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(54) R6 HIGH TOUGHNESS OFFSHORE MOORING CHAIN STEEL APPLICABLE TO ANCHOR MOORED POSITIONING CATHODIC PROTECTION FLOATING BODY AND MOORING CHAIN THEREOF

(57) The present application relates to a steel for grade R6 high strength and high toughness offshore mooring chain with tensile strength 1100-1250Mpa for use in anchoring and mooring floating bodies with cathodic protection: the chemical composition are C 0.18~0.24%, N 0.006~0.024, P 0.005~ 0.025, S ≤0.005, Si 0.15~0.35, Mn 0.20~0.40, Cr 1.40~2.60, Ni 0.80~3.20, Mo 0.35~0.75, Cu ≤0.50, Al ≤0.02, Ti ≤0.005, V 0.04~0.12, Nb 0.02~0.05, Ca 0.0005~0.004, O ≤0.0015, H ≤0.00015, the balance is Fe and unavoidable impurity elements; the total content of alloy $\sum M = (Si + Mn + Cr + Ni + Mo + Cu)$, $3.4 < \sum M \leq 6.8$; the total content of microalloy $\sum MM = (Ti + Al + Nb + V)$, $0.065 \leq \sum MM \leq 0.194$. The corrosion potential is adjusted to prevent hydrogen

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embrittlement caused by cathodic overprotection on the basic premise of maintaining the strength, toughness and low corrosion rate of the steel. Where V is only used for strengthening, and the content of N in VCN is increased, especially for the increase of the temperature for chain quenching to make M3C, M2C and VCN fully dissolved in solid solution and fully precipitated in tempering, which improves the precipitation strengthening effect and counteracts the weakening of mechanical properties that may be caused by limiting the total content of alloy, so as to produce a grade R6 complex bainitic chain steel which have low crack sensitivity and small difference between surface and internal microstructure and properties.

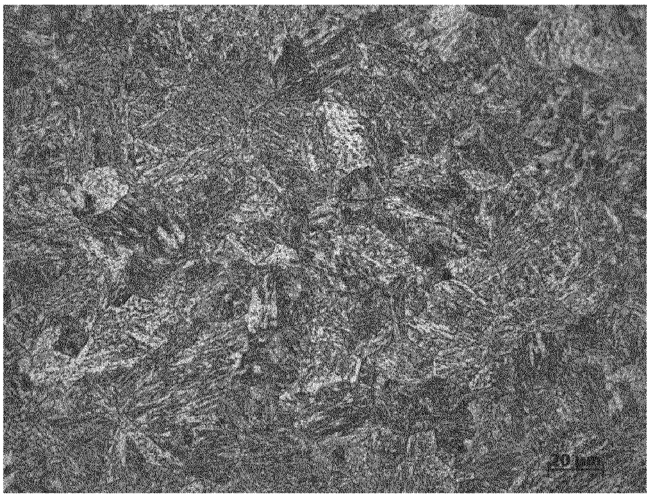

Figure 1

Description

Technical Field

[0001] The present application relates to alloy steel and ferrous metallurgical products for offshore engineering, in particular a grade R6 steel and chain for offshore mooring in the steel series for offshore mooring chain and the evaluation of its offshore environmental performance degradation resistance.

Background Art

[0002] A mooring system is acquired for positioning and mooring with floating bodies in the process of the marine exploration, deep-sea oil and gas extraction, national defense construction and so on. The main component of the mooring system is offshore mooring chain by the steel. According to the standard in DNVGL(Det Norske Veritas-Germanischer Lloyd) named Offshore Standards, DNVGL-OS-E302 Offshore mooring chain, Edition July 2018, the offshore mooring chain can be classified into six grades called R3, R3S, R4, R4S, R5, and R6 according to its strength grading. The tensile strength of the chains at all grades after overall quenching-tempering shall be equal or greater than 690 MPa, 770 MPa, 860 MPa, 960 MPa, 1000 MPa, and 1100 MPa respectively. The grade R5 is the highest grade of the mooring chain produced and used at home and abroad by the first half of the year of 2018.

[0003] The long mooring chain for positioning can be divided into two types which are stud and studless for drilling type and production type of the floating bodies respectively. The length of a single chain can reach several kilometers. Alloy steel bars of diameter 52-230 mm are used accordingly. All offshore mooring chain steels have an ultrahigh strength, as marine steel with a tensile strength above 690 MPa is ultrahigh-strength steel according to DNVGL.

[0004] The qualified mechanical properties and service performance of the offshore mooring chain are requisite in the offshore environment. When the strength of the chain is obtained by heat treatment of the final product, its toughness, especially the toughness of the flash weld area, must be ensured for the safety and reliability for resisting wild winds and huge waves. The chain is usually continuously treated in a special vertical furnace, i.e. the final performance of the chain is obtained after continuous quenching and tempering heat treatment. The accessories are forged from the steel, and their final properties are obtained through intermittent heat treatment.

[0005] It is seen that more than 51% of accidents have something to do with offshore mooring chains from the statistics of frequent accidents of floating bodies in the past decades. There have even been catastrophic accidents in which the platform capsized caused by the fracture of the chain.

[0006] From 2008 to 2018, Slow Strain Rate Testing (SSRT) in seawater was used to evaluate the degradation resistance of offshore environmental performance of the grade of the offshore mooring chain whose tensile strength ≥ 960 MPa and has high strength and toughness, so as to realize the lightweight of offshore floating bodies through ultrahigh-strength and ensure its service reliability at the same time.

[0007] DNVGL has defined grade R6 chain as the extreme technology and performance of the offshore mooring chain since 2013, and the provisional standard was not be terminated until 2018. DNVGL officially announced a standards includeing the grade R6 chain, specifying the performance of the chain and the basic process requirements of the production of the chain steel in July 2018.

[0008] DNVGL also proposed an additional standard named Class programme-DNVGL-CP-0237, Edition July 2018, Offshore mooring chain and accessories which evaluates the EAC (environment assisted cracking) of grade R6 chain under CP (cathodic protection) conditions according to the standards of ASTM G129 and ASTM E1820. The specific requirement is to carry out two tests: the one is SSRT with the applied potential of -850 mV, -1200 mV(saturated calomel electrode SCE) and strain rate of ≤ 10^{-5}/s; the other is the K_{IEAC} test (fracture toughness type I in seawater) with CT (conpact tension) specimen, applied potential of -950 mV, -1050mV (SCE) and the test speed of ≤$6x10^{-9}$m/s in seawater. So as to evaluate the degradation resistance of grade R6 chain in the seawater environment.

[0009] The seawater environment is generally considered as the service forbidden zone for ultrahigh-strength steel with yield strength over 1000MPa.

[0010] As mentioned before, the main way to lighten the chain is ultrahigh intensification. There is a restraining relationship each other between strength and toughness, and the same is true of the relationship between strength and deterioration resistance of service performance in the seawater environment. Once the strength is improved, there must be a decrease of toughness, plasticity and the degradation resistance in the seawater environment performance. But according to DNVGL, when the strength is increased, the toughness is increased instead of decreasing with its EAC evaluated at the same time.

[0011] Although there is the kind of steel meeting the mechanical properties requirements of the grade R6 chain produced by the existing technology, DNVGL proposes the above additional requirements for the evaluation of EAC of the chain by impressed cathodic protection potential of the grade R6 chain for the sake of reliability. This is a new challenge in the research and development of the ultrahigh-strength chain.

