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(54) HOT-ROLLED WIRE

(57) The present invention provides a hot rolled wire rod having high strength and excellent SSC resistance. Disclosed is a hot rolled wire rod including, in percent 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: exceeding 0% and 0.01% or less, and S: exceeding 0% and 0.01% or less, with the balance being iron and inevitable impurities. When the sulfur content in the hot rolled wire rod is measured at 300 sites or more at intervals of 200 μm using an electron beam microanalyzer, a segregation ratio (S_{max}/S_{ave}) is 30 or less, where a segregation ratio is defined as a ratio of the maximum sulfur content S_{max} (% by mass) to an average sulfur content S_{ave} (% by mass).

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Description

Technical Field

[0001] The present invention relates to hot rolled wire rods used for manufacturing steel wires. More specifically, the present invention relates to a hot rolled wire rod used to manufacture steel wires for use in parts or a reinforcing member for a flexible riser and the like to be applied under a sour environment containing hydrogen sulfide.

Background Art

[0002] The demand for oil has been recently increasing, which leads to further development of offshore oilfields. In such oilfield development, for example, a flexible riser is used to draw crude oil. The flexible riser is manufactured by using a resin pipe and a steel wire. The steel wire is used as a reinforcing material for the resin pipe. Oilfields are located in sour environments containing hydrogen sulfide, and thus the above-mentioned steel wire is required to have a high strength and to suppress sulfide stress corrosion cracking (sulfide stress cracking: SSC) (hereinafter sometimes referred to as an "SSC resistance"). For this reason, the hot rolled wire rod used as material for such a steel wire is also required to have high strength and excellent SSC resistance.

[0003] A technique proposed in Patent Document 1 is known to provide a high-strength steel material with excellent SSC resistance. The steel material disclosed in this patent document has a composition including, in percent 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%, wherein P, Ti and N are adjusted to satisfy a relationship of P / effective Ti content < 1.6, with the balance being Fe and inevitable impurities, and has a microstructure including a tempered martensite phase in which an average grain size of a prior austenite grain is 12 μm or less and a Mo segregation ratio is 1.5 or less.

[0004] The above-mentioned patent document describes a manufacturing method for the high-strength steel material. In the method, a steel material satisfying the aforesaid composition is subjected to a high-temperature heating process which involves holding the steel material at a heating temperature of more than 1,200°C to less than 1,270°C for 30 minutes or less. The heated steel material is then hot-rolled into a hot rolled steel material, which is thereafter subjected to a quenching process twice or more, followed by a tempering process. Before performing the tempering process, the quenching process is performed by holding the hot rolled steel material at a heating temperature ranging from 850 to 920°C for 5 to 10 minutes, followed by quenching to room temperature at an average cooling rate of 30°C/s or higher. Then, the tempering process is performed by holding the steel material at a temperature ranging from 600 to 680°C for 15 to 30 minutes.

Prior Art Document

Patent Document

[0005] Patent Document 1: JP 2013-227611 A

Disclosure of Invention

Problems to be Solved by the Invention

[0006] The steel material disclosed in the above-mentioned Patent Document 1 is designed to uniformize the distribution of alloy elements such as C, Cr, Mo and Nb to thereby reduce macro-segregation, and further to completely suppress coarse inclusions. Thus, the steel material attains the high strength with a yield strength (hereinafter sometimes referred to as a YS, which is an abbreviation of yield strength) of over-120 ksi (827 MPa), while maintaining the SSC resistance. However, in recent years, the requirements for the performance of steel materials have become stricter, and especially, higher strength and improved SSC resistance are required.

[0007] The present invention has been made in view of the foregoing circumstances, and it is an object of the present invention to provide a hot rolled wire rod having high strength and excellent SSC resistance.

Means for Solving the Problems

[0008] The inventors have diligently studied to further improve the SSC resistance of a hot rolled wire rod while enhancing its strength. As a result, it is found that in addition to the appropriate control of the composition of the hot rolled wire rod, the suppression of segregation of sulfur (S) that would be generated in the wire rod can improve the

SSC resistance while ensuring the strength of the wire rod. That is, sulfur (S) tends to be segregated at crystal grain boundaries. Such segregation of sulfur (S) reduces the strength of the grain boundary. When the embrittlement of the crystals due to hydrogen proceeds, the grain boundary rupture is more likely to occur. Consequently, the SSC resistance is supposed to be degraded.

