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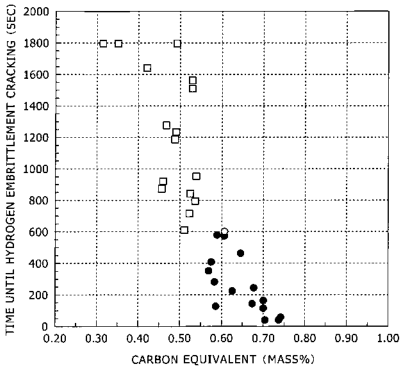
(54) HIGH-STRENGTH SPRING STEEL

(57) Provided is a spring steel that contains 0.15-0.40% carbon, 1-3.5% silicon, 0.20-2.0% manganese, 0.05-1.20% chromium, at most 0.030% phosphorus, at most 0.02% sulfur, and at least one of the following: 0.005-0.10% titanium, 0.005-0.05% niobium, and at most 0.25% vanadium. The remainder of said spring steel comprises iron and unavoidable impurities. The carbon equivalent (Ceq_1) of the provided spring steel, as calculated by formula (1), is at most 0.55.

$$(1)\ Ceq_1 = [C] + 0.108\times[Si] - 0.067\times[Mn] + 0.024\times[Cr] - 0.05\times[Ni] + 0.074\times[V]$$

(In the formula (1), each symbol in brackets represents the content (mass%) of the corresponding element.)

FIG. 1



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Description

[Technical Field]

[0001] The present invention relates to a spring steel useful as a raw material for a coil spring, and relates specifically to a spring steel used in manufacturing a coil spring and having the tensile strength of 1,900 MPa class under a condition as quenched.

[Background Art]

[0002] With respect to a spring used for automobiles and the like (suspension spring and the like), weight reduction is required in order to reduce the exhaust gas and to improve the fuel consumption, and, as a part thereof, high-strengthening is directed to. In a high-strengthened spring, the sensitivity against a defect rises, breakage from a corrosion pit caused by adhesion of a snow melting agent is liable to occur for example, and early breakage due to corrosion fatigue becomes a problem. Therefore, a spring with high strength and excellent in corrosion fatigue property has been required. For example, "UHS1900" developed by the present applicant previously as a spring steel can achieve excellent corrosion fatigue property although the tensile strength is as high as 1,900 MPa class by performing quenching and tempering after coiling into a spring shape. Accordingly, a spring obtained from the spring steel can satisfy both the high strength and excellent corrosion fatigue property.

[0003] In general, such spring is manufactured by drawing of a spring steel (wire rod), cold-finishing, thereafter heating, hot-coiling, then quenching, tempering, and setting. The quenching and tempering treatment after hot-coiling is performed in order to adjust the strength of the spring. In the heat treatment such as the quenching and tempering treatment, much CO_2 is discharged. In recent years however, aiming to reduce the load against the earth environment, reduction of CO_2 has been strongly required as one of the global warming preventive measures. Therefore, even in the manufacturing steps for a coil spring, reduction of the discharge amount of CO_2 has been required.

[0004] Also, in the patent document 1, a steel for a stabilizer is proposed in which the toughness in the ordinary temperature and the toughness in the low temperature are improved by performing water-quenching soon after hot forming and being left as water-quenched without performing tempering. The steel for a stabilizer is featured that the componential composition is adjusted to a low C-high Mn-Cr system or a low C-high Mn-B-Cr system added with one element or two elements or more of Ti, V, Nb. The stabilizer which is the object of the patent document 1 is different in the technical field from that of a coil spring. For example, the strength level is 800 MPa class where the corrosion fatigue property does not become a problem, and the stabilizer is not related with the spring of a high strength range (1,900 MPa class for example) which is required to satisfy the corrosion fatigue property simultaneously.

[0005] Also, in general, the strength of iron and steel materials increases as the hardness increases, and, as the hardness increases, the toughness drops. That is, when the strength of the iron and steel materials increases, the toughness drops, however, as a material for a spring, a fracture property capable of enduring a severe use environment of a spring is required, and it becomes necessary to secure the toughness, or the low temperature toughness in particular which becomes important when used in a cold weather region, even in springs such as a high-strengthened suspension spring and the like.

[0006] For example, the patent document 2 discloses that the ductility and toughness were improved in a high-strength spring steel by adjusting various compositions, and the patent document 3 discloses that a spring steel having both of the hardness and toughness was obtained by adjusting various compositions. However, both of the patent documents 2 and 3 focused only on the toughness in the ordinary temperature, and did not consider the low temperature toughness. Usually, the toughness in the low temperature is inferior to the toughness in the ordinary temperature, and considering the ordinary temperature toughness disclosed in the patent documents 2 and 3, the low temperature toughness in the technology of the patent documents 2 and 3 is insufficient.

[Document on Prior Art]

[Patent Document]

[0007]

[Patent Document 1] Japanese Patent No. 4406341
[Patent Document 2] Japanese Patent No. 3577411
[Patent Document 3] Japanese Patent No. 3246733

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0008] The present invention was developed considering such circumstances as described above, and its object is to provide a spring steel capable of manufacturing a coil spring achieving both of the high strength and excellent corrosion fatigue property as well as excellent in the low temperature toughness even when the tempering treatment after quenching is omitted in working into the coil spring. Also, another object of the present invention is to provide a spring obtained from the spring steel.

[Means for Solving the Problem]

[0009] A high-strength spring steel in relation with the present invention that can solve the problems contains C: 0.15-0.40% (means mass%, hereinafter the same), Si: 1-3.5%, Mn: 0.20-2.0%, and contains at least one element selected from a group consisting of Ti: 0.005-0.10%, Nb: 0.005-0.05% and V: 0.25% or less, Cr: 0.05-1.20%, P: 0.030% or less, S: 0.02% or less, with the remainder including iron and unavoidable impurities, in which a carbon equivalent Ceq_1 expressed by a formula (1) below is 0.55 or less.

$$Ceq_1=[C]+0.108\times[Si]-0.067\times[Mn]+0.024\times[Cr]-0.05\times[Ni]+0.074\times[V]\ldots(1)$$

(In the formula (1), each symbol in brackets represents the content (mass%) of the corresponding element.)

[0010] The spring steel of the present invention may contain (a) Ni: 0.05-2% and Cu: 0.05-0.50%, (b) Ni: 0.15-2% and Cu: 0.05-0.50%, (c) B: 0.005% or less and/or Mo: 0.60% or less according to the necessity.

[0011] Further, it is also preferable that the spring steel of the present invention contains at least one element selected from a group consisting of Ti: 0.035-0.10%, Nb: 0.005-0.05%, and V: 0.05-0.25%, and the grain size number after quenching is 7.5 or above.

