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(54) LONG-SERVICE-LIFE HIGH-TOUGHNESS CORROSION-RESISTANT STEEL FOR SUBSEA CHRISTMAS TREE VALVE AND HEAT TREATMENT METHOD AND PRODUCTION METHOD FOR LONG-SERVICE-LIFE HIGH-TOUGHNESS CORROSION-RESISTANT STEEL FOR SUBSEA CHRISTMAS TREE VALVE

(57) Long-service-life high-toughness corrosion-resistant steel for a subsea Christmas tree valve and a heat treatment method and production method for the long-service-life high-toughness corrosion-resistant steel for the subsea Christmas tree valve. The steel for the subsea Christmas tree valve mainly comprises the following components: C, Si, Mn, Cr, Mo, Ni, Cu, and Al. The compositions of the chemical components of the steel and the relationships and contents of the components are controlled, such that the tensile strength at the 1/4 thickness of the steel valve for the subsea Christmas tree valve is greater than or equal to 860 MPa, the yield strength is greater than or equal to 690 MPa, KV_2 at -46°C is greater than or equal to 230 J, A is greater than or equal to 20%, and Z is greater than or equal to 70%; the corrosion rate in a seawater environment is less than or equal to 0.07 mm/a; the fatigue strength is greater than or equal to 350 MPa after 2×10^7 weeks of corrosion in a seawater environment; and the performance of the steel can meet the requirements of a subsea Christmas tree in a severe environment.

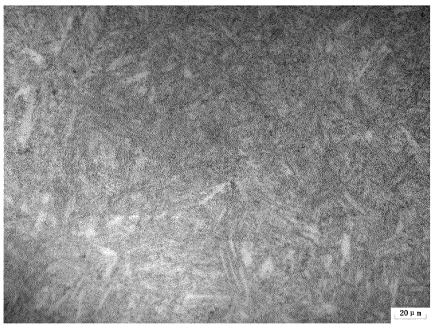

FIG. 1

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Description

FIELD

[0001] The present application relates to the technical field of alloy steel, and in particular to a long-life, high-toughness and corrosion-resistant steel for an subsea Christmas tree valve body, a heat treatment method and a production method thereof.

BACKGROUND

[0002] China is the second largest consumer of oil and the third largest consumer of natural gas. In order to improve energy self-sufficiency and energy security, China has vigorously developed domestic oil and gas drilling and production, particularly increased the development of deep-sea oil and gas resources. It is reported that the current depth of land oil and gas drilling and production in China has exceeded 7,300 meters, and the depth of offshore oil and gas drilling and production has approached 3,000 meters. The Christmas tree is an essential device for oil and gas production. The Christmas trees used in China are all imported, which seriously affects China's oil and gas security. The Christmas tree is composed of multiple modules (valve bodies), and has high requirements for the strength and toughness of the material. Especially, subsea Christmas trees have higher requirements for low-temperature toughness and corrosion resistance. The valve body of the Christmas tree is generally made of 4130 steel. However, as the deterioration of the oil and gas production environment, 4130 steel cannot meet the requirements of subsea Christmas trees.

[0003] Patent CN 102839331 A discloses a high-toughness corrosion-resistant steel and its manufacturing method for manufacturing the Christmas tree body. The Cr content in the patent is as high as 12-14%, the yield strength of the material is ≥ 517MPa, and the impact energy at -46°C is ≥ 27J. The Cr content of the patent is high, the cost is high, and the yield strength is still low although it is increased to 517MPa, and the low-temperature toughness is poor. In a more stringent low-temperature environment, the toughness will be insufficient.

[0004] Patent CN 112281069 A discloses a production method for 8630 ultra-long forgings for deep-sea Christmas tree equipment. Using the forging process of the patent, the yield strength of the obtained material is ≥ 580MPa, the impact energy at -29°C is ≥ 30J, and the low-temperature toughness of the material is low.

[0005] The performance of the Christmas tree steel disclosed in the above patents cannot meet the requirements for use at low temperatures, and the service life is not examined.

SUMMARY

[0006] The purpose of the present application is to provide a long-life, high-toughness, corrosion-resistant steel for subsea Christmas tree valve body and heat treatment method and production method thereof. The present application can achieve that the yield strength of the Christmas tree valve body is ≥ 690MPa, the impact energy at -46°C is ≥ 230J, and the corrosion rate in the seawater environment is ≤ 0.07mm/a, the fatigue strength after 2×10^7 cycles of corrosion in the seawater environment is ≥ 350MPa, which can meet the use requirements of Christmas trees in more stringent seawater environments and the method is suitable for manufacturing subsea Christmas tree valve bodies.

