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(54) **ENAMEL STEEL HAVING HIGH-TEMPERATURE BAKING HARDENABILITY AND MANUFACTURING METHOD THEREFOR**

(57) Disclosed is an enamel steel having a high-temperature baking hardenability, comprising chemical elements in mass percentage: C: 0.008-0.020%, Mn: 0.05-0.50%, S: 0.021-0.035%, Al: 0.005-0.050% or Als: 0.003-0.045%, $0 < N < 0.003\%$, $0 < O \leq 0.010\%$, and element Ti in a mass percentage meeting $N \times Ti \leq 3 \times 10^{-4}$, $S \times Ti \geq 2 \times 10^{-3}$ and $Ti \geq 3.43N + 1.5S + 0.02$, the balance being Fe and inevitable impurity elements. Also

disclosed is a method for manufacturing the above-mentioned enamel steel, comprising the steps of: a liquid iron pretreatment → smelting with a converter → refining → continuous casting → hot rolling. The enamel steel having a high-temperature baking hardenability of the present invention has a better formability, a good welding property, an excellent enamelling firing property and a good enamelling property.

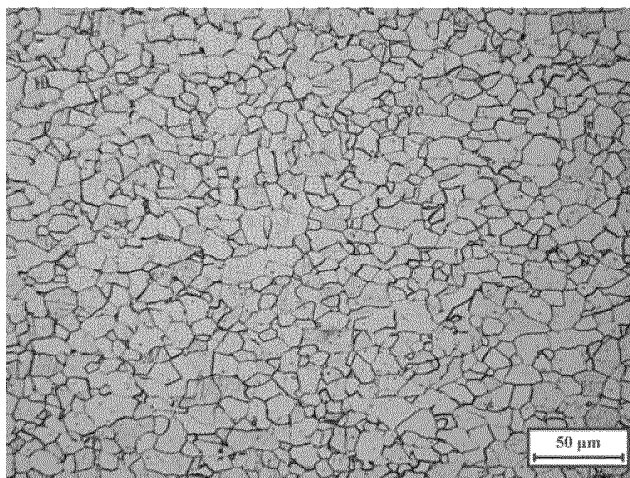


Fig. 2

Description**Technical Field**

5 **[0001]** The present invention relates to an alloy steel and a method for manufacturing the same, in particular an enamel steel and a method for manufacturing the same.

Background Art

10 **[0002]** With regard to a volume type water heater, a liner is a critical component, which determines the service safety and service life of the water heater. An enamel liner having a steel plate as a base slab has a number of features such as a good corrosion resistance, a high surface hardness, being smooth and easy to clean, and such an enamel liner significantly improves the service life and comprehensive performance of the water heater liner. When using a steel plate as a base slab to manufacture an enamel liner of a water heater, the steel plate first needs to undergo blanking, processing and forming and welding, is further subjected to enamelling, and finally fired under conditions of a high temperature of about 830°C. However, in order to satisfy the requirements of producing a high quality enamel liner, and the steel plate must meet performance requirements in various aspects of formability, strength, weldability, fish-scaling resistance, pinhole resistance, high temperature firing resistance, etc.

15 **[0003]** Previously, an enamel liner is generally formed by welding three parts, i.e., two end caps and a barrel body, and therefore one enamel liner generally has three welds, including two circumferential welds and one straight weld, wherein the two caps have relatively lower requirements on the formability. However, a new type of liner appears in the prior art, wherein this new type of liner is formed by welding two parts, i.e., an upper barrel and a lower barrel, and the primary three welds are reduced to one circumferential weld in the middle; therefore, circular rolling, hole expansion and two welds are omitted in the process of processing the new type of liner, the manufacturing process being greatly simplified. Moreover, the reduction of welds can substantially improve the pressure-resistance of the liner. In addition, since the new type of liner is stamped relatively deeply, and processes of hole expansion etc. are further performed after the stamping, the requirements for the stamping property and hole expansion property of the steel plate are obviously improved.

20 **[0004]** In order to satisfy the processing requirements of the liner, cold-rolled steel plates are mainly used, where the formability is superior to that in a hot-rolled steel plate. In the prior art, steel plates generally used for liners can meet the stamping requirements, but the hole expansion property is lower, that is to say, cracking easily occurs when hole expansion is made after deep stamping. In addition, since a mechanism of inhibiting abnormal growth of ferrite grains at a high temperature is lacked in the steel, grains in the welds and heat affected zones after welding severely grow abnormally, and grains after high-temperature enamelling firing also easy grow, the yield strengths of the base steel plate, welds, heat affected zones, etc. are decreased, finally causing that cracking and water leakage very easily occur to the liner around the welds when pressurizing. In addition, due to deficiency of hydrogen storage traps in the steel, even under conditions of enamelling on a single face of the liner, fish-scaling phenomenon will often occur.

25 **[0005]** Chinese patent document with a patent publication number of CN 1966753 A, published on February 23, 2007, and entitled "Steel plate for hot-rolled double-side enamel and method for producing same" relates to a steel plate for enamel, with various element components (wt.%) being: C: 0.02%-0.06%, Si: $\leq 0.50\%$, Mn: 0.15%-0.40%, P: $\leq 0.15\%$, S: $\leq 0.006\%$, N: $\leq 0.003\%$, Ti: 0.08%-0.20%, Als: 0.005%-0.055%, Ti/C: 2.2-5, and the balance being Fe and inevitable impurities. The structure in a hot rolled state is ferrite with a grain diameter of 2-20 μm , and TiC particles with a diameter of not greater than 20 nm are uniformly distributed in the structure. In the technical solution disclosed in the patent document, the steel plate for enamel has a higher content of element Ti and a lower content of element S.