[0012] When the spring steel is used, the spring steel is hot-coiled, is quenched, and is thereafter subjected to setting while omitting tempering, a spring achieving both of the properties can be manufactured.

[Effects of the Invention]

[0013] In the spring steel of the present invention, the element amount of a specific alloy element and the balance of mixing are properly controlled, therefore in manufacturing a coil spring using the spring steel, the tempering treatment after quenching can be omitted, and a spring achieving both of the high strength and excellent corrosion fatigue property and having excellent low temperature toughness in a state as quenched can be manufactured.

[Brief Description of the Drawings]

[0014]

[FIG. 1] FIG. 1 is a graph showing the relation between the carbon equivalent (Ceq_1) and the time until the hydrogen embrittlement cracking of a specimen obtained in the example 1.

[FIG. 2] FIG. 2 is a graph showing the relation between the tensile strength and the low temperature toughness (vE_{-50}) of a specimen obtained in the example 2.

[Best Mode for Carrying Out the Invention]

[0015] In manufacturing a spring by coiling a spring steel, the present inventors have repeatedly carried out intensive studies in order to provide a spring steel capable of manufacturing a spring achieving both of the high strength and excellent corrosion fatigue property as well as excellent in the low temperature toughness while omitting the tempering treatment after quenching performed after coiling. As a result, it was found out that, when the kind of the fundamental alloy elements contained in a spring steel was limited to C, Si, Mn, Cr, and at least an element out of Ti, Nb and V, or was limited to one in which the group of these elements was added further with (i) Ni and Cu or added further with (ii) B and/or Mo, and Si and Mn were positively contained while reducing the amount of C, Ti, Nb, V, Cr, Ni and Cu out of these elements as much as possible, the tempering treatment after quenching could be omitted in manufacturing a spring by coiling the spring steel, and a spring achieving both of the tensile strength of 1,900 MPa class and excellent corrosion fatigue property in a state as quenched as well as excellent in the low temperature toughness also achieved by more strictly adjusting the content of Ti, Nb and V could be provided, and the present invention was completed.

[0016] The spring steel of the present invention is characterized that the C amount in particular is reduced than the C amount used for an ordinary spring steel. By reducing the C amount, the amount of carbide precipitated in steel can be reduced, and therefore tempering after quenching which is performed in a usual spring manufacturing process can be omitted. That is, as described above, the spring is manufactured usually by drawing of a spring steel (wire rod), cold-finishing, thereafter heating, hot-coiling, then quenching, tempering, and setting. According to the necessity, shot peening is performed after setting, and painting is performed thereafter. However, because the C amount of the spring steel of the present invention is reduced, the strength of the spring can be secured even when setting is performed while omitting tempering after quenching.

[0017] On the other hand, in the spring steel of the present invention, Si and Mn are positively added. Si and Mn are easily obtainable elements, and stable supply is assured even when the amounts of Si and Mn are increased. Also, because Si and Mn have an action of enhancing the strength without dropping the toughness, both of the high strength and excellent corrosion fatigue property can be achieved by adding Si and Mn positively.

[0018] In order to surely achieve both of the high strength and excellent corrosion fatigue property based on the knowledge described above, it is necessary to strictly stipulate the amount of each element and to also stipulate the relation thereof. That is, in the present invention, the componential composition of the spring steel was designed as described below, and the carbon equivalent Ceq_1 expressed by the equation (1) below was made 0.55 or less. In the formula (1) below, each symbol in brackets represents the content (mass%) of the corresponding element.

<Componential composition of spring steel>

[0019] The spring steel contains C: 0.15-0.40%, Si: 1-3.5%, Mn: 0.20-2.0%, and contains at least one element selected from a group consisting of Ti: 0.005-0.10%, Nb: 0.005-0.05% and V: 0.25% or less, and Cr: 0.05-1.20%.

$$Ceq_1=[C]+0.108\times[Si]-0.067\times[Mn]+0.024\times[Cr]-0.05\times[Ni]+0.074\times[V] \ldots \quad (1)$$

The reason for setting the adding amount of each element and the reason for stipulating the carbon equivalent Ceq_1 are as described below.

[0020] The reason why C is made 0.15% or more is to enhance the quenchability and to secure the strength. Also, the reason why C is made 0.40% or less is to prevent deterioration of the toughness and corrosion fatigue property. The lower limit of the C amount is preferable to be 0.2% or more, more preferably 0.25% or more, and the upper limit of the C amount is preferable to be 0.35% or less, more preferably 0.34% or less, and especially preferably 0.33% or less.

[0021] The reason why Si is made 1% or more is to make Si act as a solid solution strengthening element and to secure the strength. When Si is below 1%, the matrix strength is insufficient. On the other hand, when the Si amount becomes excessive, dissolution of carbide becomes insufficient in heating for quenching, heating at a higher temperature becomes necessary in order to make the steel austenitic uniformly, decarbonization of the surface progresses, and the fatigue property of the spring deteriorates. Therefore, by making Si 3.5% or less, decarbonization described above can be suppressed, occurrence of oxidation of the grain boundary and the like can be suppressed, and drop of the strength due to formation of an abnormal structure can be prevented. Si is preferable to be 1.5% or more and 3.0% or less, more preferably 1.80% or more and 2.5% or less.

[0022] By making Mn 0.20% or more, the quenchability can be enhanced and the strength can be secured. Also, by formation of sulfide-based inclusions, embrittlement of the grain boundary due to S can be prevented, and the toughness and corrosion fatigue property can be improved. Also, by making Mn 2.0% or less, a supercooled structure is generated, and deterioration of the toughness and corrosion fatigue property can be prevented. Furthermore, formation and coarsening of excessive sulfide-based inclusions can be suppressed, and deterioration of the toughness and corrosion fatigue property can be prevented. The lower limit of the Mn amount is preferable to be 0.5% or more, more preferably 0.80% or more, and the upper limit of the Mn amount is preferable to be 1.8% or less, and especially preferably 1.5% or less.

[0023] The reason why Ti is made 0.005% or more is to miniaturize the former austenite grains after quenching, to improve the strength and proof stress ratio, and to improve the toughness and corrosion fatigue property. By improving the toughness, the sag resistance can be improved. Also, the reason for making Ti 0.10% or less is to prevent precipitation of coarse inclusions (Ti-nitride for example) and to suppress deterioration of the corrosion fatigue property. The lower limit of the Ti amount is preferable to be 0.01% or more (especially preferable to be 0.05% or more), and the upper limit of the Ti amount is preferable to be 0.080% or less, more preferably 0.07% or less.