[0009] Based on the result of further studies by the inventors, it has been found that a segregation ratio (S_{max}/S_{ave}) calculated from an average of the sulfur (S) content Save (% by mass) and the maximum sulfur (S) content S_{max} (% by mass) is set to 30 or less, thereby making it possible to produce a hot rolled wire rod having the high strength and excellent SSC resistance. Through this finding, the present invention has been completed.

[0010] That is, a hot rolled wire rod according to the present invention that can solve the above-mentioned problems includes, in percent 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: exceeding 0% and 0.01% or less, and S: exceeding 0% and 0.01% or less, with the balance being iron and inevitable impurities. The sulfur (S) content in the hot rolled wire rod is measured at 300 sites or more at intervals of 200 μm using an electron beam microanalyzer. When a segregation ratio (S_{max}/S_{ave}) is defined as a ratio of the maximum sulfur (S) content S_{max} (% by mass) to an average sulfur (S) content S_{ave} (% by mass), the requirement that the segregation ratio is 30 or less is satisfied.

[0011] The above-mentioned hot rolled wire rod may further include, as other elements, in percent by mass,

(a) at least one element of Cr: exceeding 0% and 1% or less and B: exceeding 0% and 0.01% or less,
(b) at least one element of Ni: exceeding 0% and 0.5% or less and Cu: exceeding 0% and 0.5% or less,
(c) at least one element of Ti: exceeding 0% and 0.1% or less and V: exceeding 0% and 0.5% or less,
(d) Mo: exceeding 0% and 1.5% or less, and
(e) Nb: exceeding 0% and 0.1% or less.

Effects of the Invention

[0012] Accordingly, the present invention appropriately controls the composition of the hot rolled wire rod and additionally suppresses the segregation of sulfur (S) generated in the wire rod, thereby making it possible to produce the hot rolled wire rod having the high strength and excellent SSC resistance.

Mode for Carrying Out the Invention

[0013] In the hot rolled wire rod according to the present invention, the segregation ratio of sulfur (S) is 30 or less, preferably 28 or less, and more preferably 27 or less. The smaller segregation ratio, the better the hot rolled wire rod becomes.

[0014] The term "segregation ratio" as used herein means a ratio of the maximum sulfur (S) content S_{max} to an average sulfur (S) content S_{ave} when the sulfur (S) content in the hot rolled wire rod is measured at 300 sites or more at intervals of 200 μm using an electron beam microanalyzer, an average S content (% by mass) is described as S_{ave}, and the maximum S content (% by mass) is described as S_{max}. Thus, when no segregation of S is observed, the average S content S_{ave} (% by mass) is equal to the maximum S content S_{max} (% by mass), and thereby the segregation ratio (S_{max}/S_{ave}) is 1.

[0015] The sulfur (S) content in the hot rolled wire rod should be measured by element mapping from an area including a center toward a surface layer of the hot rolled wire rod so that the mapping area is not biased toward the center or the surface layer.

[0016] The hot rolled wire rod of the present invention needs to appropriately control the composition, while satisfying the segregation ratio of 30 or less. That is, the hot rolled wire rod of the present invention includes, in percent 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: exceeding 0% and 0.01% or less; and S: exceeding 0% and 0.01% or less.

[0017] Carbon (C) is an element required to ensure the strength of the wire rod. The C content is 0.20% or more. The C content is preferably 0.22% or more, and more preferably 0.23% or more. However, when the C content exceeds 0.5%, the segregation of S is promoted, degrading the SSC resistance. Therefore, the C content is set at 0.5% or less, preferably 0.48% or less, and more preferably 0.47% or less.

[0018] Silicon (Si) is an element required for deoxidation and solid-solution strengthening. The Si content is set at 0.05% or more. The Si content is preferably 0.06% or more, and more preferably 0.07% or more. However, as the Si content increases, sulfur (S) is more likely to be segregated, causing the hydrogen embrittlement, thereby reducing the SSC resistance. Therefore, the Si content is set at 0.3% or less, preferably 0.27% or less, and more preferably 0.25% or less.

[0019] Manganese (Mn) is an element that improves the hardenability and enhances the strength of the wire rod. The Mn content needs to be 0.3% or more. The Mn content is preferably 0.4% or more, and more preferably 0.45% or more.