30 **[0006]** Chinese patent document with a patent publication number of CN 101684532 A, published on March 31, 2010, and entitled "Enamel steel for cold rolling water heater and manufacturing method thereof" discloses an enamel steel, with the composition of various chemical element components in contents by mass in percentage (wt.%) being: C: 0.01%-0.08%, Si: $\leq 0.03\%$, Mn: 0.10%-0.60%, P: $\leq 0.02\%$, S: 0.003%-0.02%, N: 0.001%-0.006%, Als: $\leq 0.04\%$, Ti: 0.02%-0.12%, and the balance being iron and inevitable impurities, wherein the content of excess titanium in the steel meets the relational formula: $\text{Ti} - (4 \times \text{C} + 3.43 \times \text{N} + 1.5\text{S}) \leq 0$. The enamel steel disclosed in the Chinese patent document has a yield strength after simulated enamelling firing lower than the yield strength before the simulated enamelling firing.

35 **[0007]** Chinese patent document with patent publication number of CN 101586210 A, published on November 25, 2009, entitled "High strength enamel steel and producing technology and enamel firing technology thereof" discloses an enamel steel, with the contents of various chemical elements by mass in percentage thereof being: C: 0.01-0.12, Si: ≤ 0.03 , Mn: 0.50-1.00, P: ≤ 0.070 , S: ≤ 0.015 , Nb: 0.020-0.050, Mo: 0.05-0.30, Als: 0.005-0.070, and the balance being iron and inevitable impurities. In addition, the enamel steel further meets $10\text{Nb} \geq \text{Mo}$ and $0.30 \leq 10\text{Nb} + \text{Mo} \leq 0.50$.

Summary of the Invention

[0008] An object of the present invention lies in providing an enamel steel having a high-temperature baking hardenability, which has an excellent formability, a good welding property and a good enamelling property. In addition, the enamel steel of the present invention further has an excellent enamelling firing property, and the yield strength after high-temperature enamelling firing will be significantly improved, i.e., having a high-temperature baking hardenability. In addition, the alloy addition cost of the enamel steel of the present invention is low.

[0009] In order to achieve the above-mentioned object, the present invention provides an enamel steel having a high-temperature baking hardenability, the chemical elements thereof, in mass percentage, being:

C: 0.008-0.020%;
 Mn: 0.05-0.50%;
 S: 0.021-0.035%;
 Al: 0.005-0.050% of or Al₂O₃: 0.003-0.045wt.%;
 $0 < N < 0.003\%$;
 $0 < O < 0.010\%$;

and element Ti, in a mass percentage meeting $N \times Ti \leq 3 \times 10^{-4}$, $S \times Ti \geq 2 \times 10^{-3}$ and $Ti \geq 3.43N + 1.5S + 0.02$, the balance being Fe and inevitable impurity elements.

[0010] In the present technical solution, the inevitable impurities mainly refer to elements P and Si. When the content of P is higher, segregation easily occurs at the grain boundary in the steel, thereby bubbles and black spots are easily produced when enamelling firing, which thus affects the surface quality of the enamel. When the content of Si is higher, not only the enamel properties of the steel will be damaged, but also oxide inclusions having very poor ductility may be formed, thus damaging the plasticity of the steel. With regard to the technical solution of the present invention, elements P and Si are harmful elements, the contents of these two elements in the steel needs to be as low as possible; therefore, the content of element Si can be controlled at $\leq 0.10\text{wt.}\%$, and the content of element P is controlled at $\leq 0.035\text{wt.}\%$.

[0011] The design principle of various chemical elements of the enamel steel having a high-temperature baking hardenability of the present invention is:

[0012] C and Ti, wherein firstly, the content of carbon in the steel greatly affects the formability and strength of the steel plate, the higher the content of carbon, the lower the plasticity, and the higher the strength, vice versa. Secondly, in addition to being present in the steel in a solid solution, carbon can further form a microstructure such as cementite or pearlite. In addition, after titanium alloy is added, carbon can further form titanium carbide compounds with titanium.

[0013] In the technical solution of the invention, by controlling the content of carbon and the content of element titanium reacting with carbon, and combining the subsequent process control, carbon will not form a microstructure of pearlite, but is present in a form of dispersed carbides (such as titanium carbide, cementite) or a small amount of a solid solution. Due to the substantial aggregation of cementite in the microstructure of pearlite, on the one hand, a great amount of bubbles will be formed in the process of enamelling, and on the other hand, it is not disadvantageous to improve the strength of the steel in the process of enamelling firing. When the content of carbon is higher than 0.020 wt.%, carbon very easily forms coarser cementite, and even may produce a microstructure of pearlite; on the contrary, when the content of carbon is lower than 0.008 wt.%, not only the content of cementite in the steel is small, but also the titanium carbide formed with titanium is also very less, it being impossible to have a strengthening function, and the strength of the steel is reduced, and as a result, an effect of high-temperature baking hardenability also cannot be achieved.

