

(19)



Europäisches
Patentamt
European
Patent Office
Office européen
des brevets



(11)

EP 2 172 575 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

07.04.2010 Bulletin 2010/14

(51) Int Cl.:

C22C 38/14 (2006.01)**C21D 9/48** (2006.01)**C22C 38/12** (2006.01)**C21D 8/04** (2006.01)(21) Application number: **09150416.7**(22) Date of filing: **24.09.1998**

(84) Designated Contracting States:

DE FR GB(30) Priority: **27.04.1998 JP 11678898**

(62) Document number(s) of the earlier application(s) in accordance with Art. 76 EPC:

98944222.3 / 1 002 884

(27) Previously filed application:

24.09.1998 PCT/JP98/04283(71) Applicant: **NKK Corporation****Tokyo 100-0005 (JP)**

(72) Inventors:

- **Kitano, Fusato**
Chiyoda-ku, Tokyo 100-0011 (JP)
- **Morita, Masaya**
Chiyoda-ku, Tokyo 100-0011 (JP)

• **Hosoya, Yoshihiro****Chiyoda-ku, Tokyo 100-0011 (JP)**• **Fujita, Takeshi****Chiyoda-ku, Tokyo 100-0011 (JP)**• **Inoue, Tadashi****Chiyoda-ku, Tokyo 100-0011 (JP)**• **Iwabuchi, Masahiro****Chiyoda-ku, Tokyo 100-0011 (JP)**• **Ishii, Takeo****Toyota-shi, Aichi 471-8571 (JP)**(74) Representative: **Marconnet, Sébastien****SCHMIT CHRETIEN****16, rue de la Paix****75002 Paris (FR)**Remarks:

This application was filed on 13-01-2009 as a
divisional application to the application mentioned
under INID code 62.

(54) **Cold rolled steel plate of excellent moldability, panel shape characteristics and denting resistance, molten zinc plated steel plate, and method of manufacturing these steel plates**

(57) In response to your communication pursuant to rule 58 EPC, please find herein enclosed the missing abstract.

Sincerely Yours,

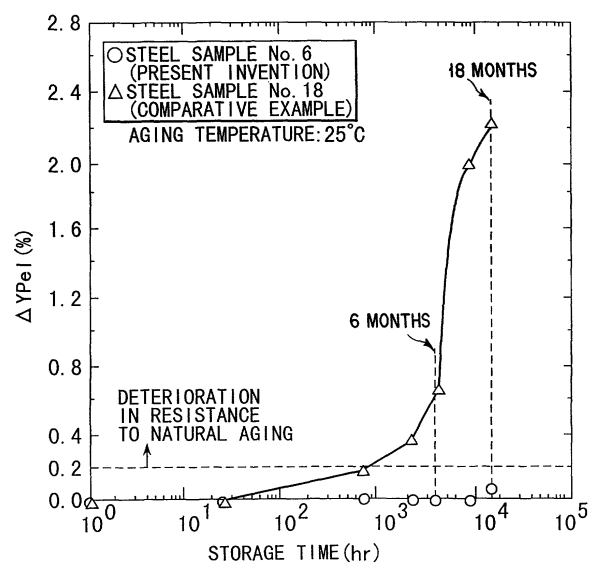


FIG. 12

EP 2 172 575 A1

Description

Technical Field

[0001] The present invention relates to a cold-rolled steel sheet and a galvanized steel sheet, which are excellent in formability, panel shapeability, and dent-resistance required for an outer panel of a motor car, and a method of manufacturing the same.

Background Art

[0002] An excellent formability, a satisfactory shape after a panel formation and a high dent-resistance (resistance to local depression) are required for a steel sheet for an outer panel of a motor car. The panel formability is evaluated by indexes such as yield strength, elongation, and an n-value (work-hardening index) of the steel sheet. Also, the panel shapeability and the dent-resistance are evaluated in many cases by yield strength and the yield strength after the working and the coating-baking treatment. If the yield strength of the steel sheet is weakened, the press formability can be improved. However, the dent-resistance after the panel formation is rendered unsatisfactory. On the other hand, if the yield strength of the steel sheet is increased, the dent-resistance is improved. However, problems are generated in terms of the press formability such as occurrence of wrinkles or cracks. Such being the situation, vigorous researches are being made in an attempt to obtain a steel sheet having a low yield point in the press forming and a high yield strength after the forming and baking as an outer panel for a motor car. As a cold-rolled steel sheet meeting these two contradictory requirements in terms of the yield strength, a bake-hardenable steel sheet, hereinafter referred to as a "BH steel sheet", utilizing a strain aging phenomenon of the carbon atoms within the steel has been developed.

[0003] Particularly, known is a method of manufacturing a BH steel sheet having a excellent deep drawability, which is a cold-rolled steel sheet prepared by adding elements capable of forming carbonitrides such as Nb and Ti to a steel having a very low carbon content of about 50 ppm, the addition amount of such an element being not larger than 1 in terms of the atomic ratio of carbon. For example, Japanese Patent Publication (Kokoku) No. 60-46166 teaches that a Nb or Ti added low-carbon steel is annealed at a high temperature close to 900°C for manufacturing the particular BH steel sheet. Also, Japanese Patent Disclosure (Kokai) No. 61-276928 teaches that an extra low carbon BH steel sheet is manufactured by annealing under a temperature region of about 700 to 850°C.

[0004] The technology disclosed in JP '166 is certainly advantageous in that the BH properties and an r-value can be improved. However, since the annealing is performed at a high temperature, the rough surface derived from enlargement of the ferrite grains is worried about. In addition, since the steel sheet itself is softened, the yield strength after the press forming and the baking steps is not acceptably high, though high BH properties may be obtained. On the other hand, in the technology disclosed in JP '928, the annealing temperature is relatively low, compared with that employed in JP '166, and, thus, is desirable in the required surface properties and the yield strength. However, it is substantially impossible to improve as desired the BH properties and the r-value. It should also be noted that these prior arts are mainly intended to improve the BH properties of a steel sheet in order to allow the steel sheet to exhibit an improved dent-resistance. Therefore, deterioration in the resistance to natural aging, i.e., occurrence of stretcher strain in the press forming, which is derived from generation of a yield point elongation during storage under room temperature, is worried about. Under the circumstances, the BH amount is suppressed at 60 MPa or less in view of the practical use of the steel sheet.

[0005] As described above, the cold-rolled sheet manufactured by the conventional method is not sufficiently satisfactory in the surface properties, the resistance to natural aging, and the dent-resistance, which are required for the steel sheet used for an outer panel of a motor car.

[0006] An object of the present invention is to provide a cold-rolled steel sheet and a galvanized steel sheet, which are satisfactory in any of the surface properties, the resistance to natural aging, and the dent-resistance, which are required for the steel sheet used for an outer panel of a motor car, and a method of manufacturing the same.

Disclosure of Invention

[0007]

(1) The present invention provides a cold-rolled steel sheet excellent in formability, panel shapeability and dent-resistance, comprising 0.005 to 0.015% by weight of C, 0.01 to 0.2% by weight of Si, 0.2 to 1.5% by weight of Mn, 0.01 to 0.07% by weight of P, 0.006 to 0.015% by weight of S, 0.01 to 0.08% by weight of sol. Al, not higher than 0.004% by weight of N, not higher than 0.003% by weight of O, 0.04 to 0.23% by weight of Nb, the amounts of Nb and C meeting the relationship given in formula (1), and a balance of Fe and unavoidable impurities, the cold-rolled steel sheet meeting the relationship given in formula (2):

$$1.0 \leq (\text{Nb}\% \times 12) / (\text{C}\% \times 93) \leq 3.0 \quad \dots (1)$$

$$\exp(\varepsilon) \times (5.29 \times \exp(\varepsilon) - 4.19) \leq \sigma / \sigma_{0.2} \leq$$

$$\exp(\varepsilon) \times (5.64 \times \exp(\varepsilon) - 4.49) \quad \dots (2)$$

where $0.002 < \varepsilon \leq 0.096$, ε represents a true strain, $\sigma_{0.2}$ represents a 0.2% proof stress, and σ represents a true stress relative to ε .

(2) The present invention provides the cold-rolled steel sheet excellent in formability, panel shapeability and dent-resistance defined in item (1) above, further comprising 0.0001 to 0.002% by weight of B.

(3) The present invention provides a galvanized steel sheet excellent in formability, panel shapeability and dent-resistance, which is obtained by applying a galvanizing to the cold-rolled steel sheet defined in item (1) or item (2) above.

(4) The present invention provides a method of manufacturing a cold-rolled steel sheet excellent in formability, panel shapeability and dent-resistance defined in item (1) or item (2) above, comprising the steps of:

preparing a molten steel and continuously casting the steel;

applying a hot-rolling process such that a finish rolling is performed at $(\text{Ar}_3 - 100)^\circ\text{C}$ or more and the rolled steel sheet is coiled at 500 to 700°C ; and

continuously applying a cold-rolling process and an annealing process to the hot-rolled steel sheet.

(5) The present invention provides a method of manufacturing a galvanized steel sheet, the steel sheet being excellent in formability, panel shapeability and dent-resistance, defined in item (3) above, comprising the steps of:

preparing a molten steel and continuously casting the steel;

applying a hot-rolling process such that a finish rolling is performed at $(\text{Ar}_3 - 100)^\circ\text{C}$ or more and the rolled steel sheet is coiled at 500 to 700°C ; and

continuously applying a cold-rolling process and a galvanizing process to the hot-rolled steel sheet.

(6) The present invention provides a cold-rolled steel sheet excellent in the surface shape of a panel and dent-resistance, comprising 0.004 to 0.015% by weight of C, 0.01 to 0.2% by weight of Si, 0.1 to 1.5% by weight of Mn, 0.01 to 0.07% by weight of P, 0.005 to 0.015% by weight of S, 0.01 to 0.08% by weight of sol. Al, not higher than 0.005% by weight of N, and at least one kind of the element selected from the group consisting of 0.02 to 0.12% by weight of Nb and 0.03 to 0.1% by weight of Ti, the amount of C, Nb, Ti, N and S meeting the relationship given in formula (1), and a balance of Fe and unavoidable impurities, the cold-rolled steel sheet meeting the relationship given in formula (2):

$$-0.001 \leq \text{C}\% - (12/93)\text{Nb}\% - (12/48)\text{Ti}^* \leq 0.001 \quad \dots (1)$$

where $\text{Ti}^* = \text{Ti}\% - (48/14)\text{N}\% - (48/32)\text{S}\%$, when Ti^* is not larger than 0, Ti^* is regarded as 0.

$$\exp(\varepsilon) \times (5.29 \times \exp(\varepsilon) - 4.19) \leq \sigma / \sigma_{0.2} \leq \exp(\varepsilon) \times (5.64 \times \exp(\varepsilon) - 4.49) \quad \dots (2)$$

where $0.002 < \varepsilon \leq 0.096$, ε represents a true strain, $\sigma_{0.2}$ represents a 0.2% proof stress, and σ represents a true stress relative to ε .

(7) The present invention provides a cold-rolled steel sheet excellent in the surface shape of a panel and dent-resistance defined in item (6) above, further comprising 0.0001 to 0.002% by weight of B.

(8) The present invention provides a galvanized steel sheet, the steel sheet being excellent in the surface shape of a panel and dent-resistance and prepared by applying a galvanizing to the cold-rolled steel sheet defined in item

(6) or item (7) above.

(9) The present invention provides a method of manufacturing a cold-rolled steel sheet excellent in the surface shape of a panel and dent-resistance and defined in item (6) or item (7) above, comprising the steps of:

applying a hot-rolling process after preparation of a molten steel and continuous casting of the steel such that a finish rolling is performed at $(Ar_3-100)^{\circ}C$ or more and the rolled steel sheet is coiled at 500 to $700^{\circ}C$; and continuously applying a cold-rolling process and an annealing process to the hot-rolled steel sheet.

(10) The present invention provides a method of manufacturing a galvanized steel sheet, the steel sheet being excellent in the surface shape of a panel and dent-resistance and defined in item (8) above, comprising the steps of:

applying a hot-rolling process after preparation of an ingot steel and continuous casting of the ingot steel such that a finish rolling is performed at $(Ar_3-100)^{\circ}C$ or more and the rolled steel sheet is coiled up at 500 to $700^{\circ}C$; and continuously applying a cold-rolling treatment and a galvanizing treatment to the hot-rolled steel band.

Brief Description of Drawings

[0008]

FIGS. 1A and 1B show the relationships between the elongation El and $(Nb \times 12)/(C \times 93)$ and between the r -value and $(Nb \times 12)/(C \times 93)$ according to a first embodiment of the present invention;

FIG. 2 shows a method of evaluating the dent-resistance and the shapeability according to the first embodiment of the present invention;

FIG. 3 is a graph showing how $P0.1$ (dent-resistance load of a panel imparted with strains of 2%, 4% and 8%) and δ (spring back amount of 2% panel) are affected by $\sigma / \sigma_{0.2}$, $\exp(\epsilon)$, and components of the steel composition according to the first embodiment of the present invention;

FIG. 4 is a graph showing how $P0.1$ (dent-resistance load of a panel imparted with strains of 2%, 4% and 8%) and δ (spring back amount of 2% panel) are affected by $\sigma / \sigma_{0.2}$, $\exp(\epsilon)$, and components of the steel composition according to the first embodiment of the present invention;

FIG. 5 is a graph showing how $P0.1$ (dent-resistance load of a panel imparted with strains of 2%, 4% and 8%) and δ (spring back amount of 2% panel) are affected by $\sigma / \sigma_{0.2}$, $\exp(\epsilon)$, and components of the steel composition according to the first embodiment of the present invention;

FIG. 6 is a graph showing how the finishing temperature and the coiling temperature have an influence on $P0.1$ (dent-resistance load of a panel imparted with strains of 2%), δ , and Wca (Arithmetic Average Waviness Height) according to the first embodiment of the present invention;

FIG. 7 shows how an experiment for evaluating the dent-resistance and the shapeability is conducted according to a second embodiment of the present invention;

FIG. 8 is a graph showing how $P0.1$ (dent-resistance load of a panel imparted with strains of 2%, 4% and 8%) and δ (spring back amount of 2% panel) are affected by $\sigma / \sigma_{0.2}$, $\exp(\epsilon)$, and components of the steel composition according to the second embodiment of the present invention;

FIG. 9 is a graph showing how $P0.1$ (dent-resistance load of a panel imparted with strains of 2%, 4% and 8%) and δ (spring back amount of 2% panel) are affected by $\sigma / \sigma_{0.2}$, $\exp(\epsilon)$, and components of the steel composition according to the second embodiment of the present invention;

FIG. 10 is a graph showing how $P0.1$ (dent-resistance load of a panel imparted with strains of 2%, 4% and 8%) and δ (spring back amount of 2% panel) are affected by $\sigma / \sigma_{0.2}$, $\exp(\epsilon)$, and components of the steel composition according to the second embodiment of the present invention;

FIG. 11 is a graph showing how the finishing temperature and the coiling temperature have an influence on $P0.1$ (dent-resistance load of a panel imparted with strains of 2%), δ , and Wca (Arithmetic Average Waviness Height) according to the second embodiment of the present invention; and

FIG. 12 is a graph showing the relationship between the storage time and $\Delta YPeI$ (recovery amount of $YPeI$ in the case of storage at $25^{\circ}C$ after the temper rolling) in Example 3 of the second embodiment of the present invention.

Best Mode of Carrying Out the Invention

[0009] The present inventors have conducted an extensive research in an attempt to obtain a cold-rolled steel sheet and a galvanized steel sheet, which are excellent in the surface properties, the resistance to natural aging and the dent-resistance required for the steel used for an outer panel of a motor car, and a method of manufacturing the same.

[0010] As a result, it has been found that the dent-resistance of a panel can be improved by an alloy design with an

emphasis placed on the work-hardening behavior in a low strain region in the panel forming step, unlike the prior art in which the dent-resistance required for an outer panel of a motor car is improved by increasing the BH value. It has also been found that good surface properties and resistance to natural aging can be imparted to the steel sheet by positively suppressing the BH value. These findings have enabled the present inventors to develop a technology for stably manufacturing a cold-rolled steel sheet and a galvanized steel sheet, being excellent in the panel surface shapeability and the dent-resistance and exhibiting such a high tensile strength as at least 340 MPa.

[0011] Some embodiments of the present invention will now be described.

(First Embodiment)

[0012] Described in the following are the reasons for using the additives, the reasons for limiting the amounts of the additives, the reasons for limiting the tensile characteristics, and the reasons for limiting the manufacturing conditions according to the first embodiment of the present invention. In the following description, "%" represents "% by weight".

(1) Amounts of Additives

C: 0.005 to 0.015%

[0013] A carbide formed together with Nb affects the work-hardening in a low strain region in panel forming step and contributes to an improvement of the dent-resistance. The particular effect cannot be obtained, if the C amount is less than 0.005%. Also, if the C amount exceeds 0.015%, the dent-resistance of the panel is certainly improved. However, the shape of the panel is impaired. It follows that the C amount should fall within a range of between 0.005 and 0.015%.

