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(54) HIGH REAMING STEEL AND MANUFACTURING METHOD THEREFOR

(57) The present invention provides a steel and a method for manufacturing therefor. The steel comprises the following components in the percentage by mass: C: 0.01-0.10%; Si: ≤0.2%; Mn: 0.5-2.0%; P: ≤0.02%; S: ≤0.003%; Al: 0.01-0.08%; N: ≤0.004%; V: 0.10-0.50%;

O: ≤0.003%; and the balance of Fe and inevitable impurities. The steel of the present invention can be applied in passenger vehicle chassis parts needing high strength and thickness reduction such as a control arm and a subframe.

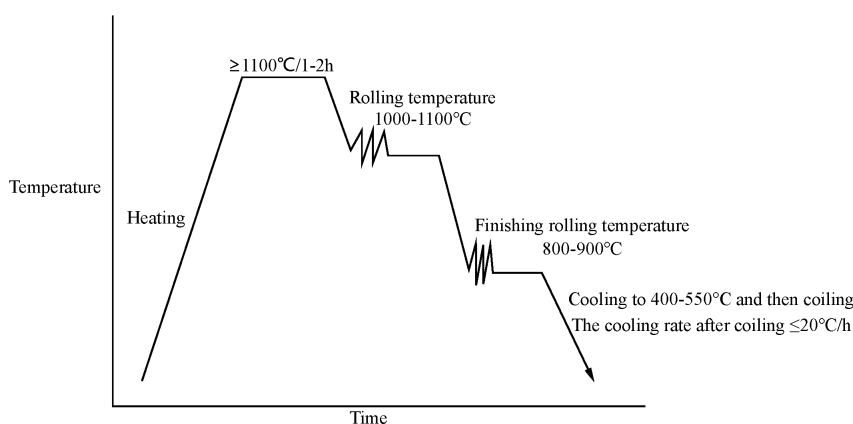


Figure 1

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Description**TECHNICAL FIELD**

- 5 **[0001]** The present invention relates to a steel and a method for manufacturing therefor, in particular to a high hole expansion steel and a method for manufacturing therefor.

BACKGROUND

- 10 **[0002]** Vehicle plays a very important role in the development of national economy. Many parts in passenger vehicle, especially some parts of the chassis and body, often require hot-rolled pickled products. Lightweight of passenger vehicle is a development trend in the automotive industry. The high strength and weight reduction of vehicles require higher grades of steel, and the structure of the chassis also needs to be improved, resulting in more complex chassis parts and higher requirements for material properties, surface conditions, and forming technologies, such as hydroforming, hot stamping, 15 laser welding, etc., thus transforming into performance requirements for materials such as high strength, stamping, flanging, rebound and fatigue performance.

- [0003]** At present, the high hole expansion steel used by domestic vehicle parts companies is basically high-strength steel with a tensile strength of 600MPa or less. There is considerable competition for high hole expansion steel with a tensile strength of 540MPa or less. At the same time, high hole expansion steel with a tensile strength of 780MPa is 20 gradually being used in batches in China. However, the elongation and hole expansion ratio, two important indicators in the forming process, are also demanding, while the requirements for performance stability are becoming more stringent.

- [0004]** In order to reduce process costs, passenger vehicle companies have further improved the performance requirements of the materials. For example, when producing vehicle chassis parts, in order to reduce the steps of the stamping process, the material is required to have high strength and high plasticity as well as a high hole expansion ratio. 25 For example, the hole expansion ratio of 780MPa grade high hole expansion steel is required to be guaranteed to be $\geq 50\%$, preferably further increase to 70% or even 80% or more. Existing high hole expansion steel, especially 780MPa grade high hole expansion steel, mostly have hot-rolled bainite structures and are strengthened with precipitated phases at the same time. Most of the process paths used are medium-temperature coiling, but the temperature control accuracy is not high and the uniformity of finished product structure is poor, resulting in ununiform properties, such as hole expansion ratio, of the 30 obtained hot-rolled steel, and stamping cracking is prone to occur during subsequent processing.

- [0005]** Prior arts of 780 MPa grade pickled high hole expansion steel are listed below:
Chinese patent CN103602895A discloses a low carbon Nb-Ti micro-alloyed high hole expansion steel, which adopts a composition design of low carbon, high silicon in combination with Nb-Ti micro-alloying, which can ensure a hole expansion ratio of $\geq 50\%$. However, the design of high silicon composition usually results in red scale on the surface 35 of the steel plate. In addition, the coiling temperature required to form bainite is usually around 500°C, which makes it difficult to control the temperature on full length of the steel coil, resulting in large fluctuations in the performance of the entire length of the steel coil.

- [0006]** Chinese patent CN105821301A discloses an 800MPa grade hot-rolled high-strength high hole expansion steel, which also adopts a composition design of low carbon and high silicon in combination with Nb-Ti micro-alloying. The Ti 40 content in the steel is very high, ranging from 0.15 to 0.18%. In the actual production process, this composition design will lead to defects such as red scale on the surface of the strip steel. On the other hand, due to the high Ti content, coarse TiN is easily formed in the steel, which is detrimental to the stability of the hole expansion ratio.

- [0007]** Chinese patent CN108570604A discloses a 780MPa grade hot-rolled pickled high hole expansion steel, which adopts a composition design of low carbon, high aluminum and high chromium, and adopts a three-stage cooling process 45 in the process design. Although there is no red scale on the surface of the strip steel, the high aluminum composition design can easily cause clogging of the casting nozzle during the actual production process. On the other hand, the production process of this steel is complex, especially the three-stage cooling process is difficult to control, resulting in a low hole expansion ratio of the steel.

- [0008]** Chinese patent CN114107792A discloses a 780MPa grade hot-rolled pickled high hole expansion steel, which 50 adopts a composition design of low carbon and high titanium and an appropriate amount of molybdenum is added to the steel. Since the phase transformation process of molybdenum-containing steel is relatively slow, the phase transformation process mainly occurs after coiling. Therefore, in the actual production process, there are problems such as low strength of the inner and outer rings of steel coils.

55 **SUMMARY**

- [0009]** In view of the above-mentioned defects in the prior arts, an objective of the present invention is to provide a steel and a method for manufacturing therefor. The steel of the present invention has high strength, high plasticity and high hole

expansion ratio, and these properties are well-matched with each other, and can be used in passenger vehicle chassis parts needing high strength and thickness reduction such as a control arm and a subframe.

[0010] To achieve the above objective, the present invention adopts the following technical solution:

In order to meet user demands for the matching of higher surface quality, better performance stability, plasticity and hole expansion property, conventional high hole expansion steel needs to be improved.

[0011] In general, the elongation of a material is inversely proportional to the hole expansion ratio, that is, the higher the elongation, the lower the hole expansion ratio; conversely, the lower the elongation, the higher the hole expansion ratio. Under the same or similar strengthening mechanism, the higher the strength of the material, the lower the hole expansion ratio. In order to obtain steel with both good plasticity and hole expansion flanging performance, a better balance between the two is needed. In order to achieve a good matching between strength, plasticity and hole expansion performance, the addition of higher amounts of silicon elements seems to be indispensable for high-strength high-plasticity high hole expansion steel. However, the compositional design of high silicon usually leads to poor surface quality of steel plates. Specifically, the red scale defects formed during the hot rolling process are difficult to be completely removed in the subsequent pickling process, resulting in appearance of stripe-shaped red scale on the surface of the pickled high-strength steel, which seriously affects the surface quality.

[0012] The present invention optimizes the chemical composition of the existing hot-rolled steel by adopting a low carbon and high vanadium element design without intentionally adding silicon element to the steel, and by adding the V element to improve the strength and plasticity of the steel by taking advantage of the nano-sized vanadium carbide it forms. A bainitic precipitation-strengthened high-strength steel with uniform structure and properties can be obtained without changing the existing hot continuous rolling production line.

