Study on Microstructure and Mechanical Properties of Titanium-bearing High-strength Hot-rolled Steels for Enamelling

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Abstract

The enamelled tank for water heater, as a new generation product featured durable, intoxic and corrosion-resistant, has been widely applied. To satisfy the requirements of forming, welding, and enamelling of inner tank, it is necessary for the steels to have high strength, excellent formability, weldability and enamellability, especially high strength after firings.

By means of simulation firing processes, the comparation of microstructure and mechanical properties of hot-rolled sheet steels with and without titanium-bearing is carried out. The results show that the titanium-bearing high-strength hot-rolled steels exhibit excellent weldability and enamellability, especially prevent the grain coarsening of ferrite thus keep higher strength after firing at high temperature, which contributed to the fine and dispersive titanium precipitates. Consequently, four levels with different yield strengths of 210MPa, 245MPa, 330MPa and 360MPa, have been developed at Baosteel.

Key words: enamelling, hot-rolled steel, high-strength, titanium, microstructure, mechanical property

1. Introduction

The enamelled tank based on hot rolled high-strength steels has the advantages of corrosion-resistance, durability and food-grade, and has been widely applied in electric water heater, and further spread into solar water heater, replaced those by stainless steels, HDG steels and plastics. The enamelling technique, including wet frit and powder spraying, is mainly one coat/one fire on one side of the substrate. To satisfy the requirements of the tank processing, especially forming, welding and enamelling, it is necessary for the steels to own good formability, weldability and enamellability. Moreover, the substrate of tank has to be with higher strength after firing at high temperature in order to withstand higher pressure.

The hot-rolled steels combined good formability, high fishscale-resistance and high-strength rely on not only the reasonable chemical ratios of C, Mn, and alloy elements, but also the processing parameters. On the basis of low carbon steels, the homogeneous microstructure and fine, equiaxed ferrite grains will be beneficial to increase the formability and strength. The sufficient amount of inclusions and precipitates in the steels are not only useful to entrap hydrogen, but also the fine and dispersive precipitates can suppress the grain growth and strengthen the substrate remarkably because of the precipitation strengthening mechanism⁽¹⁻³⁾. Ti is one of the strong compounds with C and N to form inclusions and precipitates such as TiN, TiC, TiS or $Ti_4C_2S_2$. These second particles may greatly influence the microstructure and mechanical properties of substrate during firing processes, which is investigated in this paper.

2. Chemical compositions of steels and production processing

The industrial production procedure of hot-rolled steel is as follows: steelmaking in LD converter-vacuum degassing in RH system-continuous casting-hot-rolled by hot strip tandem mill-pickling-oiling.

Table 1 shows the chemical compositions of titanium-bearing steels and compared steel, which is a type of low carbon grade steel without addition of titanium and any other alloy elements. For the Ti-bearing steels, the strength level principally depends on the content of strengthening elements such as carbon, manganese and titanium, as far as chemical

elements are concerned.

Table 1 the chemical compositions of steels (wt%)

	С	Si	Mn	P	S	Al	Ti
Ti-bearing steels	0.02~0.10	≤0.05	0.20~1.00	≤0.020	≤0.05	0.01~0.07	≤0.08
Compared steel	0.05	0.02	0.23	0.009	0.01	0.045	-

3. Relsults

3.1 Role of main chemical elements

The effect of main chemical elements on the properties is described as follows:

Carbon With the carbon content going up, the yield strength increases and the total elongation decreases. In Ti-bearing steel, carbon can mainly combine with titanium to form TiC particles. It is believed that these particles are in favor of hydrogen entrapment during enamel firing. However, high content of carbon will generate very much pinhole defects to impair the surface quality and the adhesion between steel and enamel. In that case, it is important to control the carbon content to a relatively lower range, and fix the free carbon through the addition of titanium.

Manganese Manganese is an effective element to increase strength by the strengthening mechanism of solid solute. Further, it can prevent hot embrittlement due to sulfur during hot rolling.

Nitrogen In Ti-bearing steel, nitrogen is preferential to compound with nitrogen than carbon to form TiN particles. The coarse TiN inclusions will impair the plasticity of steel, but the fine and dispersive TiN particles can increase the hydrogen entrapment. It is studied that after the deformation such as rolling and forming, a large amount of micro voids in the vicinity of second particles will be produced, which is more efficient to improve fishscale resistance.

Sulphur Sulphur and carbon combine with titanium to form TiS and $Ti_4C_2S_2$, and exist in global shape in steels, which play the same role as titanium carbide and nitride.

Titanium Titanium addition can improve the welding properties because the pinning of TiN particle to the grain boundary restrains austenitic grain growth. With the titanium content increasing, the TiN particles become coarser and more TiC will produce.