However, any excessive Mn content facilitates the segregation of impurity elements, especially sulfur (S). Further, when Mn content is excessive, the strength of the wire rod becomes extremely high, increasing the hardness thereof, thus degrading the SSC resistance. Therefore, the Mn content is set at 1.5% or less, preferably 1.40% or less, and more preferably 1.30% or less.

[0020] Aluminum (Al), like Si, is an element to be added for deoxidation. The Al content is set at 0.001% or more. The Al content is preferably 0.003% or more, and more preferably 0.005% or more. However, when the Al content exceeds 0.1%, the toughness of the wire rod is degraded. Therefore, the Al content is set at 0.1% or less. The Al content is preferably 0.09% or less, and more preferably 0.08% or less.

[0021] Phosphorus (P) is an element that tends to be segregated at the crystal grain boundaries, decreasing the strength of the grain boundary, thereby easily causing grain boundary rupture due to hydrogen. Therefore, the P content is set at 0.01% or less. The P content is preferably 0.009% or less, and more preferably 0.008% or less. The P content is preferably reduced as much as possible. Decreasing the P content to less than 0.0001% increases a cost. Thus, the P content is preferably set at 0.0001% or more.

[0022] Sulfur (S) is an element that tends to be segregated at the crystal grain boundaries and the center of the wire rod, decreasing the strength of the grain boundary, thereby easily causing grain boundary rupture due to hydrogen. Especially, in a sour environment containing hydrogen sulfide, hydrogen tends to enter the wire rod, thus degrading the SSC resistance. Therefore, the S content is set at 0.01% or less. The S content is preferably 0.009% or less, and more preferably 0.008% or less. The S content is preferably reduced as much as possible. Decreasing the S content to less than 0.0001% increases a cost. Thus, the S content is preferably set at 0.0001% or more.

[0023] The composition of the hot rolled wire rod in the present invention has been mentioned above, with the balance being iron and inevitable impurities. The wire rod may include, as other elements, in percent by mass,

(a) at least one element of Cr: exceeding 0% and 1% or less and B: exceeding 0% and 0.01% or less,
(b) at least one element of Ni: exceeding 0% and 0.5% or less and Cu: exceeding 0% and 0.5% or less,
(c) at least one element of Ti: exceeding 0% and 0.1% or less and V: exceeding 0% and 0.5% or less,
(d) Mo: exceeding 0% and 1.5% or less, and
(e) Nb: exceeding 0% and 0.1% or less.

(a) Chromium (Cr) and boron (B) are elements that effectively serve to enhance the hardenability and strength of the wire rod. To effectively exhibit such effects, the Cr content is preferably 0.05% or more, more preferably 0.1% or more, and further preferably 0.3% or more. However, any excessive Cr content possibly forms pits on the surface of the wire rod, facilitating the occurrence of rupture due to the hydrogen embrittlement, thus degrading the SSC resistance of the wire rod. Therefore, the Cr content is preferably 1% or less, more preferably 0.95% or less, and further preferably 0.9% or less.

The boron (B) content is preferably 0.0005% or more, more preferably 0.0007% or more, and further preferably 0.001% or more. However, any excessive B content tends to cause cracking during the hot rolling. Thus, the B content is preferably 0.01% or less, more preferably 0.008% or less, and further preferably 0.007% or less. Note that either Cr or B may be used singularly, or alternatively Cr and B may be used in combination.

(b) Nickel (Ni) and copper (Cu) are elements that form a coating on the surface of the wire rod to prevent the entry of hydrogen, thereby improving the SSC resistance. To exhibit such an effect, the Ni content is preferably 0.05% or more, more preferably 0.1% or more, and further preferably 0.12% or more. However, when the Ni content exceeds 0.5%, pits are formed on the surface of the wire rod, easily causing the rupture due to the hydrogen embrittlement, thus degrading the SSC resistance. Therefore, the Ni content is preferably 0.5% or less, more preferably 0.47% or less, and further preferably 0.45% or less.