[0024] V is an element effectively acting for further enhancing the quenchability and enhancing the strength. Also, V is an element enhancing the toughness to contribute to improvement of the sag resistance, and miniaturizing the grains to improve the strength and proof stress ratio. In order to exert such actions, V is preferable to be contained by 0.05% or more, more preferably 0.08% or more, and further more preferably 0.1% or more. However, when V becomes excessive, coarse carbonitride is formed, and the toughness and corrosion fatigue property deteriorate. Accordingly, V is to be 0.25% or less, preferably 0.22% or less, and more preferably 0.2% or less.

[0025] Nb is an element enhancing the toughness to contribute to improvement of the sag resistance, and is an element miniaturizing the grains to improve the strength and proof stress ratio. In order to exert such actions, the Nb amount is to be made 0.005% or more, preferably 0.008% or more, and more preferably 0.01% or more. On the other hand, when the Nb amount becomes excessive, the toughness is influenced adversely. Accordingly, the Nb amount is to be 0.05% or less, preferably 0.04% or less, and more preferably 0.03% or less.

[0026] Ti, V and Nb may be added solely, or may be added combining two elements or more. The content of Ti, V and Nb is to be Ti: 0.035-0.10%, Nb: 0.005-0.05%, V: 0.05-0.25% respectively, and it is preferable to contain at least one element thereof. Also, by containing Ti, V and Nb by these ranges, the grain miniaturizing effect can be effectively exerted, and the grain size number after quenching can be made 7.5 or above, which results in exertion of excellent low temperature toughness. The grain size number after quenching is preferable to be 8.0 or above, more preferably 9.0 or above. The low temperature toughness of the spring steel of the present invention is, for example, 50J/cm^2 or more in terms of Charpy absorbed energy at -50°C, preferably 70 J/cm^2 or more, and more preferably 80 J/cm^2 or more.

[0027] By making Cr 0.05% or more, the steel matrix is strengthened by strengthening solid solution, the quenchability is improved, and the strength can be secured. Also, Cr is an element making the rust formed on the surface layer part under a corroding condition amorphous and dense and contributing to improvement of the corrosion resistance. On the other hand, by making Cr 1.20% or less, drop of the Ms point and formation of a supercooled structure are prevented, the toughness and corrosion fatigue property can be secured, and reduction of the strength and hardness due to insufficient dissolution of Cr-carbide in quenching can be prevented. Cr is preferable to be 0.1% or more and 1.10% or less, more preferably 0.5% or more and 1.05% or less.

[0028] The remainder of the spring steel of the present invention is substantially iron. However, it is rightly allowed that the unavoidable impurities brought in due to the situation of the material such as the iron material (including scraps), auxiliary raw material, and the like as well as the manufacturing facilities and the like are included in the steel. Out of the unavoidable impurities, it was stipulated particularly that P was to be 0.030% or less and S was to be 0.02% or less. The reason why such ranges were stipulated is as described below.

[0029] The reason why P is made 0.030% or less is to suppress segregating on the former austenite grain boundary and making the grain boundary brittle and to prevent deterioration of the toughness and corrosion fatigue property. P is preferable to be 0.02% or less, more preferably 0.01% or less. Although P is preferable to be as little as possible, it is usually included by approximately 0.001%.

[0030] The reason why S is made 0.02% or less is to prevent that sulfide-based inclusions are formed in the steel, coarsened, and deteriorate the corrosion fatigue property. S is preferable to be 0.015% or less, especially preferably 0.01% or less. Similar to P, S is also preferable to be as little as possible, however it is usually included by approximately 0.001%.

[0031] The total amount of P and S is preferable to be 0.015% or less, more preferably 0.010% or less.

[0032] The reason why the carbon equivalent Ceq$_1$ is made 0.55 or less is to achieve both of the strength and corrosion fatigue property of the spring even when the tempering treatment after quenching is omitted in manufacturing a coil spring by coiling the spring steel. That is, the carbon equivalent Ceq$_1$ represents the contribution degree of an alloy element exerting influence on the hardness after quenching, the hardness of the core part of the spring can be secured by omitting the tempering treatment after quenching while reducing the value, and high strengthening can be achieved. Also, by suppressing the carbon equivalent Ceq$_1$ to 0.55 or less, the degree of dependability of the alloy element can be lowered, and stable supply can be ensured more. The carbon equivalent Ceq$_1$ is preferable to be 0.53 or less, more preferably 0.50 or less. Also, the cost can be reduced as the composition is designed so that the carbon equivalent Ceq$_1$ becomes as small as possible, however, in order to achieve both of the strength and corrosion fatigue property, it is necessary to add alloy elements to some degree. Therefore, the lower limit of the carbon equivalent Ceq$_1$ is 0.30. Also, in calculation of the formula (1) below, when there is an element not contained, calculation should be executed assuming that the content of the element is 0 mass%.

[0033] The spring steel of the present invention is to satisfy the chemical componential composition and the carbon equivalent Ceq$_1$, however aiming to further improve the property, Ni and Cu may be contained, and B and/or Mo may also be contained.

[0034] When Ni and Cu are to be contained (that is, using both of Ni and Cu simultaneously), the Ni amount is to be 0.05-2%, and the Cu amount is to be 0.05-0.50%. The reason why Ni is made 0.05% or more is to enhance the toughness, to lower the defect sensitivity, and to improve the corrosion fatigue property. Also, Ni has an action of making the rust formed amorphous and dense to improve the corrosion resistance, and has also an action of improving the setting resistance which is important as the spring property. On the other hand, by making Ni 2% or less, dropping of the Ms point and formation of a supercooled structure can be prevented, and the toughness and corrosion fatigue property can be secured. Ni is preferable to be 0.15% or more and 2% or less, more preferably 0.18% or more and 1.5% or less, further more preferably 0.20% or more and 1% or less, especially 0.5% or less.

[0035] Because Cu is an element electrochemically nobler than iron, it is an element having an action of making the rust dense and improving the corrosion resistance. Therefore, when Cu is contained, the Cu amount is to be 0.05% or more. However, even if Cu is added excessively, its effect saturates, and embrittlement of the raw material due to hot rolling may be caused adversely. Accordingly, the upper limit of the Cu amount was made 0.50% or less. Cu is preferable to be 0.1% or more and 0.4% or less, more preferably 0.15% or more (especially 0.18% or more) and 0.3% or less.

[0036] B is an element enhancing the quenchability further to enhance the grain boundary strength, enhancing the toughness to improve the setting resistance, and making the rust formed on the surface dense to improve the corrosion resistance. In order to exert such actions, B is preferable to be contained by 0.0005% or more, more preferably 0.001% or more, and further more preferably 0.0015% or more. However, when B becomes excessive, the effects saturate and coarse carbonitride is formed, and the toughness and corrosion fatigue property deteriorate. Therefore, B is to be 0.005% or less, preferably 0.004% or less, and more preferably 0.003% or less.