[0007] To achieve the above purpose, the technical solution adopted by the present application is as follows:

[0008] A long-life, high-toughness, corrosion-resistant steel for subsea Christmas tree valve body, comprising the following chemical components in weight percentage: C 0.22% to 0.28%, Si 0.15% to 0.35%, Mn 1.1% to 1.4%, Cr 1.3% to 1.5%, Mo 0.5% to 0.6%, Ni 0.30% to 0.40%, Cu 0.30% to 0.50%, Al 0.015% to 0.035%, P ≤ 0.015%, S ≤ 0.015%, N ≤ 0.0080%, O ≤0.004%, with the balance being Fe and other inevitable impurities;

wherein,

$$A=457\times(C-0.077\times Cr)+45\times Cr+80\times Si+50\times Mn+10\times Mo+96\times Cu,\ 230\% \le A \le 275\%;$$

$$D=30\times Ni+20\times Mo+16\times Cu+22\times Mn-12\times Si\times Mn+28\times C-10\times C\times Mn,\quad D \ge 52.5\%,$$

preferably D is 53 to 65%;

$$X=26\times Cu+4\times Ni+1.2\times Cr-1.5\times Si-7\times Cu\times Ni-5\times Mn,\ X \ge 5.4\%,$$

preferably X is 5.5 to 7.5%.

[0009] In order to produce a high-toughness and corrosion-resistant subsea Christmas tree valve body with excellent toughness, corrosion resistance and fatigue performance, which can meet requirements of more stringent underwater environment use, the following controls are carried out in the present application:

[0010] C: C is the cheapest strengthening element in steel. For every 0.1% increase in solid solution C, the strength can be increased by about 450MPa. C together with the alloy elements in the steel forms a precipitated phase, which plays a precipitation strengthening role. C can significantly improve the hardenability, so that the core of the large-sized Christmas tree valve body can obtain a martensitic structure. However, as the content of the martensitic structure increases, the plasticity and toughness decrease, and the high C content is harmful to the corrosion performance, so the C content is controlled at 0.22% to 0.28%.

[0011] Si: Si is an effective solid solution strengthening element in steel, which improves the strength and hardness of steel. Si can play a deoxidizing role during steelmaking and is a commonly used deoxidizer. However, Si is easy to segregate at austenite grain boundaries, which can reduce the grain boundary bonding force, and cause brittleness. In addition, Si is easy to cause element segregation in steel. Therefore, the Si content is controlled at 0.15% to 0.35%.

[0012] Mn: Mn can play a role in solid solution strengthening, and its solid solution strengthening ability is weaker than Si. Mn is an austenite stabilizing element that can significantly improve the hardenability of steel and reduce the decarburization of steel. Mn combined with S can prevent hot brittleness caused by S. However, excessive Mn will reduce the plasticity of steel. Therefore, the Mn content is controlled at 1.1% to 1.4%.

[0013] Cr: Cr is a carbide-forming element. Cr can improve the hardenability and strength of steel, but it is easy to cause temper brittleness. Cr can improve the oxidation resistance and corrosion resistance of steel, but when the Cr content is too high, it will increase the crack sensitivity. The Cr content should be controlled at 1.3% to 1.5%.

[0014] Mo: Mo mainly improves the hardenability and heat resistance of steel. Mo dissolved in the matrix can keep the structure of steel at a high stability during tempering, and can effectively reduce the segregation of impurity elements such as P, S and As at the grain boundaries, so as to improve the toughness of steel and reduce temper brittleness. Mo reduces the stability of M_7C_3. When the Mo content is high, needle-shaped Mo_2C will be formed, which will lead to a decrease in the Mo content of the matrix. Mo can improve the strength of steel through the combined effects of solid solution strengthening and precipitation strengthening, and can also change the toughness of steel by changing the precipitation of carbides. Therefore, Mo is controlled at 0.5% to 0.6%.

[0015] Ni: Ni together with Fe can form an infinitely miscible solid solution. Ni is an austenite stabilizing element, and has a function of expanding the phase region, which increases the stability of supercooled austenite, shifts the C curve to the right, and improves the hardenability of steel. Ni can refine the width of martensite laths and improve strength. Ni significantly reduces the toughness-brittle transition temperature of steel and improves low-temperature toughness. The Ni content is controlled at 0.30% to 0.40%.

[0016] Cu: Cu can expand the austenite phase region. Cu elemental substance can be used as the second phase to significantly improve the strength, and can improve the tempering stability and strength of the structure. However, excessive Cu will cause Cu brittleness. Therefore, the Cu content is controlled at 0.30% to 0.50%.

[0017] Al: Al is the main deoxidizer for steelmaking. Al combines with N to form fine and dispersed AlN, and maintains a coherent relationship with the matrix, which can play a role in strengthening and refining the organization, and can increase the resistance to fatigue crack initiation and expansion, so as to improve the endurance strength of steel. The Al content is controlled at 0.015% to 0.035%.

[0018] O and N: T.O forms oxide inclusions in steel, and T.O is controlled to be $\leq$ 0.0040%; N together with nitride-forming elements can form fine precipitated phases in steel to refine the organization, so N is controlled within 0.0080%.