The Cu content is preferably 0.05% or more, more preferably 0.1% or more, and further preferably 0.12% or more. However, even if the Cu content exceeds 0.5%, the effect exhibited by the addition of Cu becomes saturated. Thus, the Cu content is preferably 0.5% or less. The Cu content is more preferably 0.47% or less, and further preferably 0.45% or less. Note that either Ni or Cu may be used singularly, or alternatively Ni and Cu may be used in combination.

(c) Titanium (Ti) and vanadium (V) are elements that effectively serve to form trap sites for hydrogen, thereby improving the SSC resistance. That is, Ti is the element that binds to C or N in a steel to form TiC or TiN serving as the trap site for hydrogen, or a composite compound thereof, thus improving the SSC resistance. Ti is also the element that refines crystal grains to improve the toughness of the wire rod. To effectively exhibit such effects, the Ti content is preferably 0.005% or more, more preferably 0.01% or more, and further preferably 0.015% or more. However, any excessive Ti forms coarse grains of TiN, which serves as a starting point of hydrogen embrittlement. Therefore, the Ti content is preferably 0.1% or less, more preferably 0.095% or less, and further preferably 0.09% or less.

Vanadium (V) is an element that binds to C in a steel to form fine grains of VC serving as trap sites for hydrogen, thereby improving the SSC resistance. When the V content is too small, it takes more time to precipitate VC, leading to degradation in productivity. Thus, the V content is preferably 0.05% or more. The V content is more preferably 0.1% or more, and further preferably 0.15% or more. However, any excessive V increases the amount of precipitated carbides, whereby excessive dislocations are more likely to remain. The dislocation has the hydrogen trapping effect. Any excessive amount of dislocations traps too much hydrogen, and thus serves as the starting point of rupture. Thus, the V content is preferably 0.5% or less, more preferably 0.45% or less, and further preferably 0.4% or less. Note that either Ti or V may be used singularly, or alternatively Ti and V may be used in combination.

(d) Molybdenum (Mo) is an element that suppresses the segregation of sulfur (S) and effectively serves to improve the SSC resistance of the wire rod. To effectively exhibit such effects, the Mo content is preferably 0.05% or more, more preferably 0.1% or more, further preferably 0.21% or more, and particularly preferably 0.22% or more. However, any excessive Mo content increases the adsorbed hydrogen content and corrosion content, thus degrading the SSC resistance. Further, any excessive Mo content also leads to a drastic increase in cost of a steel material. The Mo content is preferably 1.5% or less, more preferably 1.45% or less, further preferably 1.4% or less, and particularly preferably 1.3% or less. Moreover, the Mo content may be 1% or less, and further 0.98% or less. The Mo may be particularly 0.95% or less, or further 0.7% or less.

(e) Niobium (Nb) is an element that refines crystal grains to improve the toughness. Further, Nb is the element that improves the corrosion resistance. To effectively exhibit such effects, the Nb content is preferably 0.01% or more, more preferably 0.03% or more, and further preferably 0.05% or more. However, any excessive Nb content sometimes reduces the toughness of the wire rod. The Nb is preferably 0.1% or less, more preferably 0.095% or less, and further preferably 0.085% or less.

[0024] A method for manufacturing the hot rolled wire rod according to the present invention will be described below.

[0025] The method for manufacturing the hot rolled wire rod in the present invention is not particularly limited and can be carried out by ordinary methods, which involve smelting and bloom rolling a steel satisfying the above-mentioned composition to produce a steel slab, and then heating and hot-rolling the steel slab.

[0026] The heating temperature of the steel slab is preferably in a range of, e.g. 700 to 1,000°C. In this temperature range, the hot-rolling should be performed.

[0027] The hot-rolling process may be performed using mills which include roughing mills, intermediate mills and finishing mills, supported by multiple stands. In the present invention, the total rolling distortion through initial three passes of the roughing mills is recommended to be 0.3 or more. The initial three passes mean initial three mills in the roughing mills.

[0028] By setting the total rolling distortion through the initial three passes to 0. 3 or more, dynamic recrystallization can occur. Consequently, sulfur (S) can be uniformly dispersed to reduce the segregation of sulfur (S), thereby improving the SSC resistance. When the total rolling distortion though the initial three passes is less than 0.3, the number of passes required is increased, leading to an increase in cost. The total rolling distortion is preferably 0.4 or more, and more preferably 0.5 or more. The upper limit of the rolling distortion is not particularly limited, but is normally 2.0 or less due to the limitation of facilities.