[0037] Mo is an element enhancing the toughness and contributing to improvement of the setting resistance, and is an element securing the quenchability and enhancing the strength and toughness of the steel. In order to exert such actions effectively, the Mo amount is preferable to be 0.05% or more, more preferably 0.08% or more, and further more preferably 0.10% or more. On the other hand, even if the Mo amount becomes excessive, the effects saturate. Therefore, the Mo amount is preferable to be 0.60% or less, more preferably 0.50% or less, and further more preferably 0.35% or less. B and Mo may be contained solely, or both may be used simultaneously.

[0038] As described above, the spring steel of the present invention is characterized that the amount of each alloy element is strictly stipulated and the relation thereof is stipulated, and when the spring steel is used, the tempering treatment after quenching performed after coiling can be omitted, and the spring achieving both of the high strength of 1,900 MPa or above tensile strength even in a state as quenched and excellent corrosion fatigue property can be manufactured. Also, by more strictly controlling the content of the elements having a grain miniaturizing action (Ti, Nb and V), the low temperature toughness can be improved. Below, a method for manufacturing a spring from the spring steel will be described.

[0039] In manufacturing a spring from the spring steel of the present invention, it is necessary to omit tempering after quenching. That is, although the process is the same with that of the prior art including the steps of drawing of a spring steel (wire rod) satisfying the chemical componential composition, cold-finishing, thereafter heating, hot-coiling to form into a spring shape, and quenching, it is necessary to perform setting while omitting tempering after quenching. Because the C amount of the spring steel of the present invention is reduced than that of the spring steel of the prior arts, when tempered after quenching, the spring steel is softened excessively, and the toughness and corrosion fatigue property deteriorate. Accordingly, it is necessary to omit tempering after quenching.

[0040] Here, "omission of tempering" means the spring is not heated to a temperature exceeding 350°C after quenching.

[0041] The setting may be performed either in a cold state or in a warm state. The temperature of cold setting can be an ordinary temperature, and the temperature of warm setting can be approximately 200-250°C.

[0042] After setting, painting may be performed after shot peening according to the necessity. The condition of shot peening and painting is not limited particularly, and the ordinary condition can be employed.

[0043] The spring thus obtained can achieve both of the high strength and excellent corrosion fatigue property, and is excellent in the low temperature toughness as well.

[0044] The manufacturing condition of the spring steel in relation with the present invention is not particularly limited, however in order to make the grain size number 7.5 or above which is a preferable aspect of the present invention, it is recommendable to make the heating temperature before quenching 925°C or below and to make the heating time 15 min or less. The lower limits of the heating temperature before quenching and the heating time are not particularly limited, however the lower limit of the heating temperature is approximately 850°C, and the lower limit of the heating time is approximately 10 min usually.

[Examples]

[0045] Although the present invention will be described below more specifically referring to examples, the present invention is not to be limited by the examples described below, it is a matter of course that the present invention can also be implemented with modifications added appropriately within the range adaptable to the purposes described previously and later, and any of them is to be included within the technical range of the present invention.

Example 1

[0046] After the steel of the chemical componential composition shown in Table 1 below (the remainder is iron and unavoidable impurities) was molten by a vacuum melting furnace of 150 kg, the steel was held at 1,200°C, was thereafter hot forged into a billet of 155 mm square, the billet was hot-rolled, and the spring steel with 13.5 mm diameter (wire rod for a spring) was manufactured. The wire rod for a spring was subjected to finish-rolling so that the diameter became 12.5 mm, was thereafter cut to the length of 70 mm, and was then quenched. Quenching was performed by heating for 10 min at the temperature of 925°C, and thereafter being dipped into an oil bath with the temperature of 50°C. After quenching, a specimen of 10 mm width×1.5 mm thickness×65 mm length was cut out by machining.

[0047] No. 29 and No. 30 shown in Table 1 are the data imitating the wire rod for a spring "UHS1900" made by Kobe Steel, Ltd., and in No. 30 out of them, the specimen was manufactured by quenching, thereafter tempering by being held for 1 hour at 400°C, and then being machined in a condition the same with the above. Table 2 shows whether tempering was performed or not.

[0048] Also, the chemical componential amount in the steel and the calculation result of the carbon equivalent (Ceq_1) calculated from the formula (1) are shown in Table 1 below.

[0049] The strength and corrosion fatigue property of the specimen obtained were examined as described below.

[0050] The strength and corrosion fatigue property of the specimen were measured imitating that setting was performed in a cold state or in a warm state. That is, when cold setting was imitated, the specimen was used for each test as it was, and when warm setting was imitated, the specimen heated for 60 min at 200°C was used for each test. Table 2 below shows which of cold setting and warm setting was imitated.

<Strength>

[0051] The strength of the specimen was evaluated by measuring the hardness of the specimen with a Rockwell hardness tester using the C scale. The measurement result of the C hardness is shown in Table 2 below. In the present invention, those with HRC of 51 or more are to be evaluated to have passed.

<Corrosion fatigue property>

[0052] The corrosion fatigue property was evaluated by performing a hydrogen embrittlement cracking test. In the hydrogen embrittlement cracking test, the specimen was immersed in the aqueous solution of a mixture of sulfuric acid (0.5 mol/L) and potassium thiocyanate (KSCN: 0.01 mol/L) while applying the stress of 1,400 MPa on the specimen by 4-point bending, the voltage of -700 mV which is lower than the SCE electrode was applied using a potentiostat, and the time until cracking occurred (hereinafter referred to as "the time until hydrogen embrittlement cracking") was measured. The measurement result of the hydrogen embrittlement cracking test is shown in Table 2 below. In the present invention, those in which the time until cracking occurs is 600 sec or more are evaluated to have passed.

[0053] Also, the criteria of 51 or above of HRC and 600 sec or more of the time until cracking occurs mean to have the property equal or better than that of a suspension spring according to the prior art (No. 30 of the Table 2 below) obtained performing tempering after quenching.

[0054] In FIG. 1, the relation between the carbon equivalent (Ceq_1) and the time until hydrogen embrittlement cracking (sec) is shown. In FIG. 1, the results of No. 1-15, 31, 33 were shown by □, the results of No. 16-29, 32 were shown by ●, and the result of No. 30 (with tempering) was shown by o.

[0055] As is clear from FIG. 1, it is known that there is a tendency that, as the carbon equivalent (Ceq_1) is reduced, the time until hydrogen embrittlement cracking can be made longer and the corrosion fatigue property can be improved.

