(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 253 590 A1

(12) # EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
04.10.2023 Bulletin 2023/40

(21) Application number: **21898421.9**

(22) Date of filing: **08.11.2021**

(51) International Patent Classification (IPC):
C22C 38/34 (2006.01) ***C22C 38/42*** (2006.01)
C22C 38/46 (2006.01)

(52) Cooperative Patent Classification (CPC):
C22C 38/34; C22C 38/42; C22C 38/46

(86) International application number:
PCT/KR2021/016119

(87) International publication number:
WO 2022/114595 (02.06.2022 Gazette 2022/22)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **27.11.2020 KR 20200163012**

(71) Applicant: **POSCO Co., Ltd**
Pohang-si, Gyeongsangbuk-do 37859 (KR)

(72) Inventors:
- **PARK, Junhak**
Pohang-si Gyeongsangbuk-do 37671 (KR)
- **KOH, Seongung**
Pohang-si Gyeongsangbuk-do 37667 (KR)
- **KIM, Yongho**
Pohang-si Gyeongsangbuk-do 37680 (KR)
- **PARK, Sewon**
Pohang-si Gyeongsangbuk-do 37765 (KR)

(74) Representative: **Nederlandsch Octrooibureau**
P.O. Box 29720
2502 LS The Hague (NL)

(54) **WIRE ROD FOR COLD WORKING WITH IMPROVED STRESS CORROSION RESISTANCE CHARACTERISTICS, STEEL WIRE, AND METHOD FOR MANUFACTURING SAME**

(57) Disclosed are a wire rod for cold working with improved stress corrosion resistance characteristics, a steel wire, and a method for manufacturing same. The wire rod for cold working with improved stress corrosion resistance characteristics, according to the present invention, comprises, by weight%, 0.3-0.6% of C, 0.5-1.0% of Mn, 0.6-2.0% of Si, 0.2-0.6% of Cr, and the remainder of Fe and inevitable impurities, wherein the thickness of an area where the ferrite fraction of a surface layer is 90% or more is 30 μm or more, and the internal microstructure includes 50% or more of pearlite.

Processed by Luminess, 75001 PARIS (FR)

Description

[Technical Field]

[0001] The present invention relates to a wire rod for cold working with improved stress corrosion resistance, a steel wire, and a method of manufacturing the same, and more specifically, to a wire rod for cold working, which is able to be manufactured into a steel wire or bar that supports the load of a transport pipe in a CO_2-rich corrosive environment of the deep sea, and a steel wire with improved stress corrosion resistance.

[Background Art]

[0002] Recently, a technique for transporting carbon dioxide (CO_2) to the deep sea has become important to store CO_2, which is generated on the ground, on the seabed. In this regard, the use of a steel wire or bar that supports the load of a transport pipe has also been increased to inject CO_2 gas collected on the ground into a transport pipe and then transport it to the seabed. In addition, as a place where CO_2 is stored moves to the deep sea, the length of a transport pipe gradually becomes longer, and accordingly, the strength of a steel wire or bar that supports the load of a transport pipe is gradually increasing.

[0003] Meanwhile, the solubility of CO_2 increases at high water pressure in the deep sea, and thus the CO_2 content in seawater increases. In this case, a load-bearing steel wire may be applied and installed on a CO_2 transport pipe to avoid direct exposure of a material to seawater at the beginning of field application. When the coating layer is peeled off during actual use in the above situation and the material is directly exposed to seawater, problems occur. In this case, the material is exposed to an environment in which stress corrosion cracking may occur by coming in contact with a CO_2-rich seawater under stress. Moreover, since stress corrosion cracking is more likely to occur in high-strength materials, this has been a major constraint in the development of a load-bearing steel wire whose strength has been increased. In other words, stress corrosion cracking in the load-bearing steel wire of the CO_2 transport pipe is a problem that needs to be solved.

[0004] Korean Laid-Open Patent Publication No. 10-2019-0064898 discloses a technique for improving the corrosion resistance of a steel wire that supports a deep-sea transport pipe. However, this technique is intended to suppress sulfide stress cracking (SSC) or hydrogen induced cracking (HIC) rather than CO_2 stress corrosion cracking, and research on a technique capable of suppressing CO_2 stress corrosion cracking of a steel wire that supports a deep-sea transport pipe is still insufficient. Therefore, there is a need for the development of a technique for a wire rod and a steel wire or bar capable of ensuring high strength and suppressing CO_2 stress corrosion cracking in a CO_2-rich environment of the deep sea.

