iron-based carbide in autotempered martensite

[0030] Size: 5 nm or more and 0.5 μm or less, Mean number of precipitated carbide grains: 5×10^4 or more per 1 mm^2

[0031] Autotempered martensite is martensite subjected to the heat treatment (autotempering treatment) performed by the method of the present invention. However, even if the mean hardness of autotempered martensite is HV ≤ 700, the workability is decreased when the autotempering treatment is improperly performed. The degree of autotempering treatment can be confirmed through the formation state (distribution state) of iron-based carbide grains in autotempered martensite. When the mean number of precipitated iron-based carbide grains each having a size of 5 nm or more and 0.5 μm or less is 5×10^4 or more per 1 mm^2, it can be judged that desired autotempering treatment has been performed. Iron-based carbide grains each having a size of less than 5 nm are removed from the target of judgment because such carbide grains do not affect the workability of autotempered martensite. On the other hand, iron-based carbide grains each having a size of more than 0.5 μm are also removed from the target of judgment because such carbide grains may decrease the strength of autotempered martensite but hardly affect the workability. If the number of iron-based carbide grains is less than 5×10^4 per 1 mm^2, it is judged that the autotempering treatment has been improperly performed because workability, particularly stretch-flangeability, is not improved. The number of iron-based carbide grains is preferably 1×10^5 or more and 1×10^6 or less per 1 mm^2, more preferably 4×10^5 or more and 1×10^6 or less per 1 mm^2. Herein, an iron-based carbide is mainly Fe_3C, and ε carbides and the like may be further contained.

[0032] To confirm the formation state of carbide grains, it is effective to observe a mirror-polished sample using a SEM (scanning electron microscope) or a TEM (transmission electron microscope). Carbide grains can be identified by, for example, performing SEM-EDS (energy dispersive X-ray spectrometry), EPMA (electron probe microanalyzer), or FE-AES (field emission-Auger electron spectrometry) on samples whose section is polished.

[0033] In the steel sheet of the present invention, the amount of autotempered martensite narrowed down by further limiting the size and number of iron-based carbide grains precipitated in the above-described autotempered martensite can be suitably set as follows.

Autotempered martensite in which the number of precipitated iron-based carbide grains each having a size of 0.1 μm or more and 0.5 μm or less is 5×10^2 or less per 1 mm^2: the area ratio of the autotempered martensite to the entire autotempered martensite is 3% or more

[0034] By increasing the ratio of autotempered martensite in which the number of precipitated iron-based carbide grains each having a size of 0.1 μm or more and 0.5 μm or less is 5×10^2 or less per 1 mm^2, ductility is further improved. To produce such an effect, the area ratio of autotempered martensite in which the number of precipitated iron-based carbide grains each having a size of 0.1 μm or more and 0.5 μm or less is 5×10^2 or less per 1 mm^2 to the entire autotempered martensite is preferably 3% or more. If a large amount of autotempered martensite in which the number of precipitated iron-based carbide grains each having a size of 0.1 μm or more and 0.5 μm or less is 5×10^2 or less per 1 mm^2 is contained in a steel sheet, workability is considerably degraded. Thus, the area ratio of such autotempered martensite to the entire autotempered martensite is preferably 40% or less, more preferably 30% or less.

[0035] When the area ratio of autotempered martensite in which the number of precipitated iron-based carbide grains each having a size of 0.1 μm or more and 0.5 μm or less is 5×10^2 or less per 1 mm^2 to the entire autotempered martensite is 3% or more, the number of fine iron-based carbide grains is increased in autotempered martensite. Therefore, the mean number of precipitated iron-based carbide grains in the entire autotempered martensite is increased. Thus, the mean number of precipitated iron-based carbide grains each having a size of 5 nm or more and 0.5 μm or less in autotempered martensite is preferably 1×10^5 or more and 5×10^6 or less per 1 mm^2, more preferably 4×10^5 or more and 5×10^6 or less per 1 mm^2.

[0036] The specific reason why ductility is further improved as described above is not clear, but it is believed to be as follows. When the area ratio of autotempered martensite in which the number of precipitated iron-based carbide grains each having a relatively large size of 0.1 μm or more and 0.5 μm or less is 5×10^2 or less per 1 mm^2 to the entire autotempered martensite is 3% or more, the autotempered martensite microstructure includes a portion that contains a large number of iron-based carbide grains having a relatively large size and a portion that contains a small number of iron-based carbide grains having a relatively large size in a mixed manner. The portion that contains a small number of iron-based carbide grains having a relatively large size is hard autotempered martensite because a large number of fine iron-based carbide grains are contained. On the other hand, the portion that contains a large number of iron-based carbide grains having a relatively large size is soft autotempered martensite. By providing the hard autotempered martensite such that the hard autotempered martensite is surrounded by the soft autotempered martensite, the degradation of stretch-flangeability caused by the hardness difference in autotempered martensite can be suppressed. Furthermore, by dispersing the hard martensite in the soft autotempered martensite, work hardenability is improved and thus ductility is improved.

[0037] The reason why the composition is set in the above-described range in the steel sheet according to the present invention will be described below. The symbol "%" below used for each component means "% by mass".

C: 0.1% or more and 0.3% or less

[0038] C is an essential element for increasing the strength of a steel sheet. A C content of less than 0.1% causes difficulty in achieving both strength and workability such as ductility or stretch-flangeability of the steel sheet. On the other hand, a C content of more than 0.3% causes a significant hardening of welds and heat-affected zones, thereby reducing weldability. Thus, in the present invention, the C content is set in the range of 0.1% or more and 0.3% or less, preferably 0.12% or more and 0.23% or less.

Si: 2.0% or less

[0039] Si is a useful element for solution hardening of ferrite, and the Si content is preferably 0.1% or more to ensure the ductility and the hardness of ferrite. However, the excessive addition of Si causes the degradation of surface quality due to the occurrence of red scale and the like and the degradation of the adhesion of a coating. Thus, the Si content is set to 2.0% or less, preferably 1.6% or less.

Mn: 0.5% or more and 3.0% or less

[0040] Mn is an element that is effective in strengthening steel, stabilizes austenite, and is necessary for ensuring the area ratio of a hard phase. To achieve this, a Mn content of 0.5% or more is required. On the other hand, an excessive Mn content of more than 3.0% causes the degradation of castability or the like. Thus, the Mn content is set in the range of 0.5% or more and 3.0% or less, preferably 1.5% or more and 2.5% or less.

P: 0.1% or less

[0041] P causes embrittlement due to grain boundary segregation and degrades shock resistance, but a P content of up to 0.1% is tolerable. Furthermore, in the case where a steel sheet is galvannealed, a P content of more than 0.1% significantly reduces the rate of alloying. Thus, the P content is set to 0.1% or less, preferably 0.05% or less.

S: 0.07% or less

[0042] S is formed into MnS as an inclusion that causes the degradation of shock resistance and causes cracks along a flow of a metal in a weld zone. Thus, the S content is preferably minimized. However, a S content of up to 0.07% is tolerable in terms of manufacturing costs. The S content is preferably 0.04% or less.