Si: 0.01 to 0.2%

[0014] Silicon is effective for strengthening the steel. However, if the Si amount is smaller than 0.01%, it is impossible to obtain a capability of the solid solution strengthening. On the other hand, if the Si amount is larger than 0.2%, the surface properties of the steel sheet are impaired. In addition, striped surface defects are generated after galvanizing. Therefore, the Si amount should fall within a range of between 0.01 and 0.2%.

Mn: 0.2 to 1.5%

[0015] Manganese serves to precipitate sulfide and to suppress deterioration of the hot ductility. Also, Mn is effective for strengthening the steel. If the Mn amount is less than 0.2%, hot brittleness of the steel sheet is brought about, leading to a low yield. In addition, a high mechanical strength characterizing the steel sheet of the present invention cannot be obtained. Further, Mn, which relates to an improvement in the workability of the steel sheet, is necessary for controlling the morphology of the MnS in the hot rolling step. It should be noted that fine MnS particles are formed by the process of resolution and re-precipitation in the hot rolling step. These MnS particles impair the grain growth of the steel. However, if Mn is added in an amount not smaller than 0.2%, it is possible to eliminate the above-noted adverse effect produced by the presence of the MnS particles. In order to control effectively the morphology of the MnS particles in the hot rolling step, it is more desirable to add Mn in an amount of at least 0.45%. However, if the Mn amount exceeds 1.5%, the steel sheet is hardened and the panel shapeability of the steel sheet are deteriorated. It follows that Mn amount should fall within a range of between 0.2% and 1.5%.

P: 0.01 to 0.07%

[0016] Phosphorus is most effective for the solid solution strengthening of steel. If the P amount is smaller than 0.01%, however, P fails to exhibit a sufficient strengthening capability. On the other hand, if the P amount exceeds 0.07%, the ductility of the steel sheet is deteriorated. Also, a defective coating is brought about in the step of the alloying treatment during the continuous galvanizing process. It follows that the P amount should fall within a range of between 0.01 and 0.07%.

S: 0.006 to 0.015%

[0017] Sulfur, if added in an amount exceeding 0.015%, brings about hot brittleness of the steel. If the S amount is smaller than 0.006%, however, the peeling capability of the scale is impaired in the hot rolling step, and surface defects tend to be generated markedly. It follows that the S amount should fall within a range of between 0.006 and 0.015%.

Sol. Al: 0.01 to 0.08%

[0018] Aluminum serves to deoxidize the steel and fix N as nitride. If the Al amount is smaller than 0.01%, however, the deoxidation and the fixation of N cannot be achieved sufficiently. On the other hand, if the Al amount is larger than 0.08%, the surface properties of the steel sheet are deteriorated. Therefore, the Al amount should fall within a range of between 0.01 and 0.08%.

$$N \leq 0.004\%$$

[0019] Nitrogen is fixed in the form of AlN. If the N amount exceeds 0.004%, however, it is impossible to obtain a desired formability of the steel sheet. Naturally, the N amount should not exceed 0.004%.

$$O \leq 0.003\%$$

[0020] Oxygen forms inclusions involving oxides so as to adversely affect the grain growth of the steel. If the O amount exceeds 0.003%, the grain growth is impaired in the annealing step, resulting in failure to obtain satisfactory formability and panel shapeability. Naturally, the O amount should not exceed 0.003%. In order to suppress the O amount at 0.003% or less in the steel of the composition specified in the present invention, it is necessary to employ optimum manufacturing conditions. For example, the sol. Al should be controlled at a suitable level, and O should be controlled up in the process steps after the secondary refining process.

Nb: 0.04 to 0.23%

[0021] Niobium is bonded to C to form fine carbide particles. These fine carbide particles affect the work-hardening behavior in the panel forming step so as to contribute to an improvement in the dent-resistance of the panel. If the Nb amount is smaller than 0.04%, however, it is impossible to obtain the particular effect. On the other hand, if the Nb amount exceeds 0.23%, the panel shapeability such as the spring back and the surface deflection is deteriorated, though the dent-resistance is certainly improved. Naturally, the Nb amount should fall within a range of between 0.04 and 0.23%.

$$(Nb \times 12)/(C \times 93): 1.0 \text{ to } 3.0$$

[0022] In the present invention, it is absolutely necessary to control $(Nb \times 12)/(C \times 93)$ in order to improve the formability of the steel sheet. If the value of $(Nb \times 12)/(C \times 93)$ is less than 1.0, C cannot be fixed sufficiently, resulting in failure to obtain a high r-value and a high ductility aimed at in the present invention. If the value exceeds 3.0, however, the amount of Nb forming a solid solution is rendered excessively high, leading to a low ductility. In this case, it is impossible to obtain a formability aimed at in the present invention. It follows that the value of $(Nb \times 12)/(C \times 93)$ should fall within a range of between 1.0 and 3.0. FIGS. 1A and 1B show the relationships between the elongation El and $(Nb \times 12)/(C \times 93)$ and between the r-value and $(Nb \times 12)/(C \times 93)$.

[0023] In order to improve the dent-resistance as desired, it is desirable to add B in an amount given below in addition to the additives described above.

B: 0.0001 to 0.002%

[0024] If B is added, the grain boundary is strengthened so as to improve the resistance to the secondary working brittleness. Also, the ferrite grains are diminished so as to ensure an absolute value of the yield strength and, thus, to improve the dent-resistance. However, these effects cannot be obtained if the B amount is smaller than 0.0001%. On the other hand, if the B amount exceeds 0.002%, the yield point is increased and, thus, the panel shapeability is impaired. It follows that the B amount should fall within a range of between 0.0001 and 0.002%.

(2) Tensile Characteristics

[0025] $\exp(\epsilon) \times (5.29 \times \exp(\epsilon) - 4.19) \leq \sigma / \sigma_{0.2} \leq \exp(\epsilon) \times (5.64 \times \exp(\epsilon) - 4.49)$, where $0.002 < \epsilon \leq 0.096$, ϵ represents a true strain, $\sigma_{0.2}$ represents a 0.2% proof stress, and σ represents a true stress relative to ϵ .

[0026] In the steel sheet of the present invention comprising the additives described in item (1) above, Fe and unavoidable impurities, a ratio of flow stress σ obtained by a tensile test under the condition that a true strain ε is larger than 0.002 and not larger than 0.096, i.e., $0.002 < \varepsilon \leq 0.096$, to a 0.2% proof stress $\sigma_{0.2}$, i.e., $\sigma / \sigma_{0.2}$, should fall within a range of between $\exp(\varepsilon) \times (5.29 \times \exp(\varepsilon) - 4.19)$ and $\exp(\varepsilon) \times (5.64 \times \exp(\varepsilon) - 4.49)$.

[0027] If the ratio $\sigma / \sigma_{0.2}$ is lower than the lower limit noted above, the dent-resistance load under the conditions of 2%P0.1, 4%P0.1, 8%P0.1 is as high as 160 to 190N as shown in FIGS. 3 to 5. For measuring the dent-resistance load, a steel sheet is formed to a model panel shown in FIG. 2 with strain of 2%, 4% or 8% imparted to the steel sheet, followed by applying a heat treatment at 170°C for 20 minutes. Then, measured is a load required for imparting a residual displacement of 0.1 mm to the model panel. However, the spring back δ (measured for a panel having a strain of 2%) is as large as 7 to 10% so as to impair the panel shapeability, if the ratio $\sigma / \sigma_{0.2}$ is lower than the lower limit noted above. On the other hand, if the ratio $\sigma / \sigma_{0.2}$ is higher than the upper limit noted above, the spring back δ is as small as 2 to 5% to improve the panel shapeability. However, the dent-resistance is as low as 140 to 175N. In other words, the dent-resistance cannot be improved. Under the circumstances, the ratio $\sigma / \sigma_{0.2}$ should fall within a range of between $\exp(\varepsilon) \times (5.29 \times \exp(\varepsilon) - 4.19)$ and $\exp(\varepsilon) \times (5.64 \times \exp(\varepsilon) - 4.49)$.

[0028] A cold-rolled steel sheet and a galvanized steel sheet excellent in the panel surface properties and the dent-resistance required for the steel used for an outer panel of a motor car can be obtained by controlling the additive components as described in item (1) above and the tensile characteristics as described in item (2) above.

[0029] The steel sheet exhibiting the particular properties can be manufactured as follows.

(3) Steel Sheet Manufacturing Process

[0030] In the first step, steel of the composition given in item (1) above is melted. A converter method is generally employed for melting the steel composition, or an electric furnace method can also be employed. After the molten steel is continuously cast to obtain a slab, the slab is heated immediately after the casting, or after the slab is once cooled, for applying a hot rolling. The hot rolling is performed under the conditions that the finishing temperature is set at temperature not less than $(Ar_3-100)^\circ\text{C}$ and that the coiling temperature is set at 500°C to 700°C . If the finishing temperature is lower than $(Ar_3-100)^\circ\text{C}$, 2%P0.1, i.e., the dent-resistance load of the panel imparted with 2% of strain) is as low as 140 to 150N, as shown in FIG. 6. In other words, the dent-resistance of the panel cannot be improved. Also, where the coiling temperature is lower than 500°C , the value of 2%P0.1 is high, i.e., 155 to 165N. However, the value of δ , i.e., the spring back amount of the panel imparted with 2% of strain, is as large as 8% to 10%, leading to a poor shapeability. On the other hand, where the coiling temperature exceeds 700°C , the value of Wca (i.e., Arithmetic Average Waviness Height; measuring length of 25 mm; average of the values measured at 10 optional points around the apex of the panel) is large, which falls within a range of between a value exceeding $0.4\ \mu\text{m}$ and $0.6\ \mu\text{m}$, leading to a poor panel shapeability. It follows that the finishing temperature should be not lower than $(Ar_3-100)^\circ\text{C}$ and that the coiling temperature should fall within a range of between 500°C and 700°C .

[0031] In the next step, the hot-rolled steel band is subjected to pickling, cold-rolling and, then, a continuous annealing. Alternatively, galvanizing is applied after the continuous annealing. The cold-rolling reduction should desirably be at least 70% in order to improve the deep drawability (r-value) of the steel sheet. The annealing should desirably be carried out within a recrystallization temperature region of the ferrite phase. Further, the coating employed in the present invention is not limited to continuous galvanizing. Specifically, even if a surface treatment such as coating with zinc phosphate or an electrolytic galvanizing is applied to the steel sheet obtained by the continuous annealing, no problem is brought about in the characteristics of the resultant steel sheet.

(Second Embodiment)

[0032] Described in the following are the reasons for using the additives, the reasons for limiting the amounts of the additives, the reasons for limiting the tensile characteristics, and the reasons for limiting the manufacturing conditions according to the second embodiment of the present invention. In the following description, "%" represents "% by weight".

(1) Amounts of Additives

C: 0.004 to 0.015%

[0033] A carbide formed together with Nb or Ti affects the work-hardening in a low strain region in the panel forming step and contributes to an improvement of the dent-resistance. The particular effect cannot be obtained, if the C amount is less than 0.004%. Also, if the C amount exceeds 0.015%, the dent-resistance of the panel is certainly improved. However, the shape of the panel is impaired. It follows that the C amount should fall within a range of between 0.004 and 0.015%.

EP 2 172 575 A1

Si: 0.01 to 0.2%

[0034] Silicon is effective for strengthening the steel. However, if the Si amount is smaller than 0.01%, it is impossible to obtain a capability of strengthening. On the other hand, if the Si amount is larger than 0.2%, the surface properties of the steel sheet are impaired. In addition, striped surface defects are generated after galvanizing. Therefore, the Si amount should fall within a range of between 0.01 and 0.2%.

Mn: 0.1 to 1.5%

[0035] Manganese serves to precipitate sulfide and to suppress deterioration of the hot ductility. Also, Mn is effective for strengthening the steel. If the Mn amount is less than 0.1%, hot brittleness of the steel sheet is brought about. However, if the Mn amount exceeds 1.5%, the steel sheet is hardened and the panel shapeability of the steel sheet is deteriorated. It follows that Mn amount should fall within a range of between 0.1% and 1.5%.

P: 0.01 to 0.07%

[0036] Phosphorus is most effective for strengthening the steel. If the P amount is smaller than 0.01%, however, P fails to exhibit a sufficient strengthening capability. On the other hand, if the P amount exceeds 0.07%, the ductility of the steel sheet is deteriorated. Also, a defective coating is brought about in the step of the alloying treatment during the process of the continuous galvanizing. It follows that the P amount should fall within a range of between 0.01 and 0.07%.

S: 0.005 to 0.015%

[0037] Sulfur, if added in an amount exceeding 0.015%, brings about hot brittleness of the steel. However, the S amount smaller than 0.005% is undesirable in terms of the manufacturing cost of the desired steel sheet because a desulfurization treatment and a degassing treatment of the molten steel are required. It follows that the S amount should fall within a range of between 0.005 and 0.015%.

Sol. Al: 0.01 to 0.08%

[0038] Aluminum serves to deoxidize the steel. If the Al amount is smaller than 0.01%, however, the deoxidation cannot be achieved sufficiently. On the other hand, if the Al amount is larger than 0.08%, the surface properties of the steel sheet are deteriorated. Therefore, the Al amount should fall within a range of between 0.01 and 0.08%.

$$N \leq 0.005\%$$

[0039] Nitrogen is fixed in the form of TiN. If the N amount exceeds 0.005%, however, the resistance to natural aging is deteriorated. Naturally, the N amount should not exceed 0.005%.

Nb: 0.02 to 0.12%

[0040] Niobium is bonded to C to form fine carbide particles. These fine carbide particles affect the work-hardening behavior in the panel forming step so as to contribute to an improvement in the dent-resistance of the panel. If the Nb amount is smaller than 0.02%, however, it is impossible to obtain the particular effect. On the other hand, if the Nb amount exceeds 0.12%, the panel shapeability such as the spring back and the surface deflection is deteriorated, though the dent-resistance is certainly improved. Naturally, the Nb amount should fall within a range of between 0.02 and 0.12%.

Ti: 0.03 to 0.1%

[0041] Like Nb, Ti forms fine carbide particles. These fine carbide particles greatly contribute to an improvement in the dent-resistance of the panel. If the Ti amount is smaller than 0.03%, however, it is impossible to obtain the particular effect. On the other hand, if the Ti amount exceeds 0.1%, the panel shapeability is deteriorated. Also, the surface of the galvanized steel sheet is impaired. Naturally, the Ti amount should fall within a range of between 0.03 and 0.1%.

$$-0.001 \leq C\% - (12/93)Nb\% - (12/48)Ti\% \leq 0.001,$$

where $Ti^* = Ti\% - (48/14)Nb\% - (48/32)S\%$, when Ti^* is not larger than 0, Ti^* is regarded as 0.

[0042] In the present invention, the value of $C\% - (12/93)Nb\% - (12/48)Ti^*$ (where $Ti^* = Ti\% - (48/14)Nb\% - (48/32)S\%$, when Ti^* is not larger than 0, Ti^* is regarded as 0, which is defined by C, Nb and Ti) should be at least -0.001% and should not exceed 0.001%. If the value exceeds 0.001%, the resistance to natural aging is deteriorated. Also, if the value is smaller than -0.001%, Nb forming a solid solution or Ti forming a solid solution is increased so as to impair the surface properties of the steel sheet and increase the yield point, leading to deterioration of the panel shapeability.

[0043] In the present invention, it is also possible to add B in an amount given below in addition to the additives described above in order to improve the resistance to the secondary working brittleness and the dent-resistance.

B: 0.0001 to 0.002%

[0044] If B is added, the grain boundary is strengthened so as to improve the resistance to the secondary working brittleness. Also, the ferrite grains are diminished so as to ensure an absolute value of the yield strength and, thus, to improve the dent-resistance. However, these effects cannot be obtained if the B amount is smaller than 0.0001%. On the other hand, if the B amount exceeds 0.002%, the yield point is increased and, thus, the panel shapeability is impaired. It follows that the B amount should fall within a range of between 0.0001 and 0.002%.

(2) Tensile Characteristics

[0045] $\exp(\varepsilon) \times (5.29 \times \exp(\varepsilon) - 4.19) \leq \sigma / \sigma_{0.2} \leq \exp(\varepsilon) \times (5.64 \times \exp(\varepsilon) - 4.49)$, where $0.002 < \varepsilon \leq 0.096$, ε represents a true strain, $\sigma_{0.2}$ represents a 0.2% proof stress, and σ represents a true stress relative to ε .

[0046] In the steel sheet of the present invention comprising the additives described in item (1) above, Fe and unavoidable impurities, a ratio of flow stress σ obtained by a tensile test under the condition that a true strain ε is larger than 0.002 and not larger than 0.096, i.e., $0.002 < \varepsilon \leq 0.096$, to a 0.2% proof stress $\sigma_{0.2}$, i.e., $\sigma / \sigma_{0.2}$, should fall within a range of between $\exp(\varepsilon) \times (5.29 \times \exp(\varepsilon) - 4.19)$ and $\exp(\varepsilon) \times (5.64 \times \exp(\varepsilon) - 4.49)$.