[0014] With regard to the technical solution of the present invention, the addition amount of titanium alloy is very important. It can be seen according to calculation of the solubility product of the formation of titanium compounds that titanium first reacts with nitrogen, then reacts with sulphur, and finally reacts with carbon; therefore, in such a precipitation order, it shall be certainly ensured that a part of titanium forms titanium carbide by reacting with carbon. When the content of element titanium in mass percentage meets the relational formula: $Ti \geq 3.43N + 1.5S + 0.02$, it can be ensured that a part of titanium reacts with carbon; in addition, by controlling the hot rolling process, cementite particles are smaller as compared to the existing cementite particles, and titanium carbide and titanium carbonitride are present in a state of fine particles so as to achieve a purpose of matrix strengthening. In addition, in the process of high-temperature enamelling firing, a part of cementite and titanium carbide and titanium carbonitride particles which are originally present in fine dispersed states will be dissolved in the subsequent heating process, but re-precipitated again in the following cooling process, and the re-precipitated particles will be finer and more dispersed, thus achieving the purpose of reaching baking hardenability by a high-temperature process. On the contrary, if the content of element titanium in mass percentage is excessively low, if lower than the content as defined in the relational formula, i.e., when $Ti < 3.43N + 1.5S + 0.02$, it will be very difficult to ensure that a certain quantity of titanium carbide and titanium carbonitride particles are present in the steel, such that the purpose of precipitation strengthening cannot be achieved. To this end, by high-temperature firing, the strength of the steel cannot be further improved. Consequently, the content of element C in the enamel steel having

a high-temperature baking hardenability of the present invention should be controlled at 0.008-0.020 wt.%, and the content of element Ti should meet $Ti \geq 3.43N + 1.5S + 0.02$.

[0015] In addition, more preferably, the content of element C is controlled in a range between 0.015-0.020 wt.%.

[0016] Mn: Manganese is a deoxidation element in the steel, and adding such an element can control the content of oxygen in the steel. Manganese can react with sulphur to produce manganese sulphide. After adding element titanium in the steel, manganese can further form a composite inclusion with the element, such as manganese titanium sulphide. Such an inclusion is in a spherical shape, and can remarkably reduce the effect of manganese sulphide on the processability. However, when the content of manganese is excessively high, the reaction at the interface of steel and enamel will be affected in the enamelling process, such that the adherence of the enamel is damaged, and defects such as bubbles are easily produced. In view of this, the content of Mn in the enamel steel having a high-temperature baking hardenability of the present invention is set as 0.05-0.50 wt.%.

[0017] Preferably, the content of Mn in the enamel steel having a high-temperature baking hardenability of the present invention is further set as 0.1-0.3 wt.%.

[0018] S: generally, sulphur is a harmful element in the steel, this is because sulphur and manganese will form an inclusion of manganese sulphide, which may damage the transverse plasticity of the steel plate. However, in the technical solution of the present invention, element S is not a harmful element, the content of S in the enamel steel needs to be controlled within a range between 0.021-0.035 wt.%, and it is further ensured that $S \times Ti \geq 2 \times 10^{-3}$. The reason why the content of sulphur is controlled within a range between 0.021-0.035 wt.% is that on the basis of adding titanium, sulphur and titanium will form titanium sulphide, a great amount of hydrogen storage traps will be formed around titanium sulphide particles, and as a result, defects of fish-scaling in the enamelling process are less likely produced. In addition, after element titanium is added in the steel, adverse effect of manganese sulphide formed in the steel on the plasticity of steel can be further reduced. However, if the content of sulphur is higher than 0.035 wt.%, more titanium and manganese need to be consumed by sulphur to form sulphides, and the formed sulphide particles will be very large, such that the plasticity of the steel will be damaged. In addition, larger particle sulphides will also have a very limited effect on the improvement of the fish-scaling resistance. In addition, sulphur can form titanium sulphide with titanium or can form composite manganese titanium sulphide with titanium and manganese. By controlling the content of sulphur and ensuring $S \times Ti \geq 2 \times 10^{-3}$, titanium sulphide may be formed in advance of manganese sulphide. The reason lies in that the greater the product of $S \times Ti$, the higher the formation temperature of titanium sulphide, and the shape of titanium sulphide particles is in a spherical shape, such that by controlling the heating and rolling steps in the subsequent hot rolling process, the shape and size of titanium sulphide can be further improved. Likewise, with regard to element manganese, manganese may also form a composite inclusion of manganese titanium sulphide, the particles shape of the composite inclusion is also a spherical shape; to this end, the formation of pure plastic manganese sulphide inclusion can be avoided in the steel, thus improving the processability of the steel.

[0019] In addition, controlling the content of S in the enamel steel at 0.021-0.03 wt.% is a more preferred technical solution.

[0020] Al or Als: Aluminium is also a strong deoxidization element. When the content of aluminium is higher, the content of oxygen in the steel will be reduced; on the contrary, when the content of aluminium is excessively low, the content of oxygen in the steel will be improved. The oxygen remaining in the steel is mainly present in a form of an oxide inclusion, which will severely damage the plasticity of the steel. An appropriate amount of aluminium can reduce the content of oxygen in the steel, and thus aluminium is one of elements to be necessarily added in the steel. To this end, with regard to the enamel steel having a high-temperature baking hardenability of the present invention, if Al is defined in a form of Alt (total aluminium), it is then required to control the content of Alt at 0.005-0.050 wt.%; and if Al is defined in a form of Als (acid soluble aluminium), Als then needs to be controlled at 0.003-0.045 wt.%.