[Disclosure]

[Technical Problem]

[0005] The present invention is directed to providing a wire rod for cold working, which has improved stress corrosion resistance in a CO_2-rich environment of the deep sea, and a steel wire

[Technical Solution]

[0006] A wire rod for cold working with improved stress corrosion resistance according to one embodiment of the present invention includes, in % by weight, 0.3 to 0.6% of C, 0.5 to 1.0% of Mn, 0.6 to 2.0% of Si, 0.2 to 0.6% of Cr, a balance of Fe, and unavoidable impurities, wherein a region of a surface layer in which a ferrite fraction is 90% or more has a thickness of 30 μm or more, and an internal microstructure includes pearlite in an amount of 50% or more.

[0007] In addition, the wire rod may further include one or more selected from the group consisting of more than 0 and 0.3% or less of Cu, more than 0 and 0.3% or less of Ni, and 0.02 to 0.1% of V.

[0008] Additionally, a ferrite particle size in the surface layer may be 8 to 50 μm.

[0009] In addition, an interlayer spacing of the pearlite may be 450 nm or less.

[0010] A method of manufacturing a wire rod for cold working with improved stress corrosion resistance according to another embodiment of the present invention includes: heating a billet including, in % by weight, 0.3 to 0.6% of C, 0.5 to 1.0% of Mn, 0.6 to 2.0% of Si, 0.2 to 0.6% of Cr, a balance of Fe, and unavoidable impurities; hot-rolling the heated billet to prepare a wire rod; cooling the rolled wire rod at 5 °C/s or less in a range of 700 to 830 °C (first cooling); and cooling the wire rod after the first cooling at 2 °C/s to 25*(1-C_{eq}) °C/s in a range of 400 to 700 °C (second cooling), wherein C_{eq} = [C] + [Si]/24 + [Mn]/6 + [Ni]/40 + [Cr]/5 + [V]/14 (here, [C], [Si], [Mn], [Ni], [Cr], and [V] refer to the weight percent of respective alloying elements).

[0011] The billet may further include one or more selected from the group consisting of more than 0 and 0.3% or less of Cu, more than 0 and 0.3% or less of Ni, and 0.02 to 0.1% of V.

[Advantageous Effects]

[0012] When manufactured into a load-bearing steel wire or bar, a wire rod for cold working with improved stress corrosion resistance according to an embodiment of the present invention can have improved stress corrosion resistance in a CO_2-rich corrosive environment of the deep sea by controlling the ferrite fraction and thickness of a surface layer.

[Modes of the Invention]

[0013] A wire rod for cold working with improved stress corrosion resistance according to an embodiment of the present invention includes, in % by weight, 0.3 to 0.6% of C, 0.5 to 1.0% of Mn, 0.6 to 2.0% of Si, 0.2 to 0.6% of Cr, a balance of Fe, and unavoidable impurities, wherein a region of a surface layer in which a ferrite fraction is 90% or more has a thickness of 30 μm or more, and an internal microstructure includes pearlite in an amount of 50% or more.

[0014] Not all details of embodiments of the present disclosure are described herein, and general descriptions in the art to which the present invention pertains or overlapping descriptions between embodiments are omitted.

[0015] In addition, a certain part "including" a certain element signifies that the certain part may further include another element instead of excluding the other element unless particularly indicated otherwise.

[0016] A singular expression includes a plural expression unless clearly indicated otherwise in the context.

[0017] Hereinafter, the present invention will be described in detail.

[0018] The inventors of the present invention have studied a method to suppress stress corrosion cracking in a CO_2-rich corrosive environment of the deep sea, and found that, when the structure of a surface layer consists of ferrite, and the thickness and particle size of the surficial ferrite layer are controlled, the surface layer has a uniform microstructure and low hardness, and as a result, stress corrosion cracking is suppressed.

[0019] In addition, the inventors have found that the control of a cooling rate in the phase transformation section of austenite is desirable in ferrite formation in a surface layer, and accordingly, proposed the present invention.