[0047] If the ratio $\sigma / \sigma_{0.2}$ is lower than the lower limit noted above, the dent-resistance load under the conditions of 2%P0.1, 4%P0.1, 8%P0.1 is as high as 160 to 210N as shown in FIGS. 8 to 10. For measuring the dent-resistance load, a steel sheet is shaped into a model panel shown in FIG. 1 with strain of 2%, 4% or 8% imparted to the steel sheet, followed by applying a heat treatment at 170°C for 20 minutes. Then, measured is a load required for imparting a residual displacement of 0.1 mm to the model panel. However, the spring back δ (measured for a panel having a strain of 2%) is as large as 7 to 11% so as to impair the panel shapeability, if the ratio $\sigma / \sigma_{0.2}$ is lower than the lower limit noted above. On the other hand, if the ratio $\sigma / \sigma_{0.2}$ is higher than the upper limit noted above, the spring back σ is as small as 1 to 5%. However, the dent-resistance is as low as 140 to 165N. In other words, the dent-resistance cannot be improved.

[0048] A cold-rolled steel sheet and a galvanizing steel sheet excellent in the panel surface properties, the resistance to natural aging and the dent-resistance required for the steel used for an outer panel of a motor car can be obtained by controlling the additive components as described in item (1) above and the tensile characteristics as described in item (2) above.

[0049] The steel sheet exhibiting the particular properties can be manufactured as follows.

(3) Steel Sheet Manufacturing Process

[0050] In the first step, steel of the composition given in item (1) above is melted. A converter method is generally employed for melting the steel composition, or an electric furnace method can also be employed. After the molten steel is continuously cast to obtain a slab, the slab is heated to 1050°C or higher immediately after the casting, or after the slab is once cooled, for applying a hot rolling. The hot rolling is performed under the conditions that the finishing temperature is set at temperature not less than $(Ar_3-100)^\circ\text{C}$ and that the coiling temperature is set at 500°C to 700°C. If the finishing temperature is lower than $(Ar_3-100)^\circ\text{C}$, 2%P0.1, i.e., the dent-resistance load of the panel imparted with 2% of strain) is as low as 140 to 155N, as shown in FIG. 11. In other words, the dent-resistance of the panel cannot be improved. Also, where the coiling temperature is lower than 500°C or higher than 700°C, the value of 2%P0.1 is high, i.e., 156 to 175N. However, the value of Wca, (i.e., Arithmetic Average Waviness Height; measuring length of 25 mm; average of the values measured at 10 optional points around the apex of the panel) is large, which falls within a range of between a value exceeding 0.2 μm and 0.6 μm , leading to a poor panel shapeability.

[0051] In the next step, the hot-rolled steel band is subjected to a pickling, cold-rolling and, then, a continuous annealing. Alternatively, galvanizing is applied after the continuous annealing step. The cold-rolling reduction should desirably be at least 70% in order to improve the deep drawability of the steel sheet. The annealing should desirably be carried out within a recrystallization temperature region of the ferrite phase and not higher than 930°C. Further, the coating employed in the present invention is not limited to galvanizing. Specifically, even if a surface treatment such as coating with zinc phosphate or an electrolytic zinc coating is applied to the steel sheet obtained by the continuous annealing, no problem

is brought about in the characteristics of the resultant steel sheet.

[0052] Some Examples of the present invention will now be described to demonstrate the prominent effects produced by the present invention.

Examples:

(Example 1)

[0053] Molten steel of the composition shown in Table 1 were prepared in a laboratory, followed by continuously casting the steel to prepare a slab having a thickness of 60 mm. Samples Nos. 1 to 7 shown in Table 1 represent the steel of the composition specified in the present invention, with samples Nos. 8 to 15 denoting the steel for Comparative Examples. The slab was treated by a blooming mill to reduce the thickness of the steel sheet to 30 mm, followed by heating the steel sheet at 1050°C for 1.5 hours under the atmosphere for the hot rolling treatment (by roughing mill). After the rough rolling, a finish rolling was applied at 900°C, followed by applying a coiling simulation at 630°C so as to obtain a hot rolled sheet having a thickness of 3 mm. Then, the hot rolled steel sheet was pickled, followed by applying a cold rolling to reduce the thickness of the steel sheet to 0.8 mm and subsequently applying a continuous annealing at 840°C for 90 seconds. Alternatively, after the continuous annealing at 840°C for 90 seconds, a galvanizing was applied at 460°C, followed by applying an alloying treatment at 530°C. Further, 1.0% of temper rolling was applied to the annealed steel sheet or the galvanized steel sheet so as to prepare samples for the experiments. These samples were used for the tensile test (test piece of JIS No. 5; tested in accordance with the method specified in JIS Z 2241) and for measuring the r-value, 2% BH amount (measured in accordance with the method specified in JIS G 3135), and ΔY_{Pe1} (restoring amount of yield point elongation of the sample stored at 25°C for 6 months after the temper rolling). Also, the sample was formed into the model panel shown in FIG. 2 (formed at three levels of the forming strain of 2, 4 and 8%). After a heat treatment was applied at 170°C for 20 minutes, the dent-resistance of the panel and the shapeability of the panel were examined. The dent-resistance was evaluated under a load of P0.1, in which 0.1 mm of residual displacement was imparted to the panel (in the following description, expressions of 2%P0.1, 4%P0.1 and 8%P0.1 are used for denoting the panel imparted with strain of 2, 4 and 8%, respectively). On the other hand, the panel shapeability was evaluated by the spring back amount δ and Wca: Arithmetic Average Waviness Height (JIS B 0610). The spring back amount δ was defined by using a curvature radius R' of the panel imparted with 2% of strain and a curvature radius R of the press mold, i.e., δ was defined by $(R'/R-1) \times 100$. Where δ was not larger than 6%, i.e., $\delta \leq 6\%$, the evaluation was marked by ○. Where δ was 7 to 10%, i.e., $\delta = 7$ to 10%, the evaluation was marked by Δ. Further, where δ was larger than 10%, i.e., $\delta > 10\%$, the evaluation was marked by x. On the other hand, the surface waviness height each having a length of 25 mm were measured at optional 10 points in the vicinity of the apex of the panel, and the average measured value is denoted by Wca. Where Wca was not larger than 0.2 μm, i.e., $Wca \leq 0.2 \mu m$, the evaluation was marked by ○. Where Wca was larger than 0.2 μm but not larger than 0.4 μm, i.e., $0.2 \mu m < Wca \leq 0.4 \mu m$, the evaluation was marked by Δ. Further, where Wca was larger than 0.4 μm and not larger than 0.6 μm, i.e., $0.4 \mu m < Wca \leq 0.6 \mu m$, the evaluation was marked by x.

[0054] Table 2 shows the results of measurements and evaluations. In samples Nos. 1 to 7 each having a composition falling within the range specified in the present invention, the value of the elongation El was as large as 41.6% to 45.0%. The average r-value, i.e., $(r_0 + 2r_{45} + r_{90})/4$, was as large as 1.80 to 2.20. The value of ΔY_{Pe1} was 0% in any of the samples of the present invention. On the other hand, the spring back amount δ and the Waviness Height Wca were small, i.e., 3% to 5% and 0.09 μm to 0.17 μm, respectively, supporting a good panel shapeability. Further, the dent-resistance P0.1 of the panel imparted with strains of 2%, 4% and 8% was as high as 158N to 193N.

[0055] On the other hand, the steel samples Nos. 8 to 15, each having a composition failing to fall within the range specified in the present invention, did not satisfy simultaneously the formability, the shapeability, and the dent-resistance. Specifically, each of Comparative Samples Nos. 8 and 9 exhibited a 2% BH as high as 33 MPa to 42 MPa and a ΔY_{Pe1} of 0.9% to 2.2%, indicating that these samples were not satisfactory in the resistance to natural aging. Also, the dent-resistance P0.1 under strains of 2% to 8% was found to be 165N to 193N, supporting a high dent-resistance. However, each of these Comparative samples was low in each of the elongation El and the r-value and large in each of the spring back amount δ and the value of Wca, supporting that these Comparative samples were not satisfactory in formability and shapeability. Comparative steel sample No. 10 was high in the elongation El and the r-value, and low in δ and Wca, supporting that this sample was satisfactory in each of formability and shapeability. However, the dent-resistance load P0.1 under strains of 2% to 8% was as low as 148 to 172N. Comparative steel sample No. 11 was high in $\sigma_{0.2}$, which was 265 MPa to 270 MPa, supporting that this sample was satisfactory in dent-resistance. However, the steel sample was high in each of δ and Wca, supporting a poor panel shape. Further, this steel sample was low in the elongation El and the r-value. Each of Comparative steel samples Nos. 12 and 13 was high in the r-value, which was 2.02 to 2.20, but low in El, which was 35.8% to 36.8%. Also, these steel samples were somewhat high in $\sigma_{0.2}$, which was 240 MPa to 250 MPa, supporting a satisfactory dent-resistance. However, since the values of δ and Wca were large, the panel

shape of each of these Comparative steel samples was not satisfactory. Further, each of Comparative steel samples Nos. 14 and 15 was low in EI, which was 37.0 to 38.5%, and in the r-value, which was 1.51 to 1.69, supporting a poor shapeability.

Table 1

Steel Sample No.	C	Si	Mn	P	S	sol.Al
1	0.0067	0.02	0.30	0.040	0.008	0.060
2	0.0080	0.06	0.65	0.020	0.012	0.035
3	0.0085	0.14	0.55	0.050	0.01	0.059
4	0.013	0.07	1.20	0.020	0.009	0.070
5	0.010	0.13	0.90	0.055	0.011	0.062
6	0.0072	0.02	0.80	0.025	0.01	0.040
7	0.011	0.04	0.60	0.040	0.013	0.030
8	0.0045*	0.05	0.65	0.055	0.01	0.063
9	0.0081	0.03	0.45	0.064	0.0075	0.055
10	0.0033*	0.05	0.55	0.035	0.007	0.059
11	0.019*	0.10	0.75	0.060	0.012	0.070
12	0.0076	0.06	0.52	0.042	0.009	0.040
13	0.010	0.05	0.80	0.039	0.01	0.040
14	0.0070	0.04	0.59	0.015	0.008	0.037
15	0.010	0.05	0.80	0.040	0.01	0.038

*: outside scope of present invention

(Continued)

Table 1

Steel Sample No.	N	Nb	B	O	(12/93)* (Nb/C)	Remarks
1	0.0022	0.062	tr.	0.0020	1.2	Present invention
2	0.0030	0.081	tr.	0.0024	1.3	Present invention
3	0.0020	0.145	tr.	0.0022	2.2	Present invention
4	0.0035	0.141	tr.	0.0017	1.4	Present invention
5	0.0018	0.202	tr.	0.0019	2.6	Present invention
6	0.0025	0.073	0.0003	0.0025	1.3	Present invention
7	0.0019	0.119	0.0008	0.0020	1.4	Present invention
8	0.0025	0.024	tr.	0.0019	0.7*	Comparative example
9	0.0022	0.050	tr.	0.0025	0.8*	Comparative example
10	0.0025	0.038*	tr.	0.0023	1.5	Comparative example
11	0.0030	0.191	tr.	0.0022	1.3	Comparative example
12	0.0025	0.200	tr.	0.0017	3.4*	Comparative example
13	0.0024	0.270*	tr.	0.0018	3.5*	Comparative example
14	0.0032	0.081	tr.	0.0036*	1.5	Comparative example
15	0.0024	0.100	tr.	0.0043*	1.3	Comparative example

*: outside scope of present invention

Table 2

Steel sample No.	Annealing method	$\sigma_{0.2}$ (MPa)	TS (MPa)	El (%)	Average r-value	2%BH (MPa)	ΔY_{Pe1} (%)	$\sigma (\epsilon = 0.02)$ (MPa)	$\sigma (\epsilon = 0.04)$ (MPa)
1	CA	225	373	42.5	1.88	0	0	283	318
	CG	227	370	42.0	1.85	0	0	286	322
2	CA	229	377	43.0	1.95	0	0	289	324
	CG	230	375	42.6	1.92	0	0	289	324
3	CA	235	388	45.0	2.20	0	0	294	328
	CG	232	390	44.6	2.10	0	0	294	327
4	CA	233	396	42.0	1.97	0	0	293	328
	CG	230	392	41.6	1.93	0	0	293	323
5	CA	230	370	42.5	2.15	0	0	288	321
	CG	230	375	42.0	2.11	0	0	286	320
6	CA	235	380	42.0	2.00	0	0	298	328
	CG	233	376	41.6	1.94	0	0	293	324
7	CA	233	385	43.0	1.99	0	0	295	323
	CG	225	380	42.0	1.93	0	0	284	316

*outside scope of formula (1)

CA: continuous annealing CG: continuous galvanizing

(Continued)

Table 2

Steel sample No.	Annealing method	$\sigma_{0.2}$ (MPa)	TS (MPa)	El (%)	Average r-value	2%BH (MPa)	ΔY_{Pe1} (%)	σ ($\epsilon=0.02$) (MPa)	σ ($\epsilon=0.04$) (MPa)
8	CA	240	343	41.0	1.70	35	1.0	270*	296*
	CG	245	345	39.7	1.65	33	0.9	276*	300*
9	CA	260	399	36.5	1.55	40	2.0	290*	315*
	CG	258	402	35.9	1.51	42	2.2	290*	311*
10	CA	213	358	43.5	2.00	0	0	280*	312*
	CG	210	357	43.0	1.97	0	0	272*	305*
11	CA	270	410	38.0	1.60	0	0	320*	363*
	CG	265	404	37.5	1.57	0	0	313*	357*
12	CA	244	386	36.8	2.20	0	0	304	339
	CG	240	385	36.0	2.10	0	0	299	335
13	CA	247	400	36.3	2.15	0	0	307	340
	CG	250	402	35.8	2.02	0	0	310	345
14	CA	228	370	38.5	1.69	0	0	288	319
	CG	225	368	38.2	1.65	0	0	282	319
15	CA	255	406	37.0	1.60	0	0	307*	342*
	CG	258	404	37.5	1.51	0	0	304*	344*

*outside scope of formula (1)

CA: continuous annealing CG: continuous galvanizing

(Continued)

Table 2

Steel Sample No.	σ ($\epsilon = 0.08$) (MPa)	2%PO.1 (N)	4%PO.1 (N)	8%PO.1 (N)	δ (%)	Wca (μm)	Remarks
1	385	158	167	183	3(O)	0.10(O)	Present invention
	389	159	168	186	3(O)	0.10(O)	Present invention
2	387	160	171	186	4(O)	0.10(O)	Present invention
	389	160	171	189	4(O)	0.15(O)	Present invention
3	397	163	173	192	5(O)	0.17(O)	Present invention
	392	163	173	190	4(O)	0.14(O)	Present invention
4	392	163	175	191	3(O)	0.15(O)	Present invention
	388	161	170	189	3(O)	0.14(O)	Present invention
5	390	160	171	190	3(O)	0.10(O)	Present invention
	388	160	169	190	3(O)	0.13(O)	Present invention
6	395	167	175	193	4(O)	0.15(O)	Present invention
	392	164	173	189	4(O)	0.12(O)	Present invention
7	390	164	174	188	4(O)	0.12(O)	Present invention
	383	159	168	184	3(O)	0.09(O)	Present invention
8	355*	166	170	185	7(Δ)	0.26(Δ)	Comparative example
	361*	165	172	188	8(Δ)	0.30(Δ)	Comparative example

*outside scope of formula (1)

CA: continuous annealing CG: continuous galvanizing

(Continued)

Table 2

Steel Sample No.	σ ($\epsilon=0.08$) (MPa)	2%PO.1 (N)	4%PO.1 (N)	8%PO.1 (N)	δ (%)	Wca (μm)	Remarks
9	374*	178	190	193	11(X)	0.50(X)	Comparative example
	372*	180	187	193	11(X)	0.49(X)	Comparative example
10	377*	154	160	172	2(O)	0.10(O)	Comparative example
	373*	148	157	170	2(O)	0.08(O)	Comparative example
11	419*	182	197	196	12(X)	0.46(X)	Comparative example
	415*	177	195	190	11(X)	0.44(X)	Comparative example
12	408	168	177	189	7(Δ)	0.25(Δ)	Comparative example
	405	166	173	188	7(Δ)	0.24(Δ)	Comparative example
13	416	168	175	191	8(Δ)	0.29(Δ)	Comparative example
	419	171	181	194	10(Δ)	0.29(Δ)	Comparative example
14	388	161	159	190	3(O)	0.12(O)	Comparative example
	382	158	160	187	3(O)	0.10(O)	Comparative example
15	416*	166	174	191	11(X)	0.27(Δ)	Comparative example
	415*	165	177	190	11(X)	0.32(Δ)	Comparative example

*outside scope of formula (1)

CA: continuous annealing CG: continuous galvanizing

(Example 2)

[0056] A molten steel having a composition of steel sample No. 2 of the present invention shown in Table 1 was prepared by melting and casting in a laboratory, followed by casting the molten steel to prepare a slab having a thickness of 50 mm. The slab was treated by a blooming mill to reduce the thickness of the steel sheet to 25 mm, followed by heating the steel sheet at 1250°C for 1 hour under the atmosphere and subsequently applying a hot rolling treatment to reduce the thickness of the steel sheet to 2.8 mm. The finishing temperature and the coiling temperature in the hot rolling treatment were changed within ranges of 770°C to 930°C and 450°C to 750°C, respectively. Then, the hot rolled steel sheet was pickled, followed by applying a cold rolling to reduce the thickness of the steel sheet to 0.75 mm and subsequently applying a soaking treatment at 825°C for 90 seconds. Further, a temper rolling was applied at an elongation of 1.2%. The mechanical characteristics and the panel characteristics of the thin steel sheet thus prepared were examined as in Example 1. Table 3 shows the results. The finishing temperature for each of steel samples Nos. 1 to 3 of the present invention was lower than (Ar₃-100)°C. Also, each of these steel samples exhibited a low P0.1 under strains of 2% to 8%, i.e., 139N to 159N, and a high Wca, i.e., 0.35 μm to 0.40 μm, indicating that these steel samples were poor in the dent-resistance and in the shapeability. Further, the r-value for these steel samples was as low as 1.69 to 1.77. The coiling temperature for each of steel samples Nos. 7 and 12 was lower than 500°C. Also, each of these steel samples exhibited a high $\sigma_{0.2}$ value, i.e., 243 MPa and 248 MPa, respectively, supporting a good dent-resistance. However, the δ value was as high as 8% and the Wca value was as high as 0.30 μm, indicating that these steel samples were poor in the panel shape. The coiling temperature for each of steel samples Nos. 11, 15 and 18 was higher than 700°C. Also, each of these steel samples exhibited a low $\sigma_{0.2}$ value, i.e., 210 MPa to 216 MPa, and such a low δ value of 2%. However, the Wca value was as high as 0.42 μm to 0.43 μm. Also, the dent-resistance load was low in each of these steel samples. On the other hand, each of steel samples Nos. 4-6, 8-10, 13, 14, 16 and 17, which fell within the scopes specified in the present invention in respect of the finishing temperature and the coiling temperature, was found to be satisfactory in each of the formability, the dent-resistance and the shapeability.