Al: 1.0% or less

[0043] Al is an element that contributes to ferrite formation and a useful element for controlling the amount of the ferrite formation during manufacturing. However, an excessive Al content degrades the quality of a slab during steelmaking. Thus, the Al content is set to 1.0% or less, preferably 0.5% or less. Since an excessively low Al content sometimes makes it difficult to perform deoxidization, the Al content is preferably 0.01% or more.

N: 0.008% or less

[0044] N is an element that most degrades the anti-aging property of steel. Therefore, the N content is preferably minimized. A N content of more than 0.008% causes significant degradation of an anti-aging property. Thus, the N content is set to 0.008% or less, preferably 0.006% or less.

[0045] If necessary, the steel sheet of the present invention can suitably contain the components described below in addition to the basic components described above.

At least one element selected from Cr: 0.05% or more and 5.0% or less, V: 0.005% or more and 1.0% or less, and Mo: 0.005% or more and 0.5% or less

[0046] Cr, V, and Mo have an effect of suppressing the formation of pearlite when a steel sheet is cooled from the annealing temperature and thus can be optionally added. The effect is produced at a Cr content of 0.05% or more, a V content of 0.005% or more, or a Mo content of 0.005% or more. On the other hand, an excessive Cr content of more than 5.0%, an excessive V content of more than 1.0%, or an excessive Mo content of more than 0.5% excessively increases the area ratio of a hard phase, thereby unnecessarily increasing the strength. Thus, when these elements are incorporated, the Cr content is preferably set in the range of 0.005% or more and 5.0% or less, the V content is preferably set in the range of 0.005% or more and 1.0% or less, and the Mo content is preferably set in the range of 0.005% or more and 0.5% or less.

[0047] Furthermore, at least one element selected from Ti, Nb, B, Ni, and Cu can be incorporated. The reason for the limitation of the content ranges is as follows.

Ti: 0.01% or more and 0.1% or less and Nb: 0.01% or more and 0.1% or less

[0048] Ti and Nb are useful for precipitation strengthening of steel and the effect is produced at a Ti content of 0.01% or more or a Nb content of 0.01% or more. On the other hand, a Ti content of more than 0.1% or a Nb content of more than 0.1% degrades the workability and shape flexibility. Thus, the Ti content and the Nb content are each preferably set in the range of 0.01% or more and 0.1% or less.

B: 0.0003% or more and 0.0050% or less

[0049] B has an effect of suppressing the formation and growth of ferrite from austenite grain boundaries and thus can be optionally added. The effect is produced at a B content of 0.0003% or more. On the other hand, a B content of more than 0.0050% decreases workability. Thus, when B is incorporated, the B content is preferably set in the range of 0.0003% or more and 0.0050% or less. Herein, when B is incorporated, the formation of BN is preferably suppressed to produce the above-described effect. Thus, B is preferably added together with Ti.

Ni: 0.05% or more and 2.0% or less and Cu: 0.05% or more and 2.0% or less

[0050] In the case where a steel sheet is galvanized, Ni and Cu promote internal oxidation, thereby improving the adhesion of a coating. The effect is produced at a Ni content of 0.05% or more or a Cu content of 0.05% or more. On the other hand, a Ni content of more than 2.0% or a Cu content of more than 2.0% degrades the workability of a steel sheet. Ni and Cu are useful elements for strengthening steel. Thus, the Ni content and the Cu content are each preferably set in the range of 0.05% or more and 2.0% or less.

At least one element selected from Ca: 0.001% or more and 0.005% or less and REM: 0.001% or more and 0.005% or less

[0051] Ca and REM are useful elements for spheroidizing the shape of a sulfide and improving an adverse effect of the sulfide on stretch-flangeability. The effect is produced at a Ca content of 0.001% or more or an REM content of 0.001% or more. On the other hand, a Ca content of more than 0.005% or an REM content of more than 0.005% increases the number of inclusions or the like and causes, for example, surface defects and internal defects. Thus, when Ca and REM are incorporated, the Ca content and the REM content are each preferably set in the range of 0.001% or more and 0.005% or less.

[0052] In the steel sheet of the present invention, components other than the components described above are Fe and incidental impurities. However, a component other than the components described above may be contained to the extent that the advantages of the present invention are not impaired.

[0053] As described below, the composition of the steel sheet according to the present invention preferably satisfies $M \geq 300°C$ that represents a relation between the composition and the area ratio of polygonal ferrite to perform stable production, that is, to suppress the variation in characteristics due to the variation in manufacturing conditions.

[0054] In the present invention, a galvanized layer or a galvannealed layer may be disposed on a surface of a steel sheet.

[0055] A preferred method for manufacturing a steel sheet according to the present invention and the reason for the limitation of the conditions will now be described.

[0056] A slab prepared to have the above-described preferred composition is produced, hot-rolled, and then cold-rolled to obtain a cold-rolled steel sheet. In the present invention, these processes are not particularly limited, and can be performed by typical methods.

[0057] The preferred manufacturing conditions will now be described below. A slab is heated to 1100°C or higher and 1300°C or lower and subjected to finish hot-rolling at a temperature of 870°C or higher and 950°C or lower, which means that the hot-rolling end temperature is set to 870°C or higher and 950°C or lower. The thus-obtained hot-rolled steel sheet is wound at a temperature of 350°C or higher and 720°C or lower. Subsequently, the hot-rolled steel sheet is pickled and cold-rolled at a reduction ratio of 40% or higher and 90% or lower to obtain a cold-rolled steel sheet.

[0058] It is assumed that the hot-rolled steel sheet is produced through the typical steps of steel making, casting, and hot-rolling, but the hot-rolled steel sheet may be produced by thin slab casting without performing part or all of the hot-rolling steps.

[0059] The resultant cold-rolled steel sheet is annealed for 15 seconds or longer and 600 seconds or shorter in a first temperature range of 700°C or higher and 950°C or lower, specifically, in an austenite single-phase region or a dual-phase region of an austenite phase and a ferrite phase. If the annealing temperature is lower than 700°C or the annealing time is shorter than 15 seconds, a carbide in the steel sheet is sometimes not sufficiently dissolved, or the recrystallization of ferrite is not completed and thus desired ductility and stretch-flangeability are sometimes not achieved. On the other hand, if the annealing temperature exceeds 950°C, austenite grains are significantly grown and the constituent phases produced by cooling performed later are coarsened, which may degrade ductility and stretch-flangeability. If the annealing time exceeds 600 seconds, a vast amount of energy is consumed and thus the cost is increased. Therefore, the annealing temperature is set in the range of 700°C or higher and 950°C or lower, preferably 760°C or higher and 920°C or lower. The annealing time is set in the range of 15 seconds or longer and 600 seconds or shorter, preferably 30 seconds or longer and 400 seconds or shorter.

[0060] In a second temperature range, which is a temperature range from the first temperature range to 420°C, the annealed cold-rolled steel sheet is cooled to 550°C from the first temperature range at a cooling rate of 3 °C/s or higher, and is then cooled from 550 to 420°C within 600 seconds. Subsequently, the steel sheet is cooled at a cooling rate of 50 °C/s or lower in a third temperature range of 250°C or higher and 420°C or lower.

