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(54) **HIGH-STRENGTH FLAT STEEL WIRE EXHIBITING SUPERIOR HYDROGEN-INDUCED CRACK RESISTANCE**

(57) A high-strength flat steel wire contains, by mass%: C: 0.25 to 0.60%; Si: greater than 0.50% and less than 2.0%; Mn: 0.20 to 1.50%; S: 0.015% or less; P: 0.015% or less; Cr: 0.005 to 1.50%; Al: 0.005 to 0.080%; N: 0.0020 to 0.0080%; and one or two of Ca: 0 to 0.0050% and Mg: 0 to 0.0050% to satisfy [Ca] + [Mg] > 0.20 × [S], with the balance composed of Fe and impurities, the high-strength flat steel wire has tensile strength of 1000 MPa or more, an average value of Hv hardness measured in a cross section perpendicular to a longitudinal direction of 320 or more and less than 450, a standard deviation σHv of the measured value of 15 or less, and a width/thickness ratio of not less than 1.5 nor more than 10. [Ca], [Mg], and [S] represent contents of respective elements by mass%.

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Description

[Technical Field]

[0001] The present invention relates to a high-strength flat steel wire used for the purpose of realizing reinforcement of tension and the like of a component used under a sour environment containing hydrogen sulfide such as a flexible pipe for transporting a high-pressure fluid such as crude oil.

[Background Art]

[0002] For a flexible pipe for transporting a high-pressure fluid such as natural gas or crude oil, a flat steel wire is used as a reinforcing material. In development of an undersea oil field, a digging depth tends to be deep as a demand for petroleum increases, and a demand for increasing strength of the reinforcing material of the flexible pipe is increasing. Further, since the flexible pipe is used under a sour environment containing hydrogen sulfide, the flat steel wire used for the reinforcing material is required to have a property causing no hydrogen induced cracking (HIC), which is, hydrogen induced cracking resistance. However, generally, the hydrogen induced cracking is likely to occur as strength of the wire becomes high, which makes it difficult for a high-strength wire material to be applied to a component such as the flexible pipe used under the sour environment. Until this time, techniques of providing high-strength wires used under the sour environment as above have been proposed.

Patent Document 1 proposes a high-strength steel material having a composition containing, by mass%, C: 0.25 to 0.35%, Si: 0.10 to 0.30%, Mn: 0.8% or less, P: 0.010% or less, S: 0.003% or less, Al: 0.003 to 0.1%, N: 0.0040% or less, Cr: 0.5 to 0.7%, Mo: 0.5 to 1.0%, Cu: 0.05 to 0.8%, Ti: 0.015 to 0.030%, Nb: 0.005 to 0.025%, V: 0.05 to 0.10%, and B: 0.0005 to 0.0015% in which P, Ti, and N are contained by being adjusted to satisfy P / effective Ti amount < 1.6 (effective Ti amount = Ti - 3.4 $\times$ N), with the balance composed of Fe and inevitable impurities, and a structure composed of a tempered martensite phase in which an Mo segregation degree is 1.5 or less and an average grain diameter of prior austenite grains is 12 μm or less.

Patent Document 2 proposes a hot-rolled wire material containing, by mass%, C: 0.20 to 0.5%, Si: 0.05 to 0.3%, Mn: 0.3 to 1.5%, Al: 0.001 to 0.1%, P: greater than 0% and equal to or less than 0.01%, S: greater than 0% and equal to or less than 0.01%, and the other elements, in which when S amounts are measured by using an electron probe microanalyzer at 300 or more points and at intervals of 200 μm, and a maximum value Smax (mass%) of the S amounts relative to an average value Save (mass%) of the S amounts is set as a segregation degree (Smax/Save), the segregation degree is 30 or less.

Patent Document 3 discloses a profiled wire having high mechanical characteristics and excellent resistance with respect to hydrogen embrittlement as a flexible tube component for digging an undersea oil field, characterized in that it contains 0.75 < C% < 0.95 and 0.30 < Mn% < 0.85, with Cr $\leq$ 0.4%, V $\leq$ 0.16%, Si $\leq$ 1.40% and preferably $\geq$ 0.15%, and possibly 0.06% or less of Al, 0.1% or less of Ni, and 0.1% or less of Cu, and in that, starting from a wire material, hot-rolled in its austenite region above 900°C and then cooled to a room temperature, it is obtained by subjecting the wire material first to thermomechanical treatment according to two successive and ordered phases, specifically isothermal tempering, which confers on it a homogeneous pearlitic microstructure, following by an operation of cold mechanical transformation, carried out with a global work-hardening ratio of between 50 and 80% at maximum, to give the wire its final profile, and in that the obtained profiled wire is then subjected to short-duration recovery heat treatment at a temperature below the Acl temperature of the steel constituting it, thus conferring on it the desired final mechanical characteristics.

[Prior Art Document]

[Patent Document]

[0003]

[Patent Document 1] Japanese Laid-open Patent Publication No. 2013-227611
[Patent Document 2] Japanese Laid-open Patent Publication No. 2015-212412
[Patent Document 3] Japanese Translation of PCT International Application Publication No. JP-T-2013-534966

[Disclosure of the Invention]

[Problems to Be Solved by the Invention]

[0004] In the technique disclosed in Patent Document 1, the Si amount is small and a sulfide is stretched in the longitudinal direction when the steel material is shaped into a flat steel wire, so that when the steel material is turned into a flat steel wire with tensile strength of 1000 MPa or more, the hydrogen induced cracking is caused under a sour environment with pH of less than 5.5, and thus there is a limit to increase strength of the flat steel wire.

[0005] In the technique disclosed in Patent Document 2, when the wire material is turned into a high-strength flat steel wire with tensile strength of 1000 MPa or more, the hydrogen induced cracking is likely to occur due to the low Si amount. Further, since a sulfide is stretched in the longitudinal direction, when the wire material is turned into a flat steel wire with tensile strength of 1000 MPa or more, the hydrogen induced cracking is likely to occur under the sour environment, and thus there is a limit to increase strength of the flat steel wire.

[0006] In the technique disclosed in Patent Document 3, the C amount is high and a hardness distribution in a cross section of the profiled wire is non-uniform, and a sulfide is stretched in the longitudinal direction when the profiled wire is shaped into a flat steel wire, so that when the profiled wire is turned into a flat steel wire with tensile strength of 1000 MPa or more, the hydrogen induced cracking is likely to occur under a severe sour environment with pH of less than 5.5, and thus there is a limit to increase strength of the flat steel wire.

[0007] The present invention has been made in view of the above-described present situation, and an object thereof is to provide a flat steel wire being a high-strength flat steel wire with tensile strength of 1000 MPa or more, which is difficult to cause hydrogen induced cracking even under a severe sour environment with pH of less than 5.5, and which can be used as a reinforcing wire material of a flexible pipe and the like.

[Means for Solving the Problems]

[0008] The present inventors conducted various studies for solving the above-described problems. As a result of this, they obtained findings of the following (a) to (d).

(a) The hydrogen induced cracking of the flat steel wire occurs from a coarse sulfide included in the flat steel wire as a starting point. Particularly, when a sulfide such as MnS is coarse, a gap is generated around the coarse sulfide at a time of performing primary wire drawing and flat rolling required as a step of performing forming from a hot-rolled wire material to a flat steel wire, which becomes a cause of facilitating the hydrogen induced cracking under a severe sour environment with pH of less than 5.5.

(b) For this reason, there is a need to make the sulfide which is inevitably included in the wire material to be as fine as possible. In order to make the sulfide finer, it is effective to add a slight amount of Ca or Mg to form MnS in which Ca or Mg is partially solid-dissolved, CaS or MgS.

(c) In order to improve the hydrogen induced cracking resistance of the flat steel wire, it is effective to make Si to be solid-dissolved in a matrix. This can be estimated because Si which is solid-dissolved in an Fe matrix being a base material functions as a trap site of hydrogen that enters the flat steel wire, which suppresses diffusion of hydrogen that exerts an adverse effect on the hydrogen induced cracking.