Table 3

No.	Steel sample No.	Finish temperature (°C)	Coiling temperature (°C)	$\sigma_{0.2}$ (MPa)	TS (MPa)	El (%)	Average r-value	σ ($\epsilon=0.02$) (MPa)
1	Steel 2	770**	540	212	375	41.3	1.73	275*
2			600	217	372	42.0	1.69	281*
3			660	215	370	42.0	1.77	280*
4		810	530	230	380	43.0	1.89	289
5			600	227	375	43.5	1.92	285
6			670	225	377	44.0	1.95	285
7		850	470**	243	382	41.0	1.80	293*
8			530	232	377	42.8	1.88	292
9			590	230	370	43.3	1.93	289
10			650	230	373	43.0	1.95	293
11			715**	216	370	43.3	1.82	281*
12			450**	248	382	41.2	1.82	301*
13		890	550	233	371	42.8	1.90	292
14			650	226	378	43.5	1.98	287
15			750**	210	367	42.7	1.83	274*
16		930	550	230	370	42.8	1.91	290
17			650	225	375	43.2	1.95	283
18			750**	212	368	43.7	1.81	277*

(Continued)

Table 3

No.	σ ($\epsilon=0.04$) (MPa)	σ ($\epsilon=0.08$) (MPa)	2%, 4%, 8% (N)	δ (%)	Wca (μm)	Remarks
1	306*	375*	139 - 153	2(O)	0.35(Δ)	Comparative example
2	313*	383*	143 - 159	2(O)	0.40(Δ)	Comparative example
3	311*	380*	144 - 156	2(O)	0.40(Δ)	Comparative example
4	322	392	152 - 179	4(O)	0.15(O)	Present invention
5	317	387	150 - 175	4(O)	0.10(O)	Present invention
6	318	388	150 - 177	3(O)	0.09(O)	Present invention
7	328*	400*	155 - 182	8(Δ)	0.30(Δ)	Comparative example
8	324	392	154 - 178	4(O)	0.10(O)	Present invention
9	320	390	151 - 178	4(O)	0.12(O)	Present invention
10	322	392	154 - 177	4(O)	0.12(O)	Present invention
11	313*	382*	144 - 156	2(O)	0.43($\times$)	Comparative example
12	334*	407*	160 - 184	8(Δ)	0.30(Δ)	Comparative example
13	325	394	155 - 180	4(O)	0.07(O)	Present invention
14	321	385	153 - 171	3(O)	0.18(O)	Present invention
15	305*	372*	139 - 152	2(O)	0.42($\times$)	Comparative example
16	321	390	152 - 178	4(O)	0.18(O)	Present invention
17	315	384	150 - 170	3(O)	0.17(O)	Present invention
18	309*	377*	142 - 155	2(O)	0.42($\times$)	Comparative example

*: outside scope of formula (1); **: outside scope of present invention

(Example 3)

[0057] Molten steel of the composition shown in Table 4 (steel samples Nos. 1 to 15 belonging to Examples of the present invention, with steel samples Nos. 16 to 29 belonging to Comparative Example) were prepared in a laboratory, followed by continuously casting the molten steel to prepare a slab having a thickness of 60 mm. The slab was treated by a blooming mill to reduce the thickness of the steel sheet to 30 mm, followed by heating the steel sheet at 1100°C for 1 hour under the air atmosphere for the hot rolling process (by roughing mill). After the roughing, a finish rolling was applied at 890°C, followed by applying a coiling simulation at 600°C so as to obtain a hot rolled sheet having a thickness of 3 mm. Then, the hot rolled steel sheet was pickled, followed by applying a cold rolling to reduce the thickness of the steel sheet to 0.75 mm and subsequently applying a continuous annealing at 850°C for 90 seconds. Alternatively, after the continuous annealing at 850°C for 90 seconds, a galvanizing was applied at 460°C, followed by applying an alloying treatment at 500°C. Further, 1.0% of temper rolling was applied to the annealed steel sheet or the galvanized steel sheet so as to prepare samples for the experiments. These samples were used for the tensile test (test piece of JIS No. 5; tested in accordance with the method specified in JIS Z 2241) and for measuring 2% BH amount (measured in accordance with the method specified in JIS G 3135), and $\Delta YPeI$ (restoring amount of yield point elongation of the sample stored at 25°C for 6 months after the temper rolling). Also, the sample was formed into the model panel shown in FIG. 7 (molded at three levels of the strain of 2, 4 and 8%). After a heat treatment was applied at 170°C for 20 minutes, the dent-resistance of the panel and the shapeability of the panel were examined. The dent-resistance was evaluated under a load of P0.1, in which 0.1 mm of residual displacement was imparted to the panel (in the following description, expressions of 2%P0.1, 4%P0.1 and 8%P0.1 are used for denoting the panel imparted with molding strain of 2, 4 and 8%, respectively). On the other hand, the panel shapeability was evaluated by the spring back amount δ and the Arithmetic Average Waviness Height Wca (JIS B 0610). The spring back amount δ was defined by using a curvature radius R' of the formed panel imparted with 2% of strain and a curvature radius R of the press mold, i.e., δ was defined by $(R'/R-1) \times 100$. Where δ was not larger than 6%, i.e., $\delta \leq 6\%$, the evaluation was marked by $\bigcirc$. Where δ was 7 to 10%, i.e., $\delta = 7$ to 10%, the evaluation was marked by Δ . Further, where δ was larger than 10%, i.e., $\delta > 10\%$, the evaluation was marked by x. On the other hand, the surface waviness height each having a length of 25 mm were measured at optional 10 points in the vicinity of the apex of the panel in accordance with the method specified in JIS B 0610, and the average measured value is denoted by Wca. Where Wca was not larger than 0.2 μm , i.e., $Wca \leq 0.2 \mu\text{m}$, the evaluation was marked by $\bigcirc$. Where Wca was larger than 0.2 μm but not larger than 0.4 μm , i.e., $0.2 \mu\text{m} < Wca \leq 0.4 \mu\text{m}$, the evaluation was marked by Δ . Further, where Wca was larger than 0.4 μm and not larger than 0.6 μm , i.e., $0.4 \mu\text{m} < Wca \leq 0.6 \mu\text{m}$, the evaluation was marked by x.

[0058] Table 5 shows the results of measurements and evaluations. In samples Nos. 1 to 15 each having a composition falling within the range specified in the present invention, the value of the 2% BH amount was 0 to 26 MPa and the $\Delta YPeI$ was 0%. Compared with the steel sample of Comparative Example No. 16, in which the amount of C was 0.0025% and the 2% BH amount was 36 to 38 MPa, 2%P0.1, 4%P0.1, 8%P0.1 of the steel samples of the present invention was high, i.e., 150 to 180N, 160 to 192N and 175 to 208N, supporting a high dent-resistance of the panel. Also, since $\delta \leq 6\%$ (evaluation of $\bigcirc$) and $Wca < 0.2 \mu\text{m}$ (evaluation of $\bigcirc$), the steel samples of the present invention were satisfactory in the panel shapeability. Further, concerning $\Delta YPeI$, the restoring amount of the yield point elongation was measured for the samples (steel sample No. 6 for the present invention and steel sample 18 for Comparative Example) stored for 18 months at 25°C after the temper annealing, with the results as shown in FIG. 12. The value of $\Delta YPeI$ after storage for 18 months for the steel sample No. 6 of the present invention was less than 0.2%, supporting an excellent resistance to natural aging. On the other hand, the value of $\Delta YPeI$ for the steel sample of Comparative Example 18 was 2.2%, supporting a marked deterioration in the resistance to natural aging.

[0059] Steel samples for Comparative Examples 16 to 29, which do not fall within the scope defined in the present invention, exhibited large values of 2%P0.1, 4%P0.1 and 8%P0.1 of 140 to 195N, 151 to 202N and 160 to 213N, respectively, supporting a satisfactory dent-resistance of the panel. However, in steel samples of Comparative Examples Nos. 16, 18, 19, 23, 24 and 29, the 2% BH was 33 to 45 MPa, $\Delta YPeI$ was not smaller than 0.2%, i.e., $\Delta YPeI \geq 0.2\%$, and Wca was larger than 0.2 μm , i.e., $Wca > 0.2 \mu\text{m}$. In other words, these steel samples of Comparative Examples were inferior to the steel samples of the present invention in the resistance to natural aging and in the panel shapeability. Also, the value of $\Delta YPeI$ was 0% in each of the steel samples for Comparative Examples Nos. 17, 20-22 and 25-28, supporting a satisfactory resistance to natural aging. However, the value of δ for these Comparative Examples was not smaller than 7%, i.e., $\delta \geq 7\%$, indicating that these steel samples were unsatisfactory in the panel shapeability.

Table 4

Steel sample No.	Chemical component (% by weight)							
	C	Si	Mn	P	S	sol.Al	N	Nb
1	0.0044	0.015	0.31	0.04	0.007	0.06	0.0025	0.04
2	0.0072	0.06	0.67	0.02	0.012	0.035	0.003	0.062
3	0.0088	0.14	0.55	0.05	0.009	0.059	0.0022	0.072
4	0.013	0.08	1	0.015	0.009	0.07	0.0035	0.097
5	0.01	0.17	0.9	0.055	0.011	0.062	0.004	0.077
6	0.0066	0.075	1.2	0.045	0.008	0.042	0.0018	0.046
7	0.011	0.053	0.85	0.033	0.013	0.025	0.0027	0.08
8	0.0059	0.01	0.75	0.06	0.01	0.055	0.0044	0.042
9	0.0071	0.065	0.8	0.045	0.011	0.059	0.0019	0.05
10	0.005	0.035	0.97	0.035	0.0065	0.04	0.0027	tr.
11	0.0095	0.04	0.69	0.05	0.012	0.053	0.0032	tr.
12	0.0066	0.02	1.3	0.039	0.009	0.037	0.002	tr.
13	0.0088	0.1	0.73	0.02	0.01	0.04	0.0025	0.062
14	0.0055	0.062	0.52	0.03	0.008	0.051	0.0024	0.02
15	0.01	0.049	0.33	0.061	0.012	0.069	0.003	tr.

(Continued)

Table 4

Steel sample No.	Chemical component (% by weight)							
	C	Si	Mn	P	S	sol.Al	N	Nb
16	0.0025*	0.05	0.65	0.055	0.01	0.063	0.0025	0.01*
17	0.003*	0.05	0.55	0.035	0.007	0.059	0.0025	0.02
18	0.005	0.1	0.75	0.06	0.012	0.07	0.003	0.026
19	0.0085	0.08	1	0.051	0.008	0.037	0.0037	0.05
20	0.01	0.05	0.8	0.039	0.01	0.04	0.0024	0.1
21	0.019*	0.03	0.45	0.064	0.0075	0.055	0.0022	0.15*
22	0.0055	0.07	0.7	0.05	0.01	0.049	0.003	0.027
23	0.011	0.055	0.59	0.04	0.01	0.045	0.002	0.056
24	0.006	0.1	0.73	0.046	0.0085	0.065	0.0032	tr.
25	0.02*	0.065	1.2	0.035	0.011	0.052	0.0025	tr.
26	0.0049	0.1	0.82	0.05	0.007	0.056	0.0024	tr.*
27	0.009	0.045	0.85	0.05	0.01	0.07	0.0029	tr.*
28	0.0055	0.08	0.7	0.05	0.009	0.052	0.002	tr.*
29	0.009	0.04	0.5	0.038	0.01	0.059	0.0026	tr.*

Note: mark * represents that the values does not fall within the scope specified in the present invention

$$Ti^* = Ti\% - (48/14)N\% - (48/32)S\%$$

(where Ti^* is not larger than 0, Ti^* is regarded as 0)

(Continued)

Table 4

Steel sample No.	Chemical component (% by weight)				C-(12/93)Nb- (12/48)Ti*	Remarks
	Ti	Zr	V	B		
1	tr.	tr.	tr.	tr.	-0.0008	Present invention
2	tr.	tr.	tr.	tr.	-0.0008	
3	tr.	tr.	tr.	tr.	-0.0005	
4	tr.	tr.	tr.	tr.	0.0005	
5	tr.	tr.	tr.	tr.	0.0001	
6	tr.	tr.	tr.	tr.	0.0007	
7	0.025	tr.	tr.	tr.	0.0007	
8	0.015	tr.	tr.	tr.	0.0005	
9	0.027	tr.	tr.	tr.	-0.0003	
10	0.037	tr.	tr.	tr.	0.0005	
11	0.07	tr.	tr.	tr.	-0.0008	
12	0.045	tr.	tr.	tr.	0.0004	
13	tr.	tr.	tr.	0.0003	0.0008	
14	0.032	tr.	tr.	0.0013	0.0000	
15	0.067	tr.	tr.	0.0006	0.0003	

Note: mark * represents that the values does not fall within
the scope specified in the present invention.

Ti* = Ti%-(48/14)N%-(48/32)S%

(where Ti* is not larger than 0, Ti* is regarded as 0)

(Continued)

Table 4

Steel sample No.	Chemical component (% by weight)				C-(12/93)Nb- (12/48)Ti*	Remarks
	Ti	Zr	V	B		
16	tr.	tr.	tr.	tr.	0.0012*	Comparative Example
17	tr.	tr.	tr.	tr.	0.0004	
18	tr.	tr.	tr.	tr.	0.0016*	
19	tr.	tr.	tr.	tr.	0.0020*	
20	tr.	tr.	tr.	tr.	-0.0029*	
21	tr.	tr.	tr.	tr.	-0.0004	
22	0.041	tr.	tr.	tr.	-0.0019*	
23	0.03	tr.	tr.	tr.	0.0017*	
24	0.041	tr.	tr.	tr.	0.0017*	
25	0.12*	tr.	tr.	tr.	-0.0037	
26	tr.*	0.075*	tr.	tr.	----*	
27	tr.*	0.11*	tr.	tr.	----*	
28	tr.*	tr.	0.025*	tr.	----*	
29	tr.*	tr.	0.035*	tr.	----*	

Note: mark * represents that the values does not fall within
the scope specified in the present invention.