[0029] The rolling distortion can be calculated by the following formula (1):

$$\text{Rolling Distortion} = \ln(S_0/S) \qquad (1)$$

where S_0 is a cross-sectional area (mm^2) of a steel slab before hot rolling, and S is a cross-sectional area (mm^2) of the steel slab at the end of initial three passes during the hot rolling.

[0030] The wire rod obtained by the hot rolling is preferably subjected to a heat treatment including quenching and tempering, to thereby have its metal microstructure converted to martensite. The quenching may involve heating the wire rod, for example, to 850 to 1,000°C, and then cooling it to the room temperature at an average cooling rate of 30°C/s or more. The upper limit of the average cooling rate is, for example, 100°C/s. The tempering may be performed by heating, for example, to 400 to 650°C.

[0031] The above-mentioned heat treatment should be applied once. By setting the number of heat treatment to one, the productivity can be improved, compared to the technique of Patent Document 1 mentioned above in which the quenching is performed twice or more.

[0032] The hot rolled wire rod obtained through such a heat treatment can be used as material for manufacturing steel wires that require the SSC resistance, such as the parts or reinforcing members of flexible risers, which are applied under sour environments containing hydrogen sulfide.

[0033] This application claims priority on Japanese Patent Application No. 2014-086532 filed on April 18, 2014, the content of which is incorporated by reference herein.

Examples

[0034] The present invention will be specifically described by way of Examples. The present invention is not limited to Examples below. It is apparent that various modifications and changes can be performed as long as they can be applied to the spirit of the present invention mentioned above and below. All of these modifications and changes are included in the technical scope of the present invention.

[0035] A steel with the composition shown in Table 1 below was smelted, and the smelted steel obtained was casted to fabricate a steel slab. The balance of the steel was made of iron and inevitable impurities. The thus-obtained steel slab was subjected to bloom rolling to form a billet, and the obtained billet was then hot-rolled into a wire rod. The billet before the hot rolling was a square block of 155 mm x 155 mm, and then hot-rolled into the wire rod having a wire diameter of 11 to 16 mm. The hot rolling was controlled such that the total rolling distortion (ε) through the initial three passes was shown in Table 2 below. The rolling distortion can be calculated by formula (1) below:

$$\text{Rolling Distortion} = \ln(S_0/S) \qquad (1)$$

where So is a cross-sectional area (mm^2) of a billet before hot rolling, and S is a cross-sectional area (mm^2) of a billet at the end of initial three passes during the hot rolling.

[0036] Then, the obtained steel wire was subjected to quenching and tempering to produce a test piece. In the quenching, the wire rod was heated to 850 to 1,000°C, held in this temperature range for 5 to 15 minutes, and then cooled to the room temperature at an average cooling rate of 30°C/s or higher. In the tempering, the quenched wire rod was held at a temperature in a range of 400 to 650°C for 50 to 70 minutes.

[0037] With regard to each obtained test piece, a metal microstructure was observed, and a segregation ratio of sulfur (S) was measured.

(Observation of Metal Microstructure)

[0038] A specimen for observation of the metal microstructure was taken from the above-mentioned test piece, and then embedded in a mount. The metal microstructure of the specimen was observed with an optical microscope at a magnification of 400x. As a result, the metal microstructure of each test piece was found to be formed of martensite.

(Segregation Ratio of sulfur (S))

[0039] Element mapping for sulfur (S) as a measurement element was executed by an electron probe microanalyzer (Electron Probe Microanalyzer; EPMA). Element mapping was carried out from an area including center of the test piece toward its surface since segregation of sulfur usually tends to occur at the center. The measurement was performed at 300 sites or more of the test piece, including its center and its surface layer, at intervals of 200 μm. The sulfur (S) content (% by mass) was calculated based on a characteristic X-ray spectrum intensity to thereby determine the average value S_{ave} (% by mass) and the maximum value S_{max} (% by mass). The segregation ratio (S_{max}/S_{ave}) is defined as the ratio of the maximum sulfur (S) content S_{max} (% by mass) to the average sulfur (S) content S_{ave} (% by mass), and the results in the test pieces are shown in Table 2 below.