(d) A wire material is worked into a flat steel wire in a manner that, for example, a rolled wire material is subjected to primary wire drawing and then subjected to profiled wire drawing using a die which is worked to have a shape of the flat steel wire or cold rolling using a cold rolling mill. In the flat steel wire manufactured through such steps, hardness at a center portion in a thickness direction of the flat steel wire tends to be high due to a working strain caused by cold working, and a large hardness dispersion is generated in a cross section of the flat steel wire. In particular, in a flat steel wire with tensile strength of 1000 MPa or more, the dispersion of hardness in a cross section thereof causes the hydrogen induced cracking, and thus there is a need to reduce the hardness dispersion in the cross section of the flat steel wire as much as possible.

[0009] The present invention has been completed based on the above-described findings, and the gist thereof lies in a high-strength flat steel wire excellent in hydrogen induced cracking resistance described in the following (1) to (4).

(1) A high-strength flat steel wire excellent in hydrogen induced cracking resistance is characterized in that it contains, by mass%: C: 0.25 to 0.60%; Si: greater than 0.50% and less than 2.0%; Mn: 0.20 to 1.50%; S: 0.015% or less; P: 0.015% or less; Cr: 0.005 to 1.50%; Al: 0.005 to 0.080%; N: 0.0020 to 0.0080%; and one or two of Ca: 0 to 0.0050% and Mg: 0 to 0.0050% to satisfy the following expression <1>, in which components which are optionally contained include: Ti: 0.10% or less; Nb: 0.050% or less; V: 0.50% or less; Cu: 1.0% or less; Ni: 1.50% or less; Mo: 1.0% or less; B: 0.01% or less; REM: 0.10% or less; and Zr: 0.10% or less, the balance is composed of Fe and impurities,

tensile strength is 1000 MPa or more, an average value of Hv hardness measured in a cross section perpendicular to a longitudinal direction is 320 or more and less than 450, a standard deviation σHv of the measured value of the Hv hardness is 15 or less, and a width/thickness ratio is not less than 1.5 nor more than 10,

$$[Ca] + [Mg] > 0.20 \times [S] \qquad \cdots <1>$$

where [Ca], [Mg], and [S] in the above expression represent contents of respective elements by mass%.

(2) The high-strength flat steel wire excellent in the hydrogen induced cracking resistance described in (1), is characterized in that it contains, by mass%, at least one or two or more selected from Ti: 0.001 to 0.10%, Nb: 0.001 to 0.050%, and V: 0.01 to 0.50%.

(3) The high-strength flat steel wire excellent in the hydrogen induced cracking resistance described in (1) or (2), is characterized in that it contains, by mass%, at least one or two or more selected from Cu: 0.01 to 1.0%, Ni: 0.01 to 1.50%, Mo: 0.01 to 1.0%, and B: 0.0002 to 0.01%.

(4) The high-strength flat steel wire excellent in the hydrogen induced cracking resistance described in any one of (1) to (3), is characterized in that it contains, by mass%, at least one or two selected from REM: 0.0002 to 0.10%, and Zr: 0.0002 to 0.10%.

[0010] Note that "impurities" in "Fe and impurities" being the balance are components which are unintentionally contained in the steel material, and indicate components mixed from an ore as a raw material, a scrap, a manufacturing environment or the like at a time of industrially manufacturing an iron and steel material.

[Effect of the Invention]

[0011] A flat steel wire of the present invention is difficult to cause hydrogen induced cracking even under a severe sour environment with pH of less than 5.5, while having high tensile strength of 1000 MPa or more, and thus it can be used as a tension reinforcing material of a flexible pipe.

[Best Mode for Carrying out the Invention]

(A) Regarding chemical components

[0012] Hereinafter, % regarding chemical components indicates mass%.

C: 0.25 to 0.60%

[0013] C is an element which strengthens a steel, and 0.25% or more thereof has to be contained. On the other hand, if the content of C exceeds 0.60%, when flat steel wires are mutually joined by welding, strength of a joint portion becomes insufficient. Further, dispersion is caused in a hardness distribution in a cross section of the flat steel wire due to segregation, which reduces the hydrogen induced cracking resistance. Therefore, an appropriate content of C is 0.25 to 0.60%. When the strength is desired to be increased more, the content of C is preferably set to 0.30% or more, and it is more preferably 0.35% or more. On the other hand, when it is desired that weldability is secured and the hydrogen induced cracking resistance is increased by reducing the segregation in the cross section of the flat steel wire as much as possible, the content of C is preferably set to 0.55% or less, and it is desirably set to 0.50% or less in order to further improve the hydrogen induced cracking resistance.

Si: greater than 0.50% and less than 2.0%

[0014] Si is an element solid-dissolved in a matrix and effective for improving the strength of the flat steel wire and improving the hydrogen induced cracking resistance, and it has to be contained in an amount of greater than 0.50%. However, if Si is contained in an amount of 2.0% or more, a problem arises such that cracking occurs in a wire material when the wire material is subjected to cold working to have a shape of the flat steel wire. Therefore, the content of Si is greater than 0.50% and less than 2.0%. When it is desired that the strength is further increased or the hydrogen induced cracking resistance is further improved, Si is preferably contained in an amount of 0.70% or more, and it is more preferably contained in an amount of 1.0% or more. When the cracking of the wire material is desired to be suppressed when the wire material is worked into the flat steel wire, Si is preferably set to 1.80% or less.

Mn: 0.20 to 1.50%

[0015] Mn is a required element for increasing hardenability of the steel to realize high strengthening, and it has to be contained in an amount of 0.20% or more. However, if the content of Mn exceeds 1.50%, the strength of the wire material becomes too high, and there arises a problem such that when the wire material is worked into the flat steel wire, cracking occurs in the wire material. For this reason, the content of Mn in the flat steel wire of the present invention is 0.20 to 1.50%. Note that when the hardenability of the flat steel wire is further increased or when the strength is further increased, Mn is only required to be contained in an amount of 0.50% or more, and it is more preferably contained in an amount of 0.70% or more. When the cracking of the wire material is desired to be suppressed when the wire material is worked into the flat steel wire, Mn is preferably set to 1.30% or less, and it is more preferably 1.10% or less.

S: 0.015% or less

[0016] S is contained as an impurity. Note that if a content of S exceeds 0.015%, MnS takes a stretched coarse form to reduce the hydrogen induced cracking resistance. For this reason, the content of S in the flat steel wire in the present invention is required to be set to 0.015% or less. In order to improve the hydrogen induced cracking resistance in the flat steel wire with the tensile strength of 1000 MPa or more, S has to be contained by considering a balance with elements such as Ca and Mg which are likely to bond with S to generate sulfides. From a viewpoint of improving the hydrogen induced cracking resistance, the content of S is preferably 0.010% or less, and more preferably 0.008% or less. Although a lower limit value of the S content is not particularly limited, to reduce the S content to 0% is technically difficult, and besides, it causes increase in a steelmaking cost. Therefore, the lower limit value of the S content may be set to 0.0005%.

P: 0.015% or less

[0017] P is contained as an impurity. Note that if a content of P exceeds 0.015%, the hydrogen induced cracking is likely to occur, and in the flat steel wire with the tensile strength of 1000 MPa or more, it is not possible to suppress the hydrogen induced cracking under the severe sour environment with pH of less than 5.5. From a viewpoint of improving the hydrogen induced cracking resistance, the content of P is preferably 0.010% or less, and more preferably 0.008% or less. Although a lower limit value of the P content is not particularly limited, to reduce the P content to 0% is technically difficult, and besides, it causes increase in a steelmaking cost. Therefore, the lower limit value of the P content may be set to 0.0005%.

Cr: 0.005 to 1.50%

[0018] Cr is a required element for increasing hardenability of the steel to realize high strengthening, similarly to Mn, and it has to be contained in an amount of 0.005% or more. However, if the content of Cr exceeds 1.50%, the strength of the wire material becomes too high, and there arises a problem such that when the wire material is worked into the flat steel wire, cracking occurs in the wire material. For this reason, an appropriate content of Cr in the flat steel wire of the present invention is 0.005 to 1.50%. Note that when the hardenability of the flat steel wire is further increased or when the strength is further increased, Cr is preferably contained in an amount of 0.10% or more, and more preferably contained in an amount of 0.30% or more. When the cracking of the wire material is desired to be suppressed when the wire material is subjected to cold working to be the flat steel wire, the Cr content is preferably set to 1.30% or less, and it is more preferably 1.10% or less.