[0020] The wire rod for cold working with improved stress corrosion resistance according to an embodiment of the present invention includes, in % by weight, 0.3 to 0.6% of C, 0.5 to 1.0% of Mn, 0.6 to 2.0% of Si, 0.2 to 0.6% of Cr, a balance of Fe, and unavoidable impurities.

[0021] In addition, the wire rod may further include one or more selected from the group consisting of more than 0 and 0.3% or less of Cu, more than 0 and 0.3% or less of Ni, and 0.02 to 0.1% of V.

[0022] Hereinafter, the reason for the numerical limitation of alloying element contents in an embodiment of the present invention will be described. Hereinafter, units are % by weight unless otherwise specified.

[0023] A C content is 0.3 to 0.6%.

[0024] C is an element favorable for improving the strength of a steel wire. When a C content is less than 0.3%, strength is degraded, and thus it is difficult to use the resulting wire rod as a load-bearing reinforcing material, and when a C content exceeds 0.6%, strength is improved, but ductility may decrease. In particular, as the C content increases, the corrosion resistance of a steel wire tends to decrease. Therefore, in the present invention, it is preferable to control the C content to 0.3 to 0.6% to ensure the strength and corrosion resistance of a steel wire.

[0025] A Mn content is 0.5 to 1.0%.

[0026] Mn is an element favorable for improving the hardenability of a steel wire and ensuring a microstructure desired in the present invention. When a Mn content is less than 0.5%, it is difficult to ensure hardenability, and thus the microstructure and strength desired in the present invention may not be ensured, and when a Mn content exceeds 1.0%, centerline segregation is promoted, and thus ductility may be substantially degraded. Therefore, in the present invention, it is preferable to control the Mn content to 0.5 to 1.0%.

[0027] A Si content is 0.6 to 2.0%.

[0028] Si is an element that greatly affects ferrite formation in a surface layer with a microstructure according to the present invention. A high Si content is desirable in ferrite formation in a surface layer, but when a Si content exceeds 2.0%, centerline segregation is promoted, and thus ductility may be substantially degraded. Therefore, in the present invention, it is preferable to control the Si content to 0.6 to 2.0%.

[0029] A Cr content is 0.2 to 0.6%.

[0030] Cr is an element that contributes to an improvement in corrosion resistance of a material by forming an oxide film on a surface layer. When a Cr content is less than 0.2, the above-described effect may not be exhibited, and when a Cr content exceeds 0.6%, hardenability is substantially increased to increase a thermal treatment time in a steel wire manufacturing process, and thus productivity may be degraded, and it may be disadvantageous in terms of alloy costs due to its high price. Therefore, in the present invention, it is preferable to control the Cr content to 0.2 to 0.6%.

[0031] Cu and Ni are elements that may be optionally added, and when Cu or Ni is added, its content is limited to more than 0 and 0.3% or less. Cu and Ni are elements that contribute to an improvement in corrosion resistance of a ferrite structure. When Cu is added alone, there is a risk of high-temperature brittleness, and therefore, it is preferable to add Cu along with Ni capable of suppressing high-temperature brittleness. However, since Cu and Ni are expensive elements, the upper limits of Cu and Ni contents are limited to 0.3% in the present invention.

[0032] V is an element that may be optionally added, and when V is added, a V content is limited to 0.02 to 0.1%. Like Si, V is an element having an effect of forming ferrite in a surface layer. When a V content is less than 0.02%, the above-described effect may not be exhibited, and when a V content exceeds 0.1%, a low-temperature structure may be caused at a centerline segregation portion, and it may be disadvantageous in terms of alloy costs. Therefore, in the present invention, when V is added, it is preferable to control the V content to 0.02 to 0.1%.

[0033] In addition to the alloying composition components, Fe is included as the remainder. The wire rod for cold working with improved stress corrosion resistance according to the present invention may include other impurities that may be included in an industrial production process of typical steel. Since descriptions of the impurities are known by those skilled in the art to which the present invention belongs, the type and content thereof are not particularly limited in the present invention.

[0034] In the case of the wire rod for cold working with improved stress corrosion resistance according to an embodiment of the present invention, a region of a surface layer in which a ferrite fraction is 90% or more may have a thickness of 30 μm or more.