[0013] Specifically, the steel according to the present invention comprises the following components in percentage by mass: C: 0.01-0.10%; Si $\leq$ 0.2%; Mn: 0.5-2.0%; P $\leq$ 0.02%; S $\leq$ 0.003%; Al: 0.01-0.08%; N $\leq$ 0.004%; V: 0.10-0.50%; O $\leq$ 0.003%; and the balance of Fe and inevitable impurities.

[0014] Preferably, the steel further comprises Ti, with an upper limit of 0.2%, preferably 0.18%, more preferably 0.015%, and a lower limit of 0.05%, preferably 0.08% in percentage by mass.

[0015] Preferably, the steel further comprises 0.1-0.5%, more preferably 0.20-0.40%, still more preferably 0.2-0.3% of Mo in percentage by mass.

[0016] Preferably, the steel further comprises one or more components selected from Nb $\leq$ 0.1%, Cu $\leq$ 0.5%, Ni $\leq$ 0.5%, Cr $\leq$ 0.5%, and B $\leq$ 0.002%, wherein Cu is more preferably 0.3% or less; Ni is more preferably 0.3% or less; Cr is more preferably 0.3% or less; Nb is more preferably 0.06% or less; B is more preferably 0.002% or less, still more preferably 0.001% or less.

[0017] Preferably, the composition of the steel satisfies one or more of the following: C: 0.03-0.07%; Si $\leq$ 0.10%; Mn: 0.8-1.6%; S $\leq$ 0.0018%; Al: 0.02-0.05%; N $\leq$ 0.003%; O $\leq$ 0.002%.

[0018] In the composition design of the steel according to the present invention:

Ca is a basic element in steel and one of the important elements in the present invention. C can expand the austenite phase area and stabilize the austenite. As an interstitial atom in steel, C plays a very important role in improving the strength of steel, among which it has the greatest impact on the yield strength and tensile strength of steel. In the present invention, since the structure to be obtained during the hot rolling stage is low carbon bainite, in order to obtain high hole expansion steel with final tensile strength reaching different strength levels, the C content must be 0.01% or more; at the same time, the C content must not be higher than 0.10%. If the C content is too high, low carbon martensite is easily formed during low-temperature coiling. Therefore, the present invention controls the C content to 0.01-0.10%, preferably 0.03-0.07%.

[0019] Si is a basic element in steel. As mentioned before, in order to meet user demands for high strength, high plasticity and high hole expansion ratio, a higher amount of Si is usually added in the composition design. However, the composition design of high silicon brings about a reduction in the surface quality of the steel plate, which has higher amount of red scale defects. In the present invention, in order to ensure good surface quality, the Si content should be strictly controlled during component design. In other words, Si is an impurity element in the present invention. Considering that Si-Mn is needed for deoxidation in actual steelmaking, it seems difficult to completely avoid the addition of Si. According to a large amount of statistical data from actual production, when the Si content is 0.2% or less, the surface red scale defects can be avoided during the hot rolling process. Usually, when the Si content is 0.10% or less, it is guaranteed that no red scale will appear. Therefore, the Si content in the steel of the present invention is controlled within 0.2%, preferably within 0.10%.

[0020] Mn is also the most basic element in steel and one of the most important elements in the present invention. It is well known that Mn is an important element in expanding the austenite phase area. It can reduce the critical quenching speed of steel, stabilize austenite, refine grains, and postpone the transformation of austenite to pearlite. In the present invention, in order to ensure the strength and grain refinement effect of the steel plate, the Mn content is usually controlled at 0.5% or more; at the same time, the Mn content should not generally exceed 2.0%, otherwise Mn segregation will easily occur during steelmaking, and hot cracking is also prone to occur during continuous casting of slabs. Therefore, the Mn content in the steel of the present invention is controlled at 0.5-2.0%, preferably 0.8-1.6%.

[0021] P is an impurity element in steel. P is very easy to segregate on the grain boundaries. When the P content in the

steel is high ($\geq 0.1\%$), Fe_2P will be formed and precipitated around the grains, reducing the plasticity and toughness of steel. Therefore, the lower its content, the better. The present invention controls the P content within 0.02%, and the steel obtained has better mechanical performances and does not increase the cost of steelmaking.

[0022] S is an impurity element in steel. S in steel usually combines with Mn to form MnS inclusions. Especially when the contents of S and Mn are both high, more MnS will be formed in the steel. MnS itself has a certain plasticity, it would deform along the rolling direction during the subsequent rolling process, which not only reduces the transverse plasticity of the steel, but also increases the anisotropy of the structure, which is detrimental to the hole expansion performance. In order to reduce the MnS content, the S content needs to be strictly controlled. The lower the S content in the steel, the better. In the present invention, the S content is controlled within 0.003%, preferably 0.0018% or less.

[0023] Al's main function in steel is to deoxidize and fix nitrogen. In the presence of strong carbide-forming elements such as Ti, the main function of Al is to deoxidize and refine grains. In the present invention, Al is a common deoxidizing element and grain refining element, and its content is usually controlled at 0.01-0.08%; when the Al content is less than 0.01%, it will not have the effect of refining grains; similarly, when the Al content is higher than 0.08%, its effect of refining grains will reach saturation. Therefore, the Al content in the steel of the present invention is controlled between 0.01-0.08%, preferably between 0.02-0.05%.

[0024] N is an impurity element in the present invention, and the lower its content, the better. However, N is an inevitable element in the steelmaking process. Although its content is low, in combination with strong carbide forming elements such as V, the VN particles formed adversely affect the performance of the steel, especially very detrimental to the hole expansion performance. Due to the square shape of VN, there is a large stress concentration between its sharp corners and the substrate. During the process of hole expansion deformation, the stress concentration between VN and the substrate can easily form crack sources, thus greatly reducing the hole expansion performance of the material. Since the present invention adopts a high vanadium design in the composition system, in order to minimize the adverse effect on hole expansion caused by VN, the present invention controls the N content to 0.004% or less, preferably 0.003% or less.

[0025] V is an important element in the present invention. Similar to Ti and Nb, V is also a strong carbide-forming element. However, vanadium carbides have low solid-solution or precipitation temperature and are usually fully solid-solutionized in austenite during the finishing rolling stage. Only when the temperature is lowered and phase transformation begins, V begins to form in the ferrite. In order to fully utilize the precipitation strengthening effect of V, the amount of V added to the steel should be at least 0.10% or more to have obvious precipitation strengthening effect; as the V content increases, the precipitation strengthening effect of V gradually increases. When the V content exceeds 0.50 %, the precipitation strengthening effect of V is saturated and the size of the vanadium carbide formed is larger, which adversely reduces the contribution to the steel strength. Therefore, the amount of V added to the steel of the present invention is controlled to be $\leq 0.50\%$. Specifically, when the V content is 0.10-0.20%, a 590MPa grade high hole expansion steel can be obtained; when the V content is 0.20-0.35%, a 780MPa grade high hole expansion steel can be obtained; when the V content is 0.35 -0.50%, a 980MPa grade high hole expansion steel can be obtained.

[0026] Mo is one of the important elements in the present invention. The addition of Mo in steel can greatly postpone the phase transformation of ferrite and pearlite, which is conducive to obtaining a bainite structure. In addition, Mo has strong resistance to welding softening. Since the main objective of the present invention is to obtain a low carbon bainite structure, and low carbon bainite is prone to softening after welding, adding a certain amount of Mo can effectively reduce the degree of welding softening. Therefore, in the present invention, the Mo content is controlled at 0.10-0.50%, preferably 0.20-0.40%, more preferably 0.2-0.3%. When combined with the sectional cooling process, Mo plays a certain inhibiting role in the formation of ferrite during the sectional cooling process. When the Mo content is within the above range, its effect can be fully realized.