[0056] From Table 2, the following study is possible.

[0057] No. 30 is an example in which tempering was performed after quenching. In the example, the hardness of the core part was secured, the strength was high, the time until hydrogen embrittlement cracking was excellent, and the corrosion fatigue property was improved. However, because the tempering treatment was performed after quenching, the discharge amount of CO_2 could not be reduced.

[0058] Although the componential composition of No. 29 is similar to that of the No. 30, it is an example of omitting tempering after quenching. In the example, because the tempering treatment is omitted, the discharge amount of CO_2 can be reduced, however, because the carbon equivalent exceeds 0.55 and tempering is omitted in spite that the amount of the alloy element is much, the hardness of the core part becomes too hard, the toughness drops, the time until hydrogen embrittlement cracking becomes short, and the corrosion fatigue property deteriorates.

[0059] No. 16-28, 32 are the examples not satisfying the requirement stipulated in the present invention, and the high strength and excellent corrosion fatigue property were not achieved simultaneously. That is, the carbon equivalent (Ceq_1) of the spring steel exceeded the range stipulated in the present invention, tempering after quenching was omitted, and the discharge amount of CO_2 therefore could be reduced, however the hardness of the core part became too hard, the toughness dropped, the time until hydrogen embrittlement cracking became short, and the corrosion fatigue property deteriorated.

[0060] No. 1-15, 33 are the examples satisfying the requirement stipulated in the present invention, and both of the high strength and excellent corrosion fatigue property were achieved. That is, while the carbon equivalent (Ceq_1) was suppressed to 0.55 or below, the discharge amount of CO_2 could be reduced because tempering after quenching was omitted, the hardness of the core part could be secured appropriately, and the high strength was achieved. Also, the time until hydrogen embrittlement cracking was long, and the corrosion fatigue property was also improved. Furthermore, because the carbon equivalent (Ceq_1) of the spring steel was suppressed to 0.55 or below, the degree of dependability of the alloy element can be lowered, and stable supply can be achieved. Accordingly, it is known that, when the spring steel of the present invention is used, a spring exerting the property of the same level with the No. 30 imitating the "UHS1900" or higher can be provided.

[0061]

[Table 1]

No.	Chemical composition (mass%)													Carbon equivalent (mass%)
	C	Si	Mn	Ni	Cr	Ti	Cu	P	S	V	B	P+S	Others	
1	0.34	1.90	0.25	0.58	1.00	0.081	0.23	0.003	0.008	—	—	0.011		0.52
2	0.33	1.76	0.21	0.40	1.07	0.69	0.28	0.002	0.004	—	—	0.006		0.51
3	0.33	1.76	0.21	0.37	1.08	0.060	0.28	0.001	0.004	0.160	—	0.005		0.53
4	0.34	1.77	0.21	0.33	1.06	0.060	0.28	0.001	0.005	0.158	—	0.006		0.54
5	0.33	2.01	1.21	0.20	0.05	0.031	0.20	0.003	0.005	—	0.002	0.008		0.46
6	0.15	2.20	1.00	0.25	0.20	0.090	0.25	0.015	0.005	—	—	0.020		0.31
7	0.29	3.00	1.70	0.20	0.05	0.032	0.20	0.003	0.005	—	—	0.008		0.49
8	0.29	2.17	0.78	0.20	0.20	0.073	0.16	0.007	0.004	—	—	0.011		0.47
9	0.29	1.76	0.21	0.30	1.06	0.061	0.28	0.001	0.003	0.161	—	0.004		0.49
10	0.15	2.20	1.00	0.25	0.20	0.090	0.25	0.015	0.005	—	0.002	0.020		0.31
11	0.28	2.01	0.48	0.26	1.05	0.060	0.21	0.002	0.006	0.158	0.002	0.008		0.49
12	0.16	2.01	0.80	0.25	1.06	0.061	0.21	0.009	0.007	0.157	0.002	0.016		0.35
13	0.40	2.01	1.20	0.19	0.05	0.031	0.20	0.006	0.005	—	0.002	0.011		0.53
14	0.29	2.01	1.21	0.20	0.05	0.031	0.20	0.007	0.006	—	0.002	0.013		0.42
15	0.40	2.01	1.20	0.19	0.05	0.031	0.20	0.006	0.005	—	0.002	0.011		0.53
16	0.60	1.73	0.88	0.08	0.20	—	0.19	0.010	0.019	0.154	—	0.029	Nb:0.020, Mo:0.03	0.74
17	0.48	1.82	0.21	0.15	1.48	0.072	0.20	0.006	0.006	0.204	—	0.012		0.71
18	0.54	1.81	0.20	0.34	1.25	0.077	0.42	0.006	0.008	0.098	—	0.014		0.74
19	0.45	1.86	0.15	0.50	0.96	0.050	0.19	0.003	0.003	0.104	—	0.006		0.65
20	0.48	2.08	—	0.78	1.50	0.091	0.060	0.007	0.002	—	—	0.009	Nb:0.002	0.70
21	0.49	2.10	0.18	0.67	1.22	0.093	0.52	0.004	0.004	—	—	0.008		0.70
22	0.48	2.10	0.32	0.73	1.12	0.072	0.20	0.007	0.005	—	—	0.012		0.68
23	0.48	2.08	0.36	0.70	1.06	0.075	0.19	0.003	0.004	0.100	—	0.007		0.68
24	0.42	1.92	0.15	0.58	1.02	0.080	0.23	0.025	0.002	0.184	—	0.027		0.63

(continued)

No.	Chemical composition (mass%)													Carbon equivalent (mass%)
	C	Si	Mn	Ni	Cr	Ti	Cu	P	S	V	B	P+S	Others	
25	0.40	2.27	1.01	0.25	0.21	0.089	0.26	0.032	0.005	—	—	0.037		0.57
26	0.42	2.24	1.01	0.25	0.21	0.088	0.26	0.040	0.004	—	0.002	0.044		0.59
27	0.41	2.17	0.79	0.25	0.21	0.010	0.27	0.014	0.004	—	0.002	0.018		0.58
28	0.42	2.27	1.21	0.25	0.20	0.015	0.26	0.012	0.005	—	—	0.017		0.58
29	0.41	1.79	0.16	0.44	1.06	0.063	0.26	0.007	0.003	0.154	—	0.010		0.61
30	0.41	1.75	0.18	0.51	1.05	0.070	0.21	0.009	0.004	0.160	—	0.013		0.61
31	0.38	1.71	0.85	0.06	1.02	0.052	0.21	0.003	0.006	0.104		0.009		0.54
32	0.39	2.98	1.70	0.21	0.05	0.035	0.21	0.007	0.005		0.002	0.012		0.59
33	0.32	2.06	1.22		0.05	0.038		0.008	0.006			0.014		0.46