Al: 0.005 to 0.080%

[0019] Al not only exhibits deoxidation action but also bonds with N to form AlN, and a pinning effect of AlN brings about an effect of making austenite grains finer during hot rolling, which produces an effect of improving the hydrogen induced cracking resistance of the flat steel wire. For this reason, Al has to be contained in an amount of 0.005% or more. From a viewpoint of improving the hydrogen induced cracking resistance, the content of Al is desirably set to 0.015% or more, and it is more desirable that Al is contained in an amount of 0.020% or more. On the other hand, if the content of Al exceeds 0.080%, the effect of Al is saturated, and not only that, coarse AlN is generated, which contrarily reduces the hydrogen induced cracking resistance of the flat steel wire. Accordingly, the content of Al is preferably 0.060% or less, and more preferably 0.050% or less.

N: 0.0020 to 0.0080%

[0020] N has an effect of improving the strength of the flat steel wire material by being solid-dissolved in a matrix. Further, N bonds with Al, Ti, or the like to generate a nitride or a carbonitride, which brings about an effect of making austenite grains finer during hot rolling, which produces an effect of improving the hydrogen induced cracking resistance of the flat steel wire. In order to obtain these effects, N has to be contained in an amount of 0.0020% or more, and it is more preferably contained in an amount of 0.0030% or more. However, even if N is excessively contained, the effect thereof is saturated, and not only that, the manufacturability is deteriorated such that cracking occurs at a time of casting the steel, so that the content of N has to be set to 0.0080% or less. In order to secure the stabilized manufacturability, the N content is preferably set to 0.0060% or less, and more preferably set to 0.0050% or less.

Ca: 0 to 0.0050%

[0021] Ca has an effect of making MnS to be finely dispersed by being solid-dissolved in MnS. By making MnS to be finely dispersed, it is possible to improve the hydrogen induced cracking resistance even in a high-strength flat steel wire. It is possible that Ca is not contained (Ca: 0%), but, in order to obtain the effect of suppressing the hydrogen induced cracking with the use of Ca, Ca is only required to be contained in an amount of 0.0002% or more, and when a higher effect is desired to be achieved, Ca is only required to be contained in an amount of 0.0005% or more. However, even if the content of Ca exceeds 0.0050%, the effect of Ca is saturated, and an oxide of Ca generated through reaction with oxygen in the steel together with Al and Mg becomes coarse, which contrarily causes reduction in the hydrogen induced cracking resistance. Therefore, when Ca is contained, an appropriate content of Ca is 0.0050% or less. From a viewpoint of improving the hydrogen induced cracking resistance, the content of Ca is preferably 0.0030% or less, and more preferably 0.0025% or less.

Mg: 0 to 0.0050%

[0022] Mg has an effect of making MnS to be finely dispersed by being solid-dissolved in MnS. By making MnS to be finely dispersed, it is possible to improve the hydrogen induced cracking resistance even in a high-strength flat steel wire. It is possible that Mg is not contained (Mg: 0%), but, in order to obtain the effect of suppressing the hydrogen induced cracking with the use of Mg, Mg is only required to be contained in an amount of 0.0002% or more, and when a higher effect is desired to be achieved, Mg is only required to be contained in an amount of 0.0005% or more. However, even if the content of Mg exceeds 0.0050%, the effect of Mg is saturated, and an oxide of Mg generated through reaction with oxygen in the steel together with Al and Ca becomes coarse, which contrarily causes reduction in the hydrogen induced cracking resistance. Therefore, when Mg is contained, an appropriate content of Mg is 0.0050% or less. From a viewpoint of improving the hydrogen induced cracking resistance, the content of Mg is preferably 0.0030% or less, and more preferably 0.0025% or less.

[0023] The flat steel wire excellent in the hydrogen induced cracking resistance of the present invention has to contain one or two of Ca and Mg, and satisfy a relationship represented by the following expression <1>,

$$[Ca] + [Mg] > 0.20 \times [S] \cdots \qquad <1>$$

where [Ca], [Mg], and [S] in the above expression represent contents of respective elements by mass%.

[0024] This is because, although the hydrogen induced cracking occurs mainly from coarse MnS as a starting point under the severe sour environment with pH of less than 5.5, by making Ca or Mg to be partially solid-dissolved in MnS, MnS is finely dispersed, which improves the hydrogen induced cracking resistance. As an amount of Ca or Mg solid-dissolved in MnS becomes larger, MnS is made finer to improve the hydrogen induced cracking resistance, so that an upper limit of the value of [Ca] + [Mg] is not particularly set. However, if the amount of Ca or Mg solid-dissolved in MnS becomes too large, MnS becomes difficult to be made finer, on the contrary, so that it is desirable that the value of [Ca] + [Mg] does not exceed a value being 1.2 times the value of [S].

(B) Regarding characteristics and manufacturing method:

[0025] Under the sour environment, as the strength of the steel becomes higher, the hydrogen induced cracking is likely to occur, and since the flat steel wire in the present invention is excellent in the hydrogen induced cracking resistance, even if the tensile strength is 1000 MPa or more, it is possible to suppress the hydrogen induced cracking under the severe sour environment with pH of less than 5.5. If adjustment of inclusions and components is performed more strictly and manufacturing conditions are optimized, the hydrogen induced cracking becomes difficult to occur even if the tensile strength is higher. The strength of the flat steel wire material is preferably 1100 MPa or more in a range of causing no hydrogen induced cracking under a certain sour environment.

[0026] The effect of the present invention can be achieved as a result of suppressing the hardness dispersion in a cross section perpendicular to a longitudinal direction by suppressing the component segregation in the cross section perpendicular to the longitudinal direction of the wire material through adjustment of components at a stage of smelting the steel, control of inclusions, and control of rolling and heating conditions, and by manufacturing conditions of the flat steel wire such as removal, through heat treatment and the like, of the working strain that is applied when the working is performed on the flat steel wire material.

[0027] When an average value of Hv hardness measured in a cross section perpendicular to a longitudinal direction of the flat steel wire is less than 320, the tensile strength as a tension reinforcing material becomes insufficient. On the contrary, when the average value is 450 or more, the strength is too high, which causes the hydrogen induced cracking. When the hydrogen induced cracking is desired to be suppressed under the severe sour environment with pH of less than 5.5, the average value of the Hv hardness in the cross section perpendicular to the longitudinal direction is desirably 430 or less, and more preferably 400 or less.

[0028] Further, in order to improve the hydrogen induced cracking resistance of the flat steel wire with the tensile strength exceeding 1000 MPa under the sour environment with pH of less than 5.5, the dispersion of the Hv hardness in the cross section perpendicular to the longitudinal direction of the flat steel wire is also required to be controlled at the same time. When the Hv hardness (Vickers hardness) in a cross section perpendicular to a longitudinal direction was measured regarding flat steel wires in which the hydrogen induced cracking did not occur under the sour environment with pH of less than 5.5, a standard deviation (σHv) of the measured value of each of the flat steel wires was 15 or less. On the contrary, the standard deviation (σHv) of the measured value of the Hv hardness in the cross section of each of the flat steel wires in which the hydrogen induced cracking occurred was greater than 15. It can be supposed that the hardness dispersion occurred in the cross section perpendicular to the longitudinal direction due to the composition segregation and the working strain applied at the stage of performing working to obtain the flat steel wire, which exerted an adverse effect on the hydrogen induced cracking. If the hardness dispersion in the cross section of the flat steel wire is as small as possible, it is effective to improve the hydrogen induced cracking resistance, and thus the standard deviation (σHv) of the measured value of the Hv hardness in the cross section is preferably 13 or less. When the hydrogen induced cracking resistance is desired to be improved more, the standard deviation (σHv) is more desirably 11 or less.

[0029] In the present invention, in order to suppress the hydrogen induced cracking, the inclusions are controlled and the component segregation in the cross section perpendicular to the longitudinal direction of the wire material is suppressed by not only the chemical components at the stage of smelting the steel but also the rolling and heating conditions and the manufacturing conditions of the flat steel wire, and the manufacturing conditions of the flat steel wire are controlled such that heat treatment is applied after the working is performed to obtain the flat steel wire, to thereby control the average hardness and the dispersion of hardness in the cross section.

[0030] If the requirements of the present invention are satisfied, it is possible to obtain the effect of the present invention without depending on the manufacturing method of the flat steel wire, and it is possible that, for example, a wire material is manufactured through the following manufacturing method, and the wire material is used as a raw material to manufacture a flat steel wire. Note that a manufacturing process to be described below is one example, and it is needless to say that even in a case where a flat steel wire having chemical components and the other requirements that fall within the range of the present invention is obtained by a process other than the process to be described below, the flat steel wire is included in the present invention.