Ti* = Ti%-(48/14)N%-(48/32)S%

(where Ti* is not larger than 0, Ti* is regarded as 0)

Table 5 (Part 1)

Steel Sample No.	Annealing	$\sigma_{0.2}$ (MPa)	TS (MPa)	El (%)	2%BH (MPa)	ΔY_{PeL} (%)	$\sigma (\epsilon = 0.2)$ (MPa)	$\sigma (\epsilon = 0.04)$ (MPa)	$\sigma (\epsilon = 0.08)$ (MPa)
1	Continuous annealing	229	370	41	0	0	285	321	388
	Continuous galvanizing	231	368	40	0	0	287	323	391
2	Continuous annealing	230	375	40.5	0	0	290	322	390
	Continuous galvanizing	230	377	39.5	0	0	289	325	388
3	Continuous annealing	237	390	39.3	0	0	296	331	403
	Continuous galvanizing	235	392	38.5	0	0	299	330	400
4	Continuous annealing	230	380	39.5	22	0	290	321	389
	Continuous galvanizing	228	383	38.6	20	0	290	320	385
5	Continuous annealing	237	395	39	2	0	299	332	403
	Continuous galvanizing	238	397	38.3	4	0	297	330	405

(Continued)

Table 5 (Part 1)

Steel Sample No.	Annealing	$\sigma_{0.2}$ (MPa)	TS (MPa)	El (%)	2%BH (MPa)	Δy_{Pe1} (%)	$\sigma (\epsilon = 0.2)$ (MPa)	$\sigma (\epsilon = 0.04)$ (MPa)	$\sigma (\epsilon = 0.08)$ (MPa)
6	Continuous annealing	235	395	39.3	24	0	296	328	398
	Continuous galvanizing	237	396	38.1	25	0	299	330	396
7	Continuous annealing	235	385	40.3	23	0	296	329	397
	Continuous galvanizing	237	385	39.1	22	0	300	333	400
8	Continuous annealing	230	392	39	20	0	290	322	389
	Continuous galvanizing	233	393	38	20	0	295	325	392
9	Continuous annealing	235	387	39.5	0	0	296	329	397
	Continuous galvanizing	237	385	38.3	0	0	300	330	400
10	Continuous annealing	232	381	40	18	0	292	323	392
	Continuous galvanizing	235	384	38.5	19	0	295	328	399

(Continued)

Table 5 (Part 1)

Steel Sample No.	2%P0.1 (N)	4%P0.1 (N)	8%P0.1 (N)	δ (%)	Wca (μm)	Remarks
1	150	160	175	4(O)	0.1(O)	Examples of present invention
	150	162	177	4(O)	0.11(O)	
2	153	162	177	4(O)	0.1(O)	
	152	163	175	4(O)	0.13(O)	
3	156	166	186	5(O)	0.1(O)	
	159	165	183	5(O)	0.1(O)	
4	165	177	193	3(O)	0.15(O)	
	162	170	188	3(O)	0.14(O)	
5	160	167	188	5(O)	0.09(O)	
	160	167	190	5(O)	0.13(O)	
6	176	186	205	4(O)	0.15(O)	
	180	188	205	4(O)	0.16(O)	
7	175	186	203	4(O)	0.17(O)	
	178	188	205	4(O)	0.15(O)	
8	163	175	190	3(O)	0.15(O)	
	170	179	195	4(O)	0.15(O)	
9	156	163	181	4(O)	0.08(O)	
	159	165	183	4(O)	0.12(O)	
10	163	173	191	3(O)	0.1(O)	
	169	181	200	4(O)	0.08(O)	

Table 5 (Part 2)

Steel Sample No.	Annealing	$\sigma_{0.2}$ (MPa)	TS (MPa)	El (%)	2%BH (MPa)	$\Delta Y_{P0.2}$ (%)	$\sigma (\epsilon = 0.2)$ (MPa)	$\sigma (\epsilon = 0.04)$ (MPa)	$\sigma (\epsilon = 0.08)$ (MPa)
11	Continuous annealing	237	395	39.3	0	0	298	331	401
	Continuous galvanizing	236	394	38.4	0	0	296	330	398
12	Continuous annealing	235	387	40	17	0	296	330	397
	Continuous galvanizing	236	389	39.8	18	0	300	330	400
13	Continuous annealing	237	378	40	26	0	297	333	401
	Continuous galvanizing	235	380	39.5	24	0	293	330	391
14	Continuous annealing	233	380	41	0	0	296	325	392
	Continuous galvanizing	235	382	40.6	0	0	294	330	397
15	Continuous annealing	238	398	39	15	0	303	336	405
	Continuous galvanizing	237	395	38.2	16	0	303	331	402

(Continued)

Table 5 (Part 2)

Steel Sample No.	Annealing	$\sigma_{0.2}$ (MPa)	TS (MPa)	El (%)	2%BH (MPa)	ΔY_{Pe1} (%)	σ ($\epsilon=0.2$) (MPa)	σ ($\epsilon=0.04$) (MPa)	σ ($\epsilon=0.08$) (MPa)
16	Continuous annealing	236	355	43	36*	0.6*	268*	293*	352*
	Continuous galvanizing	235	356	42	38*	0.5*	267*	291*	351*
17	Continuous annealing	242	368	41.5	15	0	267*	295*	357*
	Continuous galvanizing	244	370	40	13	0	273*	310*	366*
18	Continuous annealing	245	390	39	37*	0.7*	294*	318*	385*
	Continuous galvanizing	245	393	38	39*	0.6*	295*	318*	388*
19	Continuous annealing	258	400	38.2	44*	2*	310*	343*	405*
	Continuous galvanizing	255	403	37	45*	1.8*	308*	337*	409*
20	Continuous annealing	256	408	38	0	0	310*	345*	417*
	Continuous galvanizing	260	405	37.2	0	0	315*	344*	413*

Note: The mark * represents that the values do not fall within the scopes defined in the present invention.

(Continued)

Table 5 (Part 2)

Steel Sample No.	2%P0.1 (N)	4%P0.1 (N)	8%P0.1 (N)	δ (%)	Wca (μm)	Remarks
11	158	166	185	6(O)	0.13(O)	Examples of present invention
	156	165	181	5(O)	0.1 (O)	
12	168	181	197	5(O)	0.15(O)	
	173	183	200	5(O)	0.14(O)	
13	179	192	208	6(O)	0.17(O)	
	172	187	199	5(O)	0.18(O)	
14	156	163	178	4(O)	0.12(O)	Comparative Examples
	155	165	181	5(O)	0.1 (O)	
15	173	185	203	6(O)	0.15(O)	
	175	181	200	6(O)	0.15(O)	
16	160	165	177	5(O)	0.26(Δ)	
	161	165	179	5(O)	0.25(Δ)	
17	140	151	165	8(Δ)	0.15(O)	Comparative Examples
	142	152	160	8(Δ)	0.16(O)	
18	183	188	205	9(Δ)	0.25(Δ)	
	185	190	208	10(Δ)	0.26(Δ)	
19	193	202	210	13(X)	0.39(Δ)	
	195	200	212	12(X)	0.42(X)	
20	163	179	199	12(X)	0.19(O)	Comparative Examples
	170	178	195	14(X)	0.25(Δ)	

Table 5 (Part 3)

Steel Sample No.	Annealing	$\sigma_{0.2}$ (MPa)	TS (MPa)	El (%)	2%BH (MPa)	ΔY_{Pe1} (%)	$\sigma (\epsilon = 0.2)$ (MPa)	$\sigma (\epsilon = 0.04)$ (MPa)	$\sigma (\epsilon = 0.08)$ (MPa)
21	Continuous annealing	268	410	38	0	0	320*	363*	421*
	Continuous galvanizing	260	415	37	0	0	310*	345*	409*
22	Continuous annealing	256	391	39	0	0	308*	344*	410*
	Continuous galvanizing	251	393	40	0	0	303*	332*	400*
23	Continuous annealing	261	400	38.4	40*	0.8*	308*	347*	415*
	Continuous galvanizing	263	403	37.2	37*	1.2*	310*	343*	420*
24	Continuous annealing	257	394	39	40*	0.6*	309*	347*	415*
	Continuous galvanizing	262	391	38.2	37*	1*	312*	343*	416*
25	Continuous annealing	265	398	38.3	0	0	312*	350*	416*
	Continuous galvanizing	268	403	37.1	0	0	319*	351*	422*

Note: The mark * represents that the values do not fall within the scopes defined in the present invention.

(Continued)

Table 5 (Part 3)

Steel Sample No.	Annealing	$\sigma_{0.2}$ (MPa)	TS (MPa)	EL (%)	2%BH (MPa)	ΔY_{Pe1} (%)	$\sigma (\epsilon=0.2)$ (MPa)	$\sigma (\epsilon=0.04)$ (MPa)	$\sigma (\epsilon=0.08)$ (MPa)
26	Continuous annealing	258	393	38.7	0	0	308*	340*	407*
	Continuous galvanizing	258	390	37	0	0	308*	341*	410*
27	Continuous annealing	265	400	38.3	22	0	313*	345*	412*
	Continuous galvanizing	268	403	37.1	20	0	320*	350*	420*
28	Continuous annealing	237	399	39.3	18	0	310*	345*	419*
	Continuous galvanizing	239	400	38	15	0	315*	345*	422*
29	Continuous annealing	258	388	38.5	35*	0.4*	304*	347*	403*
	Continuous galvanizing	260	391	37.1	33*	0.7*	308*	343*	407*

Note: The mark * represents that the values do not fall within the scopes defined in the present invention.

(Continued)

Table 5 (Part 3)

Steel Sample No.	2%P0.1 (N)	4%P0.1 (N)	8%P0.1 (N)	δ (%)	Wca (μ m)	Remarks
21	176	193	194	14(X)	0.42(X)	Comparative Examples
	163	180	190	14(X)	0.4 (Δ)	
22	162	178	191	12(X)	0.25(Δ)	
	160	167	183	12(X)	0.27(Δ)	
23	188	202	212	13(X)	0.49(X)	
	186	199	213	13(X)	0.44(X)	
24	190	202	212	12(X)	0.23(Δ)	
	188	199	211	13(X)	0.25(Δ)	
25	163	184	200	13(X)	0.43(X)	
	175	185	205	14(X)	0.45(X)	
26	162	170	189	11(X)	0.36(Δ)	
	162	173	190	13(X)	0.35(Δ)	
27	185	195	208	13(X)	0.4 (Δ)	
	185	197	208	14(X)	0.52(X)	
28	181	193	207	7(Δ)	0.59(X)	
	183	192	207	8(Δ)	0.55(X)	
29	184	200	206	12(X)	0.44(X)	
	185	198	208	13(X)	0.53(X)	

(Example 4)

[0060] Molten steel having compositions of steel samples Nos. 2 and 14 of the present invention shown in Table 4 was prepared by melting and casting in a laboratory, followed by casting the steel to prepare a slab having a thickness of 50 mm. The slab was treated by a blooming mill to reduce the thickness of the steel sheet to 20 mm, followed by heating the steel sheet at 1200°C for 1 hour under the atmosphere and subsequently applying a hot rolling treatment to reduce the thickness of the steel sheet to 2.8 mm. The finishing temperature and the coiling temperature in the hot rolling treatment were changed within ranges of 750°C to 930°C and 440°C to 750°C, respectively. Then, the hot rolled steel sheet was pickled, followed by applying a cold rolling to reduce the thickness of the steel sheet to 0.75 mm and subsequently applying a continuous annealing (soaking treatment) at 800°C for 90 seconds. Further, a temper rolling (1.4%) was applied. The thin steel sheet thus prepared was shaped into a model panel shown in FIG. 7 with equivalent strains of 2%, 4% and 8%, followed by applying a heat treatment at 170°C for 20 minutes, said heat treatment corresponding to the coating-baking treatment. Table 6 shows the results of evaluation of the dent-resistance of the panel

(three levels of 2%, 4% and 8% of strains) and of the shapeability of the panel imparted with 2% of strain. Samples Nos. 4-7, 9-12, 15-18, 20, 21, 27-29, 32-34, and 36-39 shown in Table 6 fall within the scope of the present invention. On the other hand, samples Nos. 1-3, 8, 13, 14, 19, 22-26, 30, 31, 35 and 40 represent Comparative Examples.

[0061] The finishing temperature for samples Nos. 1-3 and 23-26 for Comparative Examples was lower than (Ar_3 -100) $^{\circ}\text{C}$, which does not fall within the scope defined in the present invention. As a result, these samples for Comparative Examples exhibited a 2% to 8%P0.1 of 140N to 158N and 140N to 165N, and Wca values of 0.38 to 0.43 μm and 0.37 to 0.59 μm , respectively, resulting in failure to obtain a good dent-resistance of the panel and a good shapeability. The coiling temperature for samples Nos. 8, 14, 31, and 35 for Comparative Examples was lower than 500 $^{\circ}\text{C}$ and, thus, each of these samples exhibited a good dent-resistance, i.e., 2 to 8%P0.1 of 160N to 189N. However, the Wca values were 0.23 to 0.45 μm and the δ values were 7 to 8%, indicating a poor panel shapeability.

[0062] Further, the coiling temperature for samples Nos. 13, 19, 22, 30, and 40 for Comparative Examples was higher than 700 $^{\circ}\text{C}$ and, thus, each of these samples exhibited an undesirable dent-resistance, i.e., 2 to 8%P0.1 of 145N to 166N. Also, the Wca values were 0.33 to 0.42 μm , indicating a poor panel shapeability.

[0063] On the other hand, each of the finishing temperature and the coiling temperature for Nos. 4-7, 9-12, 15-18, 20, 21, 27-29, 32-34, and 36-39 of the present invention fell within the scope defined in the present invention. As a result, 2 to 8%P0.1 was 153 to 188N, supporting a good dent-resistance of the panel. The samples of the present invention were also satisfactory in the δ value, i.e., $\delta \leq 5\%$, and in the Wca value, i.e., $\text{Wca} < 0.2 \mu\text{m}$, supporting a good shapeability.

Table 6

Condition No.	Steel sample No.	Finishing temperature (°C)	Coiling temperature (°C)	$\sigma_{0.2}$ (MPa)	σ ($\epsilon=0.02$) (MPa)	σ ($\epsilon=0.04$) (MPa)
1	Steel 2	780*	550	215	283*	313*
2			600	218	284*	315*
3			660	217	282*	318*
4		820	530	230	294	325
5			590	230	291	325
6			630	235	294	328
7			680	233	294	326
8		860	460*	245	299*	331*
9			550	231	295	328
10			600	233	294	327
11			640	235	296	330
12			680	230	294	328
13			730*	220	285*	318*
14		900	450*	249	303*	337*
15			540	235	298	330
16			600	232	296	328
17			650	235	299	330
18			680	230	295	330
19			725*	217	283*	316*
20		930	550	235	295	331
21			680	233	295	330
22			750*	220	285*	318*

(Continued)

Table 6

Condition No.	σ ($\epsilon = 0.08$) (MPa)	2%, 4%, 8% P0.1 (N)	δ (%)	Wca (μm)	Remarks
1	379*	140 - 155	3(O)	0.38(Δ)	Comparative example
2	384*	144 - 155	2(O)	0.4 (Δ)	Comparative example
3	381*	144 - 158	5(O)	0.43(X)	Comparative example
4	390	155 - 177	4(O)	0.12(O)	Present invention
5	387	153 - 175	4(O)	0.1 (O)	Present invention
6	394	155 - 177	4(O)	0.18(O)	Present invention
7	391	155 - 178	5(O)	0.16(O)	Present invention
8	390*	160 - 176	7(Δ)	0.23(Δ)	Comparative example
9	392	158 - 179	5(O)	0.14(O)	Present invention
10	392	157 - 179	4(O)	0.15(O)	Present invention
11	394	158 - 177	5(O)	0.08(O)	Present invention
12	391	156 - 178	5(O)	0.18(O)	Present invention
13	388*	148 - 162	3(O)	0.36(Δ)	Comparative example
14	397*	161 - 181	8(Δ)	0.26(Δ)	Comparative example
15	395	158 - 178	4(O)	0.18(O)	Present invention
16	390	157 - 177	4(O)	0.12(O)	Present invention
17	393	159 - 179	5(O)	0.1 (O)	Present invention
18	393	158 - 179	5(O)	0.12(O)	Present invention
19	385*	146 - 166	3(O)	0.42(X)	Comparative example
20	394	158 - 178	4(O)	0.15(O)	Present invention
21	394	158 - 179	5(O)	0.19(O)	Present invention
22	388*	149 - 165	3(O)	0.41(X)	Comparative example

Note: The mark * represents that the values do not fall within the scopes defined in the present invention.

Table 6 (continued)

Condition No.	Steel sample No.	Finishing temperature (°C)	Coiling temperature (°C)	$\sigma_{0.2}$ (MPa)	$\sigma (\epsilon = 0.02)$ (MPa)	$\sigma (\epsilon = 0.04)$ (MPa)
23	Steel 14	750*	450*	214	280*	315*
24			550	217	282*	320*
25			650	217	282*	318*
26			750*	215	284*	320*
27		840	550	238	303	335
28			600	235	295	333
29			650	235	297	332
30			730*	220	285*	320*
31		890	440*	247	301*	335*
32			550	235	296	334
33			650	237	297	335
34			680	237	303	335
35		920	460*	250	303*	339*
36			520	236	295	333
37			580	233	297	332
38			640	235	297	335
39			680	231	294	331
40			730*	219	284*	318*

(Continued)

Table 6 (continued)

Condition No.	σ ($\epsilon = 0.08$) (MPa)	2%, 4%, 8% P0.1 (N)	δ (%)	Wca (μm)	Remarks
23	382*	140 - 160	3(O)	0.4 (Δ)	Comparative example
24	382*	145 - 160	3(O)	0.37(Δ)	Comparative example
25	385*	145 - 165	2(O)	0.43(X)	Comparative example
26	385*	147 - 165	2(O)	0.59(X)	Comparative example
27	401	160 - 185	5(O)	0.18(O)	Present invention
28	400	156 - 183	5(O)	0.15(O)	Present invention
29	405	157 - 188	4(O)	0.15(O)	Present invention
30	388*	147 - 165	3(O)	0.33(Δ)	Comparative example
31	405*	160 - 189	8(Δ)	0.3 (Δ)	Comparative example
32	400	157 - 183	5(O)	0.19(O)	Present invention
33	401	158 - 185	5(O)	0.18(O)	Present invention
34	403	160 - 185	5(O)	0.13(O)	Present invention
35	403*	160 - 187	7(Δ)	0.45(X)	Comparative example
36	401	156 - 185	5(O)	0.19(O)	Present invention
37	403	158 - 187	5(O)	0.19(O)	Present invention
38	402	157 - 185	5(O)	0.17(O)	Present invention
39	397	155 - 181	5(O)	0.15(O)	Present invention
40	385*	145 - 166	3(O)	0.38(Δ)	Comparative example

Note: The mark * represents that the values do not fall within the scopes defined in the present invention.