[0012] There is a China Invention Patent No. CN103667953B named *An Ultra High Strength and Toughness Offshore Mooring Chain Steel with Low Environment Assisted Cracking Sensitivity and its Manufacturing Method,* which discloses the composition range of the grade R6 chain steel and its mechanical properties with quenched-tempered, and provides the service performance constant of the steel in the seawater environment, that is, corresponds to the critical hydrogen content of the determining fracture strength without hydrogen embrittlement crack and the threshold value of fracture toughness without stress corrosion crack in seawater as quenched-tempered. The invention has passed the acceptance of the expert committee organized by the Ministry of industry and information technology, as actural product, the steel and the chain in the invention meet and exceed the temporary standards of mechanical properties and seawater environmental service performance of the grade R6 chain. Vanadium are the element for refining or strengthening effect in the form of VC in the invention. The invention does not cover the technology to balance corrosion potential and cathodic protection potential to prevent embrittlement by hydrogen generation of the chain caused by cathodic overprotection, coping with new standard.

[0013] The content of evaluating the embrittlement by hydrogen generation caused by cathodic protection is added in the latest standards of DNVGL2018 under the premise of ensuring the mechanical properties of the chain. While the reliability of the chain mainly depends on the overall performance given by the steel.

[0014] There is another Chinese invention patent No. CN101161843A named *A Method to Improve the Utilization Ratio of Vanadium Alloy with V-N (vanadium-nitrogen) Micro-alloyed High Strength Steel,* which proposed the process to control the V/N ratio of air-cooled steel to the range of $4 \leq V/N \leq 6$ and the precipitation of VN. Because Al (aluminum) is the deoxidizer of low-carbon deoxidized killed steel, and there is an unavoidable residual Ti (titanium) with more affinity with N (nitrogen). When the proportion of the residual Al in the molten steel from the embodiment of the invention is 0.025-0.035wt%, and the majority of N has been consumed by TiN (titanium nitride) and AlN (aluminum nitride) formed in the early stage, it is impossible to come into being VN, and it is impossible to realize the expectation of $4 \leq V/N \leq 6$ too.

[0015] The utilization of nitrogen as austenitic grain refinement elements whose content is in the range of 0.006-0.024 for a class of offshore mooring chain steel and the precise matching technology of Ti, Al, Nb, and V are disclosed in *A Heat Treatment Method for a Class of Offshore Mooring Chain Steels and its Chain,* Invention Patent, China, No. CN201611001805.3.

[0016] And there is another China invention patent application No.201810638000.2 titled *A Kind of ultrahigh-strength and Toughness Steel with Tensile Strength of 1100 MPa and its Manufacturing Method.* The invented steel is specified to be used to manufacture the grade R6 high-performance offshore mooring chain for offshore platforms and others. The C content of this invented steel is 0.245-0.350% and the steel has the microstructure of tempered martensite and tempered bainite and retained austenite. From the embodiments in this invention No. 201810638000.2 which will be one of the contrast embodiments in present invention, it can be seen that the surface after quenching is all martensitic microstructure with low transformation temperature and strong cooling crack sensitivity. The toughness of base and weld of the chain are reduced below the qualified line by coarse eutectic niobiumcarbide. The air cooling process is impossible to be implemented in the continuous heat treatment production line to avoid the low-temperature phase transformation crack although this patent requires air cooling after heattritment. In addition, retained austenite will decompose during the high-temperature tempering although austenite is beneficial to toughness and environmental performence.

[0017] Among the steels with trance amounts of V (vanadium), the steel with high content of N has a greater driving force for precipitation, higher density of precipitation phase, and greater strengthening effect, than that with the low content of N.

Disclosure of Invention

[0018] The technical problem to be solved by the present invention is to propose a new manufacturing scheme of a grade R6 offshore mooring chain as well as its steel for use in anchoring and mooring floating bodies with cathodic protection.

[0019] The precipitation strengthening effect and the toughness and a low corrosion rate of the chain are improved on the premise of ensuring the hardenability and reduces the corrosion potential when the total contents of alloy and microalloy are narrowed, to curb the embrittlement by hydrogen generation due to the chains are received by cathodic overprotection passively.

[0020] The specific scheme adopted by the present invention is as follows.

[0021] I. The chemical composition of the steel for grade R6 offshore mooring chain with high strength and high toughness

The chemical composition by wt% (percentage by weight) are as follows: C 0.18~0.24, N 0.006 ~0.024, P 0.005~0.025,S ≤0.005,Si 0.15~0.35, Mn 0.20~0.40, Cr 1.40~2.60, Ni 0.80~3.20, Mo 0.35~0.75, Cu ≤0.50, Al ≤0.02, Ti ≤0.005, V 0.04~0.12, Nb 0.02~0.05, Ca 0.0005~0.004, O ≤0.0015, H ≤0.00015, the rest is Fe and unavoidable impurity elements.

[0022] It is further defined that $0.22<(C+N)<0.26$; the total content of alloy $\sum M$ = (Si+Mn+Cr+Ni+Mo+Cu), and

3.4<∑M≤6.8; the total content of microalloy ∑MM =(Ti + Al + Nb + V), and 0.065 <∑MM≤0.194.

[0023] The content of N in the chemical composition is 0.016-0.024.

[0024] The chain is made of round bars corresponding to the above chain steel.

[0025] The present invention further limits the content of C and N and the range of ∑M and ∑MM on the basis of the related product composition applied by two the Chinese invention patents whose publication numbers are CN103667953 B and CN106636928A.

(1.1) The total content of narrowed alloy elements is ∑M= (Si+Mn+Cr+Ni+Mo+Cu).

(1.2) The total content of narrowed microalloy elements is ∑MM = (Ti + Al + Nb + V).

(1.3) The content of N is increased by a large margin and the content of C+N is controlled to make up for the decrease of strength and toughness caused by the narrowed range of additive alloy content, and the compensation theory can be seen below.

(1.4) In prior arts, the formation of TiN by using Ti in low-alloy steel is to prevent austenite grain growing. Although the solid solubility product of Ti and N is very small, the ability to refine grains is constrained due to the large scale of TiN precipitated at high temperatures. In the present invention the content of residual Ti in the steel is controlled for two reasons: one is to reduce the consumption of N caused by Ti, ensure the N content of NbCN, and reduce its solid solubility product, so as to improve its ability of hindering the growth of austenite grain, and improve the N content of VCN; the other is to prevent Ti from polluting the steel ladle.

(1.5) The main deoxidizing element of the steel in the present invention is Al, which is used for sufficient predeoxidation. And the content of residual Al after the final deoxidation is controlled no more than 0.02 to reduce the consumption of N caused by Al.

(1.6) The Nb content in the present invention is limited to 0.02-0.05, and NbCN is precipited from the steel, and the effect of NbCN inhibiting the growth of austenite grain is stronger than that of NbC. After the steel is made into the chain link, the chain temperature is increased from ≤ 920°C to ≥ 980°C during the quenching heating, and microstructure of the chain after austenitizing is transformed into BU (upper bainite) during cooling. The initial phase transformation temperature of BU and martensite is Bs and Ms, respectively, and Bs(~500°C) is higher then Ms(~320°C). The cooling crack sensitivity decreases with the increase of the phase transformation temperature.

(1.7) The V content in the present invention is controlled to be from 0.04 to 0.12, and when the content of the residual N is ensured, VCN precipitates with an average size of 2 nm are formed in the chain during tempering, wherein nearly half of the total amount of V is in the form of VCN. These precipitates are useful for improving the strength and toughness of the steel.

[0026] II. Based on the chemical composition of the present application, the precipitation of the offshore mooring chain steel of the present application follows the rules below.