[0019] In the present application, the main precipitated phase is the precipitated phase of Cr. On the one hand, Cr consumes C to form carbides, and on the other hand, solid solution treatment of Cr in the matrix can be performed to improve strength. This is related to the content of Cr and C in the steel. The C consumed in the formation of precipitated phases in steel is 0.077×Cr. In order to ensure strength, sufficient C is required for solid solution, and the solid solution C content should be C-0.077×Cr. In order to ensure the strength, it is necessary to strengthen the composite effect of elements Cr, Si, Mn, Mo, and Cu. The contribution coefficients of these five elements to the strength are 45, 80, 50, 10, and 96 respectively. Therefore, the comprehensive strength determination factor A of steel meets that $A = 457\times(C-0.077\times Cr) +45\times Cr+80\times Si+50\times Mn+10\times Mo+96\times Cu$. To ensure the strength and plasticity, A is controlled that $230\% \leq A \leq 275\%$.

[0020] To ensure the low-temperature toughness of steel, toughening elements need to be limited. Ni is the element that can improve the toughness, and Mo is conducive to improving the tempering stability, so as to improve the toughness of steel. Cu can precipitate fine nano-copper precipitates in steel, so as to improve the toughness of steel. Therefore, the contribution coefficients of the above three elements to toughness are 30, 20, and 16 respectively. Mn can promote the selection of variants in steel during phase transformation, so as to make the microstructure fine and improve toughness, but the segregation of Si and Mn leads to a decrease in toughness. Therefore, Mn has an independent contribution to toughness and interacts with Si and Mn, so the coefficients are 22 and -12 respectively. The influence of C content on toughness also has two aspects. On the one hand, it promotes phase transformation refinement and improves toughness. On the other hand, it interacts with Mn to promote the hardening of steel, resulting in lower toughness. Therefore, C has an independent contribution to toughness and interacts with C and Mn, so the coefficients are 28 and -10 respectively. Since P and S in steel are also harmful to the toughness of steel, but the present application has set a maximum content limit for P and S content, the harm of P and S to toughness is not considered. Therefore, the toughness determination factor D of steel meets that $D=30\times Ni+20\times Mo+16\times Cu+22\times Mn-12\times Si\times Mn+28\times C-10\times C\times Mn\geq 52.5\%$.

[0021] In order to ensure that the steel has good seawater corrosion resistance, a ratio of Si, Mn, Cu, Ni and Cr needs to be limited. Since Cu can improve strength and significantly improve corrosion resistance, the coefficient is 26. Si and Mn may aggravate the segregation, resulting in uneven microstructure and thus reducing erosion performance, so the coefficients are -1.5 and -5 respectively. Ni can improve the stacking fault energy and significantly improve the low-temperature toughness, and can passivate the metal to improve the erosion performance, so the coefficient of Ni is 4. Cr can enhance the passivation film on the surface of steel, so the coefficient is 1.2 respectively. Since there is an interaction between Cu and Ni, it will offset the corrosion resistance of the elements alone, so the coefficient is -7 respectively; that is, $X = 26 \times Cu + 4 \times Ni + 1.2 \times Cr - 1.5 \times Si - 7 \times Cu \times Ni - 5 \times Mn \geq 5.4\%$.

[0022] The metallographic structure of the long-life, high-toughness and corrosion-resistant steel for subsea Christmas tree valve body is tempered sorbite, and the grain size is 20-25μm.

[0023] The long-life, high-toughness, corrosion-resistant steel for subsea Christmas tree valve body has a tensile strength of ≥ 860MPa, yield strength of ≥ 690MPa, -46°C KV_2 ≥ 230J, A ≥ 20%, and Z ≥ 70% at 1/4 thickness; the corrosion rate in seawater environment is ≤ 0.07mm/a; the fatigue strength after 2×10^7 cycles of corrosion in seawater environment is ≥ 350MPa; specifically, the long-life, high-toughness, corrosion-resistant steel for subsea Christmas tree valve body has a tensile strength of 860-920MPa, yield strength of 690-740MPa, -46°C KV_2 of 230-260J, A of 20-24%, and Z of 70-75% at 1/4 thickness; and a fatigue strength after 2×10^7 cycles of corrosion in seawater environment of 350-375MPa.

[0024] According to an embodiment of the present application, a heat treatment method of the long-life, high-toughness and corrosion-resistant steel for subsea Christmas tree valve body is provided. The method comprises following steps:

(1) Step quenching: heating the Christmas tree valve body to 900 to 940°C, keeping warm, and then water cooling; heating again to 840 to 880°C, keeping warm, and then water cooling. The wall of the subsea Christmas tree valve body is relatively thick, and step quenching can ensure that the material has a fine martensitic structure, which is conducive to strength and toughness. After the first quenching, the grain size and martensite of the steel are both refined. During the second quenching, the structure is refined before heating, which is conducive to grain nucleation and grain refinement. The temperature of the second quenching is lower than the temperature of the first quenching, which can ensure that the grains after austenite are not coarsened. After quenching, the quantity of grains and martensitic variants increases, and the microstructure is refined, which is conducive to improving strength and toughness and corrosion fatigue life.

(2) Tempering: heating the Christmas tree valve body to T=580 to 680°C, keeping warm, and then water cooling.