[0035] As the microstructure of a surface layer is more uniform and less hard, stress corrosion cracking in a CO_2-rich corrosive environment of the deep sea is suppressed. In order to satisfy the above-described conditions, when the structure of a surface layer is controlled to have a ferrite fraction of 90% or more, it is effective in terms of hardness and uniformity of the microstructure.

[0036] In addition, for a ferrite layer to be effective in suppressing stress corrosion even after cold working, the ferrite region of the wire rod needs to have a thickness of 30 μm or more before cold working.

[0037] In the case of the wire rod for cold working with improved stress corrosion resistance according to an embodiment of the present invention, a ferrite particle size in the surface layer may be 8 to 50 μm.

[0038] A ferrite particle size in the surface layer of the wire rod before cold working affects the hardness of a surface layer of a final steel wire or bar after cold working and, accordingly, is involved in the occurrence of stress corrosion cracking.

[0039] When a ferrite particle size of the wire rod before cold working is small, a hardening rate according to hardness and workability is increased, and thus hardness is increased after cold working. Accordingly, stress corrosion cracking may be more likely to occur. Therefore, by controlling the ferrite particle size of the wire rod to 8 μm or more in the present invention, the hardness of a surface layer after cold working can be lowered, and resistance to stress corrosion cracking can be ensured. However, when a ferrite particle size exceeds 50 μm, the interlayer spacing of pearlite exceeds 300 nm, and thus workability and a work hardening amount may be degraded. Therefore, in the present invention, the ferrite particle size is limited to 8 to 50 μm. In order to control the ferrite particle size according to the present invention to a large size, a long cooling time in a range of 700 to 830 °C is required in a cooling process after hot rolling of the wire rod. This will be described in detail in a method of manufacturing a wire rod for cold working with improved stress corrosion resistance, which is to be described below.

[0040] The wire rod for cold working with improved stress corrosion resistance according to an embodiment of the present invention includes pearlite in an amount of 50% or more as an internal microstructure, and the interlayer spacing of pearlite may be 450 nm or less.

[0041] Since a steel wire or bar for supporting the load of a transport pipe is manufactured by subjecting the hot-rolled wire rod to cold working, both the workability of a wire rod before working and the strength of a final material need to be ensured. Therefore, a matrix of the wire rod for cold working according to the present invention needs to include pearlite whose workability and work hardening amount are excellent and have a pearlite fraction of 50% or more.

[0042] In addition, the workability and work hardening amount of pearlite strongly depend on an interlayer spacing, and in the present invention, when the interlayer spacing of pearlite is 300 nm or less, workability and a work hardening amount may be ensured.

[0043] Next, a method of manufacturing a wire rod for cold working with improved stress corrosion resistance according to another embodiment of the present invention will be described.

[0044] The wire rod for cold working with improved stress corrosion resistance according to the present invention may be manufactured by various methods, and the manufacturing method is not particularly limited. However, as an example, manufacturing may be made by the following method.

[0045] For example, the wire rod for cold working with improved stress corrosion resistance according to the present invention may be manufactured by heating a billet having the above-described alloying composition, hot-rolling the heated billet to obtain a wire rod, and then cooling the hot-rolled wire rod.

[0046] The method of manufacturing the wire rod for cold working with improved stress corrosion resistance according to an embodiment of the present invention includes: heating a billet including, in % by weight, 0.3 to 0.6% of C, 0.5 to

1.0% of Mn, 0.6 to 2.0% of Si, 0.2 to 0.6% of Cr, a balance of Fe, and unavoidable impurities; hot-rolling the heated billet to prepare a wire rod; cooling the rolled wire rod at a cooling rate of 5 °C/s or less in a range of 700 to 830 °C (first cooling); and cooling the wire rod after the first cooling at a cooling rate of 2 °C/s to $25*(1-C_{eq})$ °C/s defined by the following equation in a range of 400 to 700 °C (second cooling), wherein C_{eq} = [C] + [Si]/24 + [Mn]/6 + [Ni]/40 + [Cr]/5 + [V]/14 (here, [C], [Si], [Mn], [Ni], [Cr], and [V] refer to the weight percent of respective alloying elements).

[0047] In addition, the billet may further include one or more selected from the group consisting of more than 0 and 0.3% or less of Cu, more than 0 and 0.3% or less of Ni, and 0.02 to 0.1% of V.

[0048] Hereinafter, the method of manufacturing the wire rod for cold working with improved stress corrosion resistance according to an embodiment of the present invention will be described in detail.