[0021] N: Nitrogen is one of inevitable residual elements in the steel. Generally, nitrogen is a solid solution element, wherein after the addition of titanium into the steel, since nitrogen is extremely easy to form a metal compound with titanium, in the steel to which titanium is added, nitrogen will be more preferential to form titanium nitride with respect to sulphur and carbon. The sequence of forming titanium nitride is related to the contents of titanium and nitrogen, and this can be calculated according to the solubility product of the formation of titanium nitride, i.e., $\lg[Ti][N] = 5.4 - 15790/T$, wherein T is the solid solution temperature of titanium nitride, the unit being K, and both Ti and N are in a content in mass percentage. The higher the contents of nitrogen and/or titanium, also the higher the content of the formed titanium nitride, and also the larger the particles. In addition, if it is required to fix 0.001 wt.% of nitrogen, 0.00343 wt.% of titanium needs to be consumed, and the mass of the titanium consumed is about 3.43 times that of nitrogen. In the processing deformation, with respect to the titanium nitride particles, tiny holes will be formed around the particles so as to be beneficial for hydrogen storage in the steel plate during the enamelling process; however, titanium nitride particles can further seriously damage the plasticity, hole expansion property and other mechanical properties of the steel plate. In addition, the titanium nitride particles also cannot improve the strength of the steel and the strength of the steel after enamelling firing. To this end, in order to avoid forming a coarse titanium nitride inclusion in the steel and reduce the consumption of titanium by nitrogen, the nitrogen in the steel should be as low as possible, and the content of nitrogen is controlled

at $0 < N < 0.003$ wt.% and meeting $N \times Ti \leq 3 \times 10^{-4}$.

[0022] O: Since the process of smelting of liquid steel mainly relies on reactions of carbon and oxygen, oxygen is inevitable in the steel. However, when the content of oxygen in the steel is excessively high, an oxide inclusion may be formed to affect the processability of the steel. On this basis, O in the enamel steel having a high-temperature baking hardenability of the present invention has to be controlled as $0 < O \leq 0.010$ wt.%.

[0023] In the technical solution of the present invention, the definition of the content of titanium in mass percentage is defined by the following three constraint formulae: 1) $N \times Ti \leq 3 \times 10^{-4}$, 2) $S \times Ti \geq 2 \times 10^{-3}$, and 3) $Ti \geq 3.43N + 1.5S + 0.02$. That is to say, the addition of element Ti is restricted and limited by the contents of elements N and S in mass percentage.

[0024] Since the content of carbon in the enamel steel of the present invention is low, most carbon will be fixed to form a titanium carbide compound after the addition of titanium into the steel, which results in that both the free state carbon and cementite has an extremely low content, which will greatly inhibit the production of pinhole defects in the enamelling process, thus substantially improving the service life of the enamel liner.

[0025] Further, the element C in the enamel steel having a high-temperature baking hardenability of the present invention is present in a dispersed carbide form.

[0026] More further, said carbide is cementite and finely granulated titanium carbide and titanium carbonitride.

[0027] More further, the grain diameter of said titanium carbide and titanium carbonitride particles are $10-30 \mu\text{m}$.

[0028] More further, the enamel steel having a high-temperature baking hardenability of the present invention further comprises at least one of $0 < Cu \leq 0.10\%$, $0 < Cr \leq 0.10\%$, $0 < Ni \leq 0.10\%$, $0 < Mo \leq 0.10\%$, $0 < Nb \leq 0.010\%$, $0 < V \leq 0.020\%$, and $0 < B \leq 0.0005\%$, with $0.05\% \leq 5 \times Nb + Cu + V + Ni + Cr + Mo + 10 \times B \leq 0.20\%$.

[0029] The fluctuations of the contents of copper, chromium, nickel and molybdenum in the steel all will affect the enamel properties of the steel plate, particularly the adherence of the steel, and surface defects may be produced, and the strength and plasticity of the steel plate will also be affected. In order to further ensure the enamelling property, etc. of the steel plate to be stable and reliable, the addition of the elements is controlled as $0 < Cu \leq 0.10\text{wt.}\%$, $0 < Cr \leq 0.10\text{wt.}\%$, $0 < Ni \leq 0.10\text{wt.}\%$, $0 < Mo \leq 0.10\text{wt.}\%$.

[0030] Adding any of niobium, vanadium and boron can improve the recrystallization temperature of the steel plate. Once the recrystallization temperature is improved, the hot rolling temperature for the steel plate also needs to be accordingly improved. With regard to thin steel plates, for example, steel plates having a finished product thickness of not greater than 2.5 mm, it is very difficult to achieve an excessively high final rolling temperature, and a problem of non-uniform temperatures at different parts of a strip steel will be caused, finally leading to defects of mixed grains and structure abnormality of the steel plate. In addition, although the increase of the recrystallization temperature has a certain effect on improving the strength of the enamel before the firing, it has not too much effect on the improvement of the strength of the enamel after the firing. In order to reduce the adverse effect of these addition elements on the microstructure after hot rolling, they need to be controlled within a certain range, i.e., $0 < Nb \leq 0.010\text{wt.}\%$, $0 < V \leq 0.020\text{wt.}\%$, and $0 < B \leq 0.0005\text{wt.}\%$.

[0031] At the same time, the above-mentioned elements, when added, further need to meet $0.05\text{wt.}\% \leq 5 \times Nb + Cu + V + Ni + Cr + Mo + 10 \times B \leq 0.20\text{wt.}\%$.

[0032] Accordingly, the present invention further provides a manufacturing method for producing the enamel steel having a high-temperature baking hardenability as described hereinabove, comprising the steps of: a liquid iron pre-treatment \rightarrow smelting with a converter \rightarrow refining \rightarrow continuous casting \rightarrow hot rolling.

[0033] Further, the method for manufacturing the enamel steel having a high-temperature baking hardenability of the present invention further comprises steps of: acid pickling \rightarrow cold rolling \rightarrow annealing \rightarrow temper rolling, after the hot rolling step.

[0034] Further, in said cold rolling step, the overall reduction ratio is controlled at greater than 70%. Further preferably, the overall reduction ratio of the cold rolling is controlled at $\geq 75\%$. In addition, in the cold rolling step, the roughness of the steel plate surface can also be controlled within a range of $0.4-2.0 \mu\text{m}$ by changing the roughness of the roll surface of the roller.