[0061] The cooling conditions in a second temperature range from the first temperature range to 420°C are essential to suppress the precipitation of phases other than intended ferrite and autotempered martensite phases. In the temperature range from the first temperature range to 550°C, pearlite transformation easily occurs. If the average cooling rate is lower than 3 °C/s in the range from 700°C, which is the lower limit temperature of the first temperature range, to 550°C, pearlite or the like is precipitated and a desired microstructure is sometimes not obtained. Therefore, the cooling rate needs to be 3 °C/s or higher, and is preferably 5 °C/s or higher. The upper limit of the cooling rate is not particularly specified, but special cooling equipment is required to achieve a cooling rate of 200 °C/s or higher. Thus, the cooling rate is preferably 200 °C/s or lower.

[0062] When the steel sheet is held for a long time in a temperature range of 550°C to 420°C, bainite transformation is caused. If the time required for cooling from 550°C to 420°C exceeds 600 seconds, bainite transformation is caused and thus a desired microstructure is sometimes not obtained. Therefore, the time required for cooling from 550°C to 420°C is 600 seconds or shorter, preferably 400 seconds or shorter.

[0063] After the process in the second temperature range, the steel sheet is processed in the third temperature range. The most important feature of the present invention is that, in the third temperature range, autotempering treatment in which martensite transformation is caused while at the same time the transformed martensite is tempered is performed to obtain autotempered martensite in which the precipitation state of carbide grains is suitably controlled.

[0064] Typical martensite is obtained by performing annealing and then performing quenching with water cooling or the like. The martensite is a hard phase, and contributes to an increase in the strength of a steel sheet but degrades workability. To change the martensite into tempered martensite having satisfactory workability, a quenched steel sheet is normally heated again to perform tempering. Fig. 1 schematically shows the steps described above. In such normal quenching and tempering treatments, after martensite transformation is completed by quenching, the temperature is increased to perform tempering. Consequently, a uniformly tempered microstructure is obtained.

[0065] In contrast, autotempering treatment is a treatment in which a steel sheet is cooled in a certain cooling-rate range in the third temperature range as shown in Fig. 2. In the autotempering treatment, quenching and tempering through reheating are not performed, which is a method with high productivity. The steel sheet including autotempered martensite obtained through this autotempering treatment has strength and workability equal to or higher than those of the steel sheet obtained by performing quenching and tempering through reheating shown in Fig. 1. In the autotempering treatment, martensite transformation and the tempering can be made to occur continuously or stepwise by performing continuous cooling (including stepwise cooling and holding) in the third temperature range. Consequently, a microstructure including martensites in different tempered states can be obtained. Although the martensites in different tempered states have different characteristics in terms of strength and workability, desired characteristics as the entire steel sheet can be achieved by suitably controlling the amounts of martensites in different tempered states through autotempering treatment. Furthermore, since the autotempering treatment is performed without rapidly cooling a steel sheet to a low temperature range in which the martensite transformation is fully completed, the residual stress in the steel sheet is low and a steel sheet having a good plate shape is obtained, which is advantageous.

[0066] In the present invention, the third temperature range is 250°C or higher and 420°C or lower. If the temperature exceeds 420°C, bainite transformation is easily caused as described above. If the temperature is lower than 250°C, autotempering treatment requires a long time and thus proceeds insufficiently in a continuous annealing line or a continuous galvanizing and galvannealing line. In the third temperature range, the cooling rate of a steel sheet needs to be 50 °C/s or lower in order to cause martensite transformation while at the same time tempering the transformed martensite and thus to obtain autotempered martensite. If the cooling rate exceeds 50 °C/s, the autotempering treatment insufficiently proceeds and the workability of martensite is sometimes not ensured. If the cooling rate is less than 0.1 °C/s, bainite transformation occurs or autotempering treatment excessively proceeds, whereby strength sometimes cannot be ensured. Thus, the cooling rate is preferably 0.1 °C/s or higher.

[0067] In the method for manufacturing a steel sheet according to the present invention, the following configuration can be suitably added if necessary.

[0068] When a steel sheet is cooled at a cooling rate of 50 °C/s or lower in a third temperature range of 250°C or higher and 420°C or lower, the steel sheet is preferably cooled at a cooling rate of 1.0 °C/s or higher and 50 °C/s or lower in a temperature range of at least (Ms temperature - 50)°C or lower. This is because, by further appropriately controlling the precipitation state of carbide grains included in autotempered martensite, the area ratio of autotempered martensite in which the number of precipitated iron-based carbide grains each having a size of 0.1 μm or more and 0.5 μm or less is 5×10^2 or less per 1 mm^2 to the entire autotempered martensite can be set to 3% or more. If the cooling rate exceeds 50 °C/s, autotempering treatment insufficiently proceeds and desired autotempered martensite is not obtained. Consequently, the workability of martensite is sometimes not ensured. If the cooling rate is less than 1.0 °C/s, 3% or more of the area ratio of autotempered martensite in which the number of precipitated iron-based carbide grains each having a size of 0.1 μm or more and 0.5 μm or less is 5×10^2 or less per 1 mm^2 to the entire autotempered martensite cannot be achieved, and desired ductility and strength are not ensured. Thus, the cooling rate is set to 1.0 °C/s or higher. Herein, Ms temperature can be obtained in a typical manner through the measurement of thermal expansion or electrical resistance during cooling. Alternatively, M obtained from an approximate expression (1) of Ms temperature described below may be used.

[0069] In the method for manufacturing a steel sheet according to the present invention, autotempering treatment can be stably performed when M represented by the approximate expression (1) below is 300°C or higher:

$$M\ (^\circ C) = 540 - 361 \times \{[C\%]/(1 - [\alpha\%]/100)\} - 6 \times [Si\%] - 40 \times [Mn\%] + 30 \times [Al\%] - 20 \times [Cr\%] - 35 \times [V\%] - 10 \times [Mo\%] - 17 \times [Ni\%] - 10 \times [Cu\%] \cdots (1)$$

where [X%] is mass% of an alloy element X and [α%] is the area ratio (%) of polygonal ferrite.

[0070] M represented by the above-described expression (1) is an empirical approximate expression of Ms temperature from which martensite transformation starts. It is believed that M is highly related to the precipitation behavior of iron-based carbide grains from martensite. Thus, M can be used as an indicator that indicates whether autotempered martensite in which the number of iron-based carbide grains each having a size of 5 nm or more and 0.5 μm or less is 5×10^4 or more per 1 mm^2 can be stably obtained. Even if M is less than 300°C, autotempered martensite is obtained. However, since the temperature is low, martensite transformation and autotempering treatment tend to slowly proceed. Compared with the case of $M \geq 300$°C, a steel sheet needs to be cooled slowly or held at a low temperature for a long time to obtain desired autotempered martensite, which may considerably lower manufacturing efficiency. Thus, M is preferably 300°C or higher.