[0031] Concretely, a steel ingot or a cast slab smelted and cast by a converter, a normal electric furnace, or the like after chemical components such as C, Si, and Mn are adjusted is subjected to a step of bloom rolling to be a raw material for product rolling being a steel billet. Before the product rolling, namely, at the time of heating in the bloom rolling or at the stage before that, the cast steel billet is subjected to heat treatment for 12 hours or more at a temperature of 1250°C or more. Consequently, a part of MnS is solid-dissolved to be made finer, and it is possible to suppress the component segregation in the rolled wire material.

[0032] After that, the steel billet is reheated and subjected to product rolling in hot working to be finally finished to a bar steel or wire material with a predetermined diameter.

[0033] The rolled wire material is subjected to primary wire drawing and then worked into a flat steel wire. At this time, a total reduction of area by working when the rolled wire material is worked into the flat steel wire is desirably 80% or less. The flat steel wire is adjusted to have a predetermined size by performing cold rolling on the primary-drawn wire material by using a cold rolling mill. In a state where the cold rolling is performed and nothing is performed thereafter, the hardness dispersion in a cross section perpendicular to a longitudinal direction is large, and thus heat treatment is performed on the flat steel wire. At this time, a heating temperature may be set to a temperature of not less than 400°C nor more than A1 point. Alternatively, it is also possible to perform quenching and tempering treatment in which after the flat steel wire is reheated to an austenite region, it is subjected to oil quenching and then tempered at a temperature of 400°C or more.

[0034] Note that when the flat steel wire is finished by the cold rolling from a wire-drawn round bar, both end faces in a thickness direction are parallel and cross sections perpendicular to the longitudinal direction of both end faces in a width direction respectively have a semi-elliptic shape or an arc shape. It is also possible that the flat steel wire is finished to have the same shape by wire drawing using a profiled die. When a width/thickness ratio being a ratio between a maximum width and a thickness in the width direction of the flat steel wire is less than 1.5, an amount of working with respect to the flat steel wire is small, and it is sometimes impossible to obtain sufficient tensile strength. Further, when the hardenability of the steel is low, there arises a problem such that the quenching cannot be performed up to an inner part of the flat steel wire, and sufficient tensile strength cannot be obtained. Further, there also arises a problem such that when the flat steel wire is mounted on a flexible pipe, it is difficult to perform bending, and cracking occurs. On the other hand, when the width/thickness ratio of the flat steel wire exceeds 10, there arises a problem such that, after the cold rolling is performed to obtain the flat steel wire or after the flat steel wire is subjected to the heat treatment, warpage occurs in the flat steel wire, and thus the flat steel wire cannot be mounted on the flexible pipe.

(C) Regarding optional components:

[0035] The high-strength flat steel wire of the present invention may contain, according to need, at least one or two or more of elements selected from Ti: 0.10% or less, Nb: 0.050% or less, V: 0.50% or less, Cu: 1.0% or less, Ni: 1.50% or less, Mo: 1.0% or less, B: 0.01% or less, REM: 0.10% or less, and Zr: 0.10% or less. Hereinafter, operations and effects of Ti, Nb, V, Cu, Ni, Mo, B, REM, and Zr being the optional elements and reasons for limiting the contents thereof will be described. % regarding the optional components indicates mass%.

Ti: 0 to 0.10%

[0036] Ti bonds with N or C to form a carbide, a nitride, or a carbonitride, and a pinning effect thereof brings about an effect of making austenite grains finer during hot rolling, which produces an effect of improving the hydrogen induced cracking resistance of the flat steel wire, so that Ti may be contained. In order to achieve this effect, Ti is only required to be contained in an amount of 0.001% or more. From a viewpoint of improving the hydrogen induced cracking resistance, the content of Ti is desirably set to 0.005% or more, and it is more desirable that Ti is contained in an amount of 0.010% or more. On the other hand, if the content of Ti exceeds 0.10%, the effect of Ti is saturated, and not only that, a large number of coarse TiN are generated, which contrarily reduces the hydrogen induced cracking resistance of the flat steel wire. Accordingly, the content of Ti is preferably 0.050% or less, and more preferably 0.035% or less.

Nb: 0 to 0.050%

[0037] Nb bonds with N or C to form a carbide, a nitride, or a carbonitride, and a pinning effect thereof brings about an effect of making austenite grains finer during hot rolling, which produces an effect of improving the hydrogen induced cracking resistance of the flat steel wire, so that Nb may be contained. In order to achieve this effect, Nb is only required to be contained in an amount of 0.001% or more. From a viewpoint of improving the hydrogen induced cracking resistance, the content of Nb is desirably set to 0.005% or more, and it is more desirable that Nb is contained in an amount of 0.010% or more. On the other hand, if the content of Nb exceeds 0.050%, the effect of Nb is saturated, and not only that, an adverse effect is exerted on the manufacturability of the steel such that cracking occurs in the steel billet in the step of performing bloom rolling on the steel ingot or the cast slab. Therefore, the content of Nb is preferably 0.035% or less, and more preferably 0.030% or less.

V: 0 to 0.50%

[0038] V bonds with C and N to form a carbide, a nitride, or a carbonitride, which enables to increase the strength of the flat steel wire. In order to achieve this purpose, 0.01% or more of V may be contained, but, if the content of V exceeds 0.50%, the strength of the flat steel wire is increased by the carbide or the carbonitride to be precipitated, which contrarily reduces the hydrogen induced cracking resistance. From a viewpoint of suppressing the hydrogen induced cracking of the flat steel wire, when V is contained, the amount of V is preferably 0.20% or less, and more preferably 0.10% or less. Note that in order to stably achieve the aforementioned effect of V, V is preferably contained in an amount of 0.02% or more.

Cu: 0 to 1.0%

[0039] Cu is an element which increases the hardenability of the steel, and thus it may be contained. Note that in order to achieve the effect of increasing the hardenability, 0.01% or more of Cu is only required to be contained. However, if the content of Cu exceeds 1.0%, the strength of the wire material becomes too high, and there arises a problem such that cracking occurs in the wire material when the wire material is worked into the flat steel wire. Therefore, when Cu is contained, the content of Cu is 0.01 to 1.0%. From a viewpoint of improving the hardenability, when Cu is contained, the content of Cu is preferably 0.10% or more, and it is more preferable that 0.30% or more of Cu is contained. Note that by considering the workability of the wire material into the flat steel wire, when Cu is contained, the content of Cu is preferably set to 0.80% or less, and it is more preferably 0.50% or less.

Ni: 0 to 1.50%

[0040] Ni is an element which increases the hardenability of the steel, and thus it may be contained. Note that in order to achieve the effect of increasing the hardenability, 0.01% or more of Ni is only required to be contained. However, if the content of Ni exceeds 1.50%, the strength of the wire material becomes too high, and there arises a problem such that cracking occurs in the wire material when the wire material is worked into the flat steel wire. Therefore, when Ni is contained, the content of Ni is 0.01 to 1.50%. From a viewpoint of improving the hardenability, when Ni is contained, the content of Ni is preferably 0.10% or more, and it is more preferable that 0.30% or more of Ni is contained. Note that by considering the workability of the wire material into the flat steel wire, when Ni is contained, the content of Ni is preferably set to 1.0% or less, and it is more preferably 0.60% or less.

Mo: 0 to 1.0%

[0041] Mo is an element which increases the hardenability of the steel, and thus it may be contained. Note that in order to achieve the effect of increasing the hardenability, 0.01% or more of Mo is only required to be contained. However, if the content of Mo exceeds 1.0%, the strength of the wire material becomes too high, and there arises a problem such that cracking occurs in the wire material when the wire material is worked into the flat steel wire. Therefore, when Mo is contained, the content of Mo is 0.01 to 1.0%. From a viewpoint of improving the hardenability, when Mo is contained, the content of Mo is preferably 0.02% or more, and it is more preferable that 0.05% or more of Mo is contained. Note that by considering the workability of the wire material into the flat steel wire, when Mo is contained, the content of Mo is preferably set to 0.50% or less, and it is more preferably 0.30% or less.