[0035] Further, in said annealing step, the annealing temperature is $650-800^\circ\text{C}$.

[0036] More further, in the above-mentioned hot rolling step, the heating temperature is $1100-1250^\circ\text{C}$, and the heating time is $\geq \text{plate thickness} \times 1 \text{ min/mm}$, wherein the unit of plate thickness is mm, and the plate thickness refers to the plate thickness of a continuous casting slab.

[0037] In order to ensure that the microstructure in the steel is formed as uniform austenite, i.e., fully austenized, and allow the cementite or pearlite aggregated in the steel slab to be dissolved, i.e., allowing some mass points formed at a high temperature, such as titanium nitride, to be dissolved or partially dissolved, the heating temperature for the continuous casting slab is set as $1100-1250^\circ\text{C}$. Certainly, the particular heating time within the range can be adjusted according to the thickness of the steel slab, and in general, the thinner the steel slab, the shorter the heating time, the heating time being required to meet $t \geq \text{plate thickness} \times 1 \text{ min/mm}$.

[0038] More further, in the above-mentioned hot rolling step, the final rolling temperature for the hot rolling is $850-930^\circ\text{C}$,

and the coiling temperature for the hot rolling is 630-780°C.

[0039] Since in the hot rolling step, carbides previously dissolved in the continuous casting process, etc., will be re-precipitated in a compound form, the final rolling temperature in the hot rolling step needs to be reasonably controlled such that the carbide is distributed in a form of a fine dispersed state in the ferrite matrix. In view of this, the final rolling

[0040] In the method for manufacturing the enamel steel having a high-temperature baking hardenability of the present invention, the cementite and titanium carbide are present in a state of fine particles by controlling the process parameters of the hot rolling process so as to achieve the purpose of matrix strengthening. In addition, by controlling the heating temperature in the continuous casting step and the final rolling temperature and the coiling temperature in the hot rolling temperature, the shape and size of titanium sulphide in the steel is further improved.

[0041] As compared to the existing enamel steels, the yield strength of the enamel steel having a high-temperature baking hardenability of the present invention after high-temperature enamelling firing will be significantly improved, thus improving the pressure-resistance of an enamel steel article and prolonging the service life.

[0042] The enamel steel having a high-temperature baking hardenability of the present invention has a better formability, an elongation of $\geq 39\%$, and a hole expansion rate of $\geq 60\%$, and is particularly suitable for manufacturing various complex shapes of water heater liners.

[0043] The enamel steel having a high-temperature baking hardenability of the present invention has a good weldability.

[0044] The enamel steel having a high-temperature baking hardenability of the present invention has an excellent enamelling property, and a long hydrogen permeation time (≥ 10 min) which is higher than that of a steel for double-side enamel in the prior art (≥ 8 min).

[0045] Since lower price alloy addition elements are used, the alloy cost of the enamel steel having a high-temperature baking hardenability of the present invention is low, and the manufacturing cost is also relatively economic.

[0046] The production process of the enamel steel having a high-temperature baking hardenability of the present invention is simple and practicable.

Description of the Drawings

[0047]

Figure 1 is a tendency graph of yield strength of an enamel steel having a high-temperature baking hardenability of Example A1 in a condition of heat preservation at 830°C over the heat preservation time.

Figure 2 is a picture of the microstructure of the enamel steel having a high-temperature baking hardenability of Example A1.

Figure 3 is a picture of the morphology of the precipitated phase in the enamel steel having a high-temperature baking hardenability of Example A1.

Particular Embodiments

[0048] The enamel steel having a high-temperature baking hardenability and method for manufacturing the same of the present invention will be further described below according to particular embodiments, but the particular embodiments and related description do not form an inappropriate definition of the technical solution of the present invention.

Examples A1-A6 and Comparative Example B1

[0049] The enamel steels in Examples A1-A5 and Comparative Example B1 are manufactured according to the following steps (1)-(5), and the enamel steel in Example A6 is manufactured according to the following steps (1)-(9):

1) Liquid iron pretreatment;

2) smelting with a converter: decarbonization, dephosphorization and removal of residual elements and harmful gases, etc. are achieved by using a top-bottom combined blowing converter;

3) Refining: the harmful gases and residual elements are further removed, alloy elements such as titanium, etc., are added, and aluminium etc. is added for deoxidation to achieve the accurate control of the chemical composition. The mass percentages of various chemical elements in Examples A1-A6 and Comparative Example B1 are controlled as shown in table 1;

4) Continuous casting: liquid steel is cast into a continuous casting slab having a thickness of 200 or 230 mm, and

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after the continuous casting slab is cooled, the surface quality is manually inspected, and the surface defects manually cleaned;

5) Hot rolling: before the hot rolling, the continuous casting slab is heated at a heating temperature of 1100-1250°C for a heating time of $t \geq \text{plate thickness} \times 1 \text{ min/mm}$, wherein the unit of plate thickness is mm; with regard to the continuous casting slab having a thickness of 200 mm, the heating time is controlled at 200-240 min or more, and with regard to the continuous casting slab having a thickness of 230 mm, the heating time is controlled at 230-260 min or more; and according to needs, the thickness at end of the hot rolling is 1.5-18 mm, and the final rolling temperature for the hot rolling is 850-930°C, and after laminar cooling to the coiling temperature, coiling is performed, the coiling temperature for hot rolling being 630-780°C;

6) Acid pickling: the acid pickling is mainly performed using dilute hydrochloric acid, or may also be performed using other methods, the purpose of the acid pickling being thoroughly removing oxide-scales on the surface;

7) Cold rolling: the overall reduction ratio is controlled at not greater than 70%;

8) Annealing: annealing is performed at 650-800°C, the purpose being achieving recrystallization and grain growth of the structure of the steel plate after the cold rolling so as to obtain a good plasticity; and

9) Temper rolling: the elongation of temper rolling is 0.8-1.2%.