[0071] The area ratio of polygonal ferrite is measured, for example, through the image processing and analysis of a SEM micrograph taken at 1000 to 3000 power. Polygonal ferrite is observed in the steel sheet that has been annealed and cooled under the above-described conditions. To ensure that M is 300°C or higher, after a cold-rolled steel sheet having a desired composition is produced, the area ratio of polygonal ferrite is measured and thus M is obtained from the expression (1) using the contents of alloy elements that can be calculated from the composition of the steel sheet. In the case where M is less than 300°C, the heat treatment conditions are suitably adjusted such that the area ratio of polygonal ferrite becomes lower, to obtain desired M. For example, the annealing temperature in the first temperature range is further increased and the average cooling rate from the first temperature range to 550°C is further increased. Alternatively, the contents of the components in the expression (1) may be adjusted.

[0072] The steel sheet of the present invention can be galvanized and galvannealed. The galvanizing and galvannealing treatments are preferably performed in a continuous galvanizing and galvannealing line while the above-described annealing and cooling conditions are satisfied. The galvanizing and galvannealing treatments are preferably performed in a temperature range of 420°C or higher and 550°C or lower. In this case, the time required for cooling a steel sheet from 550°C to 420°C, that is, the holding time in the temperature range of 420°C or higher and 550°C or lower needs to be 600 seconds or shorter, the time including galvanizing treatment time and/or galvannealing treatment time.

[0073] A method of galvanizing and galvannealing treatments is as follows. First, a steel sheet is immersed in a coating bath and the coating weight is adjusted using gas wiping or the like. In the case where the steel sheet is galvanized, the amount of dissolved Al in the coating bath is in the range of 0.12% or more and 0.22% or less. In the case where the steel sheet is galvannealed, the amount of dissolved Al is in the range of 0.08% or more and 0.18% or less.

[0074] In the case where the steel sheet is galvanized, the temperature of the coating bath is desirably 450°C or higher and 500°C or lower. In the case where the steel sheet is galvannealed by further performing alloying treatment, the temperature during alloying is preferably 450°C or higher and 550°C or lower. If the alloying temperature exceeds 550°C, an excessive amount of carbide grains are precipitated from untransformed austenite or the transformation into pearlite is caused, whereby desired strength and ductility are sometimes not achieved. Powdering is also degraded. If the alloying temperature is less than 450°C, the alloying does not proceed.

[0075] The coating weight is preferably in the range of 20 to 150 g/m^2 per surface. If the coating weight is less than 20 g/m^2, corrosion resistance is degraded. Meanwhile, even if the coating weight exceeds 150 g/m^2, the corrosion resistance is saturated, which merely increases the cost. The degree of alloying is preferably in the range of 7 to 15% by mass on a Fe content basis in the coating layer. If the degree of alloying is less than 7% by mass, uneven alloying is caused and the surface appearance quality is degraded. Furthermore, a so-called ξ phase is formed in the coating layer and thus the slidability is degraded. If the degree of alloying exceeds 15% by mass, a large amount of hard brittle Γ phase is formed and the adhesion of the coating is degraded.

[0076] In the present invention, the holding temperature in the first temperature range, in the second temperature range, or the like is not necessarily constant. Even if the holding temperature is varied, the purport of the present invention is not impaired as long as the holding temperature is within a predetermined temperature range. The same is true for the cooling rate. Furthermore, a steel sheet may be subjected to annealing and autotempering treatments with any equipment as long as heat history is just satisfied. Moreover, it is also included in the scope of the present invention that, after autotempering treatment, temper rolling is performed on the steel sheet of the present invention for shape correction.

Examples

Example 1

[0077] The present invention will now be further described with Examples. The present invention is not limited to Examples. It will be understood that modifications may be made without departing from the scope of the invention.

[0078] A slab to be formed into a steel sheet having the composition shown in Table 1 was heated to 1250°C and subjected to finish hot-rolling at 880°C. The hot-rolled steel sheet was wound at 600°C, pickled, and cold-rolled at a reduction ratio of 65% to obtain a cold-rolled steel sheet having a thickness of 1.2 mm. The resultant cold-rolled steel sheet was subjected to heat treatment under the conditions shown in Table 2. Quenching was not performed on any sample shown in Table 2. Herein, the holding time in Table 2 was a time held at the holding temperature shown in Table 2. The annealing time in a first temperature range of 700°C or higher and 950°C or lower was 600 seconds or shorter under any of the conditions shown in Table 2.

[0079] In the galvanizing treatment, both surfaces were subjected to plating in a coating bath having a temperature of 463°C at a coating weight of 50 g/m^2 per surface. In the galvannealing treatment, the alloying treatment was performed such that Fe% (iron content) in the coating layer was adjusted to 9% by mass. The resultant steel sheet was subjected to temper rolling at a reduction ratio (elongation ratio) of 0.3% regardless of the presence or absence of a coating.

Table 1

(mass%)

Steel type	C	Si	Mn	Al	P	S	N	Cr	V	Mo	Ti	Nb	B	Ni	Cu	Ca	REM	Remarks
A	0.16	1.59	2.2	0.040	0.011	0.005	0.0039	0.5	-	-	-	-	-	-	-	-	-	Suitable steel
B	0.15	1.51	2.3	0.036	0.012	0.004	0.0023	0.9	-	-	-	-	-	-	-	-	-	Suitable steel
C	0.15	1.40	2.3	0.041	0.012	0.004	0.0029	-	-	-	-	0.04	-	-	-		-	Suitable steel
D	0.15	1.00	2.2	0.039	0.009	0.004	0.0037	1.0	-	-	0.021	-	0.0010	-	-	-	-	Suitable steel
E	0.14	1.48	2.2	0.040	0.025	0.002	0.0038	-	-	-	-	-	-	-	-	-	-	Suitable steel
F	0.21	1.42	2.3	0.041	0.010	0.004	0.0037	-	-	-	-	-	-	-	-	-	-	Suitable steel
G	0.29	1.50	2.1	0.040	0.010	0.003	0.0041	-	-	-	-	-	-	-	-	-	-	Suitable steel
H	0.16	0.51	2.2	0.039	0.013	0.004	0.0032	1.5	-	-	0.020	-	0.0008	-	-	-	-	Suitable steel
I	0.15	1.49	2.8	0.037	0.012	0.003	0.0033	-	-	-	0.019	-	0.0005	-	-	-	-	Suitable steel
J	0.12	1.52	2.3	0.037	0.029	0.003	0.0041	1.0	-	-	0.020	-	0.0009	-	-	-	-	Suitable steel
K	0.21	0.49	1.6	0.037	0.029	0.003	0.0041	-	-	-	0.022	-	0.0012	-	-	-	-	Suitable steel
L	0.15	1.50	2.3	0.043	0.013	0.002	0.0043	1.0	-	-	0.050	-	0.0010	-	-	-	-	Suitable steel
M	0.11	1.48	2.0	0.039	0.013	0.003	0.0037	0.9	-	0.03	0.021	-	0.0008	-	-	-	-	Suitable steel
N	0.16	1.50	2.3	0.038	0.012	0.003	0.0041	0.8	0.10	-	-	-	-	-	-	-	-	Suitable steel
O	0.12	0.99	1.2	0.040	0.013	0.003	0.0041	1.0	-	-	-	-	-	1.00	-	-	-	Suitable steel
P	0.15	1.53	2.1	0.041	0.011	0.004	0.0029	0.5	-	-	-	-	-	-	0.3	-	-	Suitable steel
Q	0.15	1.48	2.3	0.044	0.009	0.004	0.0031	1.0	-	-	0.019	-	0.0008	-	-	-	0.002	Suitable steel
R	0.05	1.05	2.1	0.037	0.008	0.004	0.0030	-	-	-	-	-	-	-	-	-	-	Comparative steel
S	0.33	1.25	2.7	0.035	0.010	0.004	0.0042	-	-	-	-	-	-	-	-	-	-	Comparative steel

