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(54) **CHAIN STEEL FOR USE IN MINE AND MANUFACTURING METHOD THEREFOR**

(57) A steel for mining chain and a manufacturing method thereof, wherein the steel has compositions by weight percentage: C: 0.20~0.28%, Si: 0.01~0.40%, Mn: 0.50~1.50%, P≤0.015%, S≤0.005%, Cr: 0.30~2.00%, Ni: 0.50~2.00%, Mo: 0.10~0.80%, Cu: 0.01~0.30%, Al: 0.01~0.05%, Nb: 0.001~0.10%, V: 0.001~0.10%, H≤0.00018%, N≤0.0150%, O≤0.0020%, and the balance is Fe and inevitable impurities. The manufacturing method comprises steps of smelting, refining and vacuum treatment, casting, heating, forging or rolling, and quenching and tempering heat treatment processes. The steel in the present invention has high strength and good impact toughness, good elongation and reduction of area. The steel can also resist stress corrosion cracking and have good weather resistance, wear resistance and fatigue resistance, which can be used in scenarios where

the steel having high strength and toughness is required, such as construction machinery and marine engineering.

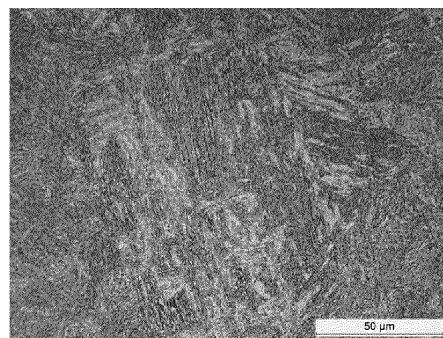


FIG. 1

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Description**TECHNICAL FIELD**

5 **[0001]** The present invention relates to steels having high strength, and specifically to a steel for mining chain having high strength and toughness and a manufacturing method thereof.

BACKGROUND

10 **[0002]** Steel bars having high strength and toughness are usually used in high-safety machinery and structural components. For example, round link chains for mines are the key wearing parts of the mining machinery. Therefore, they should have high strength, high toughness, high wear resistance, high corrosion resistance and high fatigue resistance, etc.

15 **[0003]** There are many domestic and foreign researches on steels having high strength and high roughness. Usually, those steels are produced by adopting appropriate chemical compositions and manufacturing methods such as controlled rolling and cooling process or quenching and tempering process. When the controlled rolling and cooling process is used to produce high-strength steels, the overall uniformity of the mechanical properties of the steels will be affected, since the rolling and cooling processes are difficult to control. When the quenching and tempering process is used to produce high-strength steels, the hardenability of the steels can be improved by optimizing the content of alloying elements and carbon, so that the steels can form martensite during the cooling process. Martensite-based high-strength steels have high dislocation densities, resulting in poor impact toughness. When small defects such as micro cracks appear during the stretching process, those steels will quickly fracture, showing relatively low fracture toughness.

20 **[0004]** Mn-Cr-Ni-Mo alloy steels are widely used in the fields such as construction machinery, automobiles, bridges, and marine equipment due to their good strength and toughness. Generally, the strength level for safe use of those steels is 900~1000 MPa. The application of the steels having higher strength can not only make equipment lighter, but also save resources. Therefore, alloy steels having high strength are an inevitable trend of future development. However, as the strength level of the steels increases, the manufacturing difficulty increases, and their susceptibility to hydrogen embrittlement is bound to increase. The susceptibility to hydrogen-induced delayed fracture of high-strength steels can be greatly reduced by microstructure refinement, microalloying, strengthening of grain boundaries and the addition of alloying elements.

25 **[0005]** In the Mn-Cr-Ni-Mo systems with low silicon content disclosed in the latest national standard GB/T 10560-2017 ("Steels for welded round link chains for mines"), the highest strength level of steels for mining round link chain is 1180 MPa. The mechanical properties of chain steels after quenching and tempering (quenched at 880°C and tempered at 430°C) are as follows: yield strength $R_{eL} \geq 1060$ MPa, tensile strength $R_m \geq 1180$ MPa, elongation $A \geq 10\%$, reduction of area $Z \geq 50\%$, and Charpy impact work $A_{KV} \geq 60$ J. The mechanical properties of chain steels having the highest strength grade in use in China's mining machinery after quenching and tempering (quenched at 880°C and tempered at 400°C) are as follows: yield strength $R_{eL} \geq 980$ MPa, tensile strength $R_m \geq 1180$ MPa, elongation $A \geq 10\%$, reduction of area $Z \geq 50\%$, and Charpy impact work $A_{KU} \geq 40$ J.

30 **[0006]** In the humid mines, Mn-Cr-Ni-Mo alloy steel chains are subject to large loads and dynamic shocks, and prone to stress corrosion. In some severe cases, those chains become very brittle and are easy to fracture, which might cause huge economic losses and even safety accidents.

SUMMARY

45 **[0007]** The purpose of the present invention is to provide a steel for mining chain and a manufacturing method thereof. The chain steel has good impact roughness, good elongation and reduction of area. The steel can resist stress corrosion cracking and has good weather resistance, good wear resistance and fatigue resistance. Therefore, the steel can be used in scenarios where steels having high strength and roughness are required, such as construction machinery and marine engineering.

50 **[0008]** In order to achieve the foregoing objective, the present invention provides the following technical solutions.