[0027] Nb is one of the addable elements in the present invention. Nb, similar to Ti, is a strong carbide element in steel. The addition of Nb in steel can greatly increase the non-recrystallization temperature of the steel, obtain deformed austenite with higher dislocation density during the finishing rolling stage, and refine the final phase change structure during the subsequent transformation process. However, the amount of Nb added should not be too much. On one hand, if the amount of Nb added exceeds 0.10%, it is easy to form relatively coarse niobium carbonitrides in the structure, consuming part of the carbon atoms and reducing the precipitation strengthening effect of carbides. At the same time, the higher Nb content also tends to cause anisotropy of the hot-rolled austenite structure, which is inherited to the final structure during the subsequent cooling phase transformation process, harming the hole expansion performance. Therefore, the Nb content in the steel of the present invention is controlled at $\leq 0.10\%$, preferably $\leq 0.06\%$.

[0028] Ti is an optional element in the present invention. The addition of a small amount of Ti in steel can, on one hand, combine with N to form TiN during the high-temperature stage, which can fix N and help reduce the subsequent formation of VN; on the other hand, the excess Ti after combining with N can be combined with C to form nano-TiC during the subsequent process and improve the performance of the steel with the nano-VC together. When the Ti content is higher than 0.20%, coarser TiN is prone to be formed during the high-temperature stage and deteriorates the impact toughness of the steel. Therefore, the content of the optional element Ti in the steel of the present invention is within 0.20%, preferably within 0.18%, more preferably within 0.015%, most preferably within 0.10%. On the other hand, the Ti content is preferably

0.05% or more, more preferably 0.08% or more, which provides an excellent precipitation strengthening effect.

[0029] Cu is an optional element in the present invention. The addition of Cu in steel can improve the corrosion resistance of steel. When it is added together with the P element, the corrosion resistance performance is better; when the amount of Cu added exceeds 1%, under certain conditions, an ε -Cu precipitated phase can be formed, causing a strong precipitation strengthening effect. However, the addition of Cu can easily cause the "Cu brittleness" phenomenon during the rolling process. In order to make full use of Cu's corrosion resistance improvement effect in certain applications without causing significant "Cu brittleness" phenomenon, the present invention controls the Cu content to within 0.5%, preferably within 0.3%.

[0030] Ni is an optional element in the present invention. The addition of Ni in steel has a certain degree of corrosion resistance, but the corrosion resistance effect is weaker than that of Cu. The addition of Ni in steel has little effect on the tensile performance of the steel, but can refine the structure and precipitated phases of the steel, greatly improving the low-temperature toughness of the steel; at the same time, in steel with added Cu element, adding a small amount of Ni can inhibit the occurrence of "Cu brittleness". Adding a higher amount of Ni has no significant adverse effect on the performance of the steel itself. If Cu and Ni are added at the same time, it can not only improve the corrosion resistance, but also refine the structure and precipitated phases of the steel, greatly improving the low-temperature toughness. However, since both Cu and Ni are relatively expensive alloying elements, in order to minimize the cost of the alloy design, the amount of Ni added to the steel of the present invention is $\leq 0.5\%$, preferably $\leq 0.3\%$.

[0031] Cr is an optional element in the present invention. Cr is added to steel to improve the strength of steel mainly through solid solution strengthening or microstructure refinement. Since the structure of the steel in the present invention is fine bainitic ferrite plus nano-precipitated carbides, the ratio of yield strength and tensile strength of the steel, i.e., the yield ratio, is relatively high, and usually reaches 0.90 or more. Adding a small amount of Cr can appropriately reduce the yield strength of steel, thereby reducing the yield ratio. In addition, adding a small amount of Cr can also improve corrosion resistance. Usually, the amount of Cr added is $\leq 0.5\%$, preferably $\leq 0.3\%$.

[0032] B is an optional element in the present invention. B can greatly improve the hardenability of steel, promote bainite transformation, and promote lath bainite transformation during medium-temperature bainite phase transformation. Therefore, adding a trace amount of B to the steel is conducive to obtaining a fine lath bainite structure. However, the B content should not be too much. Adding too much B will lead to the formation of martensite and more M-A islands, which is unfavorable to plasticity and hole expansion. Therefore, the amount of B added in the steel of the present invention is controlled at $\leq 0.002\%$, preferably $\leq 0.001\%$.

[0033] O is an impurity element in the present invention. In order to obtain steel with better performance, the lower the O content in the steel, the better. However, a lower oxidation amount will increase the cost of steelmaking. In order to ensure the performance of the strip steel, the O content in the steel of the present invention is controlled to be within 0.003%, preferably within 0.002%.

[0034] Existing high hole expansion steels are usually designed with high titanium composition, in which the main purpose of adding micro-alloying element Ti is to refine the grains, and the addition amount is generally within 0.1%. The present invention adopts a high vanadium composition design, and Ti is present as an optional element in the steel of the present invention. The main purpose of adding V in the present invention is to combine it with C to form dispersively distributed nano-vanadium carbide for precipitation strengthening.

[0035] The steel of the present invention obtains a steel having both high tensile strength and hole expansion ratio by including a content of V up to 0.1-0.5%. When the V content in the steel is 0.10-0.20%, the tensile strength of the steel is 590MPa, and the hole expansion ratio is $\geq 70\%$, preferably $\geq 80\%$; when the V content in the steel is 0.20-0.35%, the tensile strength of the steel is 780MPa, and the hole expansion ratio is $\geq 50\%$; when the V content in the steel is 0.35-0.50%, the tensile strength of the steel is 980MPa, and the hole expansion ratio is $\geq 30\%$, preferably $\geq 40\%$.

[0036] Most of the microstructures of existing high hole expansion steels are ferrite or ferrite plus bainite. In order to obtain higher strength, nano-titanium carbide is used for strengthening. When the high hole expansion steel of the present invention does not contain Ti, its microstructure is bainite and nano-vanadium carbide in bainite. Moreover, according to the different V content, high hole expansion steel of different strength grades can be obtained to meet the needs of downstream users for different strength grades of high hole expansion steels. When the steel of the present invention contains Ti, its microstructure is ferrite and bainite, wherein the ferrite contains nano-TiC and the bainite contains nano-VC.

[0037] The present invention also provides a method for manufacturing the steel of the present invention, including the following steps:

1) Smelting and casting

[0038] The above composition is smelted by a converter or an electric furnace, secondary refined by a vacuum furnace, and casted into billets or ingots.

2) Reheating of billets or ingots

[0039] Heating temperature $\geq 1100^{\circ}\text{C}$, preferably 1200°C or more; holding time: 1-2 hours.

3) Hot rolling and cooling.

[0040] As an embodiment of the method for manufacturing the present invention, preferably, in step 3) of the method for manufacturing the present invention, the initial rolling temperature is $1000-1100^{\circ}\text{C}$, and rough rolling of 3-5 passes is carried out under high pressure at 950°C or more to a cumulative deformation of $\geq 50\%$, then the intermediate billet is air-cooled or water-cooled to $900-950^{\circ}\text{C}$, and finishing rolling of 7 passes is carried out to a cumulative deformation of $\geq 70\%$, completing the finishing rolling between $800-900^{\circ}\text{C}$, and obtaining a steel strip, thereafter, the steel strip is water-cooled to $400-550^{\circ}\text{C}$ at a cooling rate of $\geq 10^{\circ}\text{C/s}$ and coiled, and slowly cooling to room temperature at a cooling rate of $\leq 20^{\circ}\text{C/s}$, obtaining a hot-rolled steel strip.