[0050] Reference is made in detail to table 2 for specific process parameters in the various steps.

[0051] Table 1 lists the mass percentages of various chemical elements in the enamel steels in Examples A1-A6 and Comparative Example B1 of the present case.

Table 1. (wt.%, the balance being Fe and other inevitable impurities other than P and S)

Serial number	A1	A2	A3	A4	A5	A6	B1
C	0.013	0.018	0.02	0.008	0.01	0.013	<u>0.031</u>
Mn	0.25	0.2	0.1	0.3	0.25	0.15	0.22
S	0.029	0.025	0.035	0.025	0.03	0.021	<u>0.007</u>
Al	0.041	0.035	0.035	0.028	0.005	0.02	0.031
N	0.0018	0.002	0.0025	0.0015	0.002	0.002	0.0026
O	0.005	0.006	0.003	0.005	0.003	0.003	--
P	0.011	0.015	0.009	0.01	0.008	0.011	0.01
Si	0.008	0.02	0.05	0.03	0.1	0.008	0.006
Ti	0.09	0.08	0.09	0.085	0.15	0.12	0.002
Cu	0.01	0.02	0.02	0.05	0.01	0.06	--
Cr	0.02	0.05	0.02	0.015	0.05	0.06	--
Ni	0.008	0.025	0.008	0.01	0.02	0.005	--
Mo	0.005	0.005	0.015	0.008	0.02	0.01	--
Nb	0.005	0.002	0.002	--	--	0.002	--
V	0.015	--	--	--	0.005	0.01	--
B	--	0.0002	--	--	0.0004	--	--
Relational formula 1)	0.00016	0.00016	0.00023	0.00013	0.0003	0.00024	5.2×10^{-6}
Relational formula 2)	0.0026	0.002	0.0032	0.0021	0.0045	0.0025	<u>1.4×10^{-5}</u>
Relational formula 3)	0.07	0.064	0.081	0.063	0.072	0.058	0.039
Relational formula 4)	0.02	0.016	0.009	0.022	0.078	0.062	<u>-0.037</u>
Relational formula 5)	0.08	0.11	0.07	0.08	0.11	0.16	<u>0</u>
NOTE: Relational formula 1) is $N \times Ti$, relational formula 2) is $S \times Ti$, relational formula 3) is $3.43N + 1.5S + 0.02$, relational formula 4) $Ti - (3.43 \times N + 1.5 \times S + 0.02)$, and relational formula 5) is $5 \times Nb + Cu + V + Ni + Cr + Mo + 10 \times B$.							

[0052] Table 2 lists the process parameters of the method for manufacturing the enamel steels in Examples A1-A6 and Comparative Example B1 of the present case.

Table 2.

Serial number	Thickness of continuous-casting slab (mm)	Hot rolling step					Cold rolling and annealing		Thickness of finished steel plate (mm)	
		Heating temperature (°C)	Heating time (min)	Final rolling temperature (°C)	Coiling temperature (°C)		Reduction ratio (%)	Annealing temperature (°C)	Hot rolling	Cold rolling
A1	200	1100	215	860	630				1.8	-
A2	200	1100	220	865	660				2.0	-
A3	200	1150	235	860	660				2.0	-
A4	200	1250	240	920	730				5.0	-
A5	230	1150	235	880	680				2.5	-
A6	230	1150	260	880	680		75	760	4.0	1.0
B1	200	1150	210	860	660				1.8	-

[0053] At room temperature, transverse sampling is used in any of Examples A1-A6 and Comparative Example B1, and the R_{eL} , R_m , A_{80mm} and hole expansion rate are determined. With regard to the measurement of the hydrogen storage capacities of the enamel steels in Examples A1-A6 and Comparative Example B1, the hydrogen permeation times of the steel plates are measured according to the electrochemical experiment method in Standard EN10209, and all are converted as a standard thickness of 1 mm.

[0054] Under a condition of heat preservation at 830°C, heat treatment is used after the transverse sampling in each of Examples A1-A6 and Comparative Example B1, i.e., the steel plates are taken out after heat preservation at 830°C in a constant temperature furnace for 10 min and air-cooled to room temperature. Of the sample plates after the heat treatment, the R_{eL} , R_m and A_{80mm} are measured.

[0055] Table 3 lists the mechanic property parameters of the enamel steels in Examples A1-A6 and Comparative Example B1 of the present case respectively at room temperature and under the condition of heat preservation at 830°C.

Table 3.