[0009] A steel for mining chain, comprising by weight: C: 0.20~0.28%, Si: 0.01~0.40%, Mn: 0.50~1.50%, P≤0.015%, S≤0.005%, Cr: 0.30~2.00%, Ni: 0.50~2.00%, Mo: 0.10~0.80%, Cu: 0.01~0.30%, Al: 0.01~0.05%, Nb: 0.001~0.10%, V: 0.001~0.10%, H≤0.00018%, N≤0.0150%, O≤0.0020%, and the balance being Fe and inevitable impurities; and having a coefficient $r_{M/N}$ of microalloying elements ranging from 1.0~9.9, wherein

$$r_{M/N} = ([Al]/2 + [Nb]/7 + [V]/4) / [N]$$

having trace elements as follows: $As \leq 0.05\%$, $Pb \leq 0.05\%$, $Sn \leq 0.02\%$, $Sb \leq 0.01\%$, $Bi \leq 0.01\%$, and having a coefficient J_H of harmful elements being ≤ 500 , wherein

$$J_H = ([P] + [Sn] + [As] + [Pb] + [Sb] + [Bi]) * ([Si] + [Mn]) * 10000$$

[0010] It should be noted that [Al], [Nb], [V], [N], etc. in the formulas of the present invention represent the weight percentage of the corresponding elements in the steel. Substitute [Al], [Nb], [V], [N], etc. in the formulas with the values before the percent sign when doing calculations. For example, the content of Al in Example 1 is 0.020%, then substitute [Al] in the formula with 0.020 instead of 0.00020. The substitutions of other elements are similar.

[0011] Preferably, in said inevitable impurities, $B \leq 0.0010\%$, $Ti \leq 0.003\%$, $Ca \leq 0.005\%$.

[0012] The microstructures of the steel for mining chain in the present invention are tempered martensite, bainite, and retained austenite, wherein the volume percentage of bainite is 10% or less.

[0013] The steel for mining chain in the present invention has a yield strength $R_{p0.2} \geq 1000$ MPa, a tensile strength $R_m \geq 1200$ MPa, a elongation $A \geq 12\%$, a reduction of area $Z \geq 50\%$, a Charpy impact work $A_{kv} \geq 60$ J, and a coefficient of hydrogen embrittlement $\eta(Z) \leq 15\%$.

[0014] In the composition design of said chain steel in the present invention:

C can improve the hardenability of the steel, so that the phase transformation structures with high hardness can be formed in steel in the process of quenching and cooling. Increasing the C content will increase the proportion of the hard phase and thus increase the hardness of the steel, but will lead to a decrease in toughness. If the C content is too low, the content of the phase transformation structures such as martensite and bainite will be low, and the steel having a high tensile strength cannot be obtained. In the present invention, the C content is set to 0.20~0.28%.

[0015] Si is beneficial to strength enhancement in steel. An appropriate amount of Si can avoid the formation of coarse carbides during tempering. But a high Si content will reduce the impact toughness of the steel. A composition system of low Si are adopted in the present invention, and the Si content is set to 0.01~0.40%.

[0016] Mn mainly exists in the form of solid solution in steel. It can improve the hardenability of the steel and form low-temperature phase transformation structures with high strength during quenching. Therefore, the steel having good wear resistance can be obtained. If the Mn content is too high, much retained austenite will be formed, leading to the reduction of the yield strength of the steel, and easily resulting in the central segregation in steel. In the present invention, the Mn content is set to 0.50~1.50%.

[0017] The segregation of P at the grain boundaries in steel will reduce the grain boundary binding energy and deteriorate the impact toughness of the steel. In the present invention, the P content is set to 0.015% or less. S will segregate in steel and form many sulfide inclusions, leading to the reduction of impact resistance. In the present invention, the S content is set to 0.005% or less.

[0018] Cr can improve the hardenability of the steel. It can also form hardened martensite structures, leading to the improvement of the steel strength. If the Cr content is too high, coarse carbides will be formed and the impact performance will be reduced. In the present invention, the Cr content is set to 0.30~2.00%.

[0019] Ni exists in the form of solid solution in steel, which can improve the low-temperature impact performance of the steel. However, an excessively high Ni content will lead to an excessively high content of retained austenite in steel, thereby reducing the strength of the steel. In the present invention, the Ni content is set to 0.50~2.00%.

[0020] Mo can be dissolved in the form of solid-solution in steel and help to improve the hardenability and the strength of the steel. Mo will form fine carbides when the steel is tempered at a high temperature, which can further increase the strength of the steel. Considering the cost of the precious metal Mo, in the present invention, the Mo content is set to 0.10~0.80%.

[0021] Cu can improve the strength and the corrosion resistance of the steel. If the Cu content is too high, Cu will accumulate at the grain boundaries during heating, resulting in the weakening of the grain boundaries and then the steel cracking. In the present invention, the Cu content is set to 0.01~0.30%.

[0022] Al forms fine AlN precipitates in steel, which can inhibit the growth of austenite grains. If the Al content is too high, the coarse Al oxides will be formed, those coarse and hard inclusions will result in reduced impact toughness and fatigue properties of the steel. In the present invention, the Al content is set to 0.01~0.05%.

[0023] Nb is added to the steel to form fine precipitates, which can inhibit the recrystallization of the steel and refine the grains. If the Nb content is too high, coarse NbC particles will be formed during smelting, which will reduce the impact toughness of the steel. Grain refinement plays an important role in improving the mechanical properties of the steel, especially the strength and the toughness. In the meanwhile, grain refinement also helps to reduce the hydrogen embrittlement susceptibility of the steel. In the present invention, the Nb content is set to 0.001~0.10%.

[0024] V can form precipitates with C or N in steel to improve the steel strength. If the C and V contents are too high, coarse VC particles will be formed. In the present invention, the V content is set to 0.001~0.10%.

[0025] When Ti is added to the steel, fine precipitates can be formed. But if the Ti content is too high, coarse TiN

particles with edges and corners will be formed during smelting, thereby reducing the impact toughness of the steel. In the present invention, the Ti content is set to 0.003% or less.

[0026] Since the B element is easy to segregate, the B content is limited to 0.0010% or less.