[0041] As another embodiment of the method for manufacturing the present invention, preferably, in step 3) of the method for manufacturing the present invention, the initial rolling temperature of the hot rolling is $1050-1150^{\circ}\text{C}$, and rough rolling of 3-5 passes is carried out under high pressure at 1050°C or more to a cumulative deformation of $\geq 50\%$, then an intermediate billet is heated to $950-1000^{\circ}\text{C}$, and finishing rolling of 3-7 passes are carried out to a cumulative deformation of $\geq 70\%$, and the finishing rolling temperature is $800-950^{\circ}\text{C}$, and obtaining a steel strip;

wherein the cooling is staged cooling, and after finishing rolling, the steel strip is water-cooled to $600-750^{\circ}\text{C}$ at a cooling rate of $\geq 30^{\circ}\text{C/s}$, then after air cooling for 1-10 seconds, the steel strip is cooled to $400-550^{\circ}\text{C}$ at a cooling rate of $\geq 10^{\circ}\text{C/s}$ and coiled, then cooling to room temperature at a cooling rate of $\leq 20^{\circ}\text{C/h}$, obtaining a hot-rolled strip steel.

[0042] Preferably, when the steel of the present invention contains Ti, it is carried out using the above-mentioned method including sectional cooling.

[0043] In the step 3) above, the initial rolling temperature of hot rolling is $1050-1150^{\circ}\text{C}$, and rough rolling of 3-5 passes is carried out under high pressure at 1050°C or more to a cumulative deformation is $\geq 50\%$. The main purpose is to refine the austenite grains, and retain more solid solutionized Ti at the same time.

[0044] In the rough rolling and finishing rolling stages of step 3), rolling should be completed as quickly as possible to ensure that there is more solid solutionized Ti and V in the austenite. After the high-temperature finishing rolling, the steel strip is first cooled to $600-750^{\circ}\text{C}$ at a cooling rate of $\geq 30^{\circ}\text{C/s}$, then forming ferrite and nano-TiC inside the ferrite grain at the air-cooling stage. The steel strip is subsequently water-cooled to $400-550^{\circ}\text{C}$ at a cooling rate of $\geq 10^{\circ}\text{C/s}$ to obtain bainite and nano-precipitated VC. Eventually, a microstructure dominated by ferrite and bainite and nano-precipitated TiC and VC inside ferrite and bainite is obtained.

[0045] When the steel contains both high titanium and high vanadium, the main purpose of adding more V is to make it combine with C to form dispersively distributed nano-VC for precipitation strengthening. The high titanium and high vanadium compositions together with the sectional cooling process results in the formation of nano-TiC inside the ferrite grains in the ferrite formation region, and nano-VC inside the bainite in the bainite formation region. Through the combination of compositions and processes, the excess Ti after combining with N can be formed with C into nano-TiC in the air-cooling stage after the first water-cooling stage, which serves to strengthen the ferrite. Introducing nano-TiC into ferrite can reduce the performance difference between ferrite and bainite, which is conducive to improve the hole expansion ratio; by controlling the strength of bainite through different V contents, high hole expansion steel of different strength grades can be obtained to meet the needs of downstream users for different strength grades of high hole expansion steels.

[0046] Preferably, the method further includes step 4) Pickling, wherein the pickling operating speed of the hot-rolled strip steel is 30-120m/min, the pickling temperature is $75-85^{\circ}\text{C}$, the straightening rate is $\leq 3\%$, rinsing is carried out at $35-50^{\circ}\text{C}$, and the surface drying and oiling are carried out at $120-140^{\circ}\text{C}$ to obtain pickled high hole expansion steel.

[0047] In the method for manufacturing the steel of the present invention:

The invention adopts a medium-temperature coiling process and combines it with an innovative low carbon, high vanadium and low silicon composition design to obtain a high-strength high hole expansion steel with excellent performance stability.

[0048] In the medium and low-temperature bainite transformation region, precise control of the coiling temperature ensures uniformity of performance over the entire length of the strip steel. During the medium-temperature coiling process, bainite phase transformation occurs, accompanied by nano-precipitation of V. By quantifying the content of key elements C and V in conjunction with specific coiling, a series of high hole expansion steel products with different strength grades and different hole expansion ratios can be obtained.

[0049] While the conventional high titanium high hole expansion steel mostly adopts high-temperature coiling process, the present invention adopts a medium-temperature coiling process. Therefore, during the rough rolling and finishing rolling stages, the rolling pace should be completed as quickly as possible to ensure that more V is solidly dissolved in austenite. After the high-temperature finishing rolling, the strip steel is cooled on-line to the mid-temperature region of

400-550°C at a cooling rate of $\geq 10^\circ\text{C/s}$ to obtain bainite and nano-precipitation structure.

[0050] When steel contains Ti and sectional cooling is used in the manufacturing process, the desired amount of ferrite is formed and nano-titanium carbide are precipitated inside the ferrite grains at the air-cooling stage after the first water-cooling after rolling to improve the ferrite property; in the medium-temperature coiling stage after the second water-cooling, the precipitation of V is adopted to form nano-vanadium carbide in the bainite, which improves the strength of the bainite. Through the composition and process innovations, ferrite strengthened by nano-titanium carbide and bainite structure strengthened by nano-vanadium carbide are obtained. Through different designs of V content, a series of high hole expansion steel products with different strength grades can be obtained, demonstrating the innovation of compositions and processes and the resulting uniqueness of structure and performance. Nano-TiC and VC give ferrite and bainite higher strength and more balanced properties respectively.

[0051] In the subsequent pickling process, the inhomogeneity of thermal stress and organizational stress formed within the steel coil during the medium-temperature coiling phase transformation process is fully released during pickling and straightening, which can further improve the structural uniformity. Based on this innovative design of composition and process, the present invention can obtain a series of high-surface hot-rolled pickled high hole expansion steel products with different strength grades, and excellent plasticity, hole expansion performance, and performance stability.

[0052] Compared with the prior arts, the advantages or beneficial effects of the present invention are: Compared with the high silicon composition design used in Chinese patents CN103602895A and CN105821301A, the present invention adopts a silicon-free and high vanadium composition design to avoid the appearance of red scale on the surface of the strip steel and improve the surface quality of pickled high-strength steel.

[0053] Compared with Chinese patent CN108570604A, although its Si content is 0.05-0.5%, it is still not guaranteed to completely eliminate red scale defects on the surface of the strip steel. Moreover, the three-stage cooling process is difficult to control and the performance stability is difficult to guarantee. In contrast, the present invention adopts multi-path cooling precision control technique, which can ensure the performance uniformity of the strip steel.

[0054] The present invention further adopts innovative low carbon, high titanium and high vanadium composition design, combined with innovative sectional cooling and medium-temperature coiling processes, to obtain hot-rolled pickled high hole expansion steels with excellent surface, strength, plasticity and hole expansion performance of different strength grades and good performance stability.

[0055] The steel of the present invention has a tensile strength of ≥ 590 - ≥ 980 MPa, and a good elongation (transverse $A_{50} \geq 13\%$ - $\geq 18\%$) and high hole expansion performance (hole expansion ratio $\geq 30\%$ - $\geq 80\%$) in a thickness of 1.5-6.0mm, showing matching of excellent surface, strength, plasticity and hole expansion performance, and can be applied to the manufacture of vehicle chassis, subframe and other complex parts that require high strength, thickness reduction, hole expansion and flanging, which has a very broad application prospect.

BRIEF DESCRIPTION OF THE DRAWINGS

[0056]

Figure 1 is a schematic diagram of the rolling and cooling process for the steel of Examples 1-9 of the present invention;

Figure 2 is a schematic diagram of the rolling and cooling process for the steel of Examples 10-18 of the present invention;

Figure 3 is a schematic diagram of the cooling process after rolling for the steel of Examples 10-18 of the present invention.

DETAILED DESCRIPTION

[0057] The present invention is further described below with reference to the accompanying examples and drawings.