(continued)

(mass%)

Steel type	C	Si	Mn	Al	P	S	N	Cr	V	Mo	Ti	Nb	B	Ni	Cu	Ca	REM	Remarks
T	0.23	1.51	3.5	0.040	0.008	0.004	0.0039	-	-	-	-	-	-	-	-	-	-	Comparative steel

Note) Underline means the value is outside the suitable range.

Table 2

Sample No.	Steel type	First temperature range		Second temperature range		Third temperature range	Plating^{*2}	Remarks
		Holding Temperature (°C)	Holding time (second)	Average cooling rate from first temperature range to 550°C (°C/s)	Time required for cooling from 550°C to 420°C (second)	Average cooling rate from 420°C to 250° C(°C/s)		
1	A	820	180	10	90	15	CR	Invention Example
2	B	830	100	10	60	10	GI	Invention Example
3	C	820	180	10	80	55	CR	Comparative Example
4	C	850	180	45	60	10	CR	Invention Example
5	D	830	250	40	60	10	GI	Invention Example
6	E	820	180	10	60	100	CR	Comparative Example
7	F	810	180	8	70	60	CR	Comparative Example
8	G	820	180	5	60	55	GA	Comparative Example
9	H	820	180	10	120	15	GA	Invention Example
10	I	870	180	15	60	10	CR	Invention Example
11	J	830	200	30	60	10	CR	Invention Example
12	J	830	300	7	60	5	CR	Invention Example
13	K	860	40	10	45	10	GI	Invention Example
14	L	860	90	10	60	10	CR	Invention Example
15	M	850	180	10	60	9	CR	Invention Example
16	N	800	450	10	80	10	CR	Invention Example
17	O	820	180	10	60	8	GI	Invention Example
18	P	860	400	10	75	9	GI	Invention Example

(continued)

Sample No.	Steel type	First temperature range		Second temperature range		Third temperature range	Plating[*2]	Remarks
		Holding Temperature (°C)	Holding time (second)	Average cooling rate from first temperature range to 550°C (°C/s)	Time required for cooling from 550°C to 420°C (second)	Average cooling rate from 420°C to 250° C(°C/s)		
19	Q	800	180	10	60	10	CR	Invention Example
20	R	800	180	10	80	10	CR	Comparative Example
21	S	800	180	10	80	10	CR	Comparative Example
22	I	800	180	10	80	10	CR	Comparative Example
23	A	880	200	50	20	70	CR	Comparative Example
24	E	810	200	10	90	10	CR	Invention Example
25	G	850	350	5	650	5	CR	Comparative Example
26	G	870	150	15	120	3	CR	Invention Example

*1) Underline means the value is outside the suitable range.

*2) CR: no plating (cold-rolled steel sheet), GI: galvanizing, and GA: galvannealing

[0080] The characteristics of the resultant steel sheets were evaluated by the following methods.

[0081] To examine the microstructure of the steel sheets, two test pieces were cut from each of the steel sheets. One of the test pieces was polished without performing any treatment. The other of the test pieces was polished after heat treatment was performed at 200°C for 2 hours. The polished surface was a section in the sheet thickness direction, the section being parallel to the rolling direction. By observing a steel microstructure of the polished surface with a scanning electron microscope (SEM) at a magnification of 3000x, the area ratio of each phase was measured to identify the phase structure of each crystal grain. The observation was performed for 10 fields and the area ratio was an average value of the 10 fields. The area ratios of autotempered martensite, polygonal ferrite, and bainite were obtained using the test pieces polished without performing any treatment. The area ratios of as-quenched martensite (untempered martensite) and retained austenite were obtained using the test pieces polished after heat treatment was performed at 200°C for 2 hours. The test pieces polished after heat treatment was performed at 200°C for 2 hours were prepared in order to differentiate untempered martensite from retained austenite in the SEM observation. In the SEM observation, it is difficult to differentiate untempered martensite from retained austenite. When martensite is tempered, an iron-based carbide is formed in the martensite. The iron-based carbide makes it possible to differentiate martensite from retained austenite. The heat treatment at 200°C for 2 hours does not affect the phases other than martensite, that is, martensite can be tempered without changing the area ratio of each phase. As a result, martensite can be differentiated from retained austenite due to the formed iron-based carbide. By comparing the test pieces polished without performing any treatment to the test pieces polished after heat treatment was performed at 200°C for 2 hours through SEM observation, it was confirmed that phases other than martensite were not changed.

[0082] The size and number of iron-based carbide grains included in autotempered martensite were measured through SEM observation. The test pieces were the same as those used in the microstructure observation. Obviously, the test pieces polished without performing any treatment were observed. The test pieces were observed at a magnification of 10000x to 30000x in accordance with the precipitation state and size of the iron-based carbide grains. The size of the iron-based carbide grains was evaluated using an average value of the major axis and minor axis of individual precipitates. The number of iron-based carbide grains each having a size of 5 nm or more and 0.5 μm or less was counted and thus the number of iron-based carbide grains per 1 mm^2 of autotempered martensite was calculated. The observation was performed for 5 to 20 fields. The mean number was calculated from the total number of all the fields of each sample, and the mean number was employed as the number (per 1 mm^2 of autotempered martensite) of iron-based carbide grains of each sample.

[0083] The hardness HV of autotempered martensite was measured using an ultramicro-Vickers hardness meter at a load of 0.02 N. After the microstructure of autotempered martensite in which iron-based carbide grains were precipitated was confirmed by observing an indentation with a SEM, the average value of ten or more measurement values was employed as the hardness HV.

[0084] A tensile test was performed in accordance with JIS Z2241 using a JIS No. 5 test piece taken from the steel sheet in the rolling direction of the steel sheet. Tensile strength (TS), yield strength (YS), and total elongation (T. El) were measured. The product of the tensile strength and the total elongation (TS × T. El) was calculated to evaluate the balance between the strength and the elongation. In the present invention, when TS × T. E1 ≥ 14500 (MPa·%), the balance was determined to be satisfactory.