[0049] First, a billet satisfying the above-described alloying composition is heated at 1,000 °C to 1,100 °C.

[0050] Afterward, the heated billet is hot-rolled at 950 °C to 1,050 °C to obtain a wire rod.

[0051] Subsequently, as first cooling, the hot-rolled wire rod is cooled at a cooling rate of 5 °C/s or less in a range of 700 to 830 °C. A lower cooling rate of the hot-rolled wire rod is desirable for ferrite formation in a surface layer according to the present invention. Typically, ferrite in a surface layer is known to be formed by cooling a surface layer structure in an austenite state immediately after hot rolling and subjecting the resultant to phase transformation. Particularly, it is confirmed that a cooling rate in a phase transformation section of 700 to 830 °C is associated with the phase transformation behavior, and as the cooling is made in the phase transformation section for a long time, ferrite formation in a surface layer is promoted. Therefore, in the present invention, a cooling rate in a range of 700 to 830 °C is limited to 5 °C/s or less.

[0052] As second cooling after the first cooling, the resulting wire rod is cooled at a cooling rate of 2 °C/s to $25*(1-C_{eq})$ °C/s in a range of 400 to 700 °C. In this case, C_{eq} = [C] + [Si]/24 + [Mn]/6 + [Ni]/40 + [Cr]/5 + [V]/14 (here, [C], [Si], [Mn], [Ni], [Cr], and [V] refer to the weight percent of respective alloying elements).

[0053] A cooling rate in a range of 400 to 700 °C is important in forming a pearlite microstructure according to the present invention. In order to ensure high strength and cold workability, a microstructure needs to consist of pearlite having a fine interlayer spacing. In order to ensure pearlite having a fine interlayer spacing, a cooling rate in this range needs to be 2 °C/s or more. However, when a cooling rate exceeds $25*(1-C_{eq})$ °C/s, that is, cooling is excessively rapidly made, bainite, martensite, and the like are produced, and thus workability may be rather degraded. Therefore, in the present invention, a cooling rate in a range of 400 to 700 °C is limited to 2 °C/s or more and $25*(1-C_{eq})$ °C/s.

[0054] The wire rod for cold working with improved stress corrosion resistance, which is manufactured according to the present invention, is cold-drawn at a reduction ratio of 40 to 80% to ensure a size reduction and strength, cold-rolled according to the shape of a final product as necessary, and then thermally treated in a range of 400 to 600 °C to remove dislocations formed in the internal structure through cold working, thereby being finally manufactured into a steel wire or bar that supports the load of a transport pipe.

[0055] Hereinafter, the present invention will be described in further detail with reference to examples. However, the following examples are merely presented to exemplify the present invention, and the present invention is not limited to the following examples. This is because the scope of the present invention is determined by the matters described in the claims and the matters reasonably inferred therefrom.

Examples

[0056] Each billet having an alloying composition shown in the following Table 1 was heated at 1,050 °C, hot-rolled at 1,000 °C so that a diameter became 15 mm, and then subjected to first cooling and second cooling under cooling rate conditions shown in the following Table 2.

[Table 1]

Classification	Alloying composition component system (% bv weight)						
	C	Si	Mn	Cr	Cu	Ni	V
Inventive Example 1	0.3	0.6	1	0.6	0.1	0.02	0.1
Inventive Example 2	0.4	1	0.5	0.25	0.02	0.02	0.02
Inventive Example 3	0.3	1	1	0.2	0.1	0.1	0.07
Inventive Example 4	0.5	2	0.9	0.25	0.2	0.3	0.03
Inventive Example 5	0.6	1.5	0.9	0.6	0.3	0.2	0.03
Inventive Example 6	0.4	2	0.5	0.4	0.2	0.2	0.1
Inventive Example 7	0.5	1.5	0.7	0.4	0.02	0.1	0.07

(continued)