[0025] In the step (1), the heating rate of each heating is 50 to 110°C/h, and each heat holding time is $t=0.4$ to $1.0\times S$, where S is the thickness of the wall of the valve body in mm, t is in min.

[0026] In the step (2), the heating rate is 50 to 110°C/h, and the heat holding time is $t1=0.8$ to $2.0\times S$, where S is the thickness of the wall of the valve body in mm, t1 is in min.

[0027] Under the above heating rate, the temperature at different positions of the valve body can be kept close. In a case that the heating rate is too fast, the temperature gradient at different positions of the valve body will be large, which will increase the internal stress and crack risk. In a case that the heating rate is too slow, there is a risk of tempering reaction during the heating stage, resulting in uncontrolled type and content of the precipitated phase. The heat holding time is the key to controlling the content and size of the precipitated phase. In a case that the heat holding time is too short, the precipitated phase is less and the beneficial effect is reduced. In a case that the heat holding time is too long, although the precipitated phase will increase, the size of the precipitated phase will increase, which will reduce the dispersion distribution effect of the precipitated phase. In a case that the precipitate phase is too large, the risk of internal microcracks will increase.

[0028] In the steps (1) and (2), the water cooling is performed to below 100°C.

[0029] The parameters of the tempering process should meet that $Y=T\times(S/10+\lg t1)/1000$, $24.75 \leq Y \leq 28.95$. The tempering parameters directly determine the mechanical properties and corrosion fatigue properties of the final product. In a case that the tempering parameters are too large, the softening effect of the material will be large, which results in a large decrease in the strength of the material, and the strength cannot be guaranteed. It will also cause the size of the precipitate phase to be too large, weaken the precipitation strengthening effect, and increase the risk of microcracks in the steel and reduce toughness. In a case that the tempering parameters are small, the strength of the material will not be softened enough, the structural stress and internal stress will be large, and the toughness and corrosion fatigue properties will be reduced.

[0030] According to an embodiment of the present application, a production method of the long-life, high-toughness, corrosion-resistant steel for subsea Christmas tree valve body is provided. The production method comprises the following steps: arc furnace or converter smelting → LF furnace refining → RH or VD vacuum degassing → round billet continuous casting → round billet heating → forging into valve body → heat treatment → machining → packaging and warehousing, wherein the heat treatment is carried out by the above-mentioned heat treatment method.

[0031] The diameter of the round billet is Φ380mm to Φ700mm.

[0032] The machining specifically comprises the following steps: valve body rough turning → flaw detection → valve body fine turning → grinding → flaw detection.

[0033] Compared with the conventional technology, the present application has following beneficial effects:

1. The long-life, high-toughness, corrosion-resistant steel for subsea Christmas tree valve body according to embodiments of the present application controls the composition and dosage of the chemical components in the steel, so that its performance meets the requirements of subsea Christmas trees in harsh environments;

2. The relationship between C, Cr, Si, Mn, Mo and Cu in the long-life, high-toughness, corrosion-resistant steel for subsea Christmas tree valve body according to embodiments of the present application satisfies that $A=457\times(C-0.077\times Cr)+45\times Cr+80\times Si+50\times Mn+10\times Mo+96\times Cu$, $230\% \leq A \leq 275\%$, so as to ensure that the subsea Christmas tree valve body has a higher strength;

3. The relationship between Ni, Mo, Cu, Mn, Si and C in the long-life, high-toughness, corrosion-resistant steel for subsea Christmas tree valve body according to embodiments of the present application satisfies that $30\times Ni+20\times Mo+16\times Cu+22\times Mn-12\times Si\times Mn+28\times C-10\times C\times Mn\geq 74.5\%$ to ensure the low temperature toughness of the subsea Christmas tree valve body;

4. The relationship between Cu, Ni, Cr, Si and Mn in the long-life, high-toughness and corrosion-resistant steel for subsea Christmas tree valve body according to embodiments of the present application satisfies that $26\times Cu+4\times Ni+1.2\times Cr-1.5\times Si-7\times Cu\times Ni-5\times Mn\geq 1.8\%$, so as to ensure that the subsea Christmas tree valve body has good seawater corrosion resistance;

5. The heat treatment of the long-life, high-toughness and corrosion-resistant steel for subsea Christmas tree valve body according to embodiments of the present application adopts a step quenching and a tempering process for heat treatment. The heating temperature and heat holding time during the tempering process are controlled to ensure that the overall performance of the steel for subsea Christmas tree valve body can meet the needs of subsea Christmas trees in harsh environments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0034]

FIG. 1 is a metallographic structure diagram of steel for an subsea Christmas tree valve body according to Example 3.
FIG. 2 is a metallographic structure diagram of steel for an subsea Christmas tree valve body according to Comparative Example 2.