Industrial Applicability

[0064] As described above, the present invention makes it possible to manufacture stably a cold-rolled steel sheet and a galvanized steel sheet satisfying the dent-resistance of a panel, the surface shapeability and resistance to natural aging and having a tensile strength of 340 MPa or more, which are required for steels used for an outer panel of a motor car, by specifying the steel composition, the tensile characteristics and the manufacturing conditions. It follows that the

present invention is highly valuable in the steel industries and in the motor car industries.

Claims

1. A cold-rolled steel sheet excellent in panel shapeability and dent-resistance, comprising 0.004 to 0.015% by weight of C, 0.01 to 0.2% by weight of Si, 0.1 to 1.5% by weight of Mn, 0.01 to 0.07% by weight of P, 0.005 to 0.015% by weight of S, 0.01 to 0.08% by weight of sol. Al, not higher than 0.005% by weight of N, and at least one kind of the element selected from the group consisting of 0.02 to 0.12% by weight of Nb and 0.03 to 0.1% by weight of Ti, the amount of C, Nb, Ti, N and S meeting the relationship given in formula (1), and a balance of Fe and unavoidable impurities, said cold-rolled steel sheet meeting the relationship given in formula (2):

$$-0.001 \leq (C\% - (12/93)Nb\% - (12/48)Ti^* \leq 0.001 \quad \dots (1)$$

where $Ti^* = Ti\% - (48/14)N\% - (48/32)S\%$, when Ti^* is not larger than 0, Ti^* is regarded as 0.

$$\exp(\varepsilon) \times (5.29 \times \exp(\varepsilon) - 4.19) \leq \sigma / \sigma_{0.2} \leq \exp(\varepsilon) \times (5.64 \times \exp(\varepsilon) - 4.49) \quad \dots (2)$$

where $0.002 < \varepsilon \leq 0.096$, ε represents a true strain, $\sigma_{0.2}$ represents a 0.2% proof stress, and σ represents a true stress relative to ε .

2. The cold-rolled steel sheet excellent in the surface shape of a panel and dent-resistance according to claim 1, further comprising 0.0001 to 0.002% by weight of B.
3. The galvanized steel sheet being excellent in the surface shape of a panel and dent-resistance and prepared by applying a galvanizing to the cold-rolled steel sheet defined in claim 1 or 2.
4. A method of manufacturing a cold-rolled steel sheet excellent in the surface shape of a panel and dent-resistance and defined in claim 1 or 2, comprising the steps of:

applying a hot-rolling treatment after preparation of a molten steel and continuous casting of said steel such that a finish rolling is performed at $(Ar_3 - 100)^\circ\text{C}$ or more to form a hot-rolled steel band and the rolled steel band is coiled at 500 to 700 $^\circ\text{C}$; and continuously applying a cold-rolling treatment and an annealing treatment to the hot-rolled steel band.

5. A method of manufacturing a galvanized steel sheet being excellent in the surface shape of a panel and dent-resistance and defined in claim 3, comprising the steps of:

applying a hot-rolling treatment after preparation of a molten steel and continuous casting of said steel such that a finish rolling is performed at $(Ar_3 - 100)^\circ\text{C}$ or more to form a hot-rolled steel band and the rolled steel band is coiled at 500 to 700 $^\circ\text{C}$; and continuously applying a cold-rolling treatment and a galvanizing treatment to the hot-rolled steel band.

C=0.0075wt%~0.0095wt%,
SHEET THICKNESS=0.8mmt

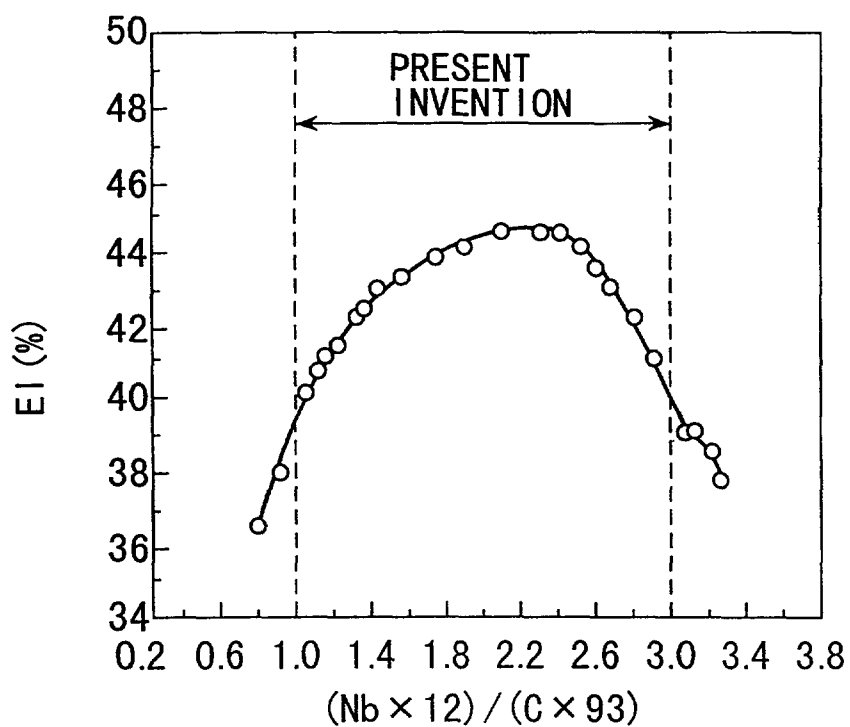


FIG. 1A

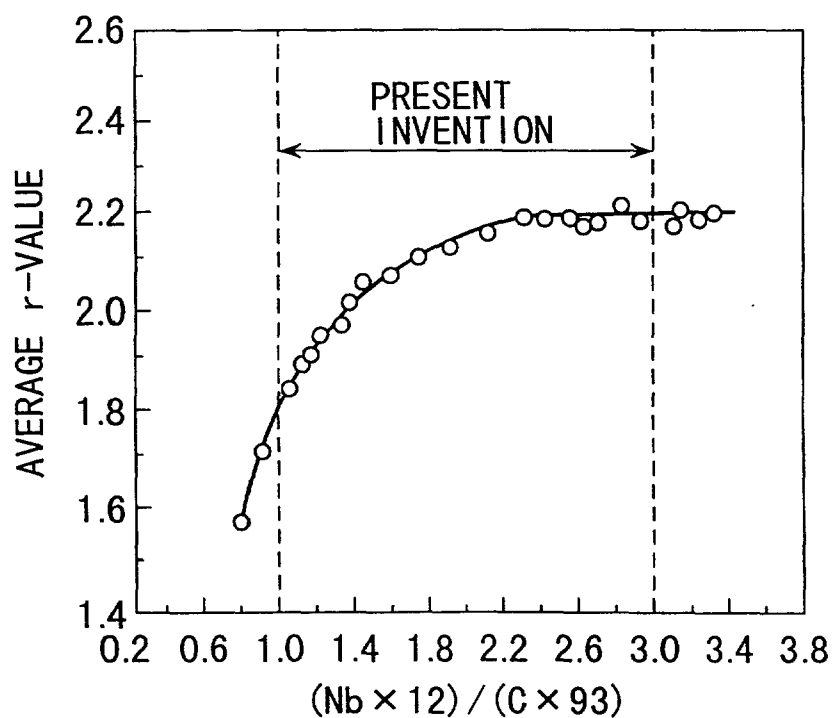


FIG. 1B

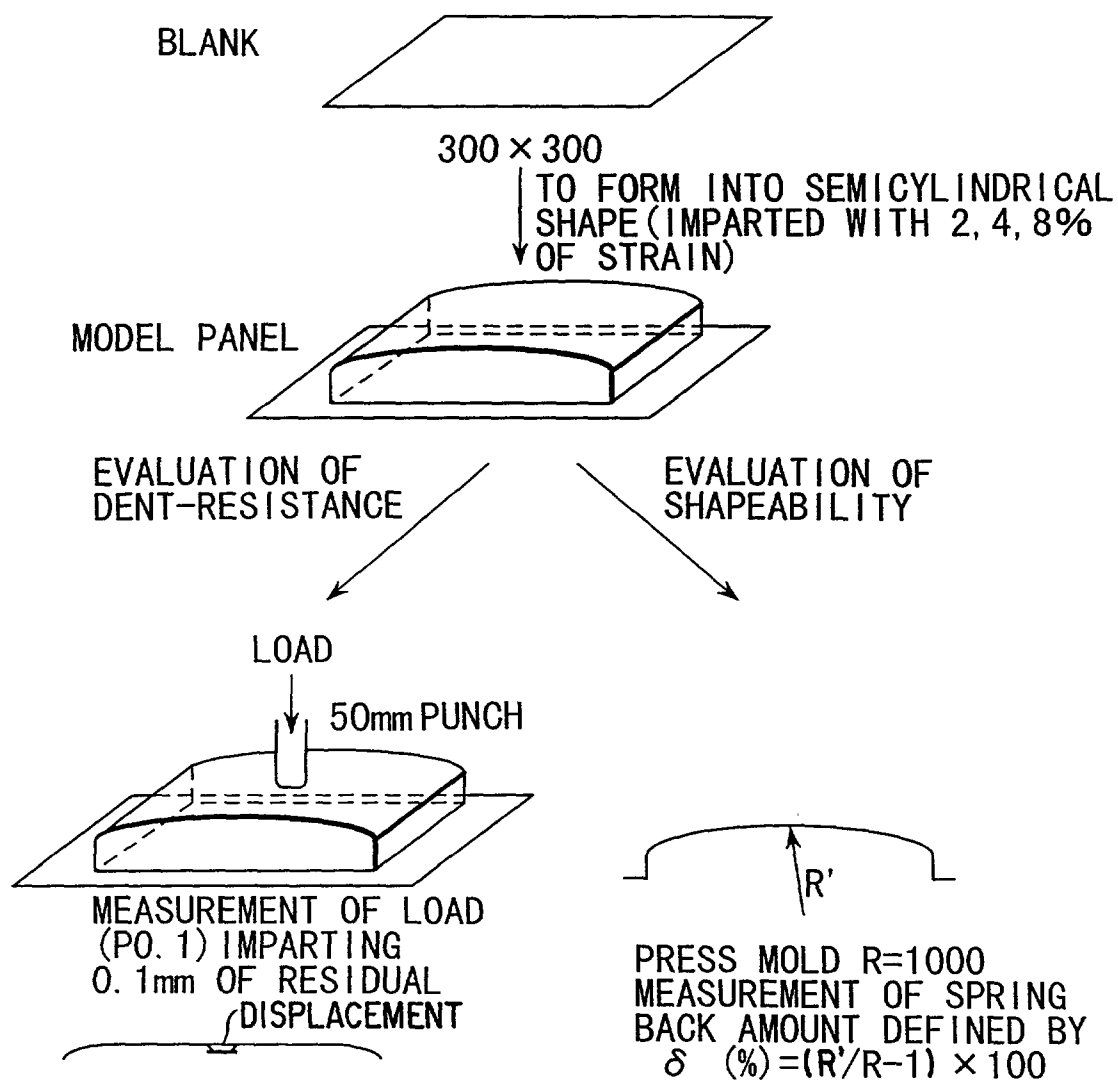


FIG. 2

C (wt%)	(Nb × 12) / (C × 93)	B (wt%)	2%BH (MPa)	2, 4, 8%P _{0.1} (N)	δ (%)	REMARKS
○ 0.0060 ~ 0.0080	1.4 ~ 1.6	0.0003 ~ 0.0006	0	165 ~ 200	3 ~ 5	STEEL OF PRESENT INVENTION
◦ 0.0060 ~ 0.0080	1.2 ~ 1.8	tr.	0	160 ~ 195		
◦ 0.0060 ~ 0.0080				160 ~ 185		
● 0.0060 ~ 0.0080	1.2 ~ 1.8	tr.	0	140 ~ 175	7 ~ 10	STEEL OF COMPARATIVE EXAMPLE
▲ 0.0020 ~ 0.0040					2 ~ 5	
△ 0.0025 ~ 0.0045	0.5 ~ 0.7	tr.	30 ~ 45	160 ~ 190	7 ~ 9	

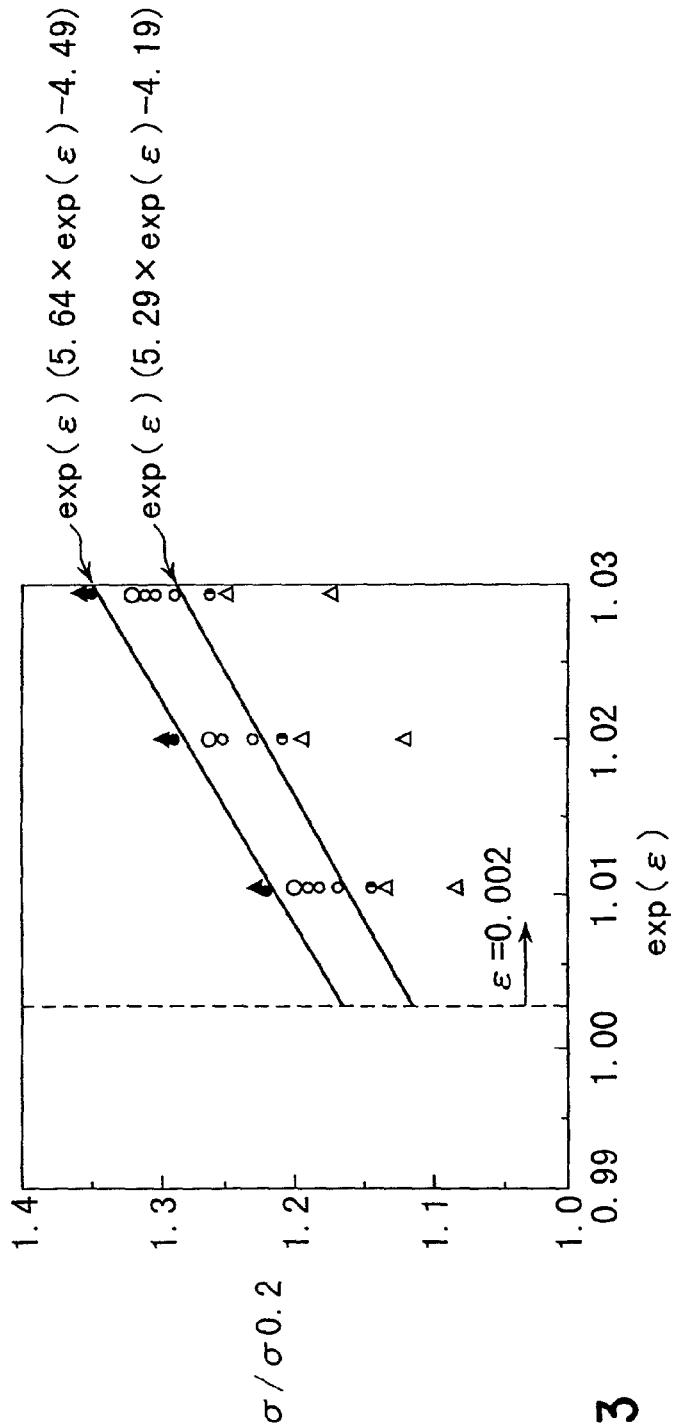


FIG. 3

C (wt%)	$(Nb \times 12) / (C \times 93)$	B (wt%)	2%BH (MPa)	2, 4, 8%PO.1 (N)	δ (%)	REMARKS
$\circ$ 0.0060 $\sim$ 0.0080	1.4 $\sim$ 1.6	0.0003 $\sim$ 0.0006	0	165 $\sim$ 200	3 $\sim$ 5	STEEL OF PRESENT INVENTION
$\circ$ 0.0060 $\sim$ 0.0080	1.2 $\sim$ 1.8	tr.	0	160 $\sim$ 195		
$\circ$ 0.0060 $\sim$ 0.0080	1.2 $\sim$ 1.8	tr.	0	160 $\sim$ 185	7 $\sim$ 10	STEEL OF COMPARATIVE EXAMPLE
$\bullet$ 0.0060 $\sim$ 0.0080	1.2 $\sim$ 1.8	tr.	0	140 $\sim$ 175	2 $\sim$ 5	
$\blacktriangle$ 0.0020 $\sim$ 0.0040	0.5 $\sim$ 0.7	tr.	30 $\sim$ 45	160 $\sim$ 190	7 $\sim$ 9	