Classification	Alloying composition component system (% bv weight)						
	C	Si	Mn	Cr	Cu	Ni	V
Inventive Example 8	0.6	0.6	0.7	0.2	0.3	0.3	0.02
Inventive Example 9	0.3	1	1	0.2	0	0.1	0.07
Inventive Example 10	0.5	2	0.9	0.25	0.2	0	0.03
Inventive Example 11	0.6	1.5	0.9	0.6	0.3	0.2	0
Comparative Example 1	0.3	1	1	0.2	0.1	0.1	0.07
Comparative Example 2	0.5	2	0.9	0.25	0.2	0.3	0.03
Comparative Example 3	0.4	1	0.5	0.25	0.02	0.02	0.02
Comparative Example 4	0.3	1	1	0.2	0.1	0.1	0.07
Comparative Example 5	0.5	2	0.9	0.25	0.2	0.3	0.03
Comparative Example 6	0.6	1.5	0.9	0.6	0.3	0.2	0.03

[Table 2]

Classification	Cooling rate (°C/s)		
	First cooling range (700 °C to 830 °C)	25*(1-C_{eq}) °C/s value	Second cooling range (400 °C to 700 °C)
Inventive Example 1	4	10	8
Inventive Example 2	3	11	10
Inventive Example 3	3	11	11
Inventive Example 4	4	5	4
Inventive Example 5	5	2	2
Inventive Example 6	3	9	8
Inventive Example 7	4	6	5
Inventive Example 8	5	5	5
Inventive Example 9	4	11	6
Inventive Example 10	4	7	5
Inventive Example 11	3	4	4
Comparative Example 1	6	11	10
Comparative Example 2	6	5	5
Comparative Example 3	3	11	12
Comparative Example 4	3	11	12
Comparative Example 5	4	5	1

(continued)

Classification	Cooling rate (°C/s)		
	First cooling range (700 °C to 830 °C)	25*(1-C_{eq}) °C/s value	Second cooling range (400 °C to 700 °C)
Comparative Example 6	5	2	1

[0057] Afterward, the pearlite fraction, interlayer spacing of pearlite, ferrite fraction of a surface layer, thickness of a ferrite layer of a surface layer, and ferrite particle size in a surface layer of each wire rod according to Examples and Comparative Examples were measured, and results thereof are shown in Table 3 below.

[0058] Subsequently, the wire rod cooled after the hot rolling was cold-drawn at a reduction ratio of 60% and cold-rolled at a reduction ratio of 40% to be manufactured into a final cold working product. The degree of stress corrosion cracking of each sample of Examples and Comparative Examples was measured, and results thereof are shown in Table 3 below.

[0059] The resistance of each product of Examples and Comparative Examples to stress corrosion cracking in a CO_2 corrosive environment was evaluated by the following method. First, to simulate a CO_2 corrosive environment, 83 g of $NaHCO_3$ with a purity of 99% or more and 105 g of Na_2CO_3 with a purity of 99% or more were dissolved in 1 L of a 3.5 wt% NaCl solution to prepare a corrosion solution. Afterward, a steel wire for cold working was cut into a length of 400 mm, the middle portion (200 mm) was completely immersed in the prepared corrosion solution and then sealed, and both sides were exposed to the outside. Afterward, while maintaining the temperature of the solution at 60 °C, the sample was repeatedly subjected to stress at a frequency of 1×10^{-3} Hz for 15 days by applying loads of 100% and 70% based on yield strength. After 15 days, the product samples of Examples and Comparative Examples were taken out to obtain cross sections of the center including the cold rolling direction and the reduction direction. Generated cracks were observed from the reduced surface in the cross section of the center, the number of cracks generated per unit length in the rolling direction was measured, and the degrees of stress corrosion cracking according to Examples and Comparative Examples were compared.

[Table 3]

Classification	Internal pearlite structure		Surficial ferrite structure			Stress corrosion cracking
	Fraction (%)	Interlayer spacing (nm)	Fraction (%)	Thickness (μm)	Particle size (μm)	# of cracks per unit length (1/mm)
Inventive Example 1	50	330	94	34	42	25
Inventive Example 2	64	310	95	35	45	23
Inventive Example 3	57	300	95	35	50	25
Inventive Example 4	97	430	94	34	35	15
Inventive Example 5	90	450	92	32	25	10
Inventive Example 6	78	320	95	35	50	22
Inventive Example 7	97	430	94	34	15	27
Inventive Example 8	97	440	90	30	8	16
Inventive Example 9	63	350	95	35	48	24

(continued)