[0058] The steel compositions of Examples 1-18 of the present invention are shown in Table 1, and the balance being Fe and inevitable impurities.

[0059] The process path of the steels of Examples 1-18 of the present invention is:

1) Smelting and casting

[0060] The composition shown in Table 1 was smelted by a converter or an electric furnace, secondary refined by a vacuum furnace, and casted into billets or ingots;

2) Reheating of billets or ingots

[0061] In Examples 1-9, the heating temperature was $\geq 1100^{\circ}\text{C}$ and between $1100-1300^{\circ}\text{C}$; in Examples 10-18, the heating temperature was 1200°C or more and between $1200-1300^{\circ}\text{C}$. The holding time was 1-2 hours.

3) Hot rolling and cooling

[0062] In Examples 1-9, primary cooling was used. Specifically, the initial rolling temperature was $1000-1100^{\circ}\text{C}$, and rough rolling of 3-5 passes was carried out under high pressure at 950°C or more to a cumulative deformation of $\geq 50\%$, then the intermediate billet was air-cooled or water-cooled to $900-950^{\circ}\text{C}$, and finishing rolling of 7 passes was carried out to a cumulative deformation of $\geq 70\%$, completing the finishing rolling between $800-900^{\circ}\text{C}$, then the steel strip was water-cooled to $400-550^{\circ}\text{C}$ at a cooling rate of $\geq 10^{\circ}\text{C/s}$ and coiled, and slowly cooled to room temperature at a cooling rate of $\leq 20^{\circ}\text{C/s}$.

4) Pickling

[0063] The pickling operating speed of the strip steel was $30-140\text{m/min}$, preferably $30-120\text{m/min}$, the pickling temperature was $75-85^{\circ}\text{C}$, the straightening rate was $\leq 3\%$, rinsing was carried out at $35-50^{\circ}\text{C}$, and surface drying and oiling were carried out at $120-140^{\circ}\text{C}$.

[0064] In Examples 10-18, secondary cooling was used in step 3 above. Specifically, the initial rolling temperature of hot rolling was $1050-1150^{\circ}\text{C}$, and rough rolling of 3-5 passes was carried out under high pressure at 1050°C or more to a cumulative deformation of $\geq 50\%$, then the intermediate billet was heated to $950-1000^{\circ}\text{C}$, and finishing rolling of 3-7 passes was carried out to a cumulative deformation of $\geq 70\%$, and the finishing rolling temperature was $800-950^{\circ}\text{C}$; cooling was staged cooling, and after finishing rolling, the steel strip was water-cooled to $600-750^{\circ}\text{C}$ at a cooling rate of $\geq 30^{\circ}\text{C/s}$, after air cooling for 1-10 seconds, the steel strip was cooled to $400-550^{\circ}\text{C}$ at a cooling rate of $\geq 10^{\circ}\text{C/s}$ and coiled, and cooled to room temperature at a cooling rate of $\leq 20^{\circ}\text{C/h}$.

[0065] Figure 1 illustrates the procedure of the method for manufacturing the present invention. Table 2 shows the manufacturing process parameters of the steel of Examples 1-18 of the present invention. Table 3 shows the performance parameters of the pickled steel of Examples 1-18 of the present invention.

[0066] The steel in Comparative Examples 1-3 is selected from CN103602895A, and the steel in Comparative Example 4 is selected from CN114107792A.

[0067] As can be seen from Table 1, none of the compositions of Comparative Example 1-4 contain V elements, while the compositions of Comparative Examples 1-3 also contain high silicon. Therefore, from the perspective of the surface quality of the steel plates, the surfaces of the steel plates of Comparative Examples 1-3 inevitably contain red scale, while the examples of the present invention are all designed with silicon-free compositions and have excellent surface quality.

[0068] In addition, all of Comparative Examples 1 to 4 only adopted high titanium composition designs, and no V was added to the steel, indicating that they adopted nano-titanium carbide precipitation strengthening; while the Examples of the present invention adopted high vanadium composition designs and used nano-vanadium carbide for strengthening.

[0069] As can be seen from Table 3, through quantitative design and precise control of compositions and key process parameters, the present invention can obtain high hole expansion steels of three different strength grades with a yield strength of $\geq 500-800\text{MPa}$, a tensile strength of $\geq 590-980\text{MPa}$, an elongation (transverse A50) of $\geq 13-18\%$, and a hole expansion ratio of $\geq 30-80\%$.

[0070] The mechanical performances of the steel in Table 3 were determined as follows:

The yield strength, tensile strength and elongation (transverse A50) of the steel were tested in accordance with GB/T 228.1-2021 "Tensile Test of Metallic Materials Part 1: Room Temperature Test Methods".

[0071] The hole expansion ratio of steel was tested in accordance with GB/T 24524-2021 "Metallic Materials, Thin plates and stripes, Hole expansion test methods".

[0072] The steel structure of Examples 1-9 is bainite, and the bainite contains nano-VC, wherein the volume fraction of nano-VC in the bainite is approximately $0.005-0.05\%$, preferably $0.005-0.03\%$.

[0073] The steel structures of Examples 10-18 are ferrite and bainite, wherein the ferrite contains nano-TiC and the bainite contains nano-VC. Specifically, the volume fraction of ferrite in steel is $10-40\%$, the volume fraction of nano-TiC in ferrite is about $0.005-0.02\%$, the volume fraction of bainite in steel is $60-90\%$, and the volume fraction of nano-VC in bainite is approximately $0.005-0.03\%$.

[0074] As can be seen from the above examples, the high hole expansion steel of the present invention has a good match of high strength, high plasticity and high hole expansion ratio, and is particularly suitable for manufacturing parts such as vehicle chassis structures that require high strength, thickness reduction, hole expansion and flanging forming, which has a broad application prospect.

Table 1 (unit: percentage by mass)

	C	Si	Mn	P	S	Al	N	V	O	Mo	Nb	Ti	Cu	Ni	Cr	B
Example 1	0.02	0.05	1.74	0.018	0.0024	0.058	0.0025	0.10	0.0022	0.5	-	0.10	-	0.3	0.2	0.0015
Example 2	0.03	0.14	1.52	0.015	0.0028	0.074	0.0024	0.15	0.0025	-	0.04	-	0.4	-	0.5	0.0012
Example 3	0.01	0.19	1.27	0.016	0.0023	0.052	0.0030	0.20	0.0018	0.4	-	0.08	0.3	0.1	-	0.0006
Example 4	0.05	0.16	1.43	0.011	0.0030	0.023	0.0029	0.27	0.0023	-	0.10	0.20	-	0.5	0.1	-
Example 5	0.07	0.08	1.99	0.009	0.0025	0.045	0.0038	0.20	0.0030	-	0.06	0.16	0.2	0.3	-	-
Example 6	0.06	0.12	1.84	0.014	0.0021	0.064	0.0035	0.35	0.0014	0.1	-	-	-	0.1	-	0.0010
Example 7	0.10	0.07	0.76	0.017	0.0026	0.011	0.0040	0.50	0.0020	-	0.08	0.05	0.5	0.2	0.4	0.0019
Example 8	0.08	0.15	0.51	0.020	0.0029	0.032	0.0037	0.36	0.0015	0.3	0.02	-	0.1	0.4	0.3	-
Example 9	0.09	0.09	1.05	0.012	0.0020	0.080	0.0028	0.44	0.0023	0.2	0.05	0.09	0.3	-	-	0.0009
Example 10	0.02	0.15	0.95	0.014	0.0013	0.061	0.0028	0.15	0.0023	-	0.10	0.08	-	0.2	-	0.0007
Example 11	0.03	0.13	0.77	0.013	0.0027	0.042	0.0024	0.10	0.0028	0.5	-	0.10	-	-	0.5	-
Example 12	0.01	0.09	0.53	0.008	0.0015	0.080	0.0040	0.20	0.0029	-	-	0.07	-	-	-	-
Example 13	0.04	0.20	1.73	0.010	0.0030	0.025	0.0027	0.28	0.0025	-	0.06	0.10	0.2	0.1	0.1	-
Example 14	0.07	0.08	1.26	0.012	0.0018	0.056	0.0033	0.34	0.0020	0.3	-	0.13	-	-	-	0.0020
Example 15	0.05	0.14	1.55	0.020	0.0025	0.073	0.0039	0.21	0.0024	-	-	0.15	0.5	-	0.3	-
Example 16	0.09	0.10	1.99	0.009	0.0027	0.011	0.0028	0.43	0.0030	-	0.02	0.12	-	-	-	-
Example 17	0.08	0.13	1.84	0.016	0.0020	0.034	0.0030	0.49	0.0026	0.1	-	0.20	-	0.4	0.2	-
Example 18	0.10	0.06	1.68	0.010	0.0026	0.057	0.0035	0.35	0.0022	-	0.05	0.17	-	0.5	-	0.0015
Comparative Example 1	0.045	<u>1.10</u>	1.70	0.010	0.0009	0.057	0.0031	-	-	-	0.045	0.13	-	-	-	-
Comparative Example 2	0.050	<u>0.85</u>	1.90	0.011	0.0020	0.024	0.0031	-	-	-	0.060	0.11	-	-	-	-
Comparative Example 3	0.080	<u>0.55</u>	1.65	0.009	0.0010	0.051	0.0045	-	-	-	0.024	0.15	-	-	-	-
Comparative Example 4	0.060	0.070	1.73	0.011	0.0024	0.063	0.0038	-	0.0022	0.45	0.010	0.15	-	-	-	-