[0027] The addition of Ca element to the steel can improve the size and morphology of sulfide inclusions and avoid the deterioration of the impact toughness. However, Ca element is easy to form inclusions and affect the fatigue performance of the final product. The Ca content is controlled at 0.005% or less.

[0028] N is a type of interstitial atoms, and is also an element for forming MX-type precipitates. In order to avoid the enrichment of N element in steel, in the present invention, the N content is set to 0.015% or less. The ratio of contents of microalloying elements Al, Nb and V to the content of N has to be controlled, and thus a coefficient of microalloying elements is defined as r_{MIN} , wherein r_{MIN} is 1.0~9.9, and

$$r_{MIN} = ([Al]/2 + [Nb]/7 + [V]/4) / [N]$$

[0029] The coefficient of microalloying elements is related to the nano-scale precipitates. A high coefficient of microalloying elements will lead to the presence of coarse precipitates in steel, which cannot achieve the effect of precipitation strengthening. In addition, the high coefficient of microalloying elements will lead to adverse effects similar to inclusions, resulting in a decrease in fatigue strength. A low coefficient of microalloying elements will lead to a small amount of precipitates, which cannot achieve the effect of dispersion strengthening. Preferably, the coefficient r_{MIN} of microalloying elements is 1.0~6.0.

[0030] Trace elements such as Sn, Sb, As, Bi, and Pb segregate to grain boundaries at the tempering temperature, leading to the weakening of the intergranular bonding force. Mn and Si can promote the segregation of those harmful elements and thus increase the embrittlement of the steel. In addition, Sn, Sb, As, Bi, and Pb are harmful to the environment, in the present invention, the contents of those elements are set as follows: As≤0.05%, Pb≤0.05%, Sn≤0.02%, Sb≤0.01%, and Bi≤0.01%. Considering the effect of P, the coefficient J_H of harmful elements is ≤500, and

$$J_H = ([P] + [Sn] + [As] + [Pb] + [Sb] + [Bi]) * ([Si] + [Mn]) * 10000$$

[0031] H will accumulate at the defects in steel. In the steel having a tensile strength greater than 1000 MPa, hydrogen-induced delayed fracture might occur. In the present invention, the tensile strength exceeds 1200 MPa, and the H content has to be controlled at 0.00018% or less. N forms nitrides or carbonitrides in steel, which plays a role of refining austenite grains. But a high N content leads to the formation of coarse particles, which will not help to refine the grains. In addition, N is an interstitial atom and will accumulate in the grain boundaries, resulting in the decrease of the impact toughness. In the present invention, the N content is controlled at 0.0150% or less. O and Al in steel form oxides and composite oxides, etc. In order to ensure the uniformity of the steel structure, and the low-temperature impact energy and the fatigue performance of the steel, in the present invention, the content of O is controlled at 0.0020% or less.

[0032] Further, in order to satisfy the welding requirements of the steel for mining chain, the carbon equivalent Ceq of the steel has to be controlled at 0.80 or less, wherein

$$Ceq = [C] + [Mn]/6 + ([Cr] + [Mo] + [V])/5 + ([Ni] + [Cu])/15$$

[0033] In order to further ensure the weather resistance of the steel for mining chain and improve the resistance to the stress corrosion cracking, the index I of atmospheric corrosion resistance is 7.0 or more, wherein

$$I = 26.0[Cu] + 3.9[Ni] + 1.2[Cr] + 1.5[Si] + 17.3[P] - 7.3[Cu][Ni] - 9.1[Ni][P] - 33.4[Cu]^2$$

[0034] The microstructures of the steel for mining chain in the present invention are tempered martensite, bainite, and retained austenite.

[0035] It is generally believed that the susceptibility to hydrogen embrittlement of different microstructures in a descending order is: original martensite > tempered martensite (tempered at a low temperature) > tempered martensite with original martensite orientation > bainite > tempered martensite (tempered at a high temperature). The chain steels have low-temperature tempered martensite structures in the prior art. However, by the adoption of the chemical composition designed by the present invention and the fully utilization of the influence of alloying elements and microalloying elements on the phase transformation and microstructures, the complex microstructures of tempered martensite, a small amount of bainite, and retained austenite are formed after quenching and tempering heat treatments. In the meanwhile,

the contents of C, P, S, N, O, and H have to be controlled to ensure the strength, impact toughness, elongation and plasticity of the steel. Therefore, steels for mining chain having matched ultra-high strength and toughness and high plasticity can be produced. Those chain steels have good weather resistance, good wear resistance, good stress corrosion resistance and good fatigue resistance.

[0036] The manufacturing method of the steel for mining chain in the present invention, comprising steps of smelting, casting, heating, forging or rolling, quenching heat treatment and tempering heat treatment processes; wherein in said heating process, the heating temperature is 1050 ~ 1250°C, the holding time is 3~24 hr.; in said forging or rolling process, the final forging temperature or the final rolling temperature is $\geq 800^\circ\text{C}$; in said quenching heat treatment, the heating temperature is 850~1000°C, the holding time is 60~240 min, and a water quenching is implemented after austenitization; in said tempering heat treatment, the tempering temperature is 350~550°C, the holding time is 60~240 min, and after tempering, a steel billet is air cooled or water cooled.

[0037] Preferably, said smelting can be smelting in electric furnace or smelting in converter, and then the molten steel is subject to refining and vacuum treatment.

[0038] Preferably, said casting is die casting or continuous casting.

[0039] Preferably, in said forging process, a steel billet is directly forged to size of final product; in said rolling process, a steel billet is directly rolled to size of final product, or a steel billet is rolled to a specified intermediate billet size, and then heated and rolled to size of final product, wherein the heating temperature of the intermediate billet is 1050~1250°C, and the holding time is 3~24 hr.