B: 0 to 0.01%

[0042] B is effective for increasing the hardenability of the steel when a slight amount thereof is added, and in order to achieve the effect, 0.0002% or more of B may be contained. Even if B is contained in an amount exceeding 0.01%, the effect is saturated, and not only that, a coarse nitride is generated, resulting in that the hydrogen induced cracking is likely to occur. Therefore, when B is contained, the content of B is 0.0002 to 0.01%. When the hardenability is desired to be increased more, the content of B is only required to be set to 0.001% or more, and it is more preferably 0.002% or more. Note that by considering the hydrogen induced cracking, when B is contained, the content of B is preferably set to 0.005% or less, and more preferably 0.003% or less.

REM: 0 to 0.10%

[0043] REM is a general term of rare earth elements, and a content of REM is a total content of rare earth elements. REM has an effect of making MnS to be finely dispersed by being solid-dissolved in MnS, similarly to Ca and Mg. By making MnS to be finely dispersed, it is possible to improve the hydrogen induced cracking resistance, so that REM may be added. In order to achieve the effect of suppressing the hydrogen induced cracking, REM is only required to be contained in an amount of 0.0002% or more, and when a higher effect is desired to be achieved, 0.0005% or more of REM is only required to be contained. However, even if the content of REM exceeds 0.10%, the effect of REM is saturated, and an oxide of REM generated through reaction with oxygen in the steel becomes coarse, which causes reduction in the hydrogen induced cracking resistance. Therefore, when REM is contained, the content of REM is 0.10% or less. From a viewpoint of improving the hydrogen induced cracking resistance, the content of REM is preferably 0.05% or less, and more preferably 0.03% or less.

Zr: 0 to 0.10%

[0044] Zr reacts with O to generate an oxide, and if a slight amount thereof is added, it exhibits an effect of making the oxide to be finely dispersed to suppress the hydrogen induced cracking, so that it may be added when the effect is desired to be achieved. In order to achieve the effect of suppressing the hydrogen induced cracking, 0.0002% or more of Zr is only required to be contained, and when a higher effect is desired to be achieved, 0.001% or more of Zr is only required to be contained. However, when the content of Zr exceeds 0.10%, the effect of Zr is saturated, and Zr reacts with N or S in the steel to generate a coarse nitride or sulfide, which contrarily causes reduction in the hydrogen induced cracking resistance. Therefore, when Zr is contained, the content of Zr is 0.10% or less. From a viewpoint of reducing inclusions which exert an adverse effect on the hydrogen induced cracking resistance, the content of Zr is preferably 0.08% or less, and more preferably 0.05% or less.

[0045] The balance is composed of "Fe and impurities". The "impurities" are components which are unintentionally contained in the steel material, and indicate components mixed from an ore as a raw material, a scrap, a manufacturing environment or the like at a time of industrially manufacturing an iron and steel material.

[Examples]

[0046] Hereinafter, the present invention will be concretely described by examples.

[0047] Concretely, steels having chemical components represented in Table 1 and Table 2 were smelted to produce flat steel wires through the following method. Note that the notation of "-" in Table 1 and Table 2 indicates that a content of the element with the notation is at an impurity level, and it can be judged that the element is not substantially contained.

[0048] Each of steels A, B having chemical components represented in Table 1 was smelted in an electric furnace, the obtained steel ingot was heated at 1250°C for 12 hours and then subjected to bloom rolling into a steel billet of 122 mm square, which was set as a raw material for rolling. Next, the raw material for rolling was heated at 1050°C to be rolled to a wire material with a diameter of 12 mm. After performing the rolling, a surface of the wire material was subjected to lubricating treatment, and then primary wire drawing was performed to obtain a wire material with a diameter of 11 mm. Thereafter, the drawn wire material was rolled by a cold rolling mill to be formed into a flat steel wire.

[0049] In order to separately produce flat steel wires having different tensile strengths and hardness dispersions in cross sections perpendicular to the longitudinal direction while having the same components, regarding test numbers A1 to A5, flat steel wires each of which was cold-rolled to have a width of 15 mm and a thickness of 3 mm were heated at 900°C for 15 minutes, then subjected to quenching treatment by being immersed into a cold oil, and subjected to heat treatment at a temperature of 400 to 600°C for 1 minute or 60 minutes, to thereby produce flat steel wires with different tensile strengths. Regarding a test number A6, the heat treatment was not performed after the cold rolling.

[0050] On the other hand, regarding test numbers B1 to B4, the cold rolling was performed to obtain flat steel wires each having a width of 13.5 mm and a thickness of 5 mm, and then, without performing the quenching treatment, the heat treatment was performed at 600°C for 10 minutes regarding the test number B1, the heat treatment was performed at 450°C for 30 seconds regarding the test number B2, the heat treatment was performed at 600°C for 240 minutes regarding B3, and then cooling was performed to a room temperature. Regarding the test number B4, no heat treatment was performed. Further, regarding a test number B5, the cold rolling was performed to obtain a flat steel wire having a width of 10 mm and a thickness of 8 mm, and the heat treatment was not performed. In a manner as described above, the flat steel wires in which the tensile strengths, the hardness dispersions in cross sections perpendicular to the longitudinal direction, and the shapes were different, were produced. Note that regarding a test number B6, a flat steel wire having a width of 17 mm and a thickness of 1.5 mm was produced, heated at 900°C for 15 minutes, and then immersed into a cold oil to be subjected to the quenching treatment. At that time, large warpage occurred in the longitudinal direction of the flat steel wire, so that a test thereafter was canceled.

[0051] Each of steels in test Nos. 1 to 31 having chemical components represented in Table 2 was smelted in an electric furnace, the obtained steel ingot was heated at 1250°C for 12 hours and then subjected to bloom rolling into a steel billet of 122 mm square, which was set as a raw material for rolling. Next, the raw material for rolling was heated at 1050°C to be rolled to a wire material with a diameter of 12 mm. After performing the rolling, a surface of the wire material was subjected to lubricating treatment, and then primary wire drawing was performed to obtain a wire material with a diameter of 11 mm. Thereafter, the drawn wire material was rolled by a cold rolling mill to be formed into a flat steel wire having a width of 15 mm and a thickness of 3 mm or a width of 13.5 mm and a thickness of 5 mm. In the test Nos. 1 to 9, 12 to 24, 28, 30, and 31, the formed flat steel wires after being subjected to the cold rolling were heated at 900°C for 15 minutes, then immersed into a cold oil to be subjected to quenching treatment, and subjected to heat treatment at a temperature of 450 to 500°C for 60 minutes. Regarding the test Nos. 10 and 11, the quenching treatment was not performed, and heating at 600°C for 2 minutes or heating at 580°C for 5 minutes was performed, and then cooling was performed to a room temperature. In each of the test Nos. 25 to 27, and 29, any of the chemical components of the steel was out of the range of the present invention, and since cracking occurred in the flat steel wire when the cold rolling was performed to obtain the flat steel wire, the test was canceled without performing the step of heat treatment and thereafter. Note that an underline in Table 2 indicates that the chemical composition is out of the range of the present invention.

[Table 1]

STEEL TYPE	C	Si	Mn	P	S	Cr	Al	N	Ca	Mg	Ti	Nb	V	Cu	Ni	Mo	B	REM	Zr	[Ca]+[Mg]	0.2*[S]
A	0.32	1.70	0.73	0.009	0.002	0.02	0.035	0.0032	0.0024	-	-	-	-	-	-	-	-	-	-	0.0024	0.0004
B	0.39	1.80	0.75	0.009	0.001	0.02	0.040	0.0035	0.0016	0.0005	-	-	-	-	-	-	-	-	-	0.0021	0.0002

[Table 2]