[0062]

[Table 21

No.	With/without tempering	Setting	Hardness (HRC)	Time until hydrogen embrittlement cracking (sec)
1	Without	Cold	55.9	717
2	Without	Cold	55.8	613
3	Without	Cold	55.6	844
4	Without	Cold	56.0	797
5	Without	Cold	55.3	876
6	Without	Cold	51.4	1800
7	Without	Cold	54.6	1797
8	Without	Cold	55.5	1280
9	Without	Cold	55.3	1188
10	Without	Cold	51.1	1800
11	Without	Cold	55.2	1235
12	Without	Cold	51.3	1800
13	Without	Cold	56.2	1562
14	Without	Warm	54.2	1640
15	Without	Warm	56.1	1510
16	Without	Cold	61.3	40
17	Without	Cold	59.5	38
18	Without	Cold	61.3	48
19	Without	Cold	58.5	466
20	Without	Cold	58.7	114
21	Without	Cold	59.0	164
22	Without	Cold	58.7	144
23	Without	Cold	59.7	246
24	Without	Cold	56.0	226
25	Without	Cold	55.7	355
26	Without	Cold	55.5	128
27	Without	Cold	55.9	284
28	Without	Cold	56.0	411
29	Without	Cold	55.8	575
30	With	Cold	52.2	603
31	Without	Cold	55.5	954
32	Without	Cold	56.8	579
33	Without	Cold	55.2	925

Example 2

[0063] After the steel of the chemical componential composition shown in Table 3 (the remainder is iron and unavoidable impurities) was molten by a vacuum melting furnace of 150 kg, the steel was casted by an ingot-making method or a continuous casting method, a billet of 155 mm square was manufactured thereafter by a blooming mill, was hot-rolled into a wire rod with the diameter of 13.5 mm which was made a test material. These test materials were heated for 10 min at the temperature of 925°C, and were thereafter put into an oil bath of 50°C for quenching. Only No. 2-24 was subjected to tempering treatment for 1 hour at 400°C after quenching.

[0064]

[Table 3]

No.	Chemical composition (mass%)												Carbon equivalent (mass%)
	C	Si	Mn	Cr	V	Ti	P	S	Ni	Cu	P+S	Others	
2-1	0.30	3.00	1.70	0.05		0.037	0.003	0.005	0.20	0.20	0.008		0.50
2-2	0.30	2.01	1.21	0.05		0.036	0.003	0.005	0.20	0.20	0.008	B:0.002	0.43
2-3	0.15	2.20	1.00	0.20	0.180	0.090	0.010	0.005	0.25	0.25	0.015		0.33
2-4	0.15	2.20	1.00	0.20		0.090	0.010	0.005	0.25	0.25	0.015	B:0.002	0.31
2-5	0.34	2.15	1.00	0.38		0.098	0.009	0.006	0.24	0.22	0.015	Nb:0.01	0.50
2-6	0.34	2.21	1.15	0.65	0.150	0.072	0.005	0.005	0.20	0.31	0.010	Mo:0.23	0.52
2-7	0.38	1.76	0.86	1.08	0.160	0.060	0.001	0.004	0.37	0.28	0.005		0.53
2-8	0.34	1.76	0.86	1.06	0.161	0.061	0.001	0.003	0.30	0.28	0.004	B:0.001	0.49
2-9	0.37	1.79	0.82	1.06	0.170	0.068	0.002	0.006	0.53	0.22	0.008		0.52
2-10	0.37	1.87	0.80	0.98	0.107	0.052	0.002	0.004	0.51	0.06	0.006		0.52
2-11	0.38	1.75	0.84	1.05	0.160	0.074	0.006	0.003	0.51	0.48	0.009		0.52
2-12	0.34	1.79	0.81	1.08	0.154	0.063	0.005	0.003	0.44	0.06	0.008		0.49
2-13	0.35	1.75	0.82	1.09		0.041	0.004	0.004	0.77	0.21	0.008		0.47
2-14	0.38	1.71	0.85	1.02	0.104	0.052	0.003	0.006	0.06	0.21	0.009		0.54
2-15	0.60	1.73	0.88	0.20	0.154		0.010	0.019	0.08	0.19	0.029	Mo:0.13, Nb:0.02	0.74
2-16	0.52	1.89	0.15	1.01	0.179	0.078	0.003	0.023	0.29	0.23	0.026		0.74
2-17	0.46	2.18	0.79	0.21		0.071	0.005	0.004			0.009		0.65
2-18	0.46	2.20	0.41	0.21		0.072	0.007	0.004	0.30		0.011		0.66
2-19	0.45	2.18	0.77			0.069	0.005	0.005	0.20	0.31	0.010		0.62
2-20	0.40	2.21	0.82	0.15			0.005	0.005	0.20	0.31	0.010		0.58
2-21	0.30	3.00	1.70	0.05			0.010	0.005	0.20	0.20	0.015		0.50
2-22	0.30	2.01	1.21	0.05			0.012	0.005	0.20	0.20	0.017	B:0.002	0.43
2-23	0.54	1.50	0.70	0.70			0.012	0.006			0.018		0.67
2-24	0.54	1.50	0.70	0.70			0.012	0.006			0.018		0.67

(continued)

No.	Chemical composition (mass%)												Carbon equivalent (mass%)
	C	Si	Mn	Cr	V	Ti	P	S	Ni	Cu	P+S	Others	
2-25	0.32	2.06	1.22	0.05		0.038	0.008	0.006			0.014		0.46
2-26	0.39	2.98	1.70	0.05		0.035	0.007	0.005	0.21	0.21	0.012	B:0.002	0.59

<Low temperature toughness>

[0065] An impact test specimen with 2 mm U-notch was taken from the test material after the quenching, and the Charpy absorbed energy at -50°C (vE_{-50}) was obtained according to JIS Z 2242. The tests were carried out on two pieces for each steel kind, and the average value thereof was made the Charpy absorbed energy of each steel kind.

<Grain size number>

[0066] At the D/4 position (D is the diameter of the wire rod) of the test material after the quenching, an optional area of 15 mm^2 was observed with an optical microscope (magnification: 400 times), and the grain size number was measured according to JIS G 0551. The measurement was performed on two fields of view, and the average value thereof was made the austenite grain size.

[0067] The result is shown in Table 4.