[0040] Then, a specimen in conformity with JIS 14A was taken from the obtained test piece, and a tensile test was performed on each specimen based on JIS Z2241 (2011), thereby measuring an yield strength (YS) of the specimen. The yield strength is expressed in units of MPa. The measurement result in each specimen was shown in Table 2 below. In the present invention, specimens having a yield strength of 900 MPa or higher were determined to have a high strength and were rated as pass.

[0041] Then, the SSC resistance of the obtained test piece was evaluated in the following procedure. A specimen for Method A defined by NACE TM0177 was taken from each obtained test piece, and the SSC resistance of the specimen was evaluated by the Method A. In the evaluation on the SSC resistance, the obtained specimen was immersed in Solution A containing 5.0% by mass of NaCl and 0.5% by mass of CH_3COOH, and the above solution was saturated with H_2S gas. Then, 80% of stress in the yield strength measured was applied to the specimen immersed in the solution, and a time to rupture of each specimen was measured. The measurement result is shown in Table 2 below. In the present invention, specimens having the time-to-rupture of 720 hours or more were rated as pass and evaluated to have excellent SSC resistance.

[Table 1]

Steel type	Composition (% by mass)													
	C	Si	Mn	P	S	Al	Ni	Cu	Cr	Ti	B	Mo	Nb	V
A	0.15	0.10	1.00	0.009	0.005	0.010	-	-	-	-	-	-	-	-
B	0.20	0.10	0.80	0.007	0.006	0.010	-	-	-	-	-	-	-	-
C	0.20	0.50	0.50	0.008	0.005	0.010	-	-	-	-	-	-	-	-
D	0.20	0.10	1.60	0.006	0.004	0.010	-	-	-	-	-	-	-	-
E	0.20	0.10	1.45	0.006	0.025	0.010	-	-	-	-	-	-	-	-
F	0.30	0.04	1.00	0.007	0.006	0.010	-	-	-	-	-	-	-	-
G	0.30	0.10	0.20	0.009	0.006	0.010	-	-	-	-	-		-	-
H	0.30	0.15	1.00	0.008	0.006	0.010	0.30	0.30	-	0.055	-	0.40	-	-
I	0.30	0.20	1.00	0.007	0.007	0.010	-	-	0.50	-	0.0056	-	-	0.10
J	0.30	0.10	1.30	0.005	0.005	0.010	-	-	-	0.080	-	-	0.10	-
K	0.35	0.30	1.00	0.007	0.005	0.010	-	-	-	-	0.0040	-	-	0.25
L	0.35	0.10	1.30	0.006	0.006	0.010	-	-	-	-	-	0.60	0.09	-
M	0.55	0.10	1.00	0.006	0.005	0.010	-	-	-	-	-	-	-	-
N	0.30	0.25	0.85	0.004	0.004	0.010	-	-	-	-	0.0018	-	0.02	-
O	0.30	0.20	0.85	0.005	0.003	0.010	-	-	-	0.025	-	1.15	-	-
P	0.30	0.05	0.75	0.006	0.006	0.010	-	-	0.85	-	-	-	-	0.40
Q	0.30	0.10	1.00	0.008	0.002	0.030	-	-	-	0.080	0.0085	-	-	-
R	0.30	0.10	1.00	0.005	0.002	0.030	-	-	-	0.080	0.0015	-	0.10	-

[Table 2]

No.	Steel type	Rolling distortion (e)	Segregation ratio	Tensile property	SSC resistance
				Yield strength (MPa)	Time-to-Rupture (Time)
1	A	0.30	23	649	≥ 720
2	B	0.30	26	928	≥ 720
3	B	0.40	17	930	≥ 720
4	B	0.50	10	914	≥ 720
5	B	0.20	39	903	654
6	C	0.30	46	954	395
7	D	0.30	40	936	461
8	E	0.30	55	911	425
9	F	0.30	11	831	≥ 720
10	G	0.30	24	848	≥ 720
11	H	0.30	20	933	≥ 720
12	I	0.30	27	912	≥ 720
13	J	0.30	23	906	≥ 720
14	K	0.30	21	920	≥ 720
15	L	0.30	27	918	≥ 720

(continued)