(2.1) The nitride and carbonitride are controlled to be precipitated in the sequence of TiN-AlN-NbCN-VCN, on the basis of the general technology that is smelting, bloom continuous casting, blooming with high-temperature heating, intermediate billet heating, forging or rolling, chain making, flash welding and heat treatment, and so on. The solubility product of [Nb] [C+N] is smaller, and the effect of inhibiting the growth of austenite grain of [Nb] [C+N] is stronger than that of NbC. The existence of NbCN allows the temperature of the chain to increase from ≤ 920°C to ≥ 980°C before quenching. In addition, there is to the drag effect of solid solution of Nb on the grain boundary.

(2.2) The existing technology shows that the strengthening effect of VCN is better than that of VC, especially for the very fine MCN carbide with an average size of 2nm precipitated by tempering. In the present invention, the quenching temperature is increased, therefore M3C, M2C and VCN is fully solid soluble. In the present patent, V is as MCN (where M = V, Mo) to precipitate and increase the strengthening effect during tempering instead of being an element to prevent the growth of austenite grain in existing technologies. As the main composition of M in MCN is V, MCN is also expressed as VCN in engineering.

(2.3) Al is used as the main deoxidizing element and the subordinate element to increase the austenite coarsening temperature. By limiting the residual acid-soluble Al, i.e. Al_S, the consumption of N by Al can be reduced, and the residual content of N combined with Nb and V can be increased, that is to say, NbCN and VCN can be formed with the former effectively improving the austenite coarsening temperature and the latter increasing the strengthening effect.

(2.4) According to the equivalent ratio, Ti:N = 3.4, A1:N = 2:1, Nb:N = 6.6, V:N= 3.6. As compared with AlN, NbN has a stronger effect of preventing the growth of austenite grain and the N consumption of Nb is nearly 30% that of Al when the content the same as Al. Based on this, this application promotes the final combination of N with Nb and V through accurate control of element content.

(2.5) Even if Ti is not added in the steelmaking process of low or medium alloy structural steel, the final precipitation is usually VC rather than VN (VCN), as there is a large consumption of N caused by Ti brought in by raw materials and refractories, and caused by the residual Al before tapping as specified in the standard. Up to now, various technologies for controlling V/N ratio are difficult to implement accurately, and the present invention solves this problem by controlling the V content and increasing the N content in VC on the basis of the technology of controlling Ti, Al and Nb by adding N. See Table 1 for the examples of estimates of precipitates, nearly half of the total amount of V corresponds to a chemical equivalent ratio of V:N=3.6 in the VCN is precipitated by tempering.

Table 1 The examples of estimates of consumption of N to form TiN, AlN, NbN and VN, if N is 0.02 wt %

Example	Ti	Consumption of N(1)	Als	Consumption of N(2)	Nb
1	Such as residual Ti 0.004	0.0012N, precipitating TiN	Such as residual Al 0.015	0.0075N, precipitating AlN	Such as 0.035
2	Such as residual Ti 0.002	0.0006N, precipitating TiN	Such as residual Al 0.01	0.005N, precipitating AlN	Such as 0.025
	Consumption of N(3)	**Residual N**	**V**	**Consumption of N(4)**	**Proportion of V forming VN to total V**
1	0.0053N, precipitating NbN	0.02-0.0012-0.0075-0,0053 =0.006	Such as 0.05	0.006N and 0.0216V	0.43
2	0.0038N, precipitating NbN	0.02-0.0006-0.005-0.0038 =0.0106	Such as 0.08	0.0106 and 0.038V	0.48

[0027] III. The characteristics of microstructure in the offshore mooring chain based on the chemical composition and precipitation rules of the present application

[0028] Due to the combination and limited amount of alloy elements, the chain link is transformed into a composite bainite microstructure consisting of BU (upper bainite) with a small amount of BL (lower bainite) and M (martensite) during the cooling process after austenitizing. Take the position that has a distance that is about a third of radius from the surface of the chain for example, the volume fraction of BL+M is no more than 10%, without granular bainite and ferrite. The bainite microstructure with a higher phase transformation temperature is favorable for the full quenching of the whole section of the large diameter chain with poor cooling conditions and solves the problems of the large difference of microstructure and properties between the surface and the internal of the large diameter chain and the sensitivity of cooling cracks.

[0029] The phase transformation temperature of BU with Bs~500°C is higher than that of the martensite with Ms of ~320°C. The cooling crack sensitivity decreases with the increase of the phase transformation temperature.

[0030] IV. Based on the chemical composition, carbide precipitating and optical microstructure, laboratory corrosion potential and EAC of the finished product chain of the application

[0031] According to the requirements of users to evaluate EAC in advance, making chain and simulated quenching-tempering of the chain link are carried out first, then EAC test is carried out by sampling.

(4.1) Corrosion potential: the flat specimen from the chain is sampled and immersed in the artificial seawater prepared in accordance with ASTM d1141, and after immersion at the room temperature of 25°C for 80 hours, the laboratory stable corrosion potential is measured to be about -610 to -650 MV (SCE, reference calomel electrode);

(4.2) EAC of the chain is evaluated in accordance with the standard of DNVGL-CP-0237.

(4.2.1) SSRT: SSRT is carried out in the atmosphere and in artificial seawater, with no potential or with potential of - 850 mV, - 1200 mV (SCE); SSRT with axial cylindrical smooth specimen whose strain rate is ≤10-5/s; Zo and Z_E are the reductions of area measured with no potential and with potential after specimens are broken respectively; the Z_0/Z_E ratio indicates the degradation degree of EAC resistance.

(4.2.2) The KIEAC test of CT specimen: in artificial seawater, hydrogen is precharged for 48 hours when the potential is not applied, or applied by -950 mV and -1050mV (SCE). Then, stretch with a speed of $\leq 6\times10^{-9}$m/s, when no potential is applied, or the potential of -950 mV and -1050 mV (SCE) is applied. KQEACo and $KQEAC_E$

are the fracture toughness of specimen without potential and with potential respectively; $KQEAC_0/KQEAC_E$ indicates the degradation degree of EAC resistance.

[0032] When the KQEAC specimen meets the plane strain condition, the K_{IC} data is obtained, and the EAC here is expressed as KIEACE, $KIEAC_0$.
[0033] KQEAC of the weld zone of the chain is also tested for comparing the performance of the weld zone with that of the base.
[0034] The examples of implementation has been listtd the results of EAC test, and the data of the present invention is favorable when -950 mV,-1050 mV potential is applied.
[0035] The chain of the present invention is made of round bar having the corresponding chemical composition, and the round bar is processed in sequence by chain making, flash butt welding, and heat treatment to obtain the final product, wherein the heat treatment include high-temperature quenching with ≥ 980°Cand tempering with 600°C to 690°C. Quenching and tempering are cooled with water less than 50°C.
[0036] Round bar is made from continuous casting bloom or ingot having corresponding chemical composition, and in sequence by heating, blooming, rolling and slow cooling, in which the heating temperature is more than 1230°C, so that nitride and carbonitride are all dissolved in austenite; in the cooling process, due to the combination of micro-alloying elements MM and the limit of C+N, the precipitation sequence of nitride and carbonitride is TiN-AlN-NbCN-MCN.
[0037] The nitride and carbonitride are controlled to be precipitated in the sequence of TiN-AlN-NbCN-MCN on the basis of the general technology, that is smelting-bloom continuous casting-blooming with high temperature heating-intermediate billet heating-forging or rolling-chain making-flash butt welding-heat treatment, and so on. The solubility product of [Nb][C+N]is smaller, the effect of inhibiting the growth of austenite grain of NbCN is stronger than that of NbC, and the existence of NbCN (and solid solution of Nb) allows the temperature of the chain to increase from ≤ 920°C to ≥ 980°C before quenching.
[0038] Compared with the available technology, the characteristics of the present invention focus on:

(1) It is a cost-effective composite bainite type grade R6 chain steel with a narrowed range of total alloy and microalloy amount, stable properties and low process crack sensitivity.
(2) The strength and toughness of the offshore mooring chain products are stable, uniform and sufficient as the chain has a specific microstructure with precipitates and is formed by the composition control of the narrowed range of total alloy and microalloy amount, being combined with the heat treatment process.
(3) It is a further description of (2). In the present invention, the precipitation strengthening effect is improved, the potential ability of C, N, and microalloy are exerted when the alloy amount is constrained, and the N amount in VCN is increased; especially the quenching temperature of the chain is improved to make the VCN carbide in steel fully dissolved in solid solution and fully precipitated in tempering, which avoids the weakening of properties of the steel.
(4) It is a further description of (2). The fine austenite is transformed into the composite bainite mainly composed of BU after quenching, which improves the transformation temperature and solves the problems including the large difference in microstructure and properties between the surface and the interior of the large diameter chain and a low phase transformation temperature leads to cooling cracks sensitivity.
5) The corrosion potential in the invention is adjusted to prevent hydrogen embrittlement caused by cathodic over-protection on the basic premise of maintaining the strength, toughness and low corrosion rate of the steel.