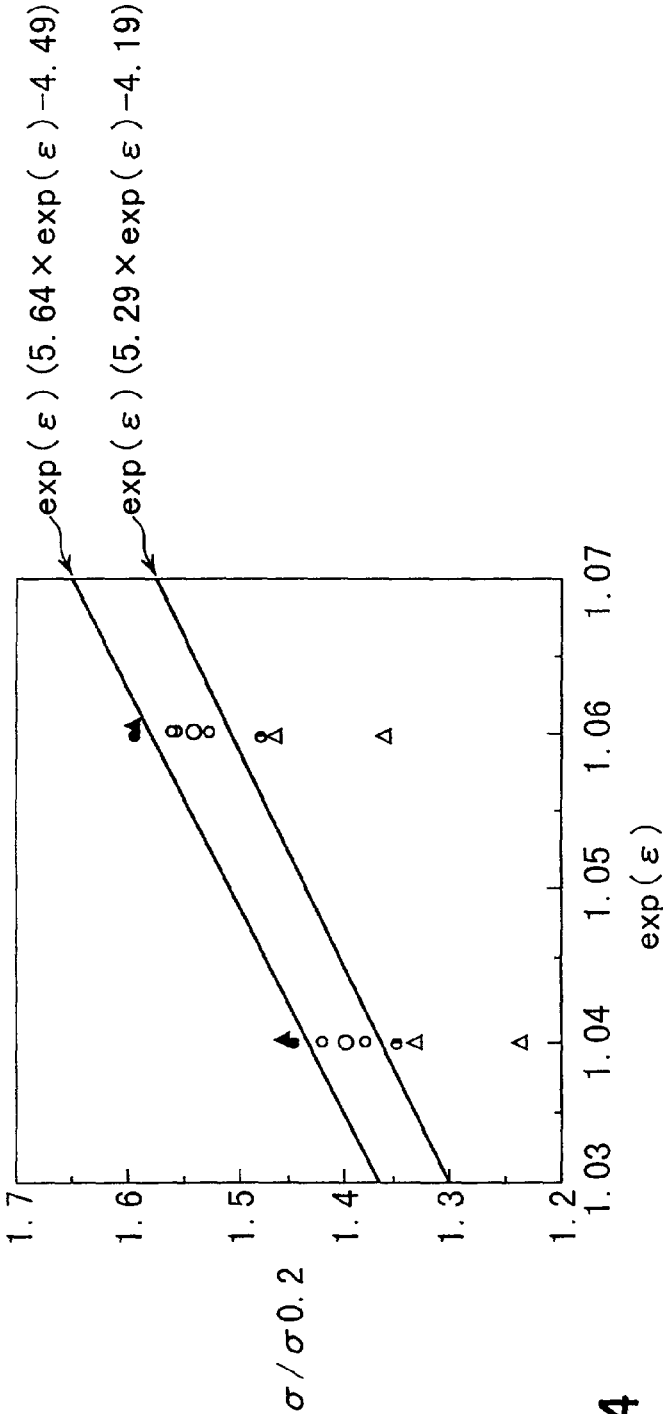


FIG. 4

	C (wt%)	(Nb × 12) / (C × 93)	B (wt%)	2%BH (MPa)	2, 4, 8%PO. 1 (N)	δ (%)	REMARKS
○	0.0060~0.0080	1.4~1.6	0.0003~0.0006	0	165~200	3~5	STEEL OF PRESENT INVENTION
◦	0.0060~0.0080	1.2~1.8	tr.	0	160~195		
◐					160~185		
●	0.0060~0.0080	1.2~1.8	tr.	0	140~175	7~10	STEEL OF COMPARATIVE EXAMPLE
▲	0.0020~0.0040					2~5	
△	0.0025~0.0045	0.5~0.7	tr.	30~45	160~190	7~9	

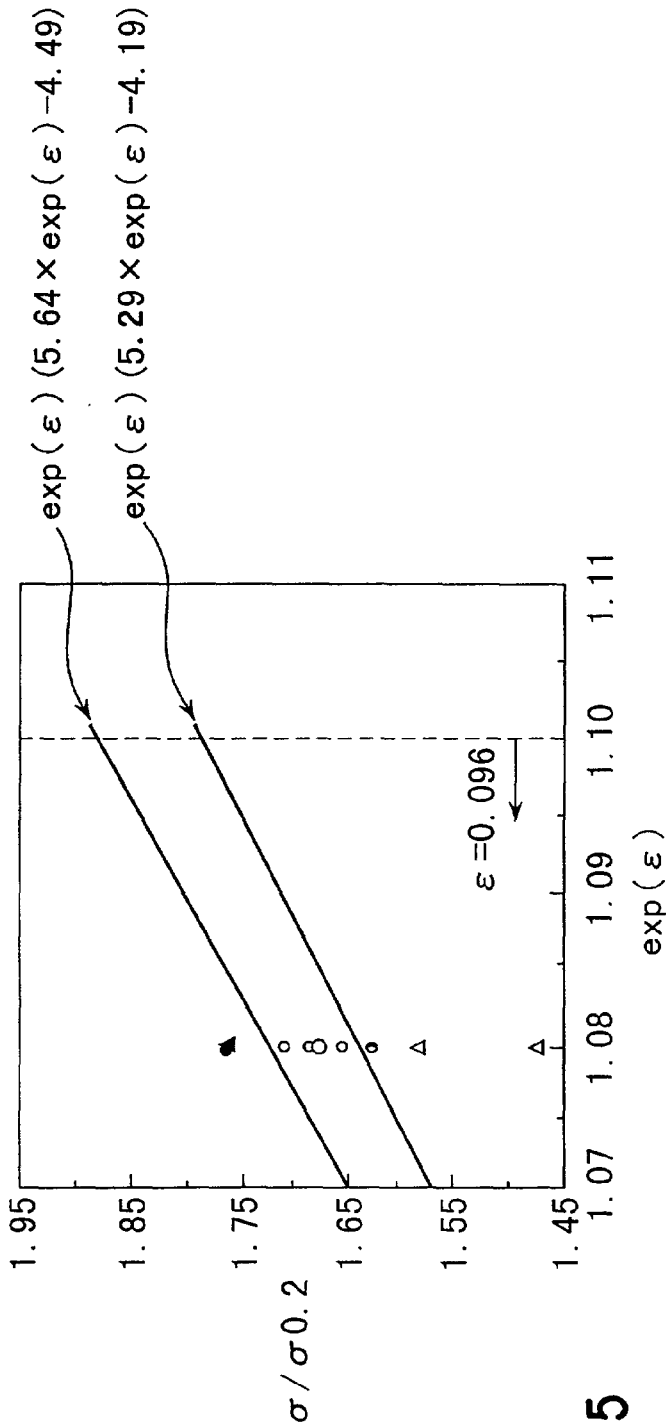


FIG. 5

STEEL SAMPLE No. 3 OF EXAMPLE 1

Wca (μm)	2%PO.1 (N)	140~150	155~165	
	$\delta\%$	≤ 4	≤ 4	8~10
≤ 0.2			○	
0.2 ~ 0.4	●			●
0.4 ~ 0.6	●			

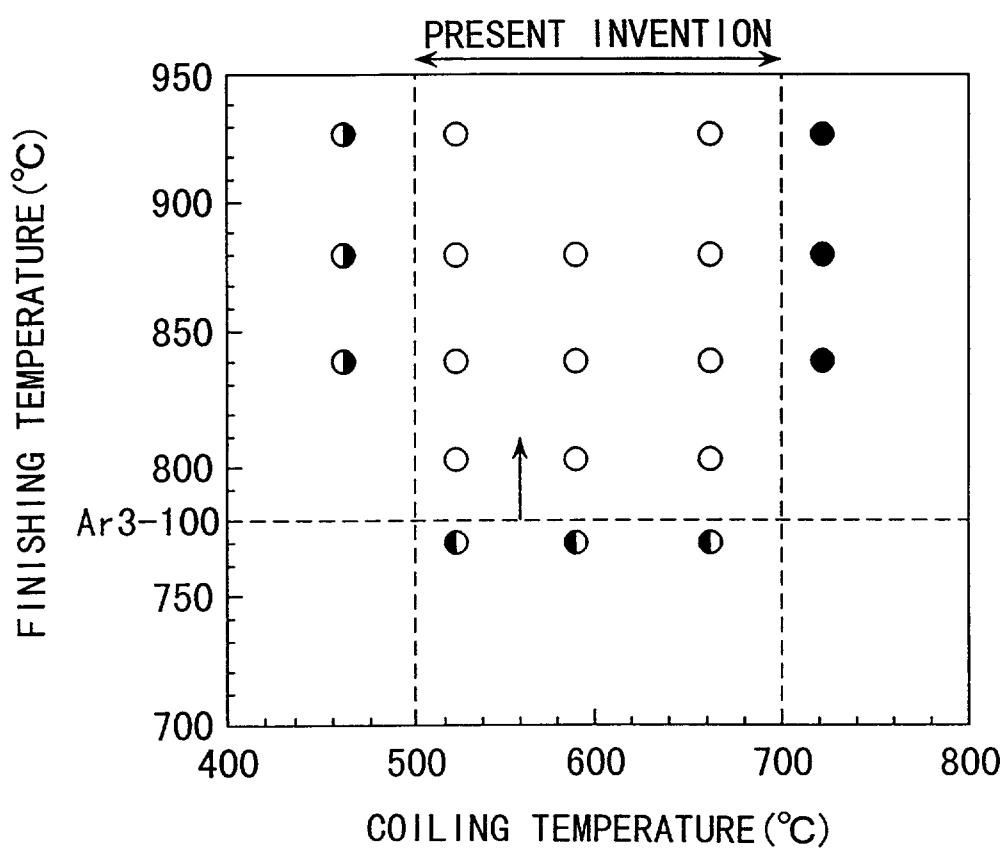


FIG. 6

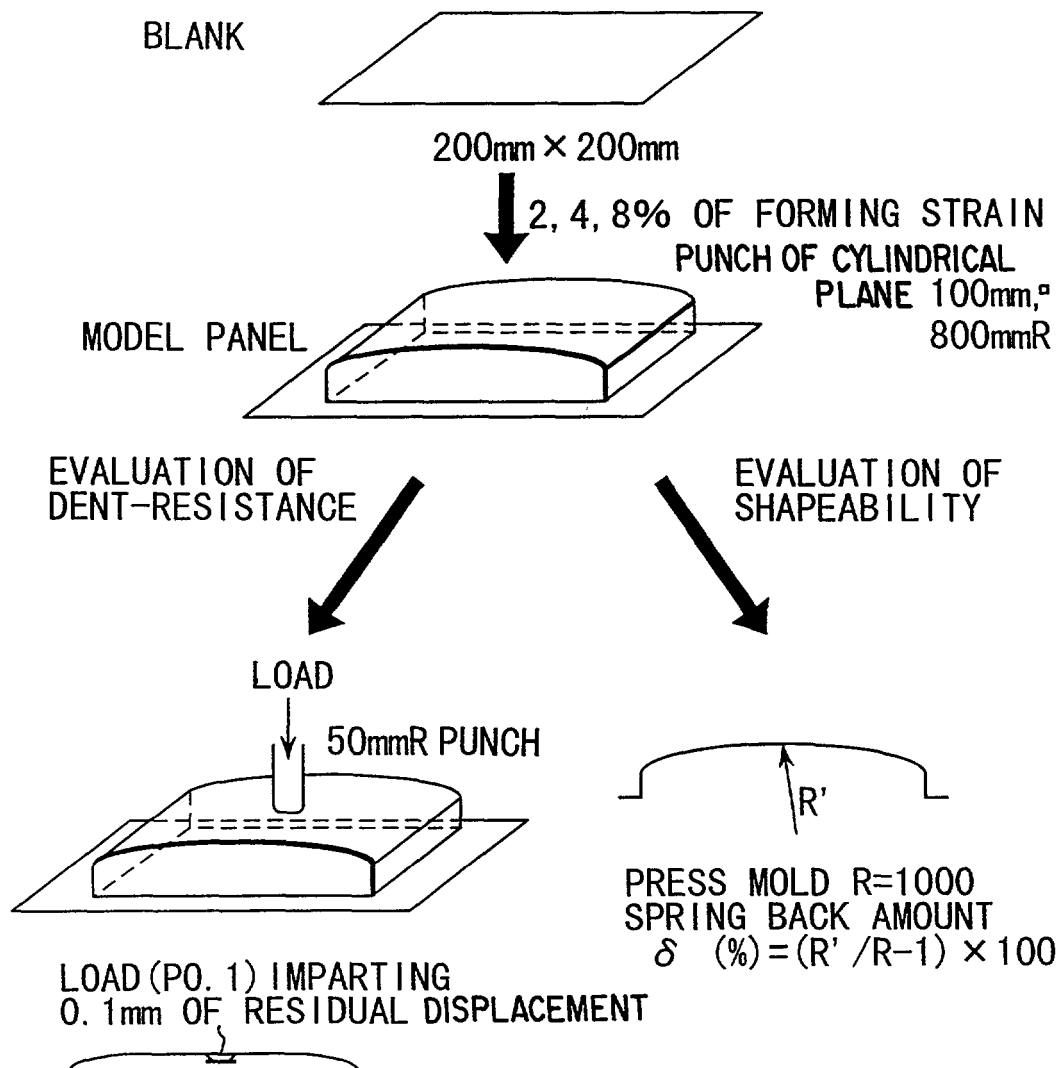


FIG. 7

$C^* = C - (12/93)Nb - (12/48)Ti^*$	CASE OF Nb OR Ti ADDITION
$C - (12/91)Zr^*$	CASE OF Zr ADDITION
	$(Zr^* = Zr - (91/14)N - (91/32)S)$
$C - (12/51)V$	CASE OF V ADDITION

		2, 4, 8% P0.1 (N)	2%BH (MPa)	δ (%)	REMARKS
C=0.004 ~0.01wt% C*=-0.0008 ~0.002wt%	○Ti, B ADDITION	170~210	0~20	2~5	STEEL OF PRESENT INVEN- TION
	△Nb ADDITION	160~200	0~15	3~6	
	□Nb, Ti ADDITION	160~190			
	▽Ti ADDITION	160~200	0~20	2~6	
	▲Nb ADDITION	180~210	30~45	7~11	STEEL OF COMPAR- ATIVE EXAMPLE
	▼Zr ADDITION	170~200	0~25		
	■V ADDITION	160~200	0~25		
	●Ti, B ADDITION	145~165	0~20		
△Nb ADDITION	140~160	0~15	1~5		
C=0.001 ~0.0035wt% C*=-0.0004 ~0.0015wt%	△Nb ADDITION	140~180	30~45	5~9	

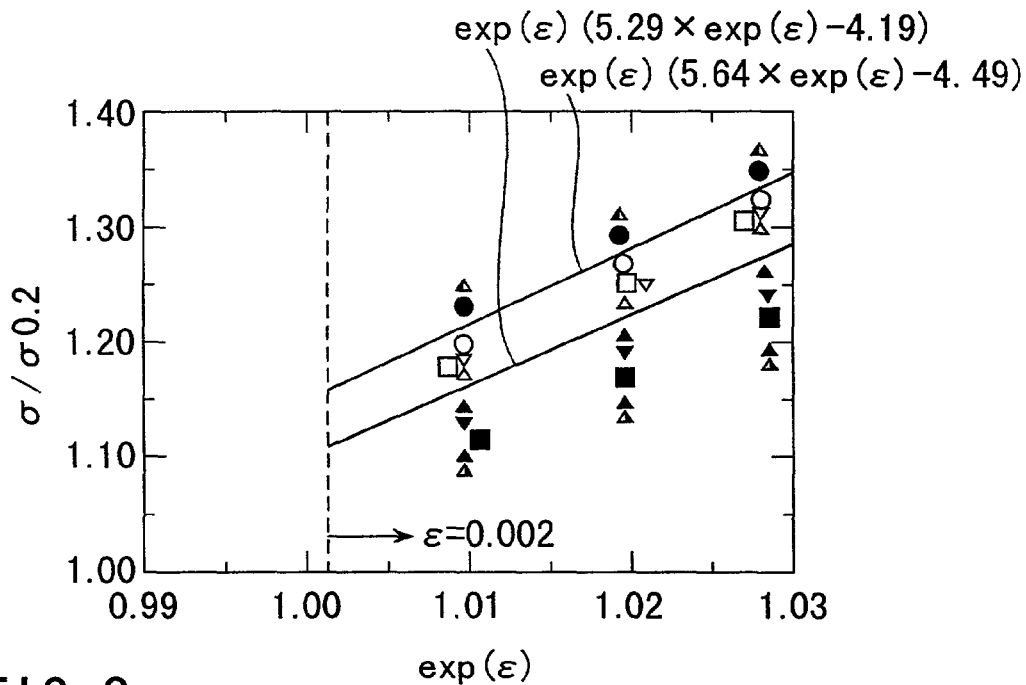


FIG. 8

$C^*=C-(12/93)Nb-(12/48)Ti^*$	CASE OF Nb OR Ti ADDITION
$C-(12/91)Zr^*$	CASE OF Zr ADDITION
	$(Zr^*=Zr-(91/14)N-(91/32)S)$
$C-(12/51)V$	CASE OF V ADDITION