[0085] Stretch-flangeability was evaluated in compliance with The Japan Iron and Steel Federation Standard JFST 1001. The resulting steel sheet was cut into pieces each having a size of 100 mm × 100 mm. A hole having a diameter of 10 mm was made in the piece by punching at a clearance of 12% of the thickness. A cone punch with a 60° apex was forced into the hole while the piece was fixed with a die having an inner diameter of 75 mm at a blank-holding pressure of 88.2 kN. The diameter of the hole was measured when a crack was initiated. The maximum hole-expanding ratio (%) was determined with Formula (2) to evaluate stretch-flangeability using the maximum hole-expanding ratio:

$$\text{Maximum hole-expanding ratio } \lambda\ (\%) = \{(D_f - D_0)/D_0\} \times 100 \quad \cdots (2)$$

where D_f represents the hole diameter (mm) when a crack was initiated, and Do represents an initial hole diameter (mm). In the present invention, λ ≥ 15% was determined to be satisfactory.

[0086] Table 3 shows the evaluation results.

Table 3

Sample No.	Steel type	Area ratio (%)					Mean hardness of autotempered martensite (HV)	Number of iron-based carbide grains per 1 mm^2 *1	M (°C)	YS (MPa)	TS (Mpa)	T. El (%)	TS × T. El (MPa·%)	λ (%)	Remarks
		Autotempered martensite	Ferrite	Retained austenite	Bainite	As-quenched martensite									
1	A	57	43	0	0	0	602	1×10^5	332	771	1255	14.8	18574	16	Invention Example
2	B	72	28	0	0	0	550	1×10^5	346	924	1341	12.0	16092	22	Invention Example
3	C	35	63	0	0	2	661	1×10^4	293	687	1238	13.4	16589	5	Comparative Example
4	C	37	52	4	7	0	601	1×10^5	330	660	1220	14.0	17080	21	Invention Example
5	D	83	17	0	0	0	526	5×10^5	361	849	1393	11.1	15462	45	Invention Example
6	E	0	72	0	0	28	857	None	261	576	1066	18.8	20041	13	Comparative Example
7	F	22	60	1	2	15	771	1×10^3	250	667	1226	14.2	17409	5	Comparative Example
8	G	58	37	0	0	5	691	5×10^3	281	817	1521	7.5	11408	1	Comparative Example
9	H	91	9	0	0	0	492	1×10^6	355	946	1385	10.9	15097	36	Invention Example
10	I	84	12	1	3	0	503	1×10^6	358	908	1392	11.0	15239	42	Invention Example
11	J	84	16	0	0	0	470	3×10^6	367	772	1270	13.9	17653	35	Invention Example

(continued)

Sample No.	Steel type	Area ratio (%)					Mean hardness of autotempered martensite (HV)	Number of iron-based carbide grains per 1 mm^2 *1	M (°C)	YS (MPa)	TS (Mpa)	T. El (%)	TS × T. El (MPa·%)	λ (%)	Remarks
		Autotempered martensite	Ferrite	Retained austenite	Bainite	As-quenched martensite									
12	J	30	67	0	0	3	667	7×10^4	288	601	1021	17.5	17868	22	Invention Example
13	K	90	10	0	0	0	523	5×10^5	389	903	1449	10.9	15794	32	Invention Example
14	L	90	10	0	0	0	505	5×10^5	359	916	1418	11.8	16732	34	Invention Example
15	M	84	15	1	0	0	480	1×10^6	386	883	1305	12.5	16313	49	Invention Example
16	N	93	7	0	0	0	495	1×10^6	357	838	1420	12.4	17608	20	Invention Example
17	O	59	39	2	0	0	513	8×10^5	378	617	1125	15.2	17100	25	Invention Example
18	P	88	12	0	0	0	503	1×10^6	372	900	1389	10.5	14585	36	Invention Example
19	Q	86	14	0	0	0	502	1×10^6	356	837	1371	12.2	16726	24	Invention Example
20	R	18	82	0	0	0	470	4×10^6	420	593	781	20.9	16323	29	Comparative Example
21	S	70	20	0	0	10	802	1×10^3	276	1081	1520	9.2	13984	1	Comparative Example
22	T	82	12	0	0	6	790	1×10^3	297	931	1481	9.6	14218	2	Comparative Example

(continued)

Sample No.	Steel type	Area ratio (%)					Mean hardness of autotempered martensite (HV)	Number of iron-based carbide grains per 1 mm^2 *1	M (°C)	YS (MPa)	TS (Mpa)	T. El (%)	TS × T. El (MPa·%)	λ (%)	Remarks
		Autotempered martensite	Ferrite	Retained austenite	Bainite	As-quenched martensite									
23	A	49	8	1	0	42	563	5×10^5	370	1123	1481	9.7	14365	10	Comparative Example
24	E	52	48	0	0	0	589	1×10^5	346	763	1197	16.1	19272	18	Invention Example
25	G	10	27	14	46	0	603	1×10^6	304	1008	1423	14.1	20064	4	Comparative Example
26	G	93	7	n	0	0	592	1×10^6	334	1118	1635	11.2	18312	19	Invention Example

*1) The size of iron-based carbide grains is 5 nm or more and 0.5 μm or less.
*2) Underline means the value is outside the suitable range.

[0087] As is clear from Table 3, any steel sheet of the present invention has a tensile strength of 900 MPa or higher, a value of TS × T. El ≥ 14500 (MPa·%), and a value of λ ≥ 15% that represents stretch-flangeability and thus has both high strength and good workability. In Invention Examples, the steel sheets having an M of 300°C or higher are excellent in stretch-flangeability, particularly stretch-flangeability that is not degraded even if strength is increased.

[0088] In contrast, in sample Nos. 6 and 7, the hardness of martensite is 700 < HV and the number of iron-based carbide grains included in martensite is less than 5×10^4 per 1 mm^2 or martensite does not include iron-based carbide grains. Therefore, a tensile strength of 900 MPa is satisfied, but a value of λ is less than 15%, which provides poor workability. This is because, in sample Nos. 6 and 7, the cooling rate in the third temperature range is high, which does not satisfy 50 °C/s. In sample Nos. 3 and 8, the hardness of martensite is satisfactorily HV ≤ 700, but the number of iron-based carbide grains included in martensite is less than 5×10^4 per 1 mm^2. Therefore, a tensile strength of 900 MPa or higher is satisfied, but a value of λ is less than 15%, which provides poor workability. This is because, in sample Nos. 3 and 8, the cooling rate in the third temperature range is 55 °C/s, which does not satisfy 50 °C/s or lower. In particular, since sample No. 8 has a relatively high C content, TS × T. El is 14500 MPa·% or less.

[0089] It can be confirmed from the above description that the steel sheet of the present invention that includes autotempered martensite sufficiently subjected to autotempering treatment such that the hardness of martensite is HV ≤ 700 and the number of iron-based carbide grains in martensite is 5×10^4 or more per 1 mm^2 has both high strength and good workability.