Classification	Internal pearlite structure		Surficial ferrite structure			Stress corrosion cracking
	Fraction (%)	Interlayer spacing (nm)	Fraction (%)	Thickness (μm)	Particle size (μm)	# of cracks per unit length (1/mm)
Inventive Example 10	94	440	94	34	36	16
Inventive Example 11	93	450	92	32	28	13
Comparative Example 1	57	310	89	29	7	31
Comparative Example 2	97	440	89	29	7	32
Comparative Example 3	49	290	93	33	38	28
Comparative Example 4	49	300	94	34	40	30
Comparative Example 5	97	455	95	36	35	29
Comparative Example 6	90	460	94	33	33	28

[0060] In the case of Inventive Examples 1 to 11 satisfying the alloying composition and manufacturing conditions of the present invention, a pearlite fraction of 50% or more and an interlayer spacing of pearlite of 450 nm or less were satisfied as an internal structure, and a surficial ferrite fraction of 90% or more, a surficial ferrite thickness of 30 μm or more, and a ferrite particle size of 8 to 50 μm were satisfied. As a result, 27 or less cracks per unit length were shown in a manufactured steel wire, and thus stress corrosion cracking resistance could be ensured.

[0061] Meanwhile, in the case of Comparative Examples 1 to 6 which satisfied the alloying composition of the present invention, but did not satisfy the cooling condition of the present invention, 28 or more cracks per unit length were shown in a manufactured steel wire, and thus a stress corrosion cracking resistance inferior to that of Examples was confirmed.

[0062] Specifically, in the case of Comparative Examples 1 and 2 in which a cooling rate in a range of 700 to 830 °C exceeded 5 °C/s, a surficial ferrite fraction did not reach 90% which is the lower limit of a ferrite fraction, a ferrite thickness did not reach 30 μm which is the lower limit of a ferrite thickness, and a ferrite particle size did not reach 8 μm which is the lower limit of a ferrite particle size. As a result, 31 and 32 cracks per unit length were shown, respectively, and thus poor stress corrosion cracking resistance was confirmed.

[0063] In the case of Comparative Examples 3 and 4 in which the alloying composition of the present invention was satisfied, but a cooling rate in a range of 400 to 700 °C exceeded a $25*(1-C_{eq})$ °C/s value, an internal pearlite fraction did not reach 50% which is the lower limit of a pearlite fraction. As a result, 28 and 30 cracks per unit length were shown, respectively, and thus poor stress corrosion cracking resistance was confirmed.

[0064] In the case of Comparative Examples 5 and 6 in which a cooling rate in a range of 400 to 700 °C was less than a $25*(1-C_{eq})$ °C value, an interlayer spacing of internal pearlite exceeded 450 nm which is the upper limit thereof, 29 and 28 cracks per unit length were shown, respectively, and thus poor stress corrosion cracking resistance was confirmed.

[0065] While exemplary embodiments of the present invention have been described above, the present invention is not limited thereto, and it may be understood by those skilled in the art that various modifications and alterations may be made without departing from the concept and scope of the following claims.

[Industrial Applicability]

[0066] According to an embodiment of the present invention, the wire rod for cold working, which has improved stress corrosion resistance in a CO_2-rich environment of the deep sea, and a steel wire can be provided.

Claims

1. A wire rod for cold working with improved stress corrosion resistance, the wire rod comprising, in % by weight, 0.3 to 0.6% of C, 0.5 to 1.0% of Mn, 0.6 to 2.0% of Si, 0.2 to 0.6% of Cr, a balance of Fe, and unavoidable impurities,

   wherein a region of a surface layer in which a ferrite fraction is 90% or more has a thickness of 30 μm or more, and an internal microstructure includes pearlite in an amount of 50% or more.

2. The wire rod of claim 1, further comprising one or more selected from the group consisting of more than 0 and 0.3% or less of Cu, more than 0 and 0.3% or less of Ni, and 0.02 to 0.1% of V.