Description of Figures

[0039]

Figure 1 The optical microscopy structure of carrying out example 2 of the invention, wherein the quenching structure is BU+BL+M, and (BL+M) ≤10%;
Figure 2 CCT schematic curve of the present invention
Figure 3 The optical microscopy structure with grain size number 9 (80%) to 7.5 (20%) original fine-grained austenite, which is shown is rolled once and quenched at 980°C after the blooming;
The size of the effective grain for toughening is smaller because of the existence of substructure;
Figure 4 The distribution of C, Cr, Mo and V atoms in type M2C and MC carbide, precipitated during quenching-tempering of the steel of the present invention, measured by three-dimensional atomic probe;
Figure 5 The sampling schematic of CT test, and z-x direction specimen is adopted in the invention;
Figure 6 The size of CT specimen according to DNVGL.
Figure 7 SSRT test by applied potential
Figure 8 CT test by applied potential

Mode(s) for Carrying Out the Invention

[0040] The present invention is further described in detail with reference to carrying out example.

[0041] Carrying out example (invention example) 1-4 and contrast example 3 are about the process wherein continuous casting bloom with the size of 390×510mm are rolled into the round bars with a diameter of 120mm, while contrast example 1, 2 and 4 are about the process that 420kg test ingots are forged into round bars with a diameter of 95mm, and then the round bars are processed in sequence by blanking, heating, bending, flash welding, forming chain and heat treatment (quenching + tempering) to obtain the finished chain. The performance data is the average value of the results of three groups of specimens. Numerical treatment of the third place after the decimal point: ≤4 discard and ≥6 into 1.

[0042] See Table 2 for the chemical composition of carrying out example 1 to 4 and contrast examples 1 to 4. See Table 3 for process parameters and performance of the chain, and see Table 4 for the size and test results of CT specimens. Some of the results of Table 4 have been collated and included in Table 3.

Table 2 The chemical composition wt,% of invention example 1 to 4 and contrast examples 1 to 4 in the present invention; the thermodynamic software estimation of the precipitation temperature of nitride(MN), carbonitride(MCN), carbide (MC)

Example	C	Si	Mn	Cr	Ni	Mo	Cu	∑M	Al	Nb	V	Ti	∑M M	N	S≤	P≤
Invention 1	0.21	0.28	0.27	1.4	1.1	0.5	0.21	3.76	0.018	0.04	0.06	0.002	0.12	0.019	0.002	0.010
Invention 2	0.22	0.34	0.38	1.75	2.1	0.48	0.25	5.30	0.016	0.036	0.047	0.002	0.101	0.020	0.002	0.010
Invention 3	0.23	0.32	0.34	1.95	3.1	0.68	0.4	6.79	0.019	0.05	0.12	0.003	0.192	0.023	0.002	0.010
Invention 4	0.22	0.17	0.23	1.45	0.84	0.49	0.28	3.46	0.01	0.022	0.06	0.001	0.093	0.018	0.002	0.010
Contrast 1	0.28	0.33	0.35	1.2	2.6	0.7	0.17	5.35	0.02	0.05	0.09	0.005	0.185	0.013	0.002	0.010
Contrast 2	0.23	0.25	0.29	1.8	0.8	0.39	0.15	3.68	0.019	0.048	0.07	0.002	0.139	0.005	0.002	0.010
Contrast 3	0.23	0.25	0.35	2.55	3.05	0.65	0.45	7.30	0.017	0.07	0.10	0.003	0.190	0.023	0.002	0.010
Contrast 4	0.24	0.25	0.35	2.10	0.95	0.49	0.11	4.25	0.05	0.05	0.09	0.006	0.196	0.018	0.002	0.010

Example	**Evaluated precipitation temperature of MN and MCN, °C**				**Precipitation sequence of MN or MC, MCN in the cooling process**
	TiN	**NbCN**	**VCN**	**AlN**	
Invention 1	1439	1079	939	1201	TiN-AlN-NbCN-VCN
Invention 2	1434	1102	928	1216	TiN-AlN-NbCN-VCN
Invention 3	1434	1105	965	1193	TiN-AlN-NbCN-VCN
Invention 4	1432	1104	949	1186	TiN-AlN-NbCN-VCN
Contrast 1	1430	1117	955	1209	TiN-AlN-NbC-VC

(continued)

Example	Evaluated precipitation temperature of MN and MCN, °C				Precipitation sequence of MN or MC, MCN in the cooling process
	TiN	NbCN	VCN	AlN	
Contrast 2	1332	1211	860	947	TiN-NbCN-AlN-VC
Contrast 3	1426	1207	948	1195	TiN-NbCN-AlN-VCN
Contrast 4	1442	1114	949	1248	TiN-AlN-NbC-VC

Table 3 Process parameters and performance of invention example of d120mm grade R6 steel and chain, as well as performance of their contrast examples

Example	C+N	∑M	∑MM	Quenching temperature of link	~Ms	~Bs	Temperin g	R_m	$R_{p0.2}$		
	wt%			°C				Base, MPa			
Stipulation	**0.22-0.26**	**3.4-6.8**	**0.065-0.194**					**1100-1250**	**(0.85-0.95) R_m**		
Invention								Average of three sets and rounded value of data			
1	0.229	3.76	0.12	980		500	610	1232	1135		
2	0.240	5.30	0.094	980		500	605	1245	1146		
3	0.253	6.79	0.192	980		500	635	1150	1041		
4	0.238	3.46	0.093	980		500	620	1211	1108		
Contrast											
1	0.293	5.35	0.185	910	320		615	1145	1064		
2	0.235	3.68	0.139	910	320		620	1080	995		
3	0.253	7.30	0.190	910		550	600	1205	1110 1123		
4	0.258	4.25	0.196	980	320		610	1170			
Example	**A**	**Z**	**CVN, -20°C**	**Rm-CVN, -20°C**	**corrosion potential**	**Δ =difference between -850mv and stable corrosion potential**	**SSRT**		**CT**		
							Applied potential, mV				
							-850	**-1200**	**-950**	**-1050**	
	Base, %		**Base, J**	**Weld, MPa-J**	**mV (SCE)**		**Z_E/Z_0**		**$K_{EAC\ E}/K_{EAC}$ or $K_{IEAC\ E}/K_{IEAC\ 0}$**		**γG No**
Stipulation	**12**	**50**	**60**	**1100-44**			**Reference**				**≥6**
Invention	**Average of three sets and rounded value of data**										
1	15	65	107	1234-66	-650	~200	65/66=~1	12/65=0.17			8.5

(continued)