Table 2

	Heating temperature °C	Initial rolling temperature °C	Cumulative deformation of rough rolling %	Intermediate billet temperature °C	Cumulative deformation of finishing rolling %	Finishing rolling temperature °C	Cooling rate after rolling °C/s	Final cooling temperature °C	Air-cooling time (s)	Water-cooling rate °C/s	Cooling temperature °C	Cooling rate °C/h
Example 1	1130	1030	71	910	93.8	810	-	-	-	35	440	12
Example 2	1100	1000	80	900	95.0	840	-	-	-	50	400	17
Example 3	1120	1010	60	905	94.0	800	-	-	-	10	420	5
Example 4	1180	1060	75	940	96.8	830	-	-	-	60	450	17
Example 5	1140	1040	65	920	95.4	820	-	-	-	40	500	13
Example 6	1160	1050	83	930	96.5	880	-	-	-	70	475	20
Example 7	1260	1100	50	950	95.6	850	-	-	-	20	520	7
Example 8	1230	1090	62	945	96.8	870	-	-	-	45	550	15
Example 9	1200	1080	70	940	93.3	900	-	-	-	25	510	10
Example 10	1250	1110	72	970	94.3	870	48	700	7	25	450	8
Example 11	1260	1120	63	980	98.4	910	30	650	1	70	400	7
Example 12	1200	1050	80	950	88.0	800	45	600	4	12	420	10
Example 13	1230	1080	60	960	97.0	860	50	680	2	54	470	13

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(continued)

	Heating temperature °C	Initial rolling temperature °C	Cumulative deformation of rough rolling %	Intermediate billet temperature °C	Cumulative deformation of finishing rolling %	Finishing rolling temperature °C	Cooling rate after rolling °C/s	Final cooling temperature °C	Air-cooling time (s)	Water-cooling rate °C/s	Cooling temperature °C	Cooling rate °C/h
Example 14	1290	1140	75	990	96.5	920	35	620	8	60	450	11
Example 15	1240	1070	58	975	95.7	830	67	730	6	38	480	15
Example 16	1300	1150	70	1000	95.7	950	56	750	3	27	500	14
Example 17	1220	1060	55	965	97.7	900	80	660	5	44	530	17
Example 18	1210	1050	66	955	93.9	850	40	710	10	18	550	20

Table 3

		Steel plate thickness, mm	Yield strength, MPa	Tensile strength, MPa	Elongation, %	Hole expansion ratio, %
5	Example 1	4.5	550	620	22	97.4
	Example 2	2.5	576	646	19	103.6
	Example 3	6.0	543	633	21	100.9
10	Example 4	2.0	746	804	19	99.2
	Example 5	4.0	770	829	18	87.5
	Example 6	1.5	758	815	20	90.7
15	Example 7	5.5	855	998	16	64.5
	Example 8	3.0	864	1035	14	53.1
	Example 9	5.0	912	1027	15	43.3
20	Example 10	4.0	564	622	19.5	89.6
	Example 11	1.5	578	634	20.5	93.4
	Example 12	6.0	601	657	20.0	75.8
25	Example 13	3.0	685	835	18.5	73.2
	Example 14	2.2	734	826	18.0	55.6
	Example 15	4.5	777	808	19.0	67.9
30	Example 16	3.2	836	1023	13.0	52.5
	Example 17	2.6	808	1004	14.0	44.3
	Example 18	5.2	842	1037	13.5	38.9
35	Comparative Example 1	2.9	720	790	19	58
	Comparative Example 2	2.8	710	820	17	65
	Comparative Example 3	4.0	750	856	15	50
	Comparative Example 4	6.0	783	832	19	96

Claims

- 40 1. A steel, comprising the following components in percentage by mass:
C: 0.01-0.10%; Si $\leq$ 0.2%; Mn: 0.5-2.0%; P $\leq$ 0.02%; S $\leq$ 0.003%; Al: 0.01-0.08%; N $\leq$ 0.004%; V: 0.10-0.50%; O $\leq$ 0.003%;
and the balance of Fe and inevitable impurities.
- 45 2. The steel as claimed in claim 1, **characterized in that**, the steel further comprises 0.05-0.2%, preferably 0.08-0.15%, more preferably 0.08-0.10% of Ti in percentage by mass.
3. The steel as claimed in claim 1 or 2, **characterized in that**, the steel further comprises one or more components selected from Nb $\leq$ 0.1%, Cu $\leq$ 0.5%, Ni $\leq$ 0.5%, Cr $\leq$ 0.5%, and B $\leq$ 0.002% in percentage by mass.
- 50 4. The steel as claimed in claim 3, **characterized in that**, the steel further comprises 0.1-0.5%, preferably 0.20-0.40%, more preferably 0.2-0.3% of Mo in percentage by mass.
- 55 5. The steel as claimed in claim 1 or 2, **characterized in that**, the components of the steel satisfy one or more of the following: C: 0.03-0.07%; Si $\leq$ 0.10%; Mn: 0.8-1.6%; S $\leq$ 0.0018%; Al: 0.02-0.05%; N $\leq$ 0.003%; O $\leq$ 0.002%.
6. The steel as claimed in claim 3, **characterized in that**, the components of the steel satisfy one or more of the following: Nb $\leq$ 0.06%, Cu $\leq$ 0.3%, Ni $\leq$ 0.3%, Cr $\leq$ 0.3%, and B $\leq$ 0.001%.