[0040] Preferably, in said rolling process, a steel billet is subjected to descaling of high pressure water when out of the heating furnace and is then rolled, and after rolling, the steel billet air cooled or slow cooled.

[0041] The steel for mining chain in the present invention has a yield strength $R_{p0.2} \geq 1000$ MPa, a tensile strength $R_m \geq 1200$ MPa, a elongation $A \geq 12\%$, a reduction of area $Z \geq 50\%$, a Charpy impact work $A_{kv} \geq 60$ J, and a coefficient of hydrogen embrittlement $\eta(Z) \leq 15\%$. This kind of steels has good strength, good plasticity, good roughness, and good weather resistance and stress corrosion resistance.

[0042] The steel for mining chain in the present invention can be used in scenarios where high-strength steel bars are required, wherein the size and gauge range Φ of the steel bar is 50 ~ 170 mm.

[0043] The steel for mining chain with high strength and roughness in the present invention is heated at 1050~1250°C to be completely austenitized. During heating, carbides, nitrides and carbonitrides of Al, Nb, V and carbides of Cr and Mo can be partially or completely dissolved in austenite. During subsequent rolling/forging and cooling processes, Al, Nb and V form fine precipitates. Mn, Cr and Mo dissolved in austenite can improve the hardenability of the steel, thereby increasing the hardness and strength of martensite. When the temperature of final rolling or final forging is $\geq 800^\circ\text{C}$, complex matrix structures of refined martensite, a small amount of bainite, and retained austenite are formed, and fine and dispersed precipitates are formed as well.

[0044] After rolling or forging, heating the steel to 850~1000°C and holding for a while, and then quenching is implemented. Sufficient austenitization is achieved during the holding process. During heating, the precipitates of the carbide forming elements such as Al, Nb, V, Cr and Mo are partially dissolved, and the undissolved precipitates can pin the grain boundaries and inhibit the coarsening of the austenite (the grain size of austenite is ≥ 6 grades). During the quenching and cooling process, the alloying elements dissolved in the austenite make the steel have high strength and good toughness. The quenched steel is subjected to tempering heat treatment at 350~550°C. Al, Nb, V, Cr and Mo will form fine precipitates with C and N, which improves the matching of the steel strength and plastic toughness. Within the temperature range of quenching and tempering in the present invention, it can be ensured that the steel has good strength and plasticity and good toughness, which is beneficial to the processing and application of the steel bars. For example, produce mining chains having good performance by forging or welding.

[0045] The present invention is compared with the prior art as follows:

The US patent US006146583 discloses an alloy steel composition and chain products fabricated in such alloy steel, wherein the components of the steel are: C: 0.15~0.28%, Cr: 0.2~1.0%, Mo: 0.1~1.0%, Ni: 0.3~1.5%, V: 0.05~0.2%, and the balance is Fe and inevitable impurities. The strength of the steel can reach 800 MPa grade, and the steel has stress corrosion resistance. The chains having high strength and roughness can be obtained by forging, welding, and heat treatment.

[0046] Compared with that US patent, the present invention adopts different Cu content in the composition and optimizes the contents of C, N, and the contents of alloying elements such as Mn, Cr, Ni, Mo, and the contents of microalloying elements such as Al, V, and Nb. The present invention adopts the composition design comprising C, Ni and Cu elements and optimizes the contents of Mn, Cr, and Mo, and thus complex microstructures of tempered martensite, a small amount of bainite, and retained austenite can be formed. In addition, the mechanical properties of the steel in the present invention are obviously better than those of the steel in the US patent.

[0047] The Chinese Patent CN103276303A discloses a high-strength steel for mining chain and the manufacturing method thereof. The components of the chain steel are: C: 0.21~0.25%, Mn: 0.20~0.25%, Si: 0.15~0.35%, Cr: 0.40~0.65%, Ni: 0.60~0.70%, Cu: 0.07~0.15%, Al: 0.02~0.05%, N $\leq$ 0.012%, S $\leq$ 0.015%, P $\leq$ 0.015%, and the balance is

Fe. The manufacturing method comprises: smelting process in electric furnace or converter, out-of-furnace refining process, billet continuous casting process, and heating and rolling process to obtain straight bars with a gauge Φ of 20~50 mm, and a high-strength steel for mining chain can be obtained after annealing.

[0048] Compared with that CN patent, the contents of Cr, Mn, Ni and Mo in the steel of the present invention are completely different. In addition, the present invention optimizes the contents of C, Cu, Al, Nb, and V, and limits the contents of N and Ca. By adopting the contents of alloy elements described in the present invention, the microstructures of tempered martensite and retained austenite are formed, and the steels show the mechanical properties of high strength and toughness. For the high-strength steel having a tensile strength greater than 1000 MPa, it will adsorb H in the environment, thereby causing delayed cracking of the steel. High-strength steel bars with heavy gauge are more sensitive to hydrogen. Therefore, the content of H in steel is controlled in the present invention, but there is no such requirement in the Chinese patent application. Therefore, the stress corrosion resistance and delayed cracking resistance of the steel in the present invention are better than those of the steel in the Chinese patent application. That patent is used to manufacture straight bars of $\Phi 20\sim 50$ mm, while the present invention can be used to manufacture steel bars of $\Phi 50\sim 170$ mm, the method of the present invention has wider application and can be used to manufacture the steels with heavier gauges. The present invention is completely different with the above-mentioned patent from the technical route in terms of composition, organization and process design. In the present invention, the steel has a tensile strength $R_m \geq 1200$ MPa, a yield strength $R_{p0.2} \geq 1000$ MPa, and an impact energy $A_{kv} \geq 60$ J. The strength grade of the steel in the present invention is greater than that of the steel in the above-mentioned patent. The steel in the present invention has excellent impact toughness and stress corrosion cracking resistance.