DETAILED DESCRIPTION OF EMBODIMENTS

[0035] According to an embodiment of the present application, a long-life, high-toughness, corrosion-resistant steel for an subsea Christmas tree valve body is provided, comprising the following chemical components in weight percentage: C 0.22% to 0.28%, Si 0.15% to 0.35%, Mn 1.1% to 1.4%, Cr 1.3% to 1.5%, Mo 0.5% to 0.6%, Ni 0.30% to 0.40%, Cu 0.30% to 0.50%, Al 0.015% to 0.035%, P ≤ 0.015%, S ≤ 0.015%, N ≤ 0.0080%, 0 ≤ 0.004%, with the balance being Fe and other inevitable impurities;
where,

$$A=457\times(C-0.077\times Cr)+45\times Cr+80\times Si+50\times Mn+10\times Mo+96\times Cu,\ 230\% \leq A \leq 275\%;$$

$$D=30\times Ni+20\times Mo+16\times Cu+22\times Mn-12\times Si\times Mn+28\times C-10\times C\times Mn,\ D \geq 52.5\%;$$

$$X=26\times Cu+4\times Ni+1.2\times Cr-1.5\times Si-7\times Cu\times Ni-5\times Mn,\ X\geq 5.4\%.$$

[0036] A production method of the long-life, high-toughness, corrosion-resistant steel for the subsea Christmas tree valve body is provided, comprising the following steps: arc furnace or converter smelting → LF furnace refining → RH or VD vacuum degassing → round billet continuous casting → round billet heating → forging into valve body → heat treatment → machining → packaging and storage.

In the production method, electric furnace smelting: oxygen is controlled before steel is tapped, and steel retention operation is adopted during steel tapping to avoid slag;

LF furnace: C, Si, Mn, Cr, Ni, Mo, Cu, and other elements are adjusted to target values;

Vacuum degassing: pure degassing time is ≥ 15 minutes, ensuring that the [H] content after vacuum treatment is ≤ 1.5ppm, avoiding the appearance of white spots in the steel and causing hydrogen embrittlement;

Continuous casting: the target temperature of the molten steel in the tundish is controlled at 10 to 40°C above the liquidus temperature, and Φ380mm to Φ700mm round billets are continuously cast.

[0037] Forging route: round billet heating → forging → slow cooling.

[0038] Valve body heat treatment: trolley furnace heating → insulation → quenching → trolley furnace heating → insulation → quenching → tempering → insulation → water cooling.

[0039] Machining route: valve body rough turning → flaw detection → valve body fine turning → grinding → flaw detection.

[0040] The heat treatment is carried out according to the following steps:

(1) Step quenching: heating the Christmas tree valve body to 900 to 940°C, keeping warm, and then water cooling to below 100°C; heating again to 840 to 880°C, keeping warm, and then water cooling to below 100°C. The heating rate of each heating is 50 to 110°C /h, and the each heat holding time is t=0.4 to 1.0×S, S is the thickness of the wall of the valve body in mm, and t is in min;

(2) Tempering: heating the Christmas tree valve body to T=580 to 680°C, keeping warm, and then water cooling to below 100°C. The heating rate is 50 to 110°C /h, the heat holding time t1 meets that t1= 0.8 to 2.0×S, S is the thickness of the wall of the valve body in mm, t1 is in min; the parameters of the tempering process should meet that $Y = T \times (S / 10 + lgt1) / 1000$, $24.75 \leq Y \leq 28.95$.

[0041] The performance test method of the long-life, high-toughness and corrosion-resistant steel for subsea Christmas tree valve body prepared by the above process is as follows.

[0042] Structure: taking samples on the valve body extension, and taking samples within the 1/4 thickness of the extension (the thickness is 400mm) for metallographic and grain size analysis.

[0043] Performance: taking samples on the valve body extension, and taking samples subjected to streching, impact, corrosion and fatigue within the 1/4 thickness of the extension (thickness is 400 mm). Performance tests were performed with reference to GB/T228, GB/T229, GB/T5776 and GB/T7733.

[0044] The present application is described in detail below in conjunction with the embodiments.

[0045] The chemical composition and weight percentage of the long-life, high-toughness and corrosion-resistant steel for subsea Christmas tree valve body in each Example and Comparative Example are shown in Table 1, with the balance being iron and inevitable impurities.

Table 1

Steel type	C	Si	Mn	Cr	Ni	Mo	Cu	Al
Example 1	0.22	0.28	1.19	1.31	0.38	0.53	0.38	0.018
Example 2	0.25	0.22	1.38	1.48	0.36	0.68	0.46	0.034
Example 3	0.28	0.34	1.24	1.42	0.31	0.56	0.39	0.021
Comparative Example 1	0.22	0.18	1.14	1.41	0.32	0.52	0.35	0.025
Comparative Example 2	0.27	0.17	1.36	1.33	0.31	0.61	0.49	0.028
Comparative Example 3	0.30	0.32	1.35	1.49	0.38	0.67	0.31	0.031

(continued)

	P	S	N	O	A value	D value	X value	
Example 1	0.009	0.009	0.0044	0.0035	237	53.8	5.6	
Example 2	0.011	0.008	0.0043	0.0032	266	62.0	6.8	
Example 3	0.010	0.009	0.0038	0.0028	274	53.3	5.5	
Comparative Example 1	0.012	0.003	0.0045	0.0031	225	51.9	5.3	
Comparative Example 2	0.008	0.004	0.0051	0.0024	271	60.4	7.5	
Comparative Example 3	0.007	0.005	0.0046	0.0033	281	58.6	3.3	

[0046] The heat treatment process parameters of the long-life, high-strength, corrosion-resistant steel for subsea tree valve body in each Example and Comparative Example are shown in Table 2.