	TEST No.	C	Si	Mn	P	S	Cr	Al	N	Ca	Mg	Ti	Nb	V	Cu	Ni	Mo	B	REM	Zr	[Ca]+ [Mg]	0.2*[S]
INVENTION EXAMPLE	1	0.30	1.65	0.90	0.009	0.005	0.05	0.040	0.0035	0.0018	0.0011	-	-	-	-	-	-	-	-	-	0.0029	0.0010
INVENTION EXAMPLE	2	0.32	1.25	0.30	0.009	0.004	0.95	0.045	0.0038	0.0020	-	-	-	-	-	-	-	-	-	-	0.0020	0.0008
INVENTION EXAMPLE	3	0.28	0.52	1.10	0.005	0.005	0.25	0.030	0.0035	0.0015	0.0005	-	-	-	-	-	-	-	-	-	0.0020	0.0010
INVENTION EXAMPLE	4	0.45	1.10	0.65	0.007	0.005	0.03	0.040	0.0038	0.0016	-	-	-	-	-	-	-	-	-	-	0.0016	0.0010
INVENTION EXAMPLE	5	0.34	1.21	0.78	0.003	0.001	0.31	0.031	0.0037	0.0019	-	-	-	-	-	-	-	-	-	-	0.0019	0.0002
INVENTION EXAMPLE	6	0.34	1.21	0.78	0.006	0.006	0.30	0.065	0.0039	0.0020	-	-	-	-	-	-	-	-	-	-	0.0020	0.0012
INVENTION EXAMPLE	7	0.35	1.24	0.81	0.005	0.005	0.31	0.018	0.0034	0.0018	-	-	-	-	-	-	-	-	-	-	0.0018	0.0010
INVENTION EXAMPLE	8	0.51	0.75	0.80	0.006	0.004	0.03	0.040	0.0042	0.0016	0.0005	-	-	-	-	-	-	-	-	-	0.0021	0.0008
INVENTION EXAMPLE	9	0.46	1.25	0.85	0.008	0.003	0.20	0.035	0.0040	0.0018	-	-	-	-	-	-	-	-	-	-	0.0018	0.0006
INVENTION EXAMPLE	10	0.35	1.80	0.78	0.005	0.006	0.01	0.035	0.0035	0.0019	-	-	-	-	-	-	-	-	-	-	0.0019	0.0012
INVENTION EXAMPLE	11	0.40	1.80	0.69	0.007	0.004	0.06	0.036	0.0036	0.0021	-	-	-	-	-	-	-	-	-	-	0.0021	0.0008
INVENTION EXAMPLE	12	0.34	1.45	0.65	0.010	0.006	0.18	0.046	0.0042	0.0028	-	0.035	-	-	-	-	-	-	-	-	0.0028	0.0012
INVENTION EXAMPLE	13	0.30	1.50	0.72	0.008	0.005	0.05	0.031	0.0036	0.0015	-	-	0.025	-	-	-	-	-	-	-	0.0015	0.0010
INVENTION EXAMPLE	14	0.30	1.49	0.60	0.008	0.004	0.45	0.039	0.0035	0.0011	0.0006	-	-	0.080	-	-	-	-	-	-	0.0017	0.0008

(continued)

	TEST No.	C	Si	Mn	P	S	Cr	Al	N	Ca	Mg	Ti	Nb	V	Cu	Ni	Mo	B	REM	Zr	[Ca]+ [Mg]	0.2*[S]
INVENTION EXAMPLE	15	0.32	1.51	0.55	0.005	0.006	0.30	0.031	0.0040	0.0025	0.0010	-	-	-	0.20	0.21	-	-	-	-	0.0035	0.0012
INVENTION EXAMPLE	16	0.35	1.05	0.60	0.006	0.005	0.09	0.042	0.0031	0.0026	-	-	-	-	-	-	0.050	-	-	-	0.0026	0.0010
INVENTION EXAMPLE	17	0.35	1.25	0.50	0.007	0.008	0.05	0.039	0.0039	0.0021	0.0009	-	-	-	-	-	-	0.0020	-	-	0.0030	0.0016
INVENTION EXAMPLE	18	0.40	1.70	0.65	0.008	0.005	0.20	0.041	0.0041	0.0016	-	-	-	-	-	-	-	-	0.0021	-	0.0016	0.0010
INVENTION EXAMPLE	19	0.31	1.10	0.80	0.008	0.006	0.15	0.035	0.0035	0.0019	0.0010	-	-	-	-	-	-	-	-	0.025	0.0029	0.0012
COMPARA-TIVE EXAM-PLE	20	0.45	0.20	0.35	0.004	0.007	0.80	0.045	0.0039	0.0012	0.0005	-	-	-	-	-	-	-	-	-	0.0017	0.0014
COMPARA-TIVE EXAM-PLE	21	0.45	1.25	0.55	0.008	0.010	0.25	0.036	0.0038	0.0010	0.0002	-	-	-	-	-	-	-	-	-	0.0012	0.0020
COMPARA-TIVE EXAM-PLE	22	0.35	1.50	0.60	0.009	0.011	0.35	0.028	0.0034	-	-	-	-	-	-	-	-	-	-	-	-	0.0022
COMPARA-TIVE EXAM-PLE	23	0.36	1.45	0.65	0.008	0.019	0.20	0.035	0.0036	0.0012	0.0005	-	-	-	-	-	-	-	-	-	0.0017	0.0038
COMPARA-TIVE EXAM-PLE	24	0.68	0.90	0.75	0.008	0.007	0.19	0.030	0.0041	0.0015	0.0003	-	-	-	-	-	-	-	-	-	0.0018	0.0014
COMPARA-TIVE EXAM-PLE	25	0.45	2.20	0.90	0.007	0.005	0.60	0.036	0.0035	0.0017	0.0005	-	-	-	-	-	-	-	-	-	0.0022	0.0010

(continued)

	TEST No.	C	Si	Mn	P	S	Cr	Al	N	Ca	Mg	Ti	Nb	V	Cu	Ni	Mo	B	REM	Zr	[Ca]+ [Mg]	0.2*[S]
COMPARATIVE EXAMPLE	26	0.48	1.50	1.80	0.006	0.004	0.65	0.050	0.0030	0.0016	0.0008	-	-	-	-	-	-	-	-	-	0.0024	0.0008
COMPARATIVE EXAMPLE	27	0.42	1.51	0.85	0.005	0.005	1.75	0.031	0.0037	0.0015	0.0007	-	-	-	-	-	-	-	-	-	0.0022	0.0010
COMPARATIVE EXAMPLE	28	0.33	1.72	0.70	0.028	0.009	0.75	0.028	0.0045	0.0012	0.0009	-	-	-	-	-	-	-	-	-	0.0021	0.0018
COMPARATIVE EXAMPLE	29	0.32	1.80	0.82	0.007	0.009	0.55	0.035	0.0155	0.0015	0.0004	-	-	-	-	-	-	-	-	-	0.0019	0.0018
COMPARATIVE EXAMPLE	30	0.30	1.69	0.65	0.010	0.008	0.47	0.132	0.0035	0.0013	0.0005	-	-	-	-	-	-	-	-	-	0.0018	0.0016
COMPARATIVE EXAMPLE	31	0.31	1.65	0.58	0.008	0.008	0.35	0.001	0.0033	0.0017	0.0002	-	-	-	-	-	-	-	-	-	0.0019	0.0016

[0052] The tensile strength, the average hardness and the standard deviation of hardness representing the hardness dispersion in the cross section perpendicular to the longitudinal direction, and the hydrogen induced cracking resistance of the flat steel wires produced through the above-described method were examined, and results thereof are presented in Table 3 and Table 4. Note that an underline in Table 3 and Table 4 indicates that the characteristic is out of the range of the present invention.

[0053] The tensile strength, the average hardness and the standard deviation representing the hardness dispersion in the cross section perpendicular to the longitudinal direction, and the hydrogen induced cracking resistance of the flat steel wires were respectively examined through methods to be described below.

(1) Examination of tensile strength of flat steel wire:

[0054] The tensile strength of the flat steel wire was measured by a break test described in JIS G 3546. The break test was carried out at a room temperature by setting a gage length to 30 mm, thereby determining the tensile strength. Note that a cross-sectional area (S (mm^2)) of the flat steel wire was calculated by using the following expression <2>, and the tensile strength was determined by dividing a maximum test force until when the test piece breaks by the cross-sectional area.

$$S = w \times t - 0.215t^2 \quad \cdots <2>$$

[0055] Here, w indicates a width (mm) of the flat steel wire, and t indicates a thickness (mm) of the flat steel wire.

(2) Examination of hardness in cross section perpendicular to longitudinal direction:

[0056] The flat steel wire was cut into a length of 10 mm, resin embedding and mirror polishing were performed so that a transverse section (a cross section perpendicular to the longitudinal direction) thereof becomes a specimen plane, and the Hv hardness was measured by using a Vickers hardness tester. A test load was 100 gf, and measurement at ten points at equal intervals in a thickness direction from a position separated by 50 μm or more from a surface was repeated nine times or more while being displaced by 1 mm in a width direction to measure a hardness distribution in the cross section, thereby determining the average hardness and the standard deviation (σHv) as an index of the hardness dispersion. The standard deviation σHv to be the index of the hardness dispersion may be determined through the following expression <3>.