3.2 Effect of firing processes on mechanical properties

The hot-rolled steel sheets, taken from two different strength levels of hot-rolled steels 210MPa and 330MPa, respectively, in 2.0mm thick, were cut into 200×300mm. Annealing test is designed to simulate the firing processes by altering holding time and temperature, in order to evaluate the softening resistance during firing. The specimens for tensile tests were taken from the annealed steel sheets in transverse direction and machined to JIS No.5 (width: 25mm, gauge length: 50mm). The average value of three specimens was measured to calculate the yield strength of the steel sheet after annealing.

Figure 1 shows the change of yield strength with holding time and soaking temperature. It is shown from Figure 1(a) and (b) that with the temperature going up, the yield strength descends. At given temperature, while the holding time not longer than 5 minutes, the yield strength increases for the steel 245MPa, and on the contrary for the 330MPa. However, when the holding time exceeds 5 minutes up to 30 minutes, the yield strength remains nearly constant.

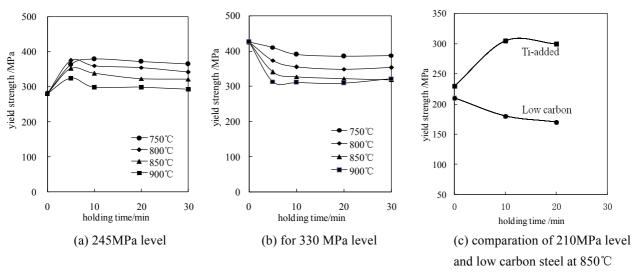


Figure 1 the relationship between mechanical properties and annealing processes

3. 3The effect of annealing process on the microstructure

The microstructures of hot-rolled steels, in transversal section to rolling direction, are shown in Figure 2. The microstructure of hot-rolled steels is composed of fine, equiaxed ferrite and very few pearlite. The average diameter of ferrite grain is about 12 micros, and the pearlite consists of fine cementite distributed on ferrite matrix, as shown in Figure 2 (b).

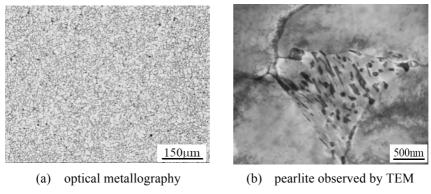


Figure 2 the microstructure of Ti-added steel as hot-rolled

The microstructures of Ti-bearing steel and compared low carbon steel after firing at 850□×5min are shown in Figure 3. The low carbon steel without Ti presents the uneven, obviously coarsening ferritic grains, and the grain size changes from 25 to 50 micros at the central layer and 100 micros at the surface layer.

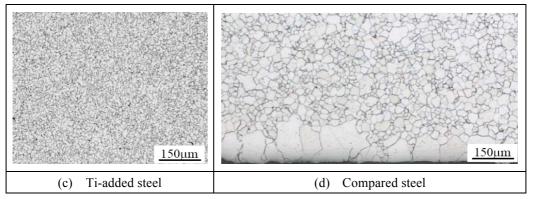


Figure 3 the microstructure of compared low carbon steel after firing at 850 □ ×5min

Figure 4 shows the microstructure evolution of Ti-added hot-rolled steel with the firing temperature and time. The microstructure of specimens after simulation firing at different processes remains the same as hot-rolled, even after the soaking temperature from $750\Box$ up to $900\Box$, and the holding time from 5 min up to 30 min. After firing at $750\Box\times5$ min, $800\Box\times10$ min, and $850\Box\times20$ min, the grain size of ferrite is about 10 micros, a little finer than that of hot-rolled. When firing up to $900\Box\times30$ min, the grain size is almost the same as hot-rolled, about 12 micros. The results feature the ability to prevent grain coarsening of steel at high temperature for extended holding time. The fine ferrite grain is helpful to intensify the steel base, especially increase the yield strength according to Hall-Pech's formula. Therefore, the steel can improve the strength after firing.

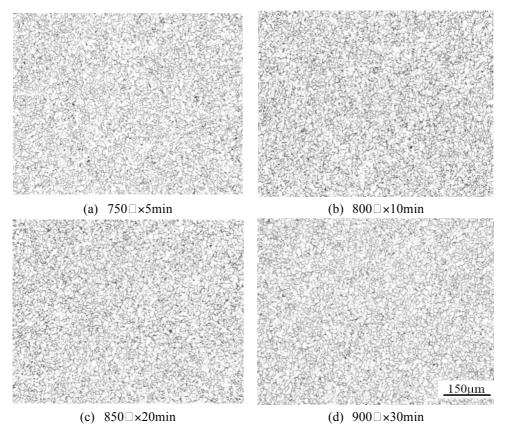
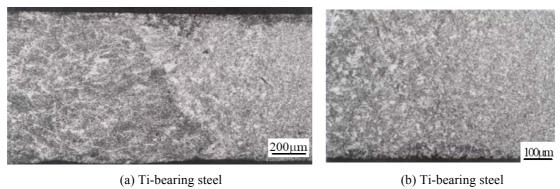
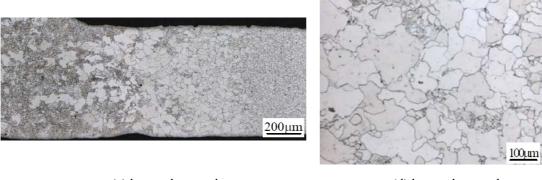