[0068]

[Table 4]

No.	Grain size number	Charpy absorbed energy **vE_{-50}(J/cm^2)**	Tensile strength **TS (MPa)**
2-1	7.5	67.7	1726
2-2	8.5	65.7	1534
2-3	8.7	91.8	1109
2-4	7.8	68.0	1137
2-5	9.0	60.9	1833
2-6	8.2	68.4	1710
2-7	9.5	81.3	1804
2-8	10.0	85.7	1638
2-9	10.8	85.8	1897
2-10	9.5	86.5	1982
2-11	9.0	81.6	1713
2-12	9.0	92.3	1857
2-13	8.8	94.3	1811
2-14	9.5	74.7	1747
2-15	10.5	12.2	2418
2-16	9.5	36.7	2409
2-17	8.2	38.5	2336
2-18	8.4	32.2	2422
2-19	8.2	38.5	2106
2-20	7.0	37.5	1823
2-21	6.0	25.5	1648
2-22	5.4	47.5	1457
2-23	6.3	7.0	2356
2-24	6.3	27.5	1565
2-25	8.2	72.5	1776
2-26	7.0	48.5	2349

[0069] In No. 2-1 to No. 2-14 of Table 4, because the requirement of the present invention was satisfied and the amounts of Ti, Nb and V were properly adjusted in particular, the steel with high strength and excellent in the low temperature toughness could be obtained.

[0070] On the other hand, in No. 2-15 to No. 2-24, because at least any one of the requirement of the present invention was not satisfied, the toughness was insufficient.

[0071] No. 2-15 to No. 2-19 are the examples in which the C amount was excessive, and the low temperature toughness dropped because the strength increased too high.

[0072] In No. 2-20 to No. 2-22, because none of Ti, Nb and V was contained, the grain miniaturizing effect was not exerted, and the low temperature toughness dropped.

[0073] Either of No. 2-23 and No. 2-24 is the steel kind equivalent to the standardized steel 9254, and No. 2-24 was subjected to the tempering treatment after quenching. In No. 2-23, the C amount was much and the strength increased excessively, none of Ti, Nb and V was contained, and therefore the low temperature toughness dropped. Also, in No. 2-24, the strength dropped compared with No. 2-23 because the tempering treatment was performed, but the low temperature toughness dropped, because none of Ti, Nb and V was contained.

[0074] FIG. 2 is a graph showing the relation between the strength and the low temperature toughness (Charpy absorbed energy at -50°C) with respect to No. 2-1 to 2-24. In FIG. 2, the results of No. 2-1 to 2-14, 2-25 were shown by □, the results of No. 2-15 to No. 2-23, 2-26 were shown by ●, and the result of No. 2-24 was shown by o. According to FIG. 2, it is known that, in all of the steel satisfying the requirement of the present invention (shown by □ in FIG. 2), the Charpy absorbed energy was 50 J/cm^2 or more and higher toughness was achieved than that in the steel not satisfying any of the requirement of the present invention (shown by ● and ○ in FIG. 2) when compared with same strength.

Claims

1. A high-strength spring steel omitting tempering, containing:

   C: 0.15-0.40% (means mass%, hereinafter the same);
   Si: 1-3.5%;
   Mn: 0.20-2.0%; and containing:
   at least one element selected from a group consisting of Ti:
   0.005-0.10%, Nb: 0.005-0.05% and V: 0.25% or less;
   Cr: 0.05-1.20%;
   P: 0.030% or less;
   S: 0.02% or less; with the remainder including iron and unavoidable impurities, wherein
   a carbon equivalent Ceq$_1$ expressed by a formula (1) below is 0.55 or less.

$$Ceq_1=[C]+0.108\times[Si]-0.067\times[Mn]+0.024\times[Cr]-0.05\times[Ni]+0.074\times[V]\ldots(1)$$

   (In the formula (1), each symbol in brackets represents the content (mass%) of the corresponding element.)

2. The high-strength spring steel according to claim 1, further containing Ni: 0.05-2% and Cu: 0.05-0.50%.

3. The high-strength spring steel according to claim 2, containing Ni: 0.15-2%.

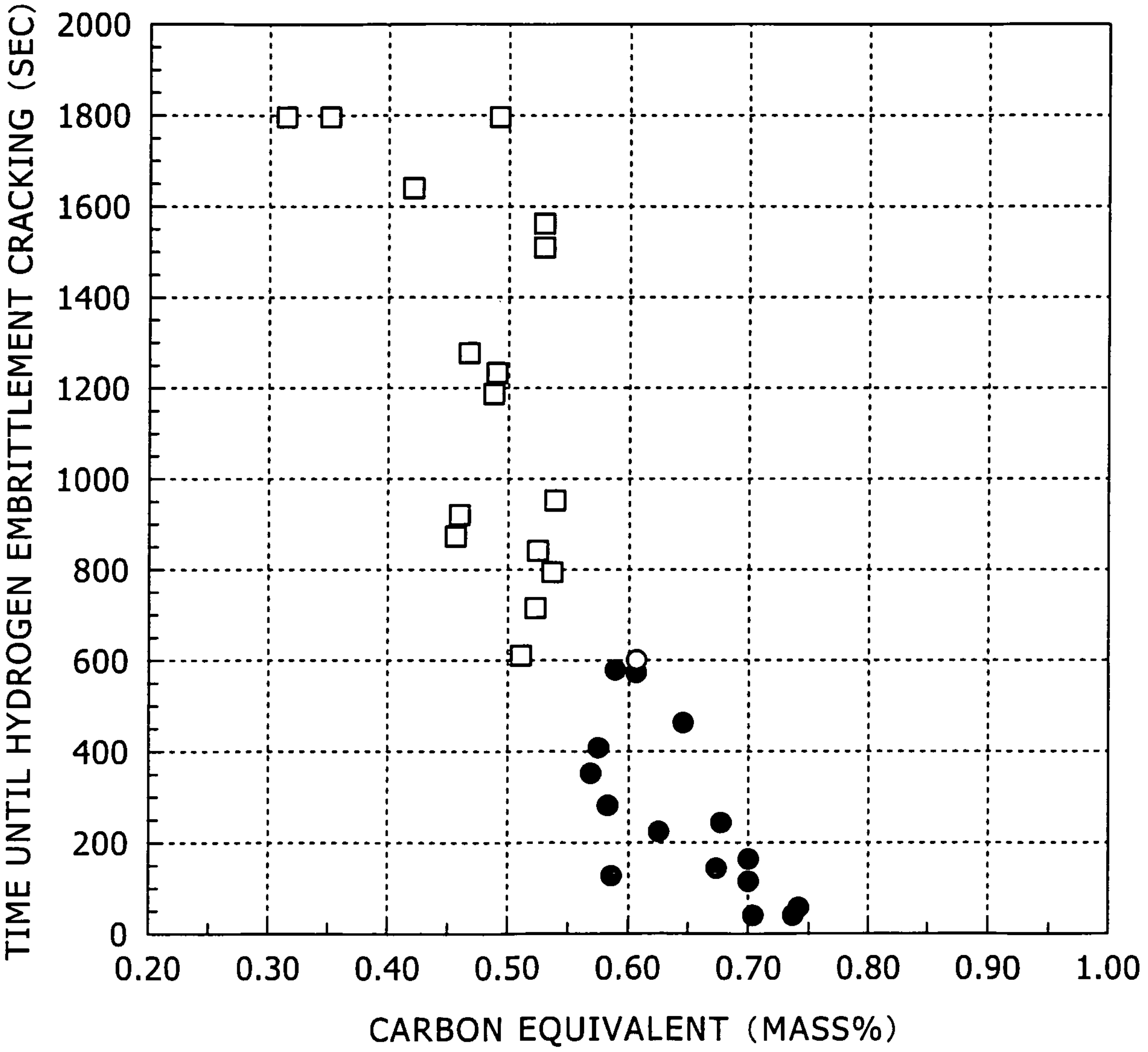
4. The high-strength spring steel according to claim 1, containing at least one element selected from a group consisting of Ti: 0.035-0.10%, Nb: 0.005-0.05%, and V: 0.05-0.25%, wherein the grain size number after quenching is 7.5 or above.