[0049] The advantages of the present invention include:

1. The present invention develops the steel having high strength and roughness by the combination of the rational design of the chemical components and the optimized processes. After rolling or forging, the quenched steel bar is subject to a tempering heat treatment to form structures of tempered martensite, a small amount of bainite, and retained austenite. Fine and dispersed precipitates are formed as well
2. The composition and manufacturing process of the steel are reasonable, and the process window is wide. The steel can be mass-produced commercially on steel bar or high-speed wire production lines.
3. The steel in the present invention has a yield strength $R_{p0.2} \geq 1000$ MPa, a tensile strength $R_m \geq 1200$ MPa, a elongation $A \geq 12\%$, a reduction of area $Z \geq 50\%$, and a Charpy impact work $A_{kv} \geq 60$ J.

[0050] In the engineering field, the change of elongation under environmental conditions is usually used to reflect the tendency of stress corrosion. In the present invention, the round section test pieces are prepared referring to the requirements of DNV (DET NORSKE VERITAS) on the susceptibility to hydrogen embrittlement and following GB/T 2975-2018 "Steel and steel products-Location and preparation of samples and test pieces for mechanical testing", wherein the diameter of the test pieces is 10 mm. The tensile testing is carried out according to the national standard GB/T 228.1, the strain rate is $\leq 0.0003/s$, and thus the reduction of area Z is obtained. The coefficient of hydrogen embrittlement $\eta(Z)$ is defined to evaluate the stress corrosion resistance of the steel:

$$\eta(Z) = (Z_1 - Z_2) / Z_1 \times 100\%$$

wherein Z_1 is the reduction of area of round steel at the tensile testing after the dehydrogenation of baking at 250°C for 2h; Z_2 is the reduction of area of round steel at the tensile testing.

[0051] A small coefficient of hydrogen embrittlement $\eta(Z)$ indicates a small stress corrosion tendency. The coefficient of hydrogen embrittlement $\eta(Z)$ of the steel in the invention is 15% or less, indicating that the steel has good stress corrosion resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0052]

FIG. 1 is a metallographic microstructure photograph of the round steel of Example 2 in the present invention (the magnification is 500 times);

FIG. 2 is a metallographic microstructure photograph of the link chain of Example 2 in the present invention (the magnification is 500 times).

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0053] The present invention is further described below with reference to the accompanying drawings and embodiments. The embodiments are only used to illustrate the present invention, but not used to limit the present invention.

[0054] The chemical components of the round steels of the examples in the present invention and comparative examples are shown in Table 1. The coefficients of components of the steels having high strength and roughness of Examples 1~7 in the present invention and those of the Comparative Examples 1~3 are shown in Table 2. It can be seen that in examples of the present invention, the coefficient r_{MIN} of microalloying elements ranges from 1.0~9.9, the carbon equivalent Ceq is 0.80 or less, and the coefficient J_H of harmful elements is 500 or less. Wherein r_{MIN} is the ratio of the content of microalloying elements Al, Nb, and V to the content of N.

[0055] The manufacturing methods of the steels of examples in the present invention and the comparative examples are shown in Table 3. Preparing test pieces for mechanical testing, the testing results of the steels in examples in the present invention and the comparative examples are shown in Table 4.

[0056] The test pieces are prepared following GB/T 2975-2018 "Steel and steel products-Location and preparation of samples and test pieces for mechanical testing". The mechanical testing is carried out following GB/T 228.1-2010 "Metallic materials-Tensile testing-Part 1: Method of test at room temperature". The impact roughness at room temperature is tested following GB/T 229-2007 "Metallic materials-Charpy pendulum impact test method". 3 samples were tested and 3 values of impact work were obtained.

Example 1

[0057] Molten steel is smelted in electric furnace and then subject to refining and vacuum treatment according to the chemical compositions shown in Table 1. After that, the molten steel is casted into continuous casting billet. Then the continuous casting billet is heated to 1050°C, the holding time is 4 hr. The steel billet is subjected to descaling of high pressure water when out of the heating furnace and is then rolled to an intermediate billet. The final rolling temperature is 850°C, and the intermediate billet size is 200 mm×200 mm. Then the intermediate billet is heated to 1050°C, the holding time is 24 hr., the intermediate billet is subjected to descaling of high pressure water when out of the heating furnace and is then rolled, the final rolling temperature is 800°C, and the size Φ of finished the steel bar is 50 mm. The steel billet is stack cooled after rolling. The quenching heating temperature is 850°C, the heating time is 60 min, the tempering temperature is 390°C, and the tempering time is 90 min. The steel billet is air cooled after tempering.

Example 2

[0058] The manufacturing method is implemented in the same way as Example 1, wherein the heating temperature is 1080°C, the holding time is 3 hr., the final rolling temperature is 880°C, and the intermediate billet size 220 mm×220 mm. The intermediate billet is heated to 1120°C, the holding time is 3h, the final rolling temperature is 850°C, and the size Φ of the finished steel bar is 75 mm. The steel billet is air cooled after rolling. The quenching heating temperature is 870°C, the heating time is 100 min, the tempering temperature is 550°C, and the tempering time is 60 min. The steel billet is water cooled after tempering.

Example 3

[0059] The manufacturing method is implemented in the same way as Example 1, wherein the heating temperature is 1120°C, the holding time is 8 hr., the final rolling temperature is 940°C, and the intermediate billet size is 260 mm×260 mm. The intermediate billet is heated to 1200°C, the holding time is 5 hr., the final rolling temperature is 880°C, and the size Φ of the finished steel bar is 100 mm. The steel billet is air cooled after rolling. The quenching heating temperature is 890°C, the heating time is 150 min, the tempering temperature is 430°C, and the tempering time is 100 min. The steel billet is air cooled after tempering.