7. The steel as claimed in claim 1, **characterized in that**, the steel has a structure of bainite and nano-precipitated VC in bainite.
8. The steel as claimed in claim 2, **characterized in that**, the steel has a structure of ferrite and bainite, wherein the ferrite contains nano-TiC and the bainite contains nano-VC.
9. The steel as claimed in any one of claims 1-8, **characterized in that**, the steel has a yield strength of 500MPa or more, a tensile strength of 590MPa or more, preferably 780MPa or more, and a transverse elongation A50 of 14% or more and 30% or less.
10. A method for manufacturing the steel of any one of claims 1-9, including the following steps:
 - 1) Smelting and casting
The composition of any one of claims 1-9 is smelted by a converter or an electric furnace, secondary refined by a vacuum furnace, and casted into billets or ingots;
 - 2) Reheating the billets or ingots
Heating temperature $\geq 1100^{\circ}\text{C}$, holding time: 1-2 hours;
 - 3) Hot rolling and cooling.
11. The method as claimed in claim 10, **characterized in that** in step 3), an initial rolling temperature is $1000-1100^{\circ}\text{C}$, and rough rolling of 3-5 passes is carried out under high pressure at 950°C or more to a cumulative deformation of $\geq 50\%$, then an intermediate billet is air-cooled or water-cooled to $900-950^{\circ}\text{C}$, and finishing rolling of 7 passes is carried out to a cumulative deformation of $\geq 70\%$, completing the finishing rolling between $800-900^{\circ}\text{C}$ and obtaining a steel strip, thereafter, the steel strip is water-cooled to $400-550^{\circ}\text{C}$ at a cooling rate of $\geq 10^{\circ}\text{C/s}$ and coiled, then slowly cooling to room temperature at a cooling rate of $\leq 20^{\circ}\text{C/s}$, obtaining a hot-rolled steel strip.
12. The method as claimed in claim 10, **characterized in that** in step 3), the initial rolling temperature of the hot rolling is $1050-1150^{\circ}\text{C}$, and rough rolling of 3-5 passes is carried out under high pressure at 1050°C or more to a cumulative deformation of $\geq 50\%$, then an intermediate billet is heated to $950-1000^{\circ}\text{C}$, and finishing rolling of 3-7 passes are carried out to a cumulative deformation of $\geq 70\%$, and the finishing rolling temperature is $800-950^{\circ}\text{C}$, obtaining a steel strip;
wherein the cooling is staged cooling, and after finishing rolling, the steel strip is water-cooled to $600-750^{\circ}\text{C}$ at a cooling rate of $\geq 30^{\circ}\text{C/s}$, then after air cooling for 1-10 seconds, the steel strip is cooled to $400-550^{\circ}\text{C}$ at a cooling rate of $\geq 10^{\circ}\text{C/s}$ and coiled, then cooling to room temperature at a cooling rate of $\leq 20^{\circ}\text{C/h}$, obtaining a hot-rolled strip steel.
13. The method as claimed in claim 11 or 12, **characterized in that**, the method further includes step 4) Pickling, wherein a pickling operating speed of the hot-rolled strip steel is 30-140m/min, preferably 30-120m/min, a pickling temperature is $75-85^{\circ}\text{C}$, a straightening rate is $\leq 3\%$, rinsing is carried out at $35-50^{\circ}\text{C}$, and surface drying and oiling are carried out at $120-140^{\circ}\text{C}$.