5. The high-strength spring steel according to claim 1, further containing B: 0.005% or less and/or Mo: 0.60% or less.

6. A method for manufacturing a high-strength spring excellent in corrosion fatigue property, comprising the steps of:

   hot-coiling the spring steel according to any one of claims 1-5;
   quenching; and
   setting thereafter while omitting tempering.

FIG. 1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1800
1600
1400
1200
1000
800
600
400
200
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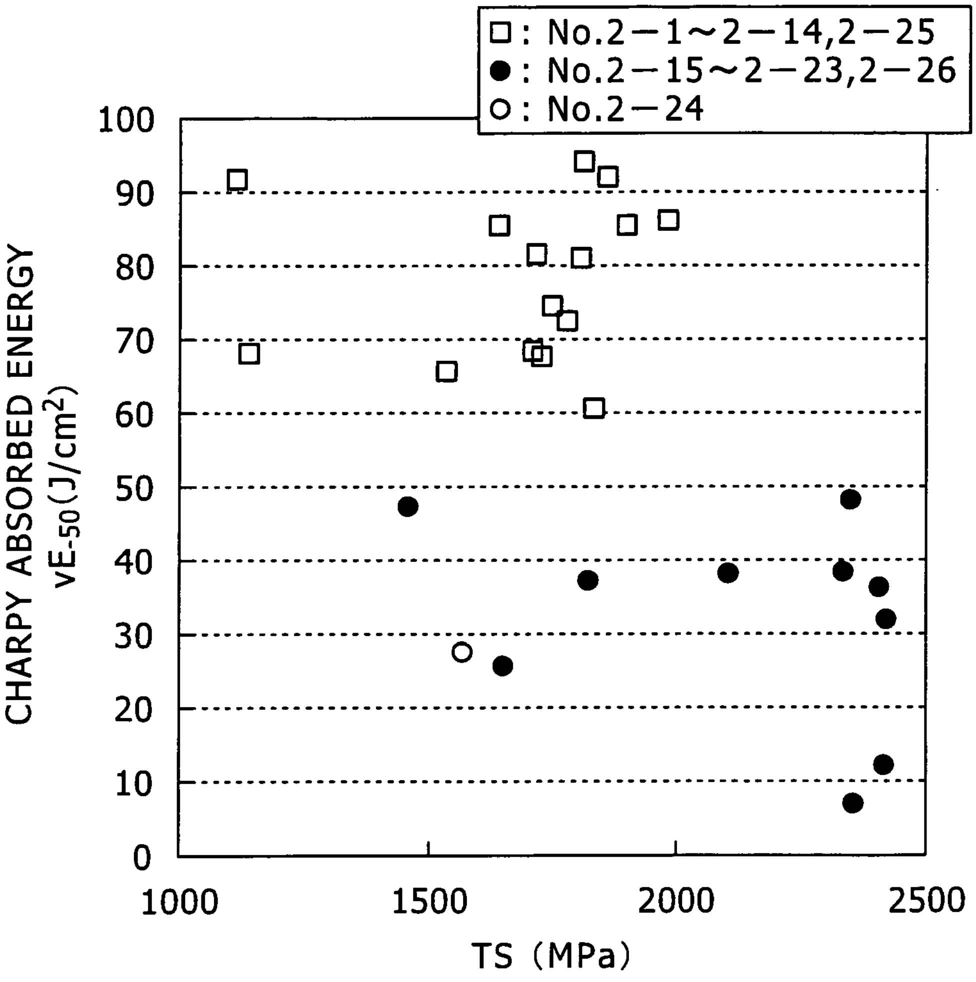
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
CARBON EQUIVALENT (MASS%)

FIG.2


□: No.2−1~2−14,2−25
●: No.2−15~2−23,2−26
○: No.2−24
CHARPY ABSORBED ENERGY
vE-50(J/cm2)
100
90
80
70
60
50
40
30
20
10
0
1000
1500
2000
2500
TS (MPa)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/073003

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D9/02*(2006.01)i, *C22C38/38*(2006.01)i, *C22C38/58*(2006.01)i, *C21D7/06*(2006.01)n

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, C21D9/02, C21D7/06

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	1996-2011
Kokai Jitsuyo Shinan Koho	1971-2011	Toroku Jitsuyo Shinan Koho	1994-2011

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.
X	JP 2001-49337 A (Kobe Steel, Ltd.), 20 February 2001 (20.02.2001), claims (Family: none)	1-6
A	JP 11-323495 A (Kobe Steel, Ltd.), 26 November 1999 (26.11.1999), Steel type no.1 & US 6206984 B1	1-6
A	JP 2004-263247 A (Daido Steel Co., Ltd.), 24 September 2004 (24.09.2004), Steel type 30 (Family: none)	1-6

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

* Special categories of cited documents:
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 04 March, 2011 (04.03.11)	Date of mailing of the international search report 15 March, 2011 (15.03.11)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/073003

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2009-46764 A (Kobe Steel, Ltd.), 05 March 2009 (05.03.2009), Steel type M & CN 101624679 A & EP 2017358 A2 & KR 10-2009-0009739 A & US 2009/0020189 A1	1-6

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REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 4406341 B **[0007]**
- JP 3577411 B **[0007]**
- JP 3246733 B **[0007]**