		2, 4, 8% P0.1 (N)	2%BH (MPa)	δ (%)	REMARKS
C=0.004 ~0.01wt% C*=-0.0008 ~0.002wt%	○Ti, B ADDITION	170~210	0~20	2~5	STEEL OF PRESENT INVEN- TION
	△Nb ADDITION	160~200	0~15	3~6	
	□Nb, Ti ADDITION	160~190			
	▽Ti ADDITION	160~200	0~20	2~6	
	▲Nb ADDITION	180~210	30~45	7~11	STEEL OF COMPAR- ATIVE EXAMPLE
	▼Zr ADDITION	170~200	0~25		
	■V ADDITION	160~200	0~25		
	●Ti, B ADDITION	145~165	0~20		
△Nb ADDITION	140~160	0~15	1~5		
C=0.001 ~0.0035wt% C*=-0.0004 ~0.0015wt%	△Nb ADDITION	140~180	30~45	5~9	

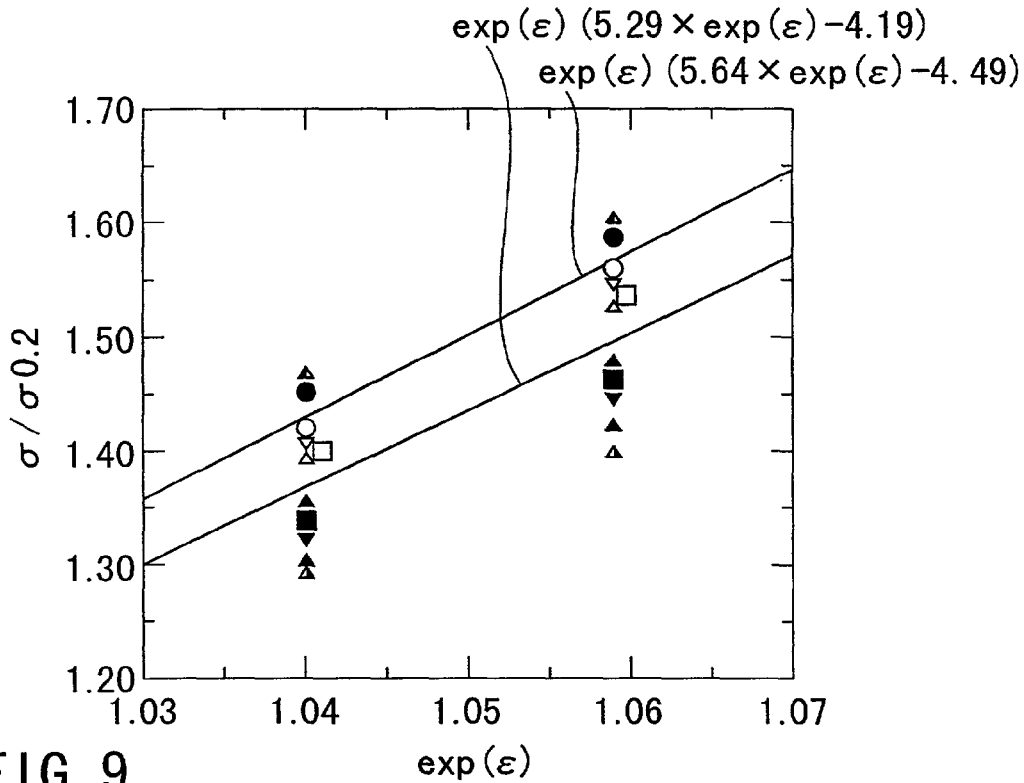


FIG. 9

$C^* = C - (12/93)Nb - (12/48)Ti^*$	CASE OF Nb OR Ti ADDITION
$C - (12/91)Zr^*$	CASE OF Zr ADDITION
	$(Zr^* = Zr - (91/14)N - (91/32)S)$
$C - (12/51)V$	CASE OF V ADDITION

		2, 4, 8% P0.1 (N)	2%BH (MPa)	δ (%)	REMARKS
C=0.004 ~0.01wt% C*=-0.0008 ~0.002wt%	○Ti, B ADDITION	170~210	0~20	2~5	STEEL OF PRESENT INVEN- TION
	△Nb ADDITION	160~200	0~15	3~6	
	□Nb, Ti ADDITION	160~190			
	▽Ti ADDITION	160~200	0~20	2~6	
	▲Nb ADDITION	180~210	30~45	7~11	STEEL OF COMPAR- ATIVE EXAMPLE
	▼Zr ADDITION	170~200	0~25		
	■V ADDITION	160~200	0~25		
	●Ti, B ADDITION	145~165	0~20		
△Nb ADDITION	140~160	0~15	1~5		
C=0.001 ~0.0035wt% C*=-0.0004 ~0.0015wt%	△Nb ADDITION	140~180	30~45	5~9	

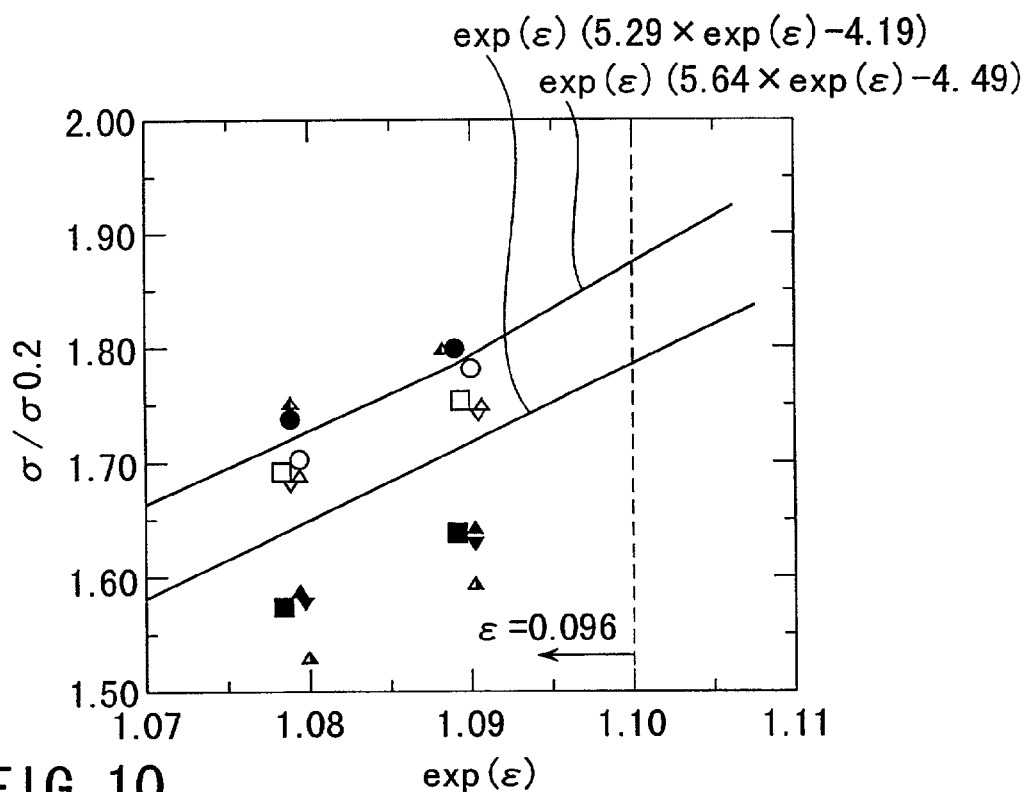


FIG. 10

STEEL SAMPLE No. 8 OF EXAMPLE 1

Wca (μm) \diagdown 2%P0.1(N)	$\delta \leq 6\%$		$\delta = 7 \sim 10\%$	
	140 ~ 155	156 ~ 165	156 ~ 165	165 ~ 175
≤ 0.2		○		
0.2 ~ 0.4	●	⊖	⊖	⊖
0.4 ~ 0.6	●	⊖		

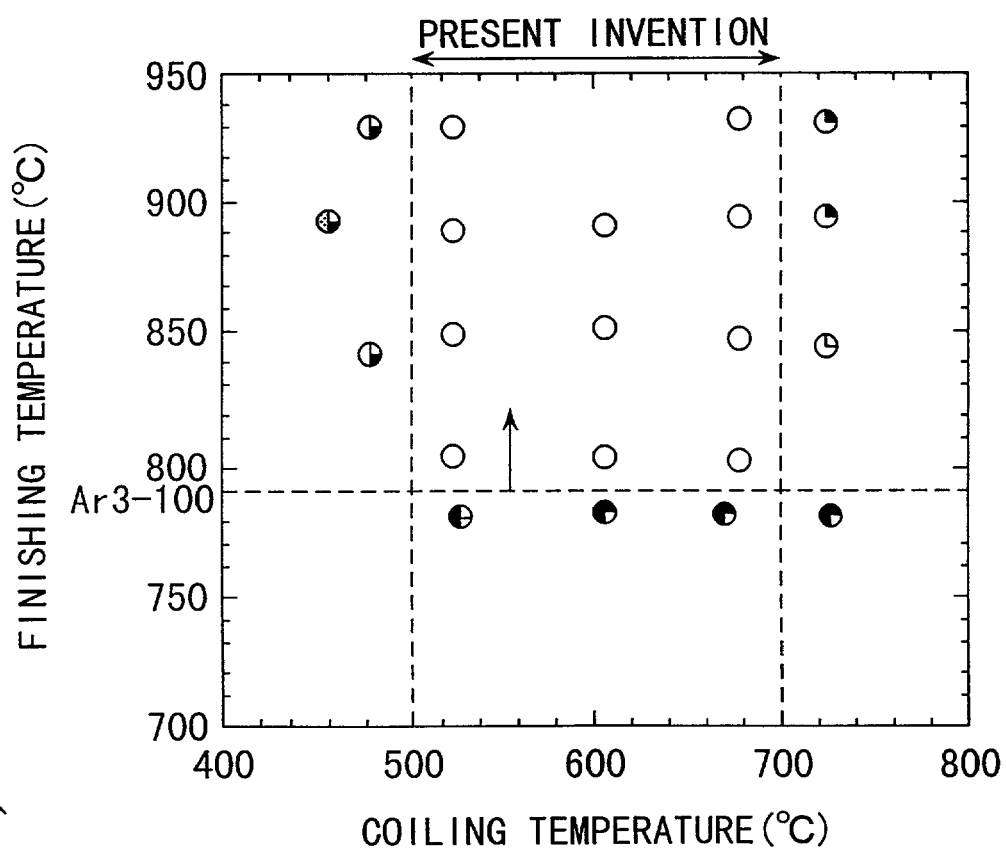


FIG. 11

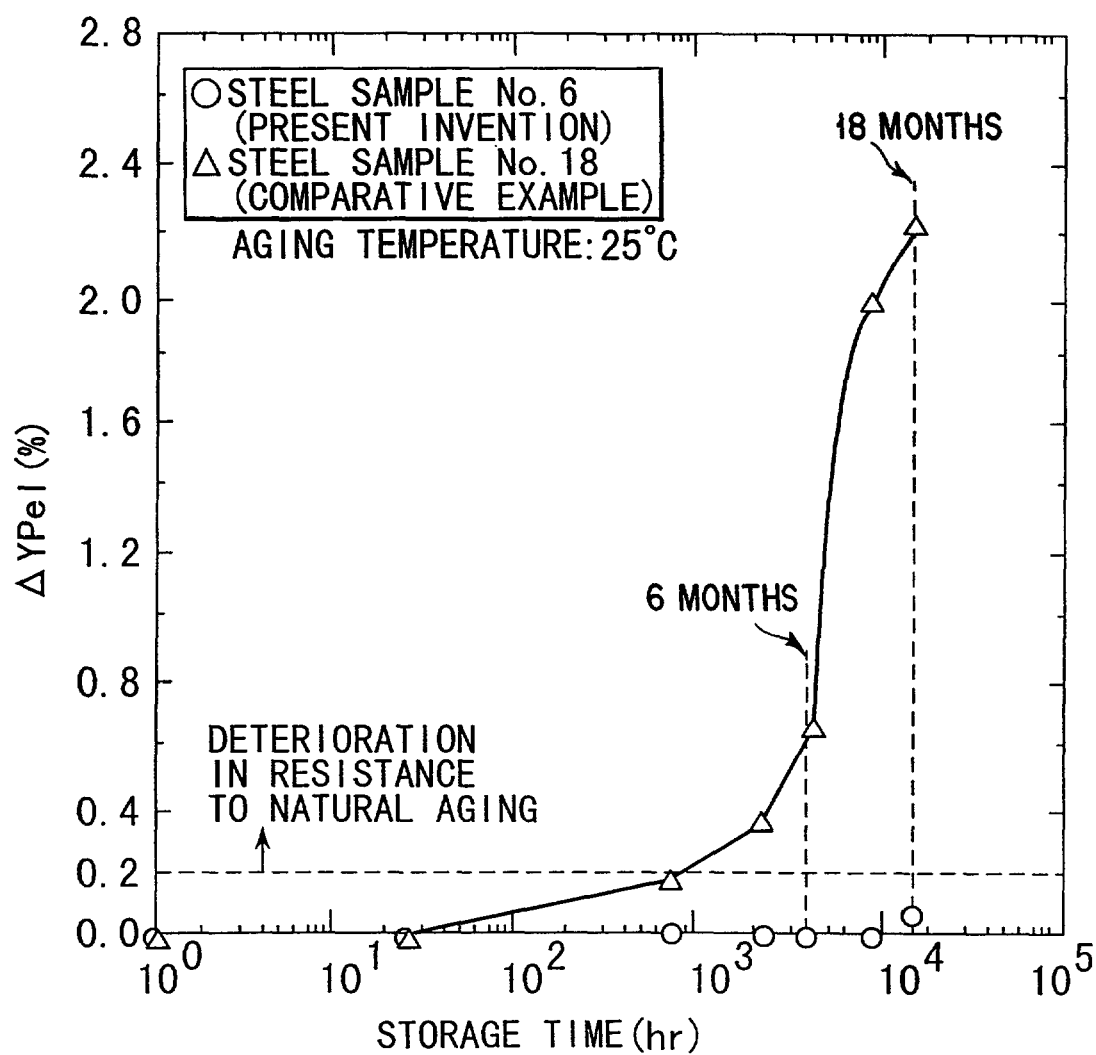


FIG. 12



EUROPEAN SEARCH REPORT

 Application Number
EP 09 15 0416

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	JP 61 064852 A (KAWASAKI STEEL CO) 3 April 1986 (1986-04-03) * abstract; figures 1-5; tables 1,2 *	1-5	INV. C22C38/14 C21D9/48 C22C38/12 C21D8/04
X	US 4 750 952 A (SATO SUSUMU [JP] ET AL) 14 June 1988 (1988-06-14) * column 9, line 60 - column 10, line 6; claims 1,2; table 1 *	1-5	
X	US 4 589 931 A (YASUDA AKIRA [JP] ET AL) 20 May 1986 (1986-05-20) * column 9, line 65 - column 10, line 11; claim 1 *	1-5	
A	US 4 504 326 A (TOKUNAGA YOSHIKUNI [JP] ET AL) 12 March 1985 (1985-03-12) * the whole document *	1-5	
A	US 4 586 966 A (OKAMOTO ATSUKI [JP] ET AL) 6 May 1986 (1986-05-06) * the whole document *	1-5	
A	EP 0 421 087 A2 (KOBE STEEL LTD [JP]) 10 April 1991 (1991-04-10) * the whole document *	1-5	
A	EP 0 444 967 A2 (KOBE STEEL LTD [JP]) 4 September 1991 (1991-09-04) * the whole document *	1-5	
A	US 4 576 656 A (SATO SUSUMU [JP] ET AL) 18 March 1986 (1986-03-18) * the whole document *	1-5	TECHNICAL FIELDS SEARCHED (IPC)
			C21D C22C
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 1 March 2010	Examiner Catana, Cosmin
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 3
EPO FORM 1503 03.82 (P04C01)

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

EP 09 15 0416

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

01-03-2010

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 61064852	A	03-04-1986	NONE	

US 4750952	A	14-06-1988	AU 560865 B2	16-04-1987
			AU 4488585 A	23-01-1986
			CA 1259827 A1	26-09-1989
			DE 3568192 D1	16-03-1989
			EP 0171208 A1	12-02-1986
			US 4818299 A	04-04-1989

US 4589931	A	20-05-1986	EP 0067878 A1	29-12-1982
			WO 8201893 A1	10-06-1982
			JP 1326241 C	16-07-1986
			JP 57089437 A	03-06-1982
			JP 60046166 B	15-10-1985

US 4504326	A	12-03-1985	EP 0108268 A1	16-05-1984

US 4586966	A	06-05-1986	JP 1025378 B	17-05-1989
			JP 1754041 C	23-04-1993
			JP 59177327 A	08-10-1984

EP 0421087	A2	10-04-1991	CA 2022907 A1	10-02-1991
			DE 69014532 D1	12-01-1995
			DE 69014532 T2	04-05-1995
			US 5085714 A	04-02-1992

EP 0444967	A2	04-09-1991	CA 2037316 A1	03-09-1991
			DE 69104747 D1	01-12-1994
			DE 69104747 T2	02-03-1995
			US 5133815 A	28-07-1992

US 4576656	A	18-03-1986	DE 3373682 D1	22-10-1987
			EP 0120976 A1	10-10-1984
			WO 8401585 A1	26-04-1984
			JP 1058255 B	11-12-1989
			JP 1616506 C	30-08-1991
			JP 59067322 A	17-04-1984

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 60046166 A [0003]
- JP 61276928 A [0003]