Example 4

[0060] The manufacturing method is implemented in the same way as Example 1, wherein the heating temperature is 1250°C, the holding time is 14 hr., and the steel billet is formed by hot continuous rolling. Wherein the final rolling temperature is 900°C, the size Φ of the finished steel bar is 150 mm. The steel billet is air cooled after rolling. The quenching heating temperature is of 990°C, heating time is 210 min, the tempering temperature is 350°C, and tempering time is 180 min. The steel billet is water cooled after tempering.

Example 5

[0061] Molten steel is smelted in converter and then subject to refining and vacuum treatment according to the chemical compositions shown in Table 1. Then the molten steel is casted into steel ingots. The heating temperature is 1180°C, the holding time is 3.5 hr., the final rolling temperature is 980°C, and the intermediate billet size is 280 mm×280 mm. The intermediate billet is heated to 1250°C, the holding time is 12 hr., the final rolling temperature is 950°C, and the size Φ of the finished steel bar is 160 mm. The steel billet is slow cooled after rolling. The quenching heating temperature is 900°C, the heating time is 210 min, the tempering temperature is 450°C, and the tempering time is 190 min. The steel billet is water cooled after tempering.

Example 6

[0062] The manufacturing method is implemented in the same way as Example 5, wherein the heating temperature is 1220°C; the holding time is 24 hr. The steel billet is formed by forging, the final forging temperature is 920°C, and the size Φ of the finished steel bar is 170 mm. The steel billet is air cooled after forging. The quenching heating temperature is 920°C, the heating time is 240min, the tempering temperature is 420°C, and the tempering time is 240 min. The steel billet is air cooled after tempering.

Example 7

[0063] The manufacturing method is implemented in the same way as Example 2, wherein the heating temperature is 1080°C, the holding time is 3 hr., the final rolling temperature is 880°C, and the intermediate billet size is 220 mm×220 mm. Then the intermediate billet is heated to 1100°C, the holding time is 3 hr., the final rolling temperature is 850°C, the size Φ of the finished steel bar is 65 mm. The steel billet is air cooled after rolling. The quenching heating temperature is 880°C, the heating time is 150min, the tempering temperature is 400°C, and the tempering time is 100min. The steel billet is water cooled after tempering.

[0064] Comparative Examples 1~3 are commercial materials from different manufacturers, the heat treatment processes refer to the recommended parameters of the supplier, see Table 3.

[0065] It can be seen that in Table 4, the Comparative Example 1 has a high Nb content and a microalloying coefficient of 10.1. It shows a poor precipitation strengthening effect, a low strength, a low impact toughness, and a short fatigue life. The Comparative Example 2 has a high P content, a coefficient of harmful elements of 678, and an index of atmospheric corrosion resistance of 5.3. It shows poor impact toughness and stress corrosion cracking resistance, and a high coefficient of hydrogen embrittlement. The Comparative Example 3 has a high S content, resulting in poor impact toughness.

[0066] The high-strength steels of Examples 1-7 in the present invention have the yield strength $R_{p0.2} \geq 1000$ MPa, the tensile strength $R_m \geq 1200$ MPa, the elongation $A \geq 12\%$, the reduction of area $Z \geq 50\%$, the Charpy impact work $A_{kv} \geq 60$ J, and the coefficient of hydrogen embrittlement $\eta(Z) \leq 15\%$. The steel of Example 6 shows relatively poor structure denseness due to the one-time heating and rolling process and the large bar size. Its strength and impact properties are slightly degraded compared with steels of other Examples. The steel of Example 7 shows degraded impact toughness, coefficient of hydrogen embrittlement, and corrosion cracking resistance due to the lower atmospheric corrosion resistance index, and has poor performance compared with steels of other Examples.

[0067] The microstructures of the round steel of Example 2 and the mining chain prepared using the steel of Example 2 were studied, and the optical microscope photographs are shown in FIGS. 1 and 2. It can be seen from the figures that the microstructures of the round steel are tempered martensite, a small amount of bainite, and retained austenite, while the microstructures of the mining chain further prepared using the round steel of Example 2 are refined tempered martensite and a small amount of bainite.

Table 1 Main Chemical Compositions of Examples in The Present Invention and Comparative Examples (wt.%)

	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Al	V	Nb	O	N	H	B	As	Pb	Sn	Sb	Bi
Example 1	0.23	0.01	1.25	0.012	0.002	0.35	1.01	0.54	0.27	0.020	0.001	0.012	0.0010	0.0051	0.00015	0.0001	0.004	0.0001	0.004	0.0002	0.0003
Example 2	0.28	0.14	1.20	0.005	0.000	0.60	1.50	0.20	0.05	0.016	0.002	0.001	0.0012	0.0060	0.00010	0.0003	0.012	0.003	0.015	0.0010	0.0010
Example 3	0.22	0.25	0.52	0.006	0.001	1.95	0.88	0.10	0.15	0.030	0.050	0.023	0.0009	0.0098	0.00008	0.0003	0.005	0.0021	0.010	0.0008	0.0007
Example 4	0.21	0.38	1.48	0.008	0.005	1.00	0.53	0.40	0.20	0.025	0.032	0.089	0.0016	0.0125	0.00015	0.0006	0.006	0.0025	0.009	0.0007	0
Example 5	0.20	0.29	0.87	0.007	0.003	1.25	1.96	0.12	0.01	0.045	0.097	0.045	0.0013	0.0103	0.00012	0.0004	0.013	0.0042	0.006	0.0012	0.0002
Example 6	0.21	0.23	1.32	0.011	0.002	0.55	1.23	0.61	0.25	0.038	0.001	0.001	0.0006	0.0145	0.00018	0.0003	0.009	0.0018	0.008	0.0006	0.0006
Example 7	0.24	0.08	1.26	0.010	0.002	0.53	0.92	0.54	0.03	0.027	0.027	0.002	0.0015	0.0051	0.00011	0.0001	0.004	0.0001	0.003	0.0012	0.0011
Comparative Example 1	0.21	0.20	1.27	0.009	0.003	0.51	1.01	0.55	0.11	0.034	0.001	0.105	0.0012	0.0032	0.00009	0.0002	0.005	0.0023	0.007	0.0003	0.0007
Comparative Example 2	0.24	0.13	1.25	0.016	0.003	0.48	0.99	0.54	0.03	0.038	0.002	0.001	0.0010	0.0057	0.00010	0.0002	0.025	0.0011	0.005	0.0012	0.0008
Comparative Example 3	0.23	0.18	1.30	0.006	0.006	0.56	0.97	0.56	0.17	0.033	0.010	0.004	0.0009	0.0078	0.00015	0.0003	0.006	0.0003	0.007	0.0007	0.0006