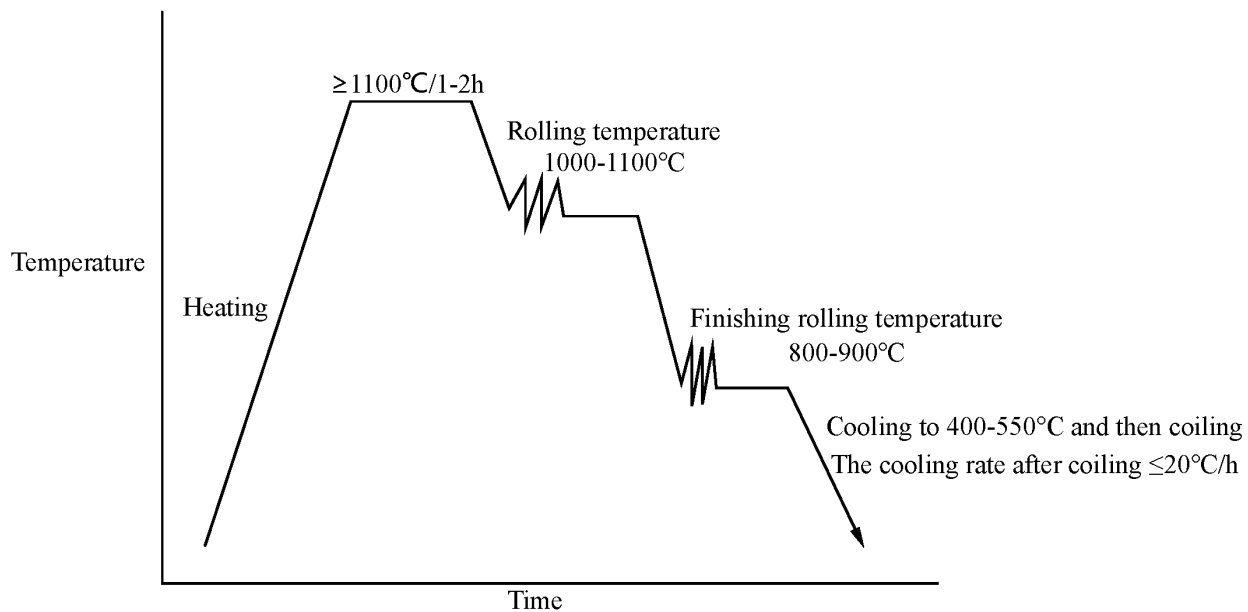


Figure 1

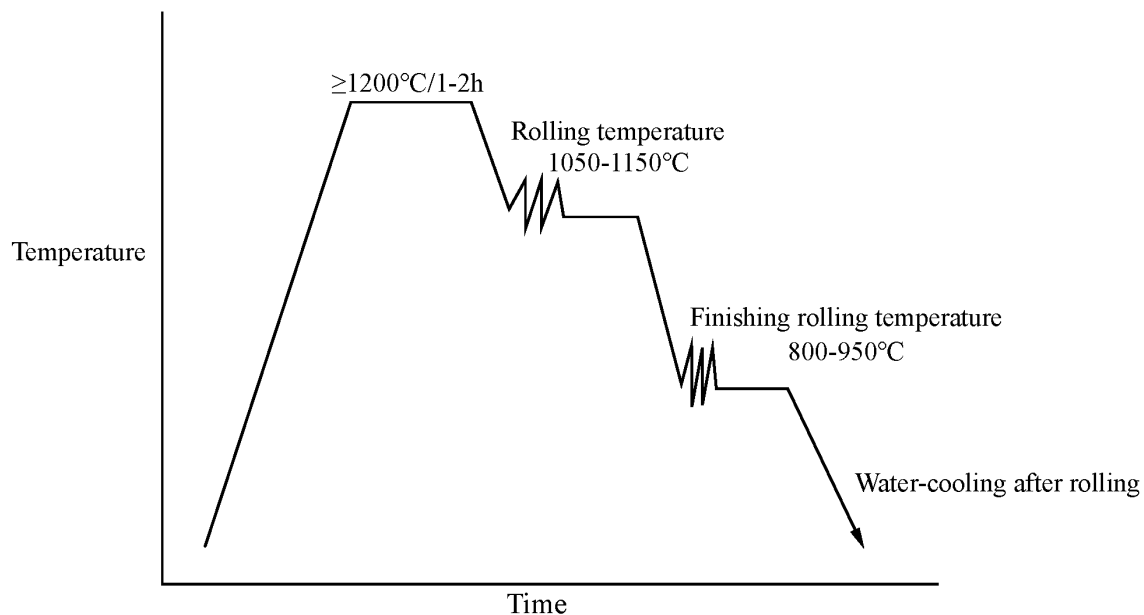


Figure 2

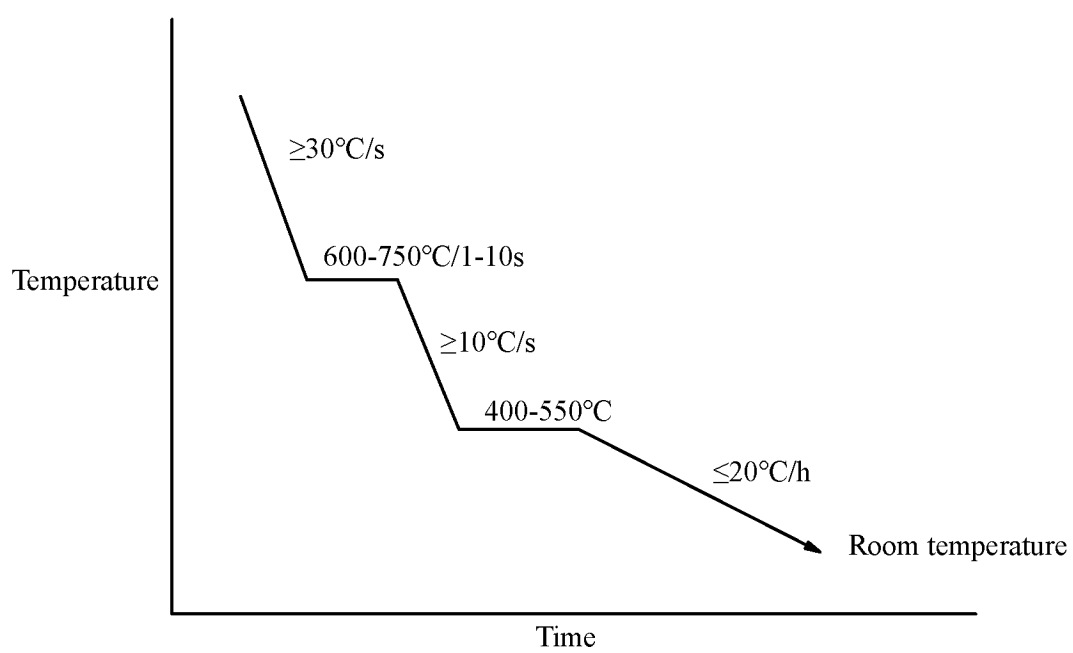


Figure 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2023/101836

A. CLASSIFICATION OF SUBJECT MATTER

C22C38/00(2006.01)i; C22C38/58(2006.01)i; C21D8/02(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)

IPC: 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, DWPI, ENTXTC, ENTXT, CNKI: 碳, 锰, 钒, 钛, 钼, 扩孔, C, carbon, Mn, manganese, mangan, V, vanadium, Ti, titan, titanium, Mo, molybdenum, hole expans+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2005256141 A (JFE STEEL K. K.) 22 September 2005 (2005-09-22) claims 1-4, and description, paragraphs 11, 18, and 43-45, and table 1 and table 2	1-6, 9, 10
X	CN 114107797 A (BAOSHAN IRON & STEEL CO., LTD.) 01 March 2022 (2022-03-01) description, paragraphs 10-13 and 32-46	4, 10, 11, 13
X	CN 103108971 A (JFE STEEL CORP.) 15 May 2013 (2013-05-15) claims 1-8, and description, paragraphs 20, 39-47, and 57-64	1-7, 9
X	CN 104968819 A (JFE STEEL CORP.) 07 October 2015 (2015-10-07) claims 1-9, and description, paragraphs 46, 70, and 89, and table 1	2-6, 8
X	CN 105734423 A (BAOSHAN IRON & STEEL CO., LTD.) 06 July 2016 (2016-07-06) description, paragraphs 9, 10, 22-24, 33-39, and 55-57	3, 6, 9, 10, 12
X	JP 2013234340 A (NIPPON STEEL & SUMITOMO METAL CORP.) 21 November 2013 (2013-11-21) claims 1-5	1-6
X	CN 102906296 A (JFE STEEL CORP.) 30 January 2013 (2013-01-30) description, paragraph 165, and table 5	2, 3

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

* Special categories of cited documents:

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“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

20 September 2023

Date of mailing of the international search report

27 September 2023

Name and mailing address of the ISA/CN

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Telephone No.

INTERNATIONAL SEARCH REPORT

International application No. PCT/CN2023/101836

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 111492076 A (SSAB TECHNOLOGY AB) 04 August 2020 (2020-08-04) claims 1-10	4
X	CN 103597100 A (THYSSENKRUPP STEEL EUROPE AG) 19 February 2014 (2014-02-19) claims 1-6, and description, paragraphs 24-29	1-6, 9
X	CN 102251170 A (BAOSHAN IRON & STEEL CO., LTD.) 23 November 2011 (2011-11-23) claims 1-6	3, 4, 6

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2023/101836

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2005256141 A	22 September 2005	JP 4293020 B2	08 July 2009
CN 114107797 A	01 March 2022	None	
CN 103108971 A	15 May 2013	EP 2617853 A1	24 July 2013
		EP 2617853 A4	16 August 2017
		EP 2617853 B1	13 February 2019
		WO 2012036312 A1	22 March 2012
		BR 112013005851 A2	17 May 2016
		US 2013276940 A1	24 October 2013
		RU 2527571 C1	10 September 2014
		JP 2012062561 A	29 March 2012
		JP 5126326 B2	23 January 2013
		KR 20130055019 A	27 May 2013
		KR 101492753 B1	11 February 2015
		MX 2013002893 A	10 April 2013
CN 104968819 A	07 October 2015	TW 201435097 A	16 September 2014
		TWI 518186 B	21 January 2016
		EP 2952600 A1	09 December 2015
		EP 2952600 A4	24 February 2016
		EP 2952600 B1	20 June 2018
		WO 2014119261 A1	07 August 2014
		KR 20150097716 A	26 August 2015
		KR 101772926 B1	30 August 2017
		US 2015368741 A1	24 December 2015
		JP 2014148698 A	21 August 2014
		JP 5610003 B2	22 October 2014
CN 105734423 A	06 July 2016	None	
JP 2013234340 A	21 November 2013	JP 5867278 B2	24 February 2016
CN 102906296 A	30 January 2013	EP 2554706 A1	06 February 2013
		EP 2554706 A4	06 December 2017
		EP 2554706 B1	28 August 2019
		US 2013133790 A1	30 May 2013
		US 9068238 B2	30 June 2015
		TW 201202441 A	16 January 2012
		TWI 425099 B	01 February 2014
		JP 2011225980 A	10 November 2011
		JP 5041084 B2	03 October 2012
		KR 20140047743 A	22 April 2014
		WO 2011122031 A1	06 October 2011
		KR 20120126126 A	20 November 2012
CN 111492076 A	04 August 2020	ES 2836707 T3	28 June 2021
		EP 3492611 A1	05 June 2019
		EP 3492611 B1	28 October 2020
		JP 2021505759 A	18 February 2021
		KR 20200090888 A	29 July 2020
		WO 2019110359 A1	13 June 2019
		US 2020308679 A1	01 October 2020
		US 11655528 B2	23 May 2023
CN 103597100 A	19 February 2014	WO 2012156428 A1	22 November 2012
		ES 2628409 T3	02 August 2017

Form PCT/ISA/210 (patent family annex) (July 2022)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2023/101836

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
		EP 2710158 A1	26 March 2014
		EP 2710158 B1	15 March 2017
		KR 20140024903 A	03 March 2014
		KR 102001648 B1	01 October 2019
		EP 2524970 A1	21 November 2012
		US 2014322559 A1	30 October 2014
		US 9650708 B2	16 May 2017
		JP 2014518945 A	07 August 2014
		JP 6193219 B2	06 September 2017
		PL 2710158 T3	29 September 2017
-----	-----	-----	-----
CN 102251170 A	23 November 2011	None	
-----	-----	-----	-----

Form PCT/ISA/210 (patent family annex) (July 2022)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- CN 103602895 A [0005] [0052] [0066]
- CN 105821301 A [0006] [0052]
- CN 108570604 A [0007] [0053]
- CN 114107792 A [0008] [0066]