Example	A	Z	CVN, -20°C	Rm-CVN, -20°C	corrosion potential	Δ =difference between -850mv and stable corrosion potential	SSRT		CT		
							Applied potential, mV				
							-850	-1200	-950	-1050	
	Base, %		Base, J	Weld, MPa-J	mV (SCE)		$Z_E/,Z_0$		$K_{EAC\,E}/K_{EAC}$ or $K_{IEAC\,E}/K_{IEAC\,0}$		γG No
Stipulation	**12**	**50**	**60**	**1100-44**			**Reference**				**≥6**
2	15	63	90	1251-58			64/63=~1	10/63=0.16		82.6/97.2=0.85 Conform to KIC	8.0
3	17	67	157		-618	~232			141.0/166.3=0.85		8.5
				1135-98					145.5/166.3=0.88 Weld line		
4	16	66	104	1189-90			66/65= ~ 1	12/66=0.18			7.5
Contrast											
1	14	57	55	1135-38			48.5/57=0 .85	7.8/56=0.14			6.0
2	17	69	61	1060-47	-						5.0
3	16	66	62	1195-44	-520	~330				78.5/104.6=0.75	6.5
4	15	65	55	1189-20							4.0

Table 4 Results of CT test with applied potential in seawater with hydrogen precharged for 48 hours

Example	B, mm	W, mm	a_0, mm	K, $MPm^{0.5}$	Potential, mV (SCE)	R_m, ~MPa	Plane strain	$K_{EAC\ E}/K_{EAC\ 0}$
Invention 2-1	25.13	49.86	32.442	97.2	Not applied	1250	satisfied	
Invention 2-2	25.14	49.84	32.476	82.6	-1050	1250	satisfied	K_{IEACE}/K_{IEAC0} =82.6/97.2=0.85
Contrast 3-1	25.08	49.72	32.070	104.6	Not applied	1200	Not satisfied	
Contrast 3-2	25.08	49.70	32.138	78.5	-1050	1200	Not satisfied	78.5/104.6=0.75
Invention 3-1	25.14	49.88	32.108	166.3	Not applied	1150	Not satisfied	
Invention 3-2	25.14	49.96	32.542	141.0	-950	1150	Not satisfied	141.0/166.3=0.85
Invention 3-3, Weld line	25.11	50.08	32.202	145.5	-950	1135	Not satisfied	145.5/166.3=0.88

[0043] Loading test: Zwick 50kN testing machine, made by Zwick Co., Germany; prefabricated fatigue crack: MTS 810 (100kN) electro-hydraulic servo testing machine system, made by MTS, Co., America; corrosion test device: seawater corrosion test container, equipped with slow tension and compact tension fixture; potentiostat: CHI660D electrochemical workstation, Shanghai Chenhua Instrument Co., China; pH value of artificial seawater is 8.2~7.0; 25 °C. See Figure 5-8 for specimens and tests.

[0044] The EAC test conditions are in accordance with DNVGL-CP-0237: EAC test is additionally required for the grade R6 chain. The SSRT and KIEAC (CT) test is included to evaluate EAC resistance. The SSRT test is carried out with no potential, potential of -850 mV, -1200 mV (SCE) and axial cylindrical smooth specimen in dry atmosphere and artificial seawater. The CT test is carried out with potential of -950, -1050 mV (SCE) and in artificial seawater. Z_E/Z_0 and $KQEAC_0$/ $KQEAC_E$ indicate the degradation degree of EAC resistance.

[0045] The results show that there is no significant difference between SSRT data of steel in a dry atmosphere and those in an artificial seawater environment, and all of them fluctuate within the error range. SSRT of the atmospheric environment is omitted in both The carrying out example and the contrast examples.

[0046] Z_0 and Z_E refer to the results of the reduction of area of SSRT without and with potential respectively. In artificial seawater, the potential is not added or added to -950 mV and -1200 mV (SCE). Strain rate $\leq 10^{-5}$/s.

[0047] $KQEAC_0$ and $KQEAC_E$ refer to the results of CT test without and with potential respectively. The CT specimen was precharged hydrogen for 48 hours. Tensile speed $\leq 6\times10^{-9}$m/s.

[0048] $KQEAC_0/KQEAC_E$ refers to the degradation degree of EAC resistance in the carrying out example and the contrast examples. When the KQEAC specimen meet the plane strain condition, the KIC data is obtained, and here $KIEAC_0$ and $KIEAC_E$ refer to the results of the CT test without and with potential respectively.

[0049] According to users' requirement of forward lead EAC evaluation (Do it in advance at the steel mill), chain making and simulated quenching-tempering are carried out first, then EAC test is carried out by sampling. KQEAC of the weld zone of the chain is also tested for the comparison of the performance of the weld zone and the base.

[0050] Carrying out example (invention example) 1-4 all conform to the range of the composition limitation of the present invention. On the premise of controlling the minimum content of Ti (controlling is inevitable in the industrial scale), the limited TiN and AlN combined with a small content of N are first precipitated in the cooling process of continuous casting bloom, according to the solubility product from small to large, which ensures the subsequent precipitation of NbCN and VCN. When the heat temperature is more than 1230°C, the continuous casting bloom is forged and rolled, AlN, NbCN, VCN, M3C and M2C was first all dissolved in austenite, and then precipitated during cooling. Among them, TiN, NbCN, and AlN do not dissolve when the chain is quenched at 980°C, which hinders the growth of austenite grain. NbCN, which is still insoluble at 1150°C, is used as the main precipitate to hinder the growth of austenite grain. M3C, M2C, and VCN are fully solid solution with a high-temperature quenching at 980°C, and then precipitated again during a high-temperature tempering. The quenching-tempering steel is strengthened by fine and dense VCN, so as to make up for the loss of strengthening effect caused by reducing the total content of alloy in the present invention. There are excellent mechanical properties such as strength, plasticity and toughness and others, and it is outstanding that the low-temperature impact value of the base and the weld are higher than the standard requirements. And mechanical properties value is abundant. The processing properties are well too, which can be seen from that B_S is about 500°C which is about 180°C higher than contrast example's Ms 320°C, the phase transformation temperature is higher, and the crack sensitivity is lower.

[0051] In the carrying out example 1, 2 and 4, the SSRT specimen was slowly stretched with applied potential -850mV (SCE) in artificial seawater at a strain rate of ≤ 10^{-5}/s, compared with the specimen without potential, the result shows that Z_E/Z_0=1, that is, the plasticity did not decrease. The contrast example 1, Z_E/Z_0=0.85. But when -1200mV (SCE) is applied, the slow tensile specimen is seriously embrittled as $Z_E/Z_0 \leq 0.18$ in both the carrying out example 1, 2, 4 and the contrast example 1.

[0052] In the carrying out example 2, with -1050mV (SCE) applied, $KIEAC_E/KIEAC_0$=0.85, which means that the EAC resistance did not significantly decrease. $KIEAC_E$ and KIEACo meet the plane strain condition and KIC criterion. This is the first KIEAC data of grade R6 steel obtained in the world.

[0053] In the carrying out example 3, with - 950mv (SCE) applied, the value of $KQEAC_0/KQEAC_E$ of the chain base and the weld are 0.85 and 0.88 respectively. And the EAC resistance of the weld is higher than that of the chain base. The KQEAC very high.

[0054] In the contrast example 3, with -1050 mV (SCE) applied, $KQEAC_0/KQEAC_E$ =0.75, which means that the EAC resistance decreases .

[0055] As a reference, the potential measured after immersion in seawater for 80 hours is used as the corrosion potential under laboratory conditions. The difference between corrosion potential and applied potential is overprotection potential.