Table 2 Element Coefficients of Examples in the Present Invention and Comparative Examples

Coefficient	Coefficient of Microalloying Elements r_{MIN}	Carbon Equivalent C_{eq}	Index of Atmospheric Corrosion Resistance I	Coefficient of Harmful Elements J_H
Example 1	2.3	0.702	7.1	260
Example 2	1.4	0.744	7.5	496
Example 3	3.1	0.795	8.4	189
Example 4	2.7	0.792	7.0	487
Example 5	5.2	0.770	9.7	367
Example 6	1.3	0.761	8.0	481
Example 7	4.0	0.733	5.0	260
Comparative Example 1	<u>10.1</u>	0.709	6.6	357
Comparative Example 2	3.4	0.721	5.3	<u>678</u>
Comparative Example 3	2.5	0.749	7.0	305

Table 3 Manufacturing Methods of Examples in the Present Invention and Heat Treatment Processes of Comparative Examples

Example	Smelting, Refining, and Casting Processes	Heating Process of Steel Billet	Temperature of Final Rolling or Forging /°C	Intermediate Billet Size /mm	Heat Temperature of Intermediate Billet	Final Rolling Temperature /°C	Bar Size /mm	Cooling Pattern after Rolling or Forging	Quenching Process	Tempering Process
Example 1	smelting in electric furnace + refining + continuous casting	1050°C×4h	850	200×200	1050°C×24h	800	φ50	Stack Cooling	850°C×60min	390°C×90min
Example 2	smelting in electric furnace + refining + continuous casting	1080°C×3h	880	220×220	1120°C×3h	850	φ75	Air Cooling	870°C×100min	550°C×60min
Example 3	smelting in electric furnace + refining + continuous casting	1120°C×8h	940	260×260	1200°C×5h	880	φ100	Air Cooling	890°C×150min	430°C×100min
Example 4	smelting in electric furnace + refining + continuous casting	1250°C×14h	900	-	-	-	φ150	Air Cooling	990°C×210min	350°C×180min
Example 5	smelting in converter + refining + die casting	1180°C×3.5h	980	280×280	1250°C×12h	950	φ160	Slow Cooling	900°C×210min	450°C×190min

(continued)

	Smelting, Refining, and Casting Processes	Heating Process of Steel Billet	Temperature of Final Rolling or Forging /°C	Intermediate Billet Size /mm	Heat Temperature of Intermediate Billet	Final Rolling Temperature /°C	Bar Size /mm	Cooling Pattern after Rolling or Forging	Quenching Process	Tempering Process
Example 6	smelting in converter + refining + die casting	1220°C×24h	920	-	-	-	Φ170	Air Cooling	920°C×240min	420°C×240min
Example 7	smelting in electric furnace + refining + continuous casting	1080°C×3h	880	220×220	1100°C×3h	850	Φ65	Air Cooling	880°C×150min	400°C×100min
Comparative Example 1	smelting in electric furnace + refining + continuous casting	-	-	-	-	-	Φ50	-	900°C×150min	430°C×90min
Comparative Example 2	smelting in electric furnace + refining + continuous casting	-	-	-	-	-	Φ65	-	880°C×150min	410°C×90min
Comparative Example 3	Smelting in electric furnace + refining + continuous casting	-	-	-	-	-	Φ50	-	870°C×150min	410°C×90min

Table 4 Mechanical Properties of Examples in the Present Invention and Comparative Examples

	Yield Strength $R_{p0.2}$ /MPa	Tensile Strength R_m /MPa	Elongation A /%	Reduction of Area Z /%	Charpy Impact Work A_{kv} /J	Coefficient of Hydrogen Embrittlement $\eta(Z)$ /%
Example 1	1145	1293	14.5	55	101/96/98	9.5
Example 2	1062	1288	13.0	57	93/110/103	8.2
Example 3	1043	1251	16.5	62	103/91/94	10
Example 4	1036	1247	13.5	54	91/97/99	6.5
Example 5	1021	1238	15.0	61	111/102/89	8.8
Example 6	1013	1205	12.5	55	98/76/93	12
Example 7	1161	1325	12.5	60	95/90/85	15
Comparative Example 1	1004	<u>1189</u>	14.5	61	<u>65/93/78</u>	10
Comparative Example 2	1105	1333	15.0	64	<u>42/58/43</u>	16
Comparative Example 3	1075	1274	14.0	62	<u>48/60/58</u>	8