Table 2

Steel type	Heat treatment process (thickness of valve body is 400 mm)		Parameter Y
	Quenching	Tempering	
Example 1	Heating to 920°C at a rate of 60°C /h, keeping warm for 300 minutes, and water cooling; then heating to 860°C at a rate of 80°C /h, keeping warm for 330 minutes, and then water cooling	Heating to 620°C at a rate of 70°C/h, then keeping warm for 720 minutes, and water cooling	26.57
Example 2	Heating to 900°C at a rate of 75°C /h, keeping warm for 400 minutes, and water cooling; then heat to 840°C at a rate of 95°C /h, keeping warm for 360 minutes, and then water cooling	Heating to 640°C at a rate of 90°C/h, then keeping warm for 480 minutes and water cooling	27.32
Example 3	Heating to 940°C at a rate of 100°C/h, keeping warm for 300 minutes, and water cooling; then heating to 860°C at a rate of 95°C/h, keeping warm for 380 minutes, and then water cooling	Heating to 660°C at a rate of 80°C/h, then keeping warm for 440 minutes and water cooling	28.14
Comparative Example 1	Heating to 920°C at a rate of 60°C/h, keeping warm for 380 minutes, and water cooling; then heating to 870°C at a rate of 90°C/h, keeping warm for 360 minutes, and then water cooling	Heating to 620°C at a rate of 90°C/h, then keeping warm for 680 minutes, and water cooling	26.56
Comparative Example 2	Heating to 840°C at a rate of 95°C/h, keeping warm for 400 minutes, and water cooling; then heating to 980°C at a rate of 90°C/h, keeping warm for 380 minutes, and water cooling	Heating to 680°C at a rate of 100°C/h, then keeping warm for 840 minutes, and water cooling	29.19
Comparative Example 3	Heating to 910°C at a rate of 60°C/h, keeping warm for 400 minutes, and water cooling; then heating to 870°C at a rate of 80°C/h, keeping warm for 360 minutes, and then water cooling	Heating to 630°C at a rate of 80°C/h, then keeping warm for 680 minutes, and water cooling	26.98

[0047] The test results of the mechanical properties of the long-life, high-strength, corrosion-resistant steel for subsea tree valve body in each Example and Comparative Example are shown in Table 3.

Table 3 The mechanical performance detection list of each Example and Comparative Example.

Steel type	Metallographic structure	Grain size/μm	Properties after heat treatment					Corrosion rate in seawater environment (mm/year)	Corrosion fatigue strength in seawater environment (2×10^7cycle) (MPa)
			R_m/MPa	$R_{p0.2}$/MPa	A/%	Z/%	-46°C KV_2/J		
Example 1	Tempered sorbite	24.6	867	698	22.5	73.5	243	0.07	353
Example 2	Tempered sorbite	20.9	889	716	21.5	71.5	256	0.06	367
Example 3	Tempered sorbite	23.9	913	730	21.5	70.5	233	0.07	371
Comparative Example 1	Tempered sorbite	24.6	833	643	18.5	70.5	178	0.10	324
Comparative Example 2	Tempered sorbite	29.7	843	665	16.5	58.5	163	0.09	336
Comparative Example 3	Tempered sorbite	24.6	903	727	11.5	52.5	198	0.15	348

[0048] It can be seen from the above data that the strength, plasticity, toughness and corrosion resistance of the steels in Examples 1-3 controlled according to the present application are all better. In Comparative Example 1, though the content of each chemical composition and the heat treatment process are controlled according to the scope of the present application, the improper control of A value, D value and X value leads to low material strength, and insufficient plastic toughness, corrosion resistance and fatigue performance. In Comparative Example 2, although the composition design is reasonable, the heat treatment process is improper, resulting in coarse grains of the material, and insufficient strength, toughness, and insufficient corrosion and fatigue performance. In Comparative Example 3, due to improper control of the content of some chemical components and the A value and X value, the material strength is too low, the toughness is insufficient, and the corrosion and fatigue properties are insufficient.

[0049] The detailed description of the long-life, high-strength, corrosion-resistant, corrosion-resistant steel for subsea tree valve body and its heat treatment and production methods as described above with reference to the examples is illustrative rather than restrictive. Several examples can be illustrated according to the limited scope. Therefore, changes and modifications without departing from the general concept of the present application shall fall within the protection scope of the present application.