Example 2

[0090] To confirm the effect of further improvement in ductility achieved by suitably controlling the distribution state of iron-based carbide grains included in autotempered martensite, samples were manufactured in the same manner as the samples shown in Table 2, except that the cooling rate in a temperature range of 250°C or higher and (Ms temperature - 50)°C or lower of the third temperature range was changed as shown in Table. 4. In Table 4, sample Nos. 9, 11, 13, 14, and 26 are the same as those shown in Table 2 and listed in Table 4 to clarify the temperature range of 250°C or higher and (Ms temperature - 50)°C or lower. Note that M (°C) was used as the Ms temperature.

Table 4

Sample No.	Steel type	First temperature range		Second temperature range		Third temperature range		Plating*1	Remarks
		Holding temperature (°C)	Holding time (second)	Average cooling rate from first temperature range to 550°C (°C/s)	Time required for cooling from 550°C to 420°C (second)	Average cooling rate from 420°C to 250°C (°C/s)	Average cooling rate from (Ms temperature - 50)°C to 250°C (°C/s)		
9	H	820	180	10	120	15	0.8	GA	Invention Example
11	J	830	200	30	60	10	20	CR	Invention Example
13	K	860	40	10	45	10	0.5	GI	Invention Example
14	L	860	90	10	60	10	0.8	CR	Invention Example
26	G	870	150	15	120	3	10	CR	Invention Example
27	H	820	180	10	120	15	30	GA	Invention Example
28	J	830	200	30	60	10	0.5	CR	Invention Example
29	K	860	40	10	45	10	25	GI	Invention Example
30	L	860	90	10	60	10	20	CR	Invention Example
31	G	870	150	15	120	3	0.4	CR	Invention Example

*1) CR: no plating (cold-rolled steel sheet), GI: galvanizing, and GA: galvannealing

[0091] The characteristics of the thus-obtained steel sheets were evaluated in the same manner as in Example 1. Herein, the amount of autotempered martensite in which the number of precipitated iron-based carbide grains each having a size of 0.1 μm or more and 0.5 μm or less is 5×10^2 or less per 1 mm^2 in the entire autotempered martensite was obtained as follows.

[0092] As described above, the test pieces polished without performing any treatment were observed at a magnification of 10000x to 30000x using a SEM. The size of the iron-based carbide grains was evaluated using an average value of the major axis and minor axis of individual precipitates. The area ratio of autotempered martensite in which the iron-based carbide grains have a size of 0.1 μm or more and 0.5 μm or less was measured. The observation was performed for 5 to 20 fields.

Table 5 shows the results.

[0093] As is apparent from Table 5, in sample Nos. 11, 26, 27, 29, and 30 with a cooling rate of 1.0 °C/s or higher and 50 °C/s or lower in the temperature range of 250°C or higher and (Ms temperature - 50)°C or lower, the distribution state of iron-based carbide grains included in autotempered martensite is suitably controlled and thus TS × T. El $\geq$ 17000 MPa·% is exhibited, that is, ductility is improved.

Table 5

Sample No.	Steel type	Area ratio (%)					Mean hardness of autotempered martensite (HV)	Number of iron-based carbide grains (5 nm to 0.5 μm) per 1 mm2	Area ratio of autotempered martensite in which the number of precipitated iron-based carbide grains (5 nm to 0.5 μm) is 5 × 102 or less per 1 mm2 to the entire autotempered martensite (%)	M (°C)	YS (MPa)	TS (MPa)	T. El (%)	TS × T.El (MPa·%)	λ (%)	Remarks
		Autotempered martensite	Ferrite	Retained austenite	Bainite	As-quenched martensite										
9	H	91	9	0	0	0	492	1x106	2	355	946	1385	10.9	15097	36	Invention Example
11	J	84	16	0	0	0	470	3 × 106	14	367	772	1270	13.9	17653	35	Invention Example
13	K	90	10	0	0	0	523	5 × 105	1	389	903	1449	10.9	15794	32	Invention Example
14	L	90	10	0	0	0	505	5 × 105	2	359	916	1418	11.8	16732	34	Invention Example
26	G	93	7	0	0	0	592	1 × 106	16	334	1118	1635	11.2	18312	19	Invention Example
27	H	91	9	0	0	0	564	1 × 106	24	355	952	1538	11.1	17072	32	Invention Example
28	J	84	16	0	0	0	460	3 × 106	2	367	797	1207	13.8	16657	36	Invention Example
29	K	90	10	0	0	0	553	5 × 105	16	389	907	1524	11.2	17069	29	Invention Example

(continued)

Sample No.	Steel type	Area ratio (%)					Mean hardness of autotempered martensite (HV)	Number of iron-based carbide grains (5 nm to 0.5 μm) per 1 mm2	Area ratio of autotempered martensite in which the number of precipitated iron-based carbide grains (5 nm to 0.5 μm) is 5 × 102 or less per 1 mm2 to the entire autotempered martensite (%)	M (°C)	YS (MPa)	TS (MPa)	T. El (%)	TS × T.El (MPa·%)	λ (%)	Remarks
		Autotempered martensite	Ferrite	Retained austenite	Bainite	As-quenched martensite										
30	L	90	10	0	0	0	526	5 × 105	14	359	918	1457	12.1	17630	30	Invention Example
31	G	93	7	0	0	0	541	1 × 106	0	334	1094	1497	11.3	16916	18	Invention Example

Claims

1. A high strength steel sheet having a tensile strength of 900 MPa or higher, comprising a composition including, on a mass basis:

   C: 0.1% or more and 0.3% or less;
   Si: 2.0% or less;
   Mn: 0.5% or more and 3.0% or less;
   P: 0.1% or less;
   S: 0.07% or less;
   Al: 1.0% or less; and
   N: 0.008% or less, with the balance Fe and incidental impurities,
   wherein a steel microstructure includes, on an area ratio basis, 5% or more and 80% or less of ferrite, 15% or more of autotempered martensite, 10% or less of bainite, 5% or less of retained austenite, and 40% or less of as-quenched martensite; a mean hardness of the autotempered martensite is HV ≤ 700; and the mean number of precipitated iron-based carbide grains each having a size of 5 nm or more and 0.5 μm or less and included in the autotempered martensite is 5×10^4 or more per 1 mm^2.

2. The high strength steel sheet according to Claim 1, further comprising, on a mass basis, at least one element selected from:

   Cr: 0.05% or more and 5.0% or less;
   V: 0.005% or more and 1.0% or less; and
   Mo: 0.005% or more and 0.5% or less.

3. The high strength steel sheet according to Claim 1 or 2, further comprising, on a mass basis, at least one element selected from:

   Ti: 0.01% or more and 0.1% or less;
   Nb: 0.01% or more and 0.1% or less;
   B: 0.0003% or more and 0.0050% or less;
   Ni: 0.05% or more and 2.0% or less; and
   Cu: 0.05% or more and 2.0% or less.

4. The high strength steel sheet according to any one of Claims 1 to 3, further comprising, on a mass basis, at least one element selected from:

   Ca: 0.001% or more and 0.005% or less; and
   REM: 0.001% or more and 0.005% or less.