[Mathematical expression 1]

$$\sigma_{Hv} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(Hv_i - Hv_{AV}\right)^2} \quad \cdots <3>$$

[0057] Here, n indicates the number of hardness measurement points in the cross section, Hv_{AV} indicates the average hardness, and Hv_i indicates the hardness at a position of a measurement point i.

(3) Examination of hydrogen induced cracking resistance:

[0058] The flat steel wire cut into a length of 150 mm was used to evaluate the hydrogen induced cracking resistance. With respect to a 5% NaCl + CH_3COOH solution, HCl was applied to adjust a pH to be 5.0. The deaeration was performed using a nitrogen gas, and then a mixed gas of hydrogen sulfide (H_2S) and carbon dioxide (CO_2) was introduced, and the flat steel wire was immersed into the solution to examine occurrence of cracking. At this time, a partial pressure of the hydrogen sulfide is 0.01 MPa, a test temperature is 25°C, and a test time is 96 hours. After the test, the presence/absence of the occurrence of cracking was checked in the thickness direction of the flat steel wire by an ultra-sonic test (UST). The total area of the cracking-occurred portion in which the ultra-sonic test judged that the cracking occurred was determined through image analysis, and a hydrogen induced cracking occurrence rate (χ (%)) was determined by using the following expression <4>.

[Mathematical expression 2]

$$\chi = \left(A_f / (w \times L) \right) \times 100 \quad \cdots < 4 >$$

[0059] Here, A_f indicates the total area (mm^2) of the cracking-occurred portion measured by the UST, w indicates the width (mm) of the flat steel wire, and L indicates the length (mm) of the flat steel wire.

[Table 3]

TEST No.	STEEL	SHAPE OF FLAT STEEL WIRE (THICKNESS × WIDTH)	QUENCHING TEMPERATURE (°C)	TEMPERING (°C)	HEATING TIME (min)	TENSILE STRENGTH (MPa)	AVERAGE HARDNESS	STANDARD DEVIATION OF HARDNESS σ Hv	HYDROGEN INDUCED CRACKING OCCURRENCE RATE χ (%)	
A1	A	3×15	900	400	60	1489	463	13.5	25.0	COMPARATIVE EXAMPLE
A2	A	3×15	900	420	60	1398	408	10.8	0.0	INVENTION EXAMPLE
A3	A	3×15	900	450	60	1256	385	11.1	0.0	INVENTION EXAMPLE
A4	A	3×15	900	500	60	1206	368	10.1	0.0	INVENTION EXAMPLE
A5	A	3×15	900	600	1	1102	349	9.6	0.0	INVENTION EXAMPLE
A6	A	3×15	-	-	-	1401	413	19.1	85.0	COMPARATIVE EXAMPLE
B1	B	5×13.5	-	600	10	1105	356	9.8	0.0	INVENTION EXAMPLE
B2	B	5×13.5	-	450	0.5	1231	381	16.9	65.0	COMPARATIVE EXAMPLE
B3	B	5×13.5	-	600	240	935	300	9.5	0.0	COMPARATIVE EXAMPLE
B4	B	5×13.5	-	-	-	1318	392	18.5	90.0	COMPARATIVE EXAMPLE
B5	B	8×10	-	-	-	985	324	16.0	35.0	COMPARATIVE EXAMPLE
B6	B	1.5×17	900	-	-	-	-	-	-	COMPARATIVE EXAMPLE

[0060] Based on Table 3, each of the test numbers A2 to A5, and B1 being the examples of the present invention satisfied the chemical components and the requirements of the present invention, and the manufacturing conditions of the steel materials were appropriate, so that although the tensile strength thereof was 1000 MPa or more, the hydrogen induced cracking did not occur and thus there is no problem.

[0061] On the contrary, in each of the test numbers A1, A6, B2, and B4, the average hardness or the standard deviation (σHv) representing the hardness dispersion in the cross section was out of the range of the present invention, and the hydrogen induced cracking occurred.

[0062] In the test number A1, the average Hv hardness in the cross section exceeded 450, and thus the hardness was too high, resulting in that the hydrogen induced cracking occurrence rate was 10% or more.

[0063] In each of the test numbers A6 and B4, the working was performed to obtain the flat steel wire and then the heat treatment was not conducted, in which the standard deviation of hardness (σHv) in the cross section was 15 or more and thus the dispersion of hardness in the cross section was large, resulting in that the hydrogen induced cracking occurrence rate was 10% or more.

[0064] In the test number B2, the working was performed to obtain the flat steel wire and then the heat treatment was conducted, in which the standard deviation of hardness (σHv) in the cross section was 15 or more and thus the dispersion of hardness in the cross section was large, resulting in that the hydrogen induced cracking occurrence rate was 10% or more.

[0065] In the test number B3, the working was performed to obtain the flat steel wire and then the heat treatment was conducted, in which the average hardness was less than Hv320, and the tensile strength was less than 1000 MPa.

[0066] In the test number B5, the shape of the flat steel wire was out of the range of the present invention, and since the amount of working with respect to the flat steel wire was small, the tensile strength was less than 1000 MPa. Besides, since no heat treatment was conducted, the standard deviation of hardness (σHv) in the cross section was 15 or more, and the hydrogen induced cracking occurrence rate was 10% or more.

[0067] In the test number B6, the shape of the flat steel wire was out of the range of the present invention, so that large warpage occurred in the longitudinal direction of the flat steel wire during the quenching treatment, and thus the test such as the tensile test was not carried out.

[Table 4]

	TEST No.	SHAPE OF FLAT STEEL WIRE (THICKNESS × WIDTH)	QUENCHING TEMPERATURE (°C)	TEMPERING (°C)	HEATING TIME (min)	TENSILE STRENGTH (MPa)	AVERAGE HARDNESS	STANDARD DEVIATION OF HARDNESS σHv	HYDROGEN INDUCED CRACKING OCCURRENCE RATE χ (%)	REMARKS
INVENTION EXAMPLE	1	3×15	900	450	60	1285	385	10.9	0.0	
INVENTION EXAMPLE	2	5×13.5	900	450	60	1355	410	10.6	0.0	
INVENTION EXAMPLE	3	5×13.5	900	450	60	1205	365	8.6	0.0	
INVENTION EXAMPLE	4	3×15	900	450	60	1320	399	8.2	0.0	
INVENTION EXAMPLE	5	5×13.5	900	450	60	1323	403	10.2	0.0	
INVENTION EXAMPLE	6	5×13.5	900	450	60	1320	402	10.0	0.0	
INVENTION EXAMPLE	7	5×13.5	900	450	60	1326	405	9.8	0.0	
INVENTION EXAMPLE	8	5×13.5	900	450	60	1380	418	8.5	5.0	
INVENTION EXAMPLE	9	3×15	900	450	60	1420	430	9.8	5.0	
INVENTION EXAMPLE	10	5×13.5	-	600	2	1120	358	10.1	5.0	
INVENTION EXAMPLE	11	5×13.5	-	580	5	1185	368	9.6	5.0	
INVENTION EXAMPLE	12	3×15	900	450	60	1279	380	9.8	0.0	
INVENTION EXAMPLE	13	3×15	900	450	60	1199	360	9.1	0.0	

(continued)

	TEST No.	SHAPE OF FLAT STEEL WIRE (THICKNESS × WIDTH)	QUENCHING TEMPERATURE (°C)	TEMPERING (°C)	HEATING TIME (min)	TENSILE STRENGTH (MPa)	AVERAGE HARDNESS	STANDARD DEVIATION OF HARDNESS σHv	HYDROGEN INDUCED CRACKING OCCURRENCE RATE χ (%)	REMARKS
INVENTION EXAMPLE	14	3×15	900	500	60	1305	392	13.1	0.0	
INVENTION EXAMPLE	15	3×15	900	450	60	1275	376	10.5	0.0	
INVENTION EXAMPLE	16	3×15	900	480	60	1259	372	9.9	0.0	
INVENTION EXAMPLE	17	3×15	900	450	60	1182	364	7.5	0.0	
INVENTION EXAMPLE	18	3×15	900	450	60	1356	409	10.1	0.0	
INVENTION EXAMPLE	19	3×15	900	500	60	1125	340	9.8	0.0	
COMPARATIVE EXAMPLE	20	3×15	900	450	60	1355	412	11.8	50.0	
COMPARATIVE EXAMPLE	21	3×15	900	450	60	1368	420	9.6	85.0	
COMPARATIVE EXAMPLE	22	3×15	900	450	60	1298	390	8.5	95.0	
COMPARATIVE EXAMPLE	23	3×15	900	450	60	1285	385	9.6	90.0	
COMPARATIVE EXAMPLE	24	3×15	900	480	60	1385	421	<u>18.9</u>	80.0	
COMPARATIVE EXAMPLE	25	3×15	-	-	-	-	-	-	-	CRACKING OCCURRED
COMPARATIVE EXAMPLE	26	3×15	-	-	-	-	-	-	-	CRACKING OCCURRED