Claims

1. A long-life, high-toughness and corrosion-resistant steel for an subsea Christmas tree valve body, comprising the following chemical components in weight percentage: C 0.22% to 0.28%, Si 0.15% to 0.35%, Mn 1.1% to 1.4%, Cr 1.3% to 1.5%, Mo 0.5% to 0.6%, Ni 0.30% to 0.40%, Cu 0.30% to 0.50%, Al 0.015% to 0.035%, P ≤ 0.015%, S ≤ 0.015%, N ≤ 0.0080%, O ≤ 0.004%, with the balance being Fe and other inevitable impurities;

   wherein, $A=457\times(C-0.077\times Cr)+45\times Cr+80\times Si+50\times Mn+10\times Mo+96\times Cu$, $230\% \leq A \leq 275\%$;

   $$D=30\times Ni+20\times Mo+16\times Cu+22\times Mn-12\times Si\times Mn+28\times C-10\times C\times Mn,\ D\geq 52.5\%;$$

   $$X=26\times Cu+4\times Ni+1.2\times Cr-1.5\times Si-7\times Cu\times Ni-5\times Mn,\ X\geq 5.4\%;$$

   a metallographic structure of the long-life, high-toughness and corrosion-resistant steel for the subsea Christmas tree valve body is tempered sorbite, and a grain size is 20-25 μm.

2. The long-life, high-toughness and corrosion-resistant steel for an subsea Christmas tree valve body according to claim 1, wherein the long-life, high-toughness and corrosion-resistant steel for the subsea Christmas tree valve body has a tensile strength of ≥ 860MPa, a yield strength of ≥ 690MPa, -46°C KV_2 ≥ 230J, A ≥ 20%, and Z ≥ 70% at 1/4 thickness; a corrosion rate in seawater environment of ≤0.07mm/a; and a fatigue strength after 2×10^7 cycles of corrosion in seawater environment of ≥350MPa.

3. A heat treatment method for the long-life, high-toughness and corrosion-resistant steel for the subsea Christmas tree valve body according to claim 1 or 2, wherein the heat treatment method comprises the following steps:

(1) step quenching: heating the Christmas tree valve body to 900 to 940°C, keeping warm, and then water cooling; then heating to 840 to 880°C, keeping warm, and then water cooling; and
(2) tempering: heating the Christmas tree valve body to T=580 to 680°C, keeping warm, and then water cooling.

4. The heat treatment method according to claim 3, wherein in the step (1), heating rate of each heating is 50 to 110°C/h, and each heat holding time is t=0.4 to 1.0×S, wherein S is a thickness of a wall of the Christmas tree valve body in mm, and t is in min.

5. The heat treatment method according to claim 3, wherein in the step (2), heating rate is 50 to 110°C/h, and heat holding time is t1=0.8 to 2.0×S, wherein S is a thickness of the Christmas tree valve body in mm, and t1 is in min.

6. The heat treatment method according to claim 5, wherein parameters of the tempering process meet the following conditions: $Y=T\times(S/10+\lg t1)/1000$, $24.75\leq Y\leq 28.95$.

7. A production method for the long-life, high-toughness and corrosion-resistant steel for an subsea Christmas tree valve body according to claim 1 or 2, wherein the production method comprises the following steps: arc furnace or converter smelting → LF furnace refining → RH or VD vacuum degassing → round billet continuous casting → round billet heating → forging into valve body → heat treatment → machining → packaging and warehousing, wherein the heat treatment is carried out by the heat treatment method as described in any one of claims 3 to 6.

8. The production method according to claim 7, wherein a diameter of the round billet is Φ380mm to Φ700mm.

9. The production method according to claim 7, wherein the machining comprises: valve body rough turning → flaw detection → valve body fine turning → grinding → flaw detection.