Serial number	Mechanical property at room temperature					Mechanical property after heat preservation at 830°C for 10 min		
	R_{eL}/MPa	R_m/MPa	$A_{80}/\%$	Hole expansion rate/%	Hydrogen permeation time/min	R_{eL}/MPa	R_m/MPa	$A_{80}/\%$
A1	259	344	40	71	15	361	426	41
A2	241	335	42	80	14	371	429	43
A3	265	360	39	70	16	390	448	44.5
A4	197	315	43.5	72	12	315	420	43
A5	220	321	42	75	22	335	412	40
A6	235	330	44	75	20	375	430	41
B1	194	322	38	48	7	180	301	42

[0056] As can be seen from table 3, at room temperature, the yield strengths in Examples A1-A6 are all ≥ 197 MPa, the tensile strengths are all ≥ 315 MPa, the elongations A_{80} are $\geq 39\%$, the hole expansion rates are $\geq 70\%$, and the hydrogen permeation times are ≥ 12 min; and, under the condition of heat preservation at 830°C, the yield strengths in Examples A1-A6 are improved to ≥ 315 MPa, the tensile strengths are all ≥ 412 MPa, and the elongations A_{80} are $\geq 40\%$; it can be indicated therefrom that, not only the enamel steel of the present invention has a higher elongation, a longer hydrogen permeation time, and a higher hole expansion rate, but also both the yield strengths and tensile strengths in all the examples after heat preservation at 830°C for 10 min are substantially improved, which indicates that the enamel steel involved in this technical solution has a good high-temperature baking hardenability, which is beneficial for significantly improving the pressure-resistance and service life of an enamel steel article.

[0057] The hydrogen penetration time of the enamel steel of the present invention is ≥ 12 min. Generally, when the hydrogen penetration time is ≥ 8 min, the steel plate can meet the requirements of fish-scaling resistance for double-side enamel, that is to say, whatever type of glaze is used in actual productions, and this type of steel plate can meet the requirements of fish-scaling resistance. Since the requirements of fish-scaling resistance for double-side enamel are more rigorous than those for single-side enamel, the enamel steel of the present invention can fully meet the requirements for single-side enamel.

[0058] Figure 1 shows tendency graph of yield strength of an enamel steel having a high-temperature baking hardenability of Example A1 in a condition of heat preservation at 830°C over time.

[0059] As shown in figure 1, under the condition of heat preservation at 830°C, when the enamel steel in Example A1 has not achieved the specified heat preservation time (about 10 min), the yield strength of the enamel steel in Example A1 increases over the heat preservation time; however, after the specified heat preservation time is reached, the yield strength decreases over the heat preservation time. Nevertheless, even though the preservation time under the condition of heat preservation at 830°C is longer, the yield strength is still significantly improved with respect to the yield strength under the condition of room temperature.

[0060] Figure 2 shows the microstructure of the enamel steel in Example A1, and figure 3 shows the picture of the morphology of the precipitated phase in the enamel steel.

[0061] As shown in figures 2 and 3, the microstructure of the enamel steel in Example A1 is a uniform ferrite structure, wherein no pearlite structure and larger size cementite particles can be seen, the precipitated phase is in a fine dispersed

distribution, mainly having titanium carbide or titanium carbonitride.

[0062] It should be noted that the examples listed above are only the specific examples of the present invention, and obviously the present invention is not limited to the above examples and can have many similar changes. All variations which can be directly derived from or associated with the disclosure of the invention by those skilled in the art should be within the scope of protection of the present invention.

Claims

1. An enamel steel having a high-temperature baking hardenability, the chemical elements thereof, in mass percentage, being: C: 0.008-0.020%, Mn: 0.05-0.50%, S: 0.021-0.035%, Al: 0.005-0.050% or Als: 0.003-0.045%, $0 < N < 0.003\%$, $0 < O \leq 0.010\%$, and element Ti in a mass percentage meeting $N \times Ti \leq 3 \times 10^{-4}$, $S \times Ti \geq 2 \times 10^{-3}$ and $Ti \geq 3.43N + 1.5S + 0.02$, the balance being Fe and inevitable impurity elements.
2. The enamel steel having a high-temperature baking hardenability of claim 1, **characterized in that** said element C is present in a dispersed carbide form.
3. The enamel steel having a high-temperature baking hardenability of claim 2, **characterized in that** said carbide is cementite and finely granulated titanium carbide and titanium carbonitride.
4. The enamel steel having a high-temperature baking hardenability of claim 3, **characterized in that** the grain size of said titanium carbide and titanium carbonitride particles is 10-30 μm .
5. The enamel steel having a high-temperature baking hardenability of claim 1, **characterized by** further comprising at least one of $0 < Cu \leq 0.10\%$, $0 < Cr \leq 0.10\%$, $0 < Ni \leq 0.10\%$, $0 < Mo \leq 0.10\%$, $0 < Nb \leq 0.010\%$, $0 < V \leq 0.020\%$, and $0 < B \leq 0.0005\%$, with $0.05\% \leq 5 \times Nb + Cu + V + Ni + Cr + Mo + 10 \times B \leq 0.20\%$.
6. The enamel steel having a high-temperature baking hardenability of claim 1, **characterized in that** the content of said element C is 0.015-0.020%.
7. The enamel steel having a high-temperature baking hardenability of claim 1, **characterized in that** the content of said element S is 0.021-0.030%.
8. The enamel steel having a high-temperature baking hardenability of claim 1, **characterized in that** the content of said element Mn is 0.1-0.3%.
9. A method for manufacturing the enamel steel having a high-temperature baking hardenability of any one of claims 1-8, **characterized by** comprising the steps of: a liquid iron pretreatment \rightarrow smelting with a converter \rightarrow refining \rightarrow continuous casting \rightarrow hot rolling.
10. The method for manufacturing the enamel steel having a high-temperature baking hardenability of claim 9, **characterized by** further comprising the steps of: acid pickling \rightarrow cold rolling \rightarrow annealing \rightarrow temper rolling, after said hot rolling step.
11. The method for manufacturing the enamel steel having a high-temperature baking hardenability of claim 10, **characterized in that** in said cold rolling step, the overall reduction ratio is controlled at greater than 70%.
12. The method for manufacturing the enamel steel having a high-temperature baking hardenability of claim 10, **characterized in that** in said annealing step, the annealing temperature is 650-800°C.
13. The method for manufacturing the enamel steel having a high-temperature baking hardenability of claim 9, **characterized in that** in said hot rolling step, the heating temperature is 1100-1250°C, and the heating time is \geq plate thickness $\times 1$ min/mm, wherein the unit of the plate thickness is mm.
14. The method for manufacturing the enamel steel having a high-temperature baking hardenability of claim 9, **characterized in that** in said hot rolling step, the final rolling temperature for the hot rolling is 850-930°C, and the coiling temperature for the hot rolling is 630-780°C.