5. The high strength steel sheet according to any one of Claims 1 to 4, wherein the area ratio of autotempered martensite in which the number of precipitated iron-based carbide grains each having a size of 0.1 μm or more and 0.5 μm or less is 5×10^2 or less per 1 mm^2 to the entire autotempered martensite is 3% or more.

6. The high strength steel sheet according to any one of Claims 1 to 5, wherein a galvanized layer is disposed on a surface of the steel sheet.

7. The high strength steel sheet according to any one of Claims 1 to 5, wherein a galvannealed layer is disposed on a surface of the steel sheet.

8. A method for manufacturing a high strength steel sheet, comprising the steps of hot-rolling and then cold-rolling a slab to be formed into a steel sheet having the composition according to any one of Claims 1 to 4 to form a cold-rolled steel sheet; annealing the cold-rolled steel sheet in a first temperature range of 700°C or higher and 950°C or lower for 15 seconds or longer and 600 seconds or shorter; in a second temperature range, which is a temperature range from the first temperature range to 420°C, cooling the steel sheet from the first temperature range to 550°C at an average cooling rate of 3 °C/s or higher and cooling the steel sheet from 550°C to 420°C within 600 seconds; and cooling the steel sheet at a cooling rate of 50 °C/s or lower in a third temperature range of 250°C or higher and 420°C or lower to perform, in the third temperature range, autotempering treatment in which martensite transformation

is caused while at the same time the transformed martensite is tempered.

9. The method for manufacturing a high strength steel sheet according to Claim 8, wherein when the steel sheet is cooled at a cooling rate of 50 °C/s or lower in the third temperature range of 250°C or higher and 420°C or lower, the steel sheet is cooled at a cooling rate of 1.0 °C/s or higher and 50 °C/s or lower in a temperature range of at least (Ms temperature - 50)°C or lower to perform, in the third temperature range, autotempering treatment in which martensite transformation is caused while at the same time the transformed martensite is tempered.

10. The method for manufacturing a high strength steel sheet according to Claim 8 or 9, wherein martensite start temperature Ms of the slab is approximated by M represented by Formula (1) below, and the M is 300°C or higher:

$$M\ (^\circ C) = 540 - 361 \times \{[C\%]/(1 - [\alpha\%]/100)\} - 6 \times [Si\%] - 40 \times [Mn\%] + 30 \times [Al\%] - 20 \times [Cr\%] - 35 \times [V\%] - 10 \times [Mo\%] - 17 \times [Ni\%] - 10 \times [Cu\%] \cdots (1)$$

where [X%] is mass% of a constituent element X of the slab and [α%] is an area ratio (%) of polygonal ferrite.

FIG.1

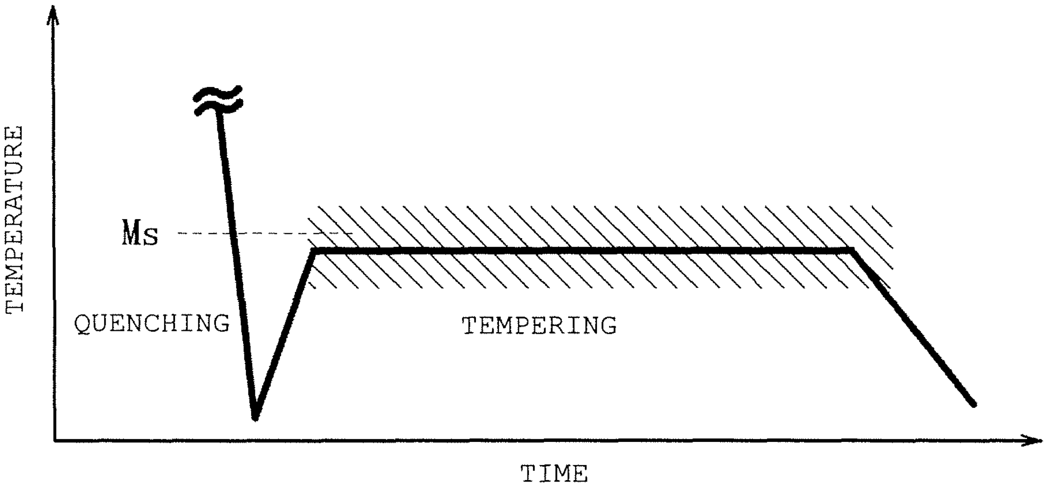
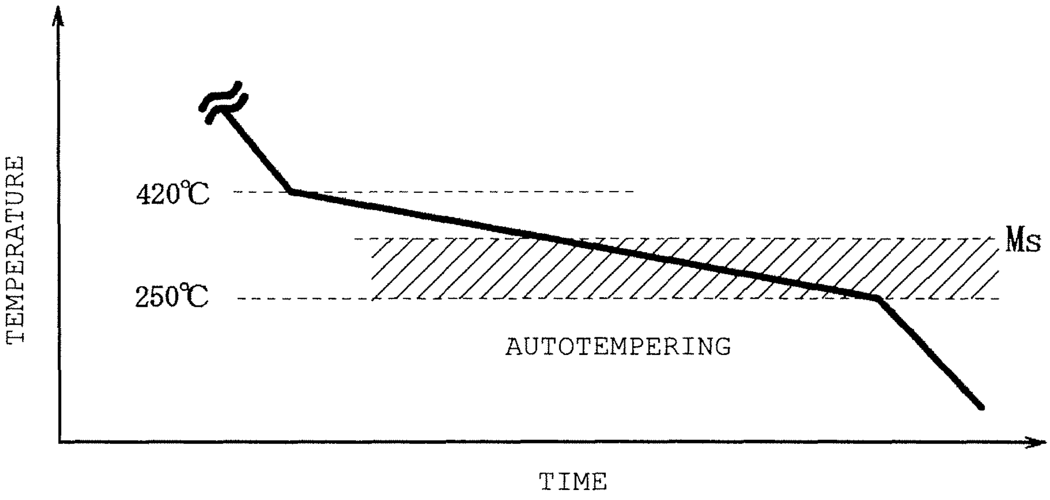

TEMPERATURE
Ms
QUENCHING
TEMPERING
TIME

FIG.2


TEMPERATURE
420℃
250℃
Ms
AUTOTEMPERING
TIME

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/051915

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/60(2006.01)i, *C21D9/46*(2006.01)i, *C23C2/06*(2006.01)i, *C23C2/28*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00-38/60, C21D9/46-9/48, C22C38/60, C23C2/00-2/40

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2007-138262 A (JFE Steel Corp.), 07 June, 2007 (07.06.07), Claims; tables 1, 2 (Family: none)	1-10
A	JP 2005-256089 A (Nippon Steel Corp.), 22 September, 2005 (22.09.05), Claims; tables 1, 3 & US 2007/0190353 A1 & EP 1724371 A1 & WO 2005/087965 A	1-10
A	JP 2005-171321 A (JFE Steel Corp.), 30 June, 2005 (30.06.05), Claims; Par. No. [0026]; tables 1 to 3 (Family: none)	1-10

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

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 21 April, 2009 (21.04.09)	Date of mailing of the international search report 12 May, 2009 (12.05.09)
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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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