[0056] Among them, the overprotection potential to - 850mV(SCE) in In the carrying out example 1 and 3 is about 200 and 232mV (SCE) respectively, which are within the allowable range. However, the overprotection potential to -1200mV (SCE) is about 550 and 580mv (SCE) respectively, which is hard to bear.

[0057] The carrying out example 1, 2 is compared with the contrast example 4, the strength is increased by 62-75 MPa by adopting similar quenching-tempering treatment, which shows that the strengthening effect of VCN is better than that of VC.

[0058] In the contrast example 1, Ms is low, it is sensitive to cooling crack, and C+N = 0.293, which is exceeded the scope of the invention, and the impact value is unqualified. Coarse NbCN particles of 100 μm class were found. There are only VC precipitates, no VCN precipitates.

[0059] In the contrast example 2, Ms is low, and it is sensitive to cooling crack; N has a low content, N is exhausted by first precipitated NbCN, and is not enough to form AlN. The impact value is 61J, which barely conform with the standard, but the tensile strength is as low as 1080 MPa, which is unqualified. There are only VC, no VCN.

[0060] In the contrast example 3, the total content of alloy exceeds the scope of the invention. The difference between -850 mV and its corrosion potential of -520 mV, that is, the overprotection potential is about 330 mV (SCE). SSRT test show a tendency of embrittlement. The content of Nb is as high as 0.07, and NbCN is precipitated before AlN.

[0061] In the contrast example 4, Ms is low, it is sensitive to cooling crack; with the increase of Al and Ti, the total content of micro-alloy elements exceeds the scope of the invention. Due to the consumption of N, N was exhausted when NbCN was precipitated. There are only VC, no VCN. The yield ratio is 0.96 and greater than regulation 0.95. The strengthening and toughening effects are not obvious when the quenching temperature is at 980°C. Impact toughness is unqualified.

[0062] In a word, there is no VCN precipitation in the contrast examples 1, 2 and 4, only VC is precipitated in tempering, and the precipitation strengthening effect of V is not ideal. And austenite grains are coarsened or begin to coarsen at 910 °C in all contrast examples; compared with all contrast example wherein there are fine austenite grains at the chain temperature of 980°C and the tempering temperature is allowed to increase (up to 635 °C when in the contrast example 3), the performance and process parameters of the contrast examples are entirety lower than those of the carrying out example of the present application.

[0063] Besides the above carrying out example, the present invention further includes other carrying out examples, and any technical solution formed by equivalent transformation or equivalent substitution shall fall within the protection scope of claims of the present invention.

Claims

1. A steel for grade R6 offshore mooring chain with high strength and high toughness for use in anchoring and mooring floating bodies with cathodic protection, wherein the chemical composition by wt% (percentage by weight) are as follows: C 0.18~0.24, N 0.006~0.024, P 0.005~0.025, S ≤0.005, Si 0.15~0.35, Mn 0.20~0.40, Cr 1.40~2.60, Ni 0.80~3.20, Mo 0.35~0.75, Cu ≤0.50, Al ≤0.02, Ti ≤0.005, V 0.04~0.12, Nb 0.02~0.05, Ca 0.0005~0.004, O ≤0.0015,

H ≤0.00015, the balance is Fe and unavoidable impurity elements;
It is further defined that 0.22 ≤ (C+N) ≤ 0.26; the total content of alloy ∑M = (Si + Mn + Cr + Ni + Mo + Cu), 3.4 ≤∑M ≤ 6.8; the total content of micro-alloy ∑MM = (Ti + Al + Nb + V), 0.065≤∑ MM ≤ 0.194.

2. The steel for grade R6 offshore mooring chain with high strength and high toughness for use in anchoring and mooring floating bodies with cathodic protection according to claim 1, wherein wt% of N in the chemical composition is 0.016-0.024.

3. A grade R6 offshore mooring chain with high strength and high toughness for use in anchoring and mooring floating bodies with cathodic protection, wherein the chemical composition by wt% (percentage by weight) are as follows:

C 0.18~0.24, N 0.006~0.024, P 0.005~0.025, S ≤0.005, Si 0.15~0.35, Mn 0.20~0.40, Cr 1.40~2.60, Ni 0.80~3.20, Mo 0.35~0.75, Cu ≤0.50, Al ≤0.02, Ti ≤0.005, V 0.04~0.12, Nb 0.02~ 0.05, Ca 0.0005~0.004, O ≤0.0015, H ≤0.00015 the balance is Fe and unavoidable impurity elements;
It is further defined that 0.22 ≤ (C+N) ≤ 0.26; the total content of alloy ∑ M = (Si + Mn + Cr + Ni + Mo + Cu), 3.4 ≤∑ M ≤ 6.8; the total content of micro-alloy ∑ MM = (Ti + Al + Nb + V), 0.065 ≤∑ MM ≤ 0.194.

4. The grade R6 offshore mooring chain with high strength and high toughness for use in anchoring and mooring floating bodies with cathodic protection according to claim 3, wherein wt% of N in the chemical composition is from 0.016 to 0.024.

5. The grade R6 high strength and high toughness offshore mooring chain for use in anchoring and mooring floating bodies with cathodic protection according to claim 3, wherein: with the combination and limitation of alloy element , composite bainite is transformed during the cooling process after the chain is austenitized, wherein the composite bainite is composed of upper bainite (BU), a small amount of lower bainite (BL) and martensite (M), and the microstructure does not include granular bainite or ferrite; at the position that has a distance that is about a third of radius from the surface of the chain, the volume fraction of BL + M is no more than 10% and the grain size of the prior austenite is between grade 7.5 and grade 9.0.

6. The grade R6 high-strength and high-toughness offshore mooring chain for use in anchoring and mooring floating bodies with cathodic protection according to claim 3, wherein: with the combination and limited content of micro-alloyed elements MM and the limited content of C+N, the chain microstructure contains the precipitated extremely fine MCN type carbonitride with an average size of 2nm, the carbonitride is VMoCN or VCN because its main composition of M(metal elements) is V, is written as VCN.

7. The grade R6 high-strength and high-toughness offshore mooring chain for use in anchoring and mooring floating bodies with cathodic protection according to claim 6, wherein: with the combination and limited content of microalloyed elements MM and the limited content of C+N, the N content of MCN type carbonitride is significantly increased, wherein nearly half of the total amount of V is in the form of VCN, when calculated in terms of chemical equivalent ratio of Ti: N = 3.4, Al: N = 2:1, Nb: N = 6.6, and V: N = 3.6.

8. The grade R6 high-strength and high-toughness offshore mooring chain for use in anchoring and mooring cathodic floating bodies with protection according to claim 3, wherein: the flat specimen of the chain is sampled and immersed in the artificial seawater prepared in accordance with ASTM d1141, and after immersion at the room temperature of 25°C for 80 hours, the laboratory stable corrosion potential is measured to be about -610 to -650 MV (SCE).

9. The grade R6 high-strength and high-toughness offshore mooring chain for use in anchoring and mooring floating bodies with cathodic protection according to claim 8, wherein: according to the standards of DNVGL, SSRT is carried out in artificial seawater under the condition of without electric potential, with the electric potential of -850 mV, -1200 mV (SCE), respectively, and the strain rate of cylindrical smooth specimen is $\leq 10^{-5}$/s; Zo and Z_E refer to the reduction of area without electric potential and with the electric potential of -850 mV or -1200 mV (SCE) respectively; when the applied potentials are -850 mV and -1200 mV (SCE), the value of Z_e/Z_0 are 1 and ≤ 0.18 respectively, that is, no embrittlement and serious embrittlement.