(continued)

	TEST No.	SHAPE OF FLAT STEEL WIRE (THICKNESS × WIDTH)	QUENCHING TEMPERATURE (°C)	TEMPERING (°C)	HEATING TIME (min)	TENSILE STRENGTH (MPa)	AVERAGE HARDNESS	STANDARD DEVIATION OF HARDNESS σHv	HYDROGEN INDUCED CRACKING OCCURRENCE RATE χ (%)	REMARKS
COMPARATIVE EXAMPLE	27	3×15	-	-	-	-	-	-	-	CRACKING OCCURRED
COMPARATIVE EXAMPLE	28	3×15	900	450	60	1325	403	9.0	75.0	
COMPARATIVE EXAMPLE	29	3×15	-	-	-	-	-	-	-	CRACKING OCCURRED
COMPARATIVE EXAMPLE	30	3×15	900	450	60	1288	386	11.9	45.0	
COMPARATIVE EXAMPLE	31	3×15	900	450	60	1275	378	10.9	80.0	

[0068] Based on Table 4, each of the test numbers 1 to 19 being the examples of the present invention satisfied the chemical components and the requirements of the present invention, and the manufacturing conditions of the steel materials were appropriate, so that although the tensile strength thereof was 1000 MPa or more, the hydrogen induced cracking did not occur or the hydrogen induced cracking occurrence rate was less than 10%, and thus there is no problem.
[0069] Regarding each of the test numbers 20 to 24, 28, 30, and 31, any of the chemical components or the expression <1> was not satisfied, so that the hydrogen induced cracking occurred at the hydrogen induced cracking occurrence rate of 10% or more.
[0070] In each of the test numbers 25 to 27, and 29, any of the chemical components of the steel was out of the range of the present invention, and the cracking occurred in the flat steel wire when the cold rolling was performed to obtain the flat steel wire, so that the test was canceled without performing the step of heat treatment and thereafter.
[0071] In the test number 20, the content of Si was out of the range of the present invention, so that the hydrogen induced cracking occurred at the hydrogen induced cracking occurrence rate of 10% or more.
[0072] In the test number 21, although the chemical components were within the range of the present invention, the expression <1> was not satisfied, so that the hydrogen induced cracking occurred at the hydrogen induced cracking occurrence rate of 10% or more.
[0073] In the test number 22, both of Ca and Mg were not added, and the expression <1> was also not satisfied, so that the hydrogen induced cracking occurred at the hydrogen induced cracking occurrence rate of 10% or more.
[0074] In the test number 23, the content of S was out of the range of the present invention, so that the hydrogen induced cracking occurred at the hydrogen induced cracking occurrence rate of 10% or more.
[0075] In the test number 24, the content of C was out of the range of the present invention, and the standard deviation representing the hardness dispersion in the cross section exceeded 15, so that the hydrogen induced cracking occurred at the hydrogen induced cracking occurrence rate of 10% or more.
[0076] In the test number 25, the content of Si was out of the range of the present invention, and the cracking occurred in the flat steel wire when the cold rolling was performed to obtain the flat steel wire.
[0077] In the test number 26, the content of Mn was out of the range of the present invention, and the cracking occurred in the flat steel wire material when the cold rolling was performed to obtain the flat steel wire.
[0078] In the test number 27, the content of Cr was out of the range of the present invention, and the cracking occurred in the flat steel wire material when the cold rolling was performed to obtain the flat steel wire.
[0079] In the test number 28, the content of P was out of the range of the present invention, so that the hydrogen induced cracking occurred at the hydrogen induced cracking occurrence rate of 10% or more.
[0080] In the test number 29, the content of N was out of the range of the present invention, and the cracking occurred in the flat steel wire material when the cold rolling was performed to obtain the flat steel wire.
[0081] In each of the test numbers 30 and 31, the content of Al was out of the range of the present invention, so that the hydrogen induced cracking occurred at the hydrogen induced cracking occurrence rate of 10% or more.
[0082] The entire disclosure of Japanese Patent Application No. 2016-043961 filed on March 7, 2016 is incorporated into the present specification by reference.
[0083] All documents, patent applications, and technical standards described in the present specification are incorporated into the present specification by reference at a degree at which individual documents, patent applications and technical standards are concretely and individually described.

Claims

1. A high-strength flat steel wire excellent in hydrogen induced cracking resistance, containing, by mass%:

C: 0.25 to 0.60%;
Si: greater than 0.50% and less than 2.0%;
Mn: 0.20 to 1.50%;
S: 0.015% or less;
P: 0.015% or less;
Cr: 0.005 to 1.50%;
Al: 0.005 to 0.080%;
N: 0.0020 to 0.0080%; and
one or two of Ca: 0 to 0.0050% and Mg: 0 to 0.0050% to satisfy the following expression <1>, wherein:

components which are optionally contained include:

Ti: 0.10% or less;

Nb: 0.050% or less;
V: 0.50% or less;
Cu: 1.0% or less;
Ni: 1.50% or less;
Mo: 1.0% or less;
B: 0.01% or less;
REM: 0.10% or less; and
Zr: 0.10% or less;
the balance is composed of Fe and impurities; and
tensile strength is 1000 MPa or more, an average value of Hv hardness measured in a cross section perpendicular to a longitudinal direction is 320 or more and less than 450, a standard deviation σHv of the measured value is 15 or less, and a width/thickness ratio is not less than 1.5 nor more than 10,

$$[Ca] + [Mg] > 0.20 \times [S] \qquad \cdots <1>$$

where [Ca], [Mg], and [S] in the above expression <1> represent contents of respective elements by mass%.

2. The high-strength flat steel wire excellent in the hydrogen induced cracking resistance according to claim 1, further containing, by mass%, at least one or two or more selected from Ti: 0.001 to 0.10%, Nb: 0.001 to 0.050%, and V: 0.01 to 0.50%.

3. The high-strength flat steel wire excellent in the hydrogen induced cracking resistance according to claim 1 or 2, further containing, by mass%, at least one or two or more selected from Cu: 0.01 to 1.0%, Ni: 0.01 to 1.50%, Mo: 0.01 to 1.0%, and B: 0.0002 to 0.01%.

4. The high-strength flat steel wire excellent in the hydrogen induced cracking resistance according to any one of claims 1 to 3, further containing, by mass%, at least one or two selected from REM: 0.0002 to 0.10%, and Zr: 0.0002 to 0.10%.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/009081

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/34*(2006.01)i, *C22C38/54*(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00-38/60

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	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 6-235024 A (Nippon Steel Corp.), 23 August 1994 (23.08.1994), claim 1; examples (Family: none)	1-4
A	JP 11-501986 A (Institut Francais du Petrole), 16 February 1999 (16.02.1999), claim 1 & US 5922149 A claim 1 & WO 1996/28575 A1 & FR 2731371 A1	1-4

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 May 2017 (26.05.17)	06 June 2017 (06.06.17)

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INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2017/009081

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 2000-517381 A (Institut Francais du Petrole), 26 December 2000 (26.12.2000), claim 1 & US 6291079 B1 claim 1 & WO 1998/10113 A1 & FR 2753206 A1	1-4
A	WO 2014/171472 A1 (Nippon Steel & Sumitomo Metal Corp.), 23 October 2014 (23.10.2014), paragraphs [0043] to [0044] & US 2016/0060744 A1 paragraphs [0112] to [0115] & CN 105121687 A	1-4

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2013227611 A **[0003]**
- JP 2015212412 A **[0003]**
- JP 2013534966 W **[0003]**
- JP 2016043961 A **[0082]**