3. The wire rod of claim 1, wherein a ferrite particle size in the surface layer is 8 to 50 μm.

4. The wire rod of claim 1, wherein an interlayer spacing of the pearlite is 450 nm or less.

5. A method of manufacturing a wire rod for cold working with improved stress corrosion resistance, the method comprising:

   heating a billet including, in % by weight, 0.3 to 0.6% of C, 0.5 to 1.0% of Mn, 0.6 to 2.0% of Si, 0.2 to 0.6% of Cr, a balance of Fe, and unavoidable impurities;
   hot-rolling the heated billet to prepare a wire rod;
   cooling the rolled wire rod at 5 °C/s or less in a range of 700 to 830 °C (first cooling); and
   cooling the wire rod after the first cooling at 2 °C/s to 25*(1-C_{eq}) °C/s in a range of 400 to 700 °C (second cooling),
   wherein C_{eq} = [C] + [Si]/24 + [Mn]/6 + [Ni]/40 + [Cr]/5 + [V]/14 (here, [C], [Si], [Mn], [Ni], [Cr], and [V] refer to the weight percent of respective alloying elements).

6. The method of claim 5, wherein the billet further includes one or more selected from the group consisting of more than 0 and 0.3% or less of Cu, more than 0 and 0.3% or less of Ni, and 0.02 to 0.1% of V.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2021/016119

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/34(2006.01)i; **C22C 38/42**(2006.01)i; **C22C 38/46**(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)

C22C 38/34(2006.01); B21B 1/16(2006.01); C21D 7/02(2006.01); C21D 8/06(2006.01); C22C 38/00(2006.01); C22C 38/04(2006.01); C22C 38/18(2006.01); C22C 38/38(2006.01)

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

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 응력부식(stress corrosion), 강선(steel wire), 크롬(Cr), 규소(Si), 망간(Mn), 냉각(cooling), 페라이트(ferrite)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2021216 B1 (KABUSHIKI KAISHA KOBE SEIKO SHO (KOBE STEEL, LTD.)) 11 September 2019 (2019-09-11) See paragraphs [0026], [0057]-[0061] and [0064]-[0067] and claims 1-2.	1-6
A	KR 10-2120699 B1 (POSCO) 09 June 2020 (2020-06-09) See claims 1 and 4-5.	1-6
A	KR 10-1674750 B1 (POSCO) 10 November 2016 (2016-11-10) See claims 1 and 6.	1-6
A	KR 10-1655006 B1 (NIPPON STEEL & SUMITOMO METAL CORPORATION) 06 September 2016 (2016-09-06) See claim 1.	1-6
A	JP 2006-291291 A (KOBE STEEL LTD.) 26 October 2006 (2006-10-26) See paragraphs [0051]-[0055].	1-6

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

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

Date of the actual completion of the international search	Date of mailing of the international search report
10 February 2022	**10 February 2022**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office **Government Complex-Daejeon Building 4, 189 Cheongsa-ro, Seo-gu, Daejeon 35208**	
Facsimile No. **+82-42-481-8578**	Telephone No.

Form PCT/ISA/210 (second sheet) (July 2019)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2021/016119

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
KR 10-2021216 B1	11 September 2019	CN 107429352 A	01 December 2017
		CN 107429352 B	19 July 2019
		JP 2016-186099 A	27 October 2016
		JP 6479527 B2	06 March 2019
		TW 201708568 A	01 March 2017
		TW I601833 B	11 October 2017
		US 2018-0066344 A1	08 March 2018
		WO 2016-158361 A1	06 October 2016
KR 10-2120699 B1	09 June 2020	CN 112840058 A	25 May 2021
		EP 3825435 A1	26 May 2021
		US 2021-0180152 A1	17 June 2021
		WO 2020-040388 A1	27 February 2020
KR 10-1674750 B1	10 November 2016	CN 105671458 A	15 June 2016
		CN 105671458 B	20 April 2018
KR 10-1655006 B1	06 September 2016	CN 104350167 A	11 February 2015
		CN 104350167 B	31 August 2016
		JP 5655986 B2	21 January 2015
		JP WO2013-183648 A1	01 February 2016
		WO 2013-183648 A1	12 December 2013
JP 2006-291291 A	26 October 2006	AT 492660 T	15 January 2011
		CN 1847438 A	18 October 2006
		CN 1847438 B	20 April 2011
		EP 1712653 A1	18 October 2006
		EP 1712653 B1	22 December 2010
		ES 2355835 T3	31 March 2011
		JP 4476863 B2	09 June 2010
		KR 10-2006-0107915 A	16 October 2006
		US 2006-0225819 A1	12 October 2006
		US 8043444 B2	25 October 2011

Form PCT/ISA/210 (patent family annex) (July 2019)

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- KR 1020190064898 **[0004]**