10. The grade R6 high-strength and high-toughness offshore mooring chain for use in anchoring and mooring floating bodies with cathodic protection according to claim 8, wherein: according to the standards of DNVGL, the compact tensile (CT) test with the tension speed of $\leq 6\times10^{-9}$m/s is carried out in artificial seawater under the condition of without electric potential, with the electric potential of -950, -1050mv (SCE), respectively; KQEACo and $KQEAC_E$

represent the results of the compact tensile test without electric potential and with electric potential respectively; when the CT specimen with precracking was precharged with hydrogen for 48 hours, the results of KQEACo and $KQEAC_E$ with applied potential of -1050 mV are met plane strain conditions, the criteria of KIC is satisfied, and the value of $KIEAC_E/KIEAC_0$ is 0.85; with an applied potential of -950 mV, the value of $KQEAC_0/KQEAC_E$ of the welding line is 0.88;When $KQEAC_0/KQEAC_E \geq 0.80$, the reduction of EAC resistance is within the controllable range, and the values of KIC and KQ of the chain are higher.

11. The grade R6 high-strength and high-toughness offshore mooring chain for use in anchoring and mooring floating bodies with cathodic protection according to claim 3, wherein: the chain is made of round bar having corresponding chemical composition, and the round bar is processed in sequence by chain making, flash butt welding, and heat treatment to obtain the final product, wherein the heat treatment include high-temperature quenching and tempering, with the high-temperature quenching temperature of ≥ 980°C, water quenching with the water temperature of lower than 50°C; and the tempering temperature is from 600°C to 690 °C, water cooling with the water temperature is lower than 50°C.

12. The grade R6 high-strength and high-toughness offshore mooring chain for use in anchoring and mooring floating bodies with cathodic protection according to claim 10, wherein: the round bar is made from continuous casting bloom or ingot having corresponding chemical composition, which is processed in sequence by heating, blooming, rolling and slow cooling, in which the heating temperature is more than 1230°C, so that nitride and carbonitride are all dissolved in austenite; in the cooling process, due to the combination of microalloying elements and the limited content of C+N, the precipitating sequence of nitride and carbonitride is TiN-AlN-NbCN-MCN.

13. The grade R6 high-strength and high-toughness offshore mooring chain for use in anchoring and mooring floating bodies with cathodic protection according to claim 1, which is also suitable for the production of long and flat structural steel with high strength and toughness.

14. The grade R6 high-strength and high-toughness offshore mooring chain steel for use in anchoring and mooring floating bodies with cathodic protection according to claim 1, which is also suitable for the production of long and flat structural steel with high strength and toughness and with the resistance to deterioration of seawater environmental service performance.