Figure 4 metallographic microstructure of the steels after different firing processes

3.4 HAZ microstructure of TIG welding





(c) low-carbon steel

(d) low-carbon steel

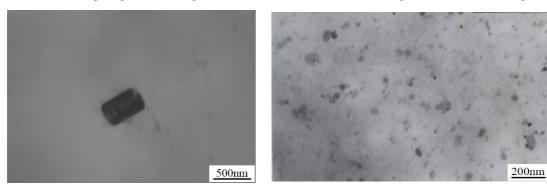
Figure 5 microstructures of TIG welding

The microstructure of weld, HAZ and matrix of two steels by conventional TIG welding process are shown in Figure 5. It is shown obviously that for Ti-bearing steel, the microstructures of are too much finer than that without Ti. The low carbon steel without Ti exists abnormal grain growth, which seriously impair the strength and toughness of weld and HAZ.

4. Discussion

The addition of titanium in low carbon manganese steel can form titanium compounds, mainly nitrid, carbides and sulfides. The typical TEM morphology of titanium nitride and titanium carbide is shown in Figure 5. It was studied [4] that precipitates such as TiC and TiN particles can improve the hydrogen entrapment and suppress the hydrogen diffusion in the steel. These kinds of the second particles, distributed dispersively in the steel base are the excellent sites to entrap hydrogen, thus to prevent the occurrence of fishscale.

The fine particles of titanium nitride can be strongly suppressed the austenitic grain coarsening during welding. A large amount of fine titanium carbides impede the migration of ferrite grain boundary during and after high temperature firing. Therefore, titanium precipitates make great contribution to the refinement of grain and the increasing of strength.



(a) titanium nitride

(b) titanium carbides

Figure 6 TEM morphology of titanium nitride and carbides

Table 2 shows the requirements of mechanical properties of the hot-rolled steels for enameled tank of water heater. The steel grades cover four strength levels according to the different lower limits of yield strength. The higher the strength, the total elongation is greater. The purpose is to satisfy the every demands of punch and pressure of water tank. As mentioned above, the change of strength is achieved by means of the different content of C, Mn and Ti, and also the hot-rolling processes.

Table 2 requirements of mechanical properties of the steels

Steel grades	R _{p0.2} /MPa	R _m /MPa	A ₅₀ /%	Strength level
BTC210R	≥210	≥300	≥28	210MPa
BTC245R	≥245	≥340	≥26	245MPa

BTC330R	≥330	≥400	≥22	330MPa
BTC360R	≥360	≥400	≥22	360MPa

5. Conclusions

The investigation of microstructure and mechanical properties of hot-rolled sheet steels with and without titanium-bearing is carried out by means of simulation firing processes. The results show that the titanium-bearing high-strength hot-rolled steels have the advantages over low carbon steel in many aspects.

- (1) The types of precipitates in Ti-bearing steels are mainly composed of TiN and TiC particles. The fine, dispersive particles are helpful to refine ferrite grains and strengthen the steel substrate, especially during and after firing processes.
- (2) The improvement of weldability of titanium-bearing steels is attributed to the grain growth hindrance of TiN particles.
- (3) Fine and dispersive particles of titanium nitride and carbide are irreversible traps in the steels.
- (4) Based on preferred chemical elements including carbon, manganese and titanium, four yield strength levels of hot-rolled steels have been developed at Baosteel.

References

- 1. Quanshe Sun, Lei Jin, "Study on Hydrogen Permeability of Tti-bearing Ultra Low Carbon Sheet Steels", Shanghai Jinshu, Vol. 26, No. 2 (March, 2004), 9-11, 4.
- 2. Quanshe Sun, Xianjin Wang, "Effect of RE,Ti and Nb on Recrystallization and Formability of ULC Cold-Rolled Enamel Sheets", Journal of Iron and Steel Research, Vol. 16, No. 3 (June, 2004), 49-54.
- 3. A. Yasuda, K. Ito and K. Tsunoyama. "Hot and Cold-Rolled Steel Sheets", Edited by R. Pradhan and G. Ludkovsky, The Metallurgical Society, 1988, 273-285.
- 4. Quanshe Sun, Lei Jing, Feng Lv, et al. "Study on Hydrogen Permeability of Titanium-Bearing Ultra Low Carbon Sheet Steel", Prodeedings of the 4th International HSLA Steels' 2000(in Xi'an), edited by Liu Guoquan, Wang Fuming, Wang Zubin, Zhang Hongtao, organized by the Chinese Society for Metals, 635-638.

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