Claims

1. A steel for mining chain, comprising by weight: C: 0.20~0.28%, Si: 0.01~0.40%, Mn: 0.50~1.50%, P≤0.015%, S≤0.005%, Cr: 0.30~2.00%, Ni: 0.50~2.00%, Mo: 0.10~0.80%, Cu: 0.01~0.30%, Al: 0.01~0.05%, Nb: 0.001~0.10%, V: 0.001~0.10%, H≤0.00018%, N≤0.0150%, O≤0.0020%, and the balance being Fe and inevitable impurities; and having a coefficient r_{MIN} of microalloying elements ranging from 1.0 to 9.9, wherein

$$r_{MIN} = ([Al]/2 + [Nb]/7 + [V]/4) / [N]$$

having trace elements as follows: As≤0.05%, Pb≤0.05%, Sn≤0.02%, Sb≤0.01%, Bi≤0.01%, and having a coefficient J_H of harmful elements being ≤500, wherein

$$J_H = ([P] + [Sn] + [As] + [Pb] + [Sb] + [Bi]) * ([Si] + [Mn]) * 10000$$

2. The steel for mining chain of claim 1, having Ceq ≤0.80, wherein

$$Ceq = [C] + [Mn]/6 + ([Cr] + [Mo] + [V])/5 + ([Ni] + [Cu])/15$$

3. The steel for mining chain of claim 1, having an index I of atmospheric corrosion resistance being ≥7.0, wherein

$$I = 26.0[Cu] + 3.9[Ni] + 1.2[Cr] + 1.5[Si] + 17.3[P] - 7.3[Cu][Ni] - 9.1[Ni][P] - 33.4[Cu]^2$$

4. The steel for mining chain of claim 1, wherein in said inevitable impurities, B≤0.0010%, Ti≤0.003%, Ca≤0.005%.
5. The steel for mining chain of any of claims 1-4, having microstructures of tempered martensite, bainite, and retained austenite.
6. The steel for mining chain of any of claims 1-4, having a yield strength $R_{p0.2}$ ≥1000 MPa, a tensile strength R_m ≥1200 MPa, a elongation A≥12%, a reduction of area Z≥50%, a Charpy impact work A_{kv} ≥60 J, and a coefficient of hydrogen

embrittlement $\eta(Z) \leq 15\%$.

7. A manufacturing method of the steel for mining chain of any of claims 1-6, comprising steps of smelting, casting, heating, forging or rolling, quenching heat treatment, and tempering heat treatment processes, wherein

in said heating process, the heating temperature is 1050 ~ 1250°C, the holding time is 3~24 hr.;
in said forging or rolling process, the final forging temperature or the final rolling temperature is $\geq 800^\circ\text{C}$;
in said quenching heat treatment, the heating temperature is 850~1000°C, the holding time is 60~240 min, and a water quenching is implemented after austenitization;
in said tempering heat treatment, the tempering temperature is 350~550°C, the holding time is 60~240 min, and an air cooling or water cooling is implemented after tempering.

8. The manufacturing method of the steel for mining chain of claim 7, wherein said smelting comprises smelting in electric furnace or smelting in converter, and refining and vacuum treatment; said casting is die casting or continuous casting.

9. The manufacturing method of the steel for mining chain of claim 7, wherein in said forging process, a steel billet is directly forged to size of final product; in said rolling process, a steel billet is directly rolled to size of final product; or a steel billet is rolled to a specified intermediate billet size, and then heated and rolled to size of final product, wherein the heating temperature of the intermediate billet is 1050~1250°C, and the holding time is 3~24 hr.

10. The manufacturing method of the steel for mining chain of claims 7 or 9, wherein in said rolling process, a steel billet is subjected to descaling of high pressure water when out of the heating furnace and is then rolled, and after rolling, the steel billet is air cooled or slow cooled.

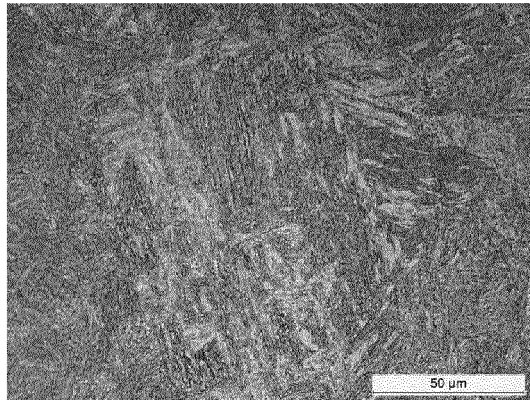


FIG. 1

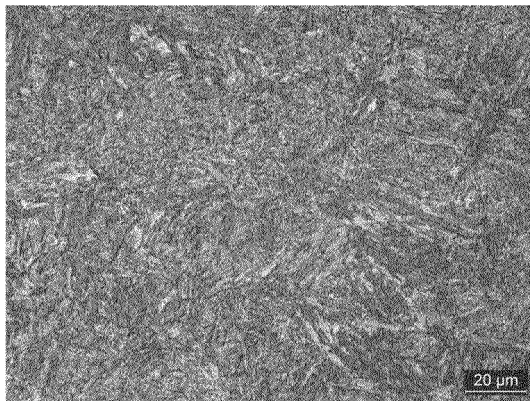


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2021/077430

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/02(2006.01)i; C22C 38/08(2006.01)i; C22C 38/18(2006.01)i; C22C 38/22(2006.01)i; C22C 38/24(2006.01)i;
C22C 38/26(2006.01)i; C21D 8/06(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; C21D

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)

CNABS, CNTXT, CNKI, EPODOC, DWPI, SIPOABS: 链条, 钢, 铁合金, 铬, 镍, 铝, 钒, 铌, Cr, Ni, Al, V, Nb, chain, steel, iron alloy, chrome, chromium, nickel, aluminium, aluminum, vanadium, columbium, niobium

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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A	CN 106854738 A (SHANGHAI BRANCH OF CHONGQING GELICI DIE TECHNOLOGY CO., LTD.) 16 June 2017 (2017-06-16) entire document	1-10
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A	CN 108004469 A (UNIVERSITY OF SCIENCE AND TECHNOLOGY BEIJING) 08 May 2018 (2018-05-08) entire document	1-10
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☒ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:	"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
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

30 April 2021

Date of mailing of the international search report

20 May 2021

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2021/077430**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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