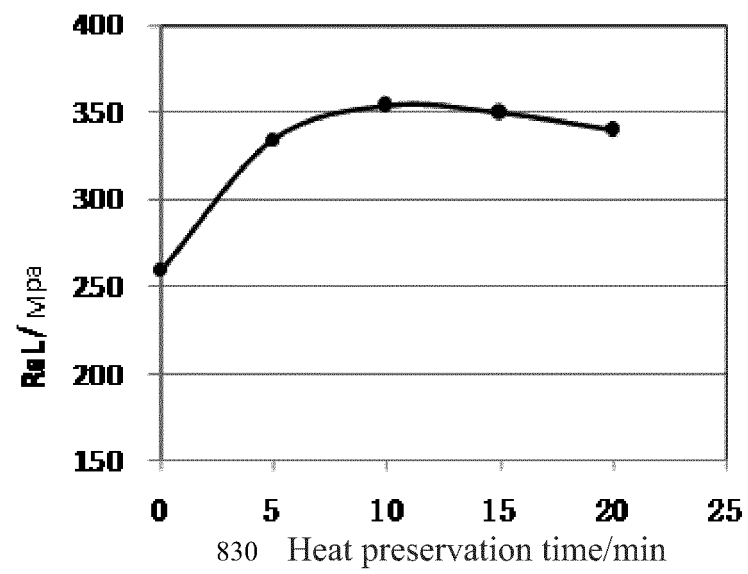


Fig. 1

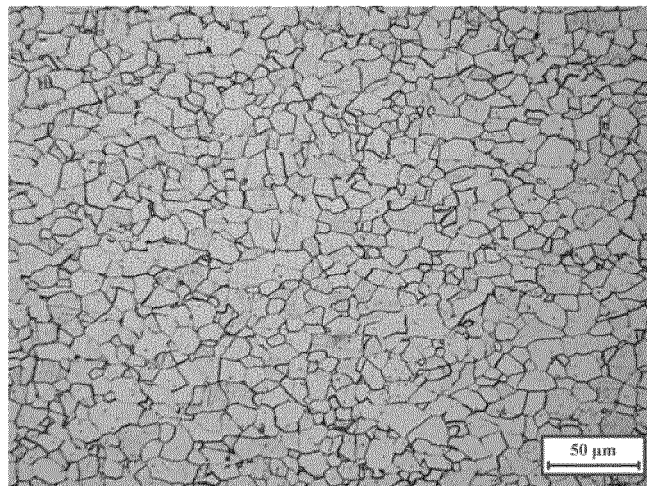


Fig. 2

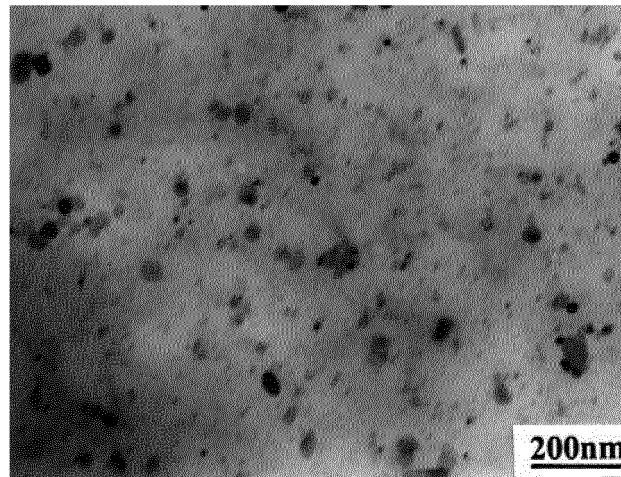


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/089695

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/14 (2006.01) i; C21D 8/02 (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)

C22C 38; C21D 8

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, DWPI, EPODOC, CNKI, steel, enamel+, titanium, Ti, sulphur, S, nitrogen, N, oxygen, O

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 102251192 A (BAOSHAN IRON & STEEL CO LTD) 23 November 2011 (23.11.2011) description, paragraphs [0015]-[0067] and [0126]-[0129], tables 1 and 2	1-14
X	CN 102747309 A (BAOSHAN IRON & STEEL CO LTD) 24 October 2012 (24.10.2012) description, paragraphs [0011]-[0049]	1-14
X	JP 58-197254 A (NIPPON STEEL CORP.) 16 November 1983 (16.11.1983) description, page 2 column 4 to page 3 column 8 and tables 1 and 2	1-14
PX	CN 104250705 A (BAOSHAN IRON&STEEL CO LTD) 31 December 2014 (31.12.2014) claims 1-14	1-14

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

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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	"&" document member of the same patent family

Date of the actual completion of the international search

02 December 2015

Date of mailing of the international search report

23 December 2015

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2015/089695

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN 102251192 A	23 November 2011	None	
CN 102747309 A	24 October 2012	WO 2014015823 A1	30 January 2014
JP 58-197254 A	16 November 1983	None	
CN 104250705 A	31 December 2014	None	

REFERENCES CITED IN THE DESCRIPTION

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