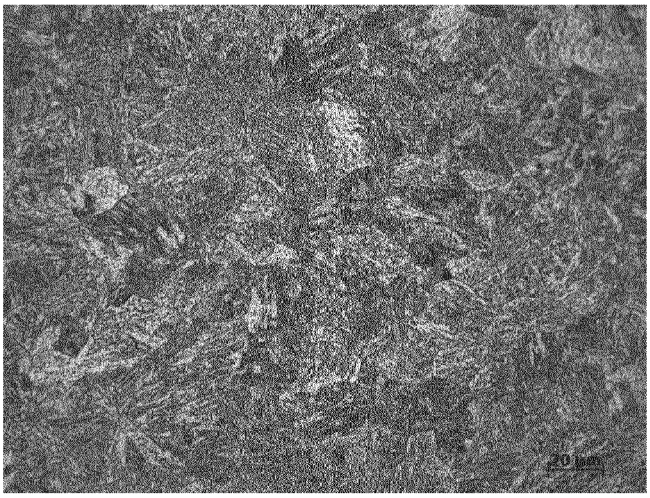

Figure 1

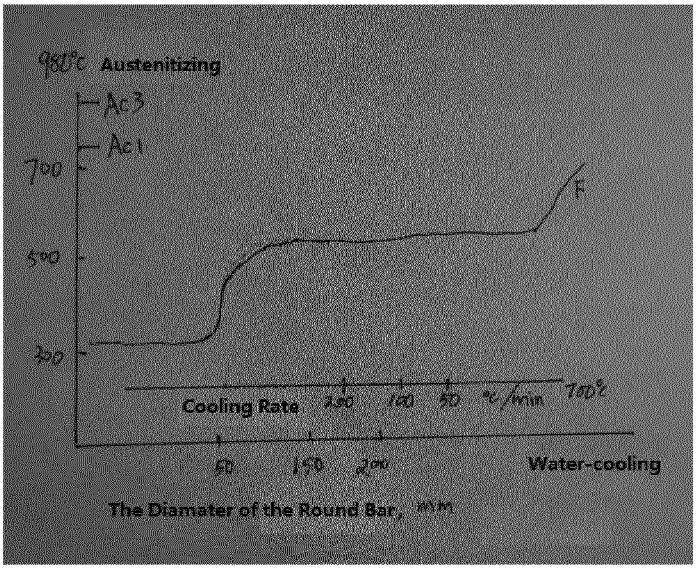

Figure 2

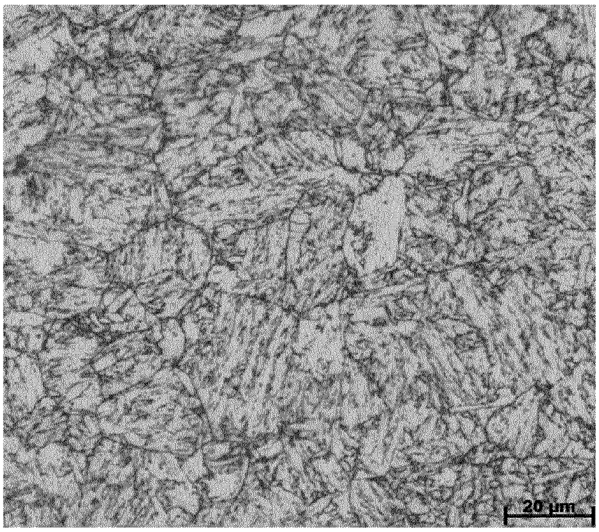

Figure 3

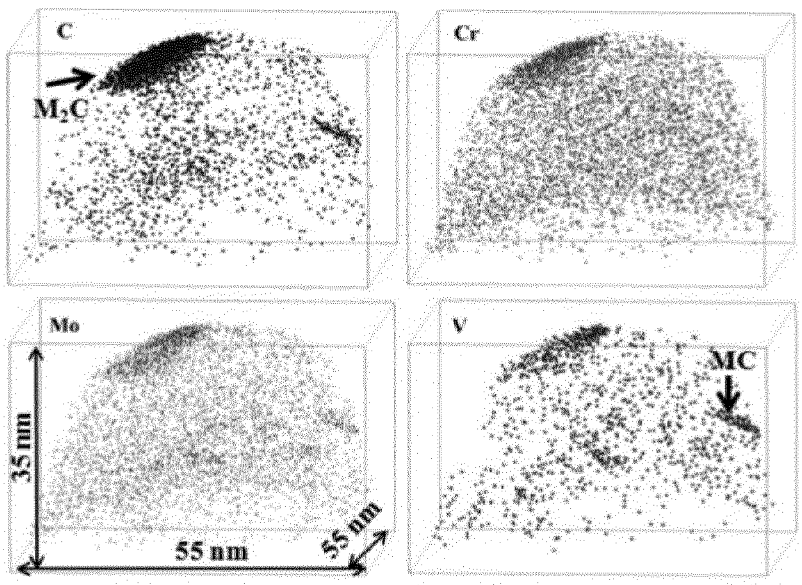

Figure 4

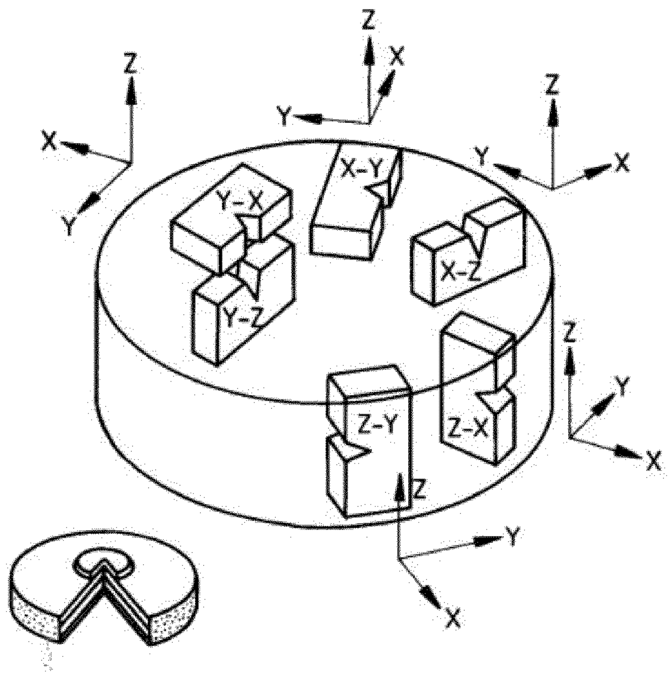

Figure 5

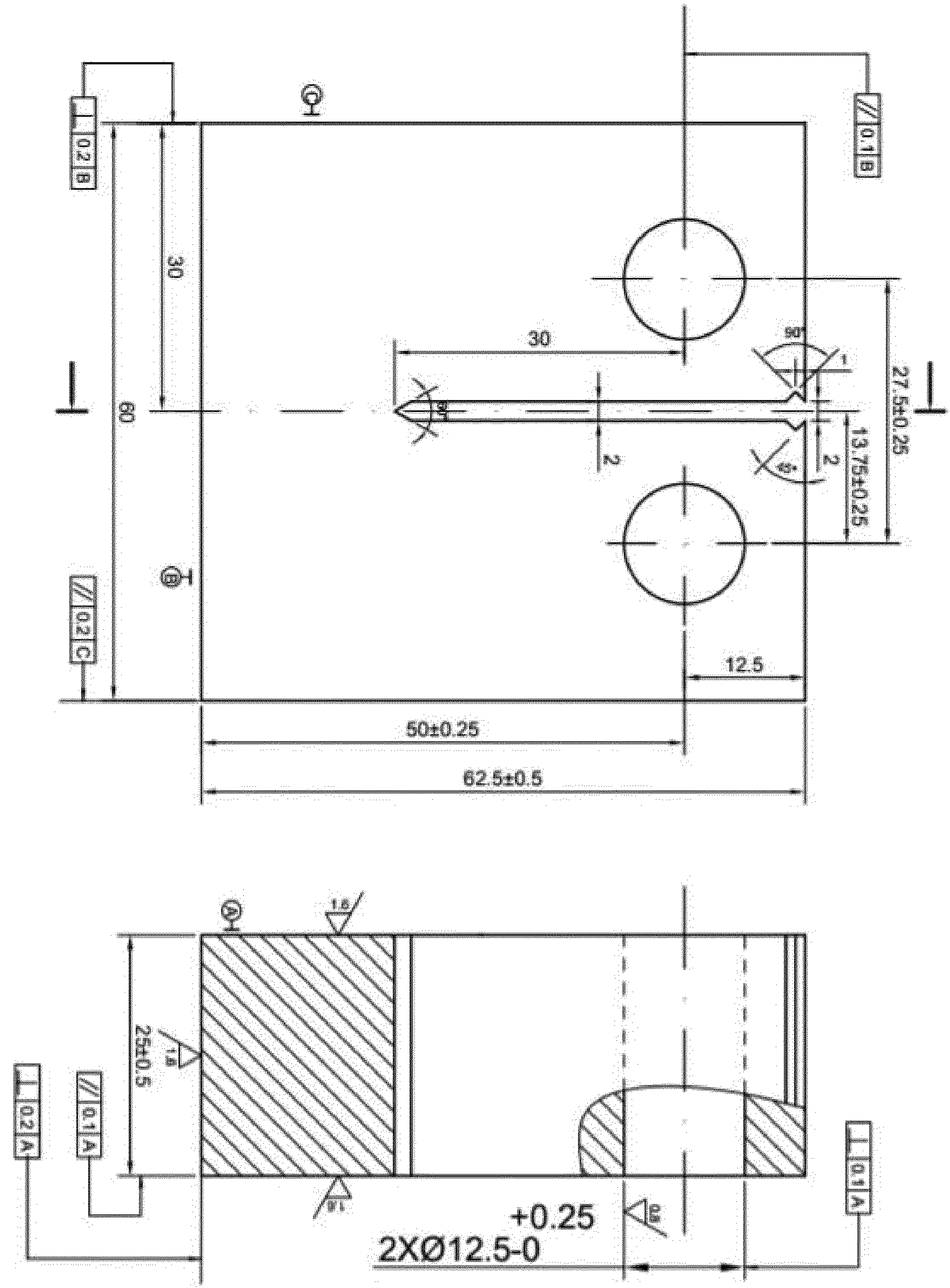
0.2 B
0.1 B
C
30
30
90°
1
27.5±0.25
60
2
2
45°
13.75±0.25
B
0.2 C
12.5
50±0.25
62.5±0.5
A
1.6
25±0.5
0.2 A
0.1 A
0.1 A
+0.25
2XØ12.5-0

Figure 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2019/087168

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/02(2006.01)i; C22C 38/04(2006.01)i; C22C 38/06(2006.01)i; C22C 38/42(2006.01)i; C22C 38/44(2006.01)i; C22C 38/46(2006.01)i; C22C 38/48(2006.01)i; C22C 38/50(2006.01)i; C21D 8/06(2006.01)i; C21D 1/18(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)

C22C 38，C21D 8，C21D 1

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)

DWPI, CNKI, CNABS, VEN: 泊链, 钢, 碳, 氮, 磷, 硫, 硅, 锰, 铬, 镍, 钼, 铜, 铝, 钛, 钒, 铌, 钙, 氧, 氢, 锚, 贝氏体, 马氏体, 腐蚀, 电位, 淬火, 回火, 加热, mooring chain, steel, carbon, nitrogen, phosphorus, sulfur, silicon, manganese, chromium, nickel, molybdenum, copper, aluminum, titanium, vanadium, niobium, calcium, oxygen, hydrogen, anchor, bainite, martensite, corrosion, potential, quenching, tempering, heating

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 103667953 A (ASIAN STAR ANCHOR CHAIN CO., LTD. JIANGSU) 26 March 2014 (2014-03-26) claims 1-11, description, pages 6-7, table 8	1-14
X	CN 106636928 A (YIN, Jiang) 10 May 2017 (2017-05-10) table 1	1-14
A	CN 101519751 A (BAOSHAN IRON & STEEL CO., LTD.) 02 September 2009 (2009-09-02) entire document	1-14
A	JP 54115618 A (KAWASAKI STEEL CORPORATION) 08 September 1979 (1979-09-08) entire document	1-14

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

* Special categories of cited documents:
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07 January 2020	**15 January 2020**
Name and mailing address of the ISA/CN **China National Intellectual Property Administration (ISA/CN)** **No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088** **China**	Authorized officer
Facsimile No. **(86-10)62019451**	Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2019/087168

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 103667953 A	26 March 2014	CN 103667953 B	28 September 2016
CN 106636928 A	10 May 2017	None	
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REFERENCES CITED IN THE DESCRIPTION

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