No.	Steel type	Rolling distortion (e)	Segregation ratio	Tensile property	SSC resistance
				Yield strength (MPa)	Time-to-Rupture (Time)
16	L	0.20	36	924	679
17	L	0.50	21	931	≥ 720
18	M	0.40	41	1067	374
19	N	0.40	13	913	≥ 720
20	O	0.40	27	957	≥ 720
21	P	0.40	14	966	≥ 720
22	Q	0.40	22	936	≥ 720
23	R	0.40	23	940	≥ 720

[0042] Based on Tables 1 and 2, the following consideration can be made. Specimens Nos. 2 to 4, 11 to 15, 17 and 19 to 23 are the examples satisfying the requirements specified by the present invention. In each example, the composition and the segregation ratio of sulfur (S) were controlled appropriately, whereby the high yield strength of 900 MPa or higher was achieved, and the SSC resistance was improved.

[0043] In contrast, specimens Nos. 1, 5 to 10, 16 and 18 are comparative examples which do not satisfy the requirements specified by the present invention. Among them, in the specimen No. 1, the C content was too small, whereby the yield strength of the wire rod became less than 900 MPa. In each of specimens Nos. 5 and 16, the rolling distortion induced through the initial three passes was less than 0.3, leading to the segregation of sulfur (S). The segregation ratio of sulfur (S) exceeded 30, thereby failing to improve the SSC resistance of the wire rod. Specimen No. 6 contained the excessive amount of Si, and the segregation ratio of sulfur (S) exceeded 30, thereby failing to improve the SSC resistance of the wire rod. Specimen No. 7 contained the excessive amount of Mn, and the segregation ratio of S exceeded 30, thereby failing to improve the SSC resistance of the wire rod. Specimen No. 8 contained the excessive amount of S, and the segregation ratio of S exceeded 30, thereby failing to improve the SSC resistance of the wire rod. In specimen No. 9, the Si content was excessively small, whereby the solid-solution strengthening became insufficient, leading to inadequate yield strength of less than 900 MPa. In specimen No. 10, the Mn content was excessively small, whereby the hardenability became insufficient, resulting in a yield strength of less than 900 MPa. In specimen No. 18, the C content,was excessive, and the segregation ratio of S exceeded 30, thus failing to improve the SSC resistance.

Claims

1. A hot rolled wire rod comprising, in percent 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: exceeding 0% and 0.01% or less, and
S: exceeding 0% and 0.01% or less, with the balance being iron and inevitable impurities, wherein

when the sulfur content in the hot rolled wire rod is measured at 300 sites or more at intervals of 200 μm using an electron beam microanalyzer, a segregation ratio (S_{max}/S_{ave}) is 30 or less, where a segregation ratio is defined as a ratio of the maximum sulfur content S_{max} (% by mass) to an average sulfur content Save (% by mass).

2. The hot rolled wire according to claim 1, further comprising, as other elements, any one or more of elements listed in the following (a) to (e), in percent by mass:

(a) at least one element of Cr: exceeding 0% and 1% or less and B: exceeding 0% and 0.01% or less,
(b) at least one element of Ni: exceeding 0% and 0.5% or less and Cu: exceeding 0% and 0.5% or less,
(c) at least one element of Ti: exceeding 0% and 0.1% or less and V: exceeding 0% and 0.5% or less,

(d) Mo: exceeding 0% and 1.5% or less, and
(e) Nb: exceeding 0% and 0.1% or less.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/06*(2006.01)i, *C22C38/54*(2006.01)i, *C21D8/06* (2006.01)n, *C21D9/52*(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, C21D8/06, C21D9/52

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

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Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus/JST7580(JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 4-2720 A (Nippon Steel Corp.), 07 January 1992 (07.01.1992), entire text; all drawings (Family: none)	1-2
A	JP 11-501986 A (Institut Francais du Petrole, Coflexip), 16 February 1999 (16.02.1999), entire text & US 5922149 A & WO 1996/028575 A1 & FR 2731371 A1	1-2

☒ 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
10 April 2015 (10.04.15)	12 May 2015 (12.05.15)

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2000-517381 A (Institut Francais du Petrole), 26 December 2000 (26.12.2000), entire text & US 6291079 B1 & WO 1998/010113 A1 & FR 2753206 A1	1-2
A	JP 2013-227611 A (JFE Steel Corp.), 07 November 2013 (07.11.2013), entire text; all drawings (Family: none)	1-2

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2013227611 A **[0005]**
- JP 2014086532 A **[0033]**