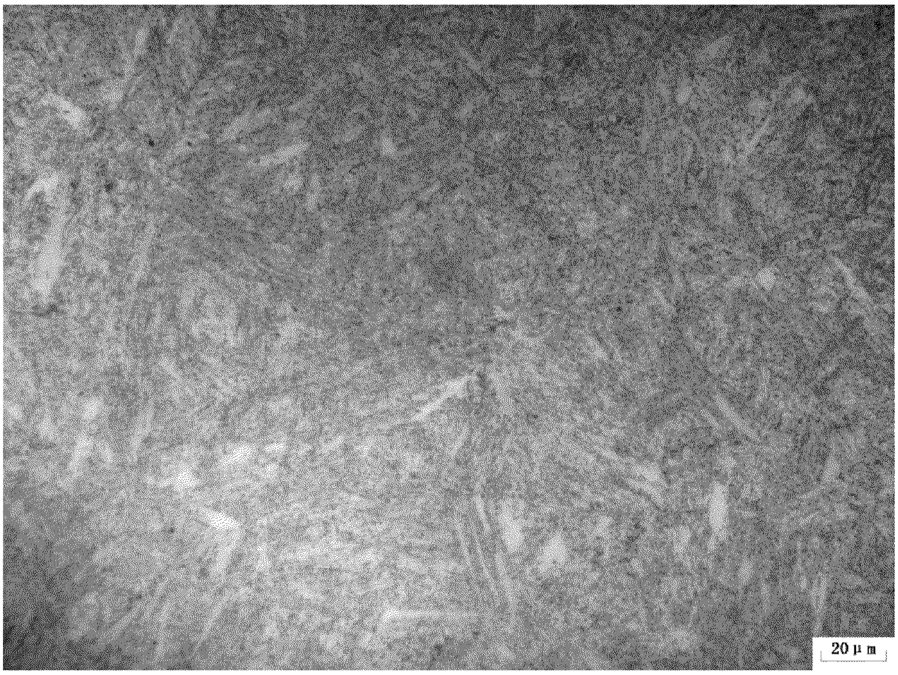

FIG. 1

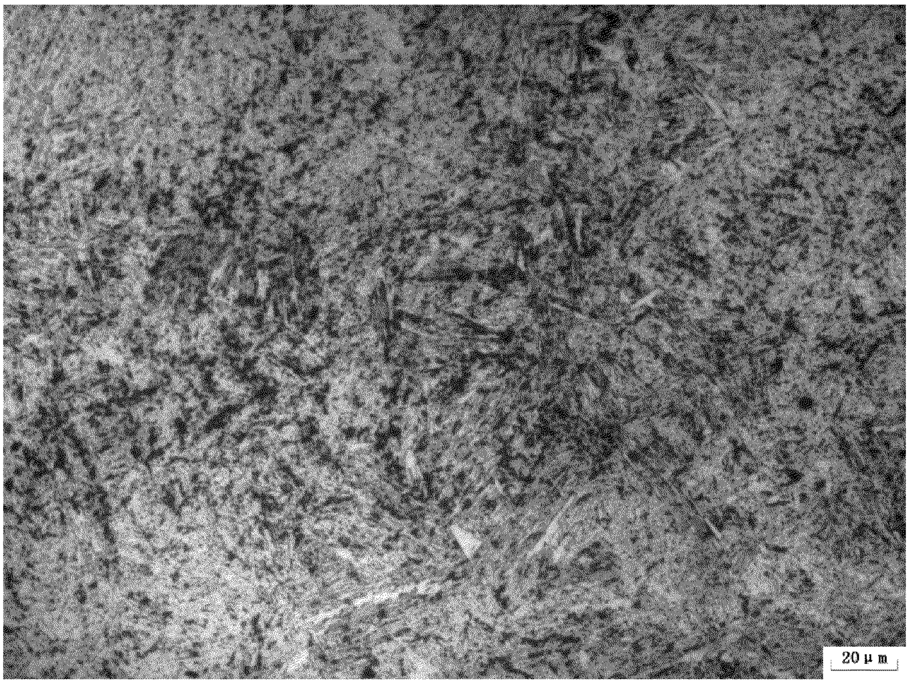

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/079637

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/02(2006.01)i; C22C38/04(2006.01)i;C22C38/44(2006.01)i;C22C38/42(2006.01)i;C21D1/18(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，C21D1

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

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

CNTXT, WPABSC, WPABS, ENTXT, DWPI, ENTXTC, Patentics: 马鞍山钢铁股份有限公司, 杨志强, 汪开忠, 胡芳忠, 王自敏, 陈世杰, 吴林, 杨少朋, 金国忠, 碳, 硅, 锰, 铬, 钼, 镍, 铜, 铝, 回火索氏体, 淬火, 回火, 阀, 耐蚀, 腐蚀, 耐腐, C, carbon, Si, silicon, Mn, manganese, Cu, copper, Ni, nickel, Cr, chromium, Mo, molybdenum, Al, alumin?um, valve, quench, temper, sorbite, sorbitic, corrosion

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 114561593 A (MAANSHAN IRON & STEEL CO., LTD.) 31 May 2022 (2022-05-31) claims 1-10	1-9
A	CN 101440460 A (SHANDONG MOLONG PETROLEUM MACHINERY CO., LTD.) 27 May 2009 (2009-05-27) description, page 2, paragraph 4, page 3, paragraph 1, and page 8, paragraph 2	1-9
A	CN 1948538 A (TIANJIN STEEL PIPE GROUP CO., LTD.) 18 April 2007 (2007-04-18) entire document	1-9
A	CN 113493882 A (MAANSHAN IRON & STEEL CO., LTD.) 12 October 2021 (2021-10-12) entire document	1-9
A	CN 101892443 A (TIANJIN PIPE (GROUP) CORP.) 24 November 2010 (2010-11-24) entire document	1-9
A	CN 102199730 A (BAOSHAN IRON & STEEL CO., LTD.) 28 September 2011 (2011-09-28) entire document	1-9

☑ 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
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"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
09 May 2023	**15 May 2023**

Name and mailing address of the ISA/CN	Authorized officer
China National Intellectual Property Administration (ISA/CN) **China No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088**	 Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/079637

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2023/079637

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CN 1948538 A	18 April 2007	None	
CN 113493882 A	12 October 2021	None	
CN 101892443 A	24 November 2010	None	
CN 102199730 A	28 September 2011	None	
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