

DEVELOPMENT AND APPLICATION OF THE HOT-ROLLED SHEET FOR ENAMELING AT ANSTEEL



XXI International Enamellers Congress

18 - 22 May 2008 Shanghai - China





Development and Application of the Hot-rolled Sheet for Enameling At Ansteel

Wang Dongming, Zhang Wanshan, Dong Enshan, Liu Zhiwei,
Liu Fenglian, Guo Xiaohong, Zhang Xuping

Angang Steel Co., Ltd., Anshan, Liaoning, 114001

Abstract This article introduces the technical characteristics, actual performance and application of hot-rolled sheet for two-coat enameling. The research shows that the ratio of Ti and C is an important factor to affect the enameling property of hot rolled sheet. The hydrogen permeation time has the correlation of monotone increasing with Ti content and Ti/C. When the Ti/C ratio is more than 2.5, the steel sheet will have more steady ability of hydrogen trapping, which will be better if Ti exists in steel in the form of precipitates. By heating at 1300°C and lower, the compound of N, S and Ti will not vary in the number of precipitates when the temperature changes. During the rolling and heat treatment, the number of TiC precipitates is adjustable. Such the precipitate is the main source of hydrogen trap. In consideration of fish scaling resistance, adhesiveness and bubbling resistance, the hot-rolled steel sheet with good two-coat enameling property can be produced by means of Ti alloying and proper control of Ti/C ratio and in the number of precipitates as hydrogen traps. The hot-rolled coil and sheet containing Ti for two-coat enameling and the medium and heavy plate for enamel glass vessel, developed by Ansteel, have the good mechanical property and enameling property and can be used widely for the manufacture of enamel structural members.

Key words Enamel, fish scaling, hot-rolled steel sheet, precipitate, hydrogen trap

1. Preface

The enameling steel sheet plays an important role in the national economy and it is closely related with the daily life of peoples. It is used widely in the light industry, electrical household appliance industry, metallurgical industry, chemical industry and building industry, etc. for the manufacture of kitchen utensils, sanitary ware, oven, geyser liner, roofing sheet, reaction vessel, etc.. Ansteel is a pioneer to develop the steel sheet special for enameling in China. Since 1980, Ansteel has developed a series of cold-rolled enameling steel sheet TC1、TC2、05MnTi、09TiRe and a series of hot-rolled enameling steel sheet and seamless pipe 06TiA、09MnTi、09MnTiNb、09MnTiNbRe. At the time, those products met well the demands in the domestic market and fill in the gap in this field although in a small number of production. However, owing to the change in the market environment and the technical modification, Ansteel stopped the production and supply of enameling steel sheet for a time period after 1977. In 2004, on the basis of the essential change of technology and equipment conditions, Ansteel placed again the production of Ti enameling steel sheet into its product mix. When the opportunity appeared in the market, we developed the hot-rolled steel sheet for two-coat enameling promptly.

2. Hot-rolled plate for two-coat enameling

2.1 Hot-rolled medium and heavy plate for enamel glass vessel

Two kinds of steel plates for enamel glass vessel, developed by Ansteel, are introduced as follows. One is Steel grade 235MPa 09MnTi, the other is steel grade 345MPa 09MnTiNb. Both have the good enameling property, weldability and toughness. The steel plate is produced in the medium and heavy plate mill. After hitting the target thickness, the plate structure will be adjusted by

normalization to improve the property. The chemical composition of both steel grades is shown in Table 1.

Table 1 Chemical Composition of the Steel Plates for Enamel Glass Vessel

| Steel grade | Element | C | Si | Mn | Ti/C | Ti | Nb | P | S |
|-------------|----------|-------|-------|-------|---------|-----------|--------|--------|--------|
| 09MnTiNb | Required | ≤0.12 | ≤0.50 | ≤1.60 | 1~3.5 | 0.10~0.22 | ≤0.030 | ≤0.035 | ≤0.035 |
| | Actual | N/A | | | 1.2~3.3 | 0.13~0.20 | ≤0.030 | ≤0.024 | ≤0.018 |
| 09MnTi | Required | ≤0.12 | ≤0.40 | ≤1.00 | 1~3.5 | 0.08~0.22 | - | ≤0.035 | ≤0.035 |
| | Actual | N/A | | | 1.2~3.3 | 0.10~0.18 | - | ≤0.024 | ≤0.018 |

The mechanical property of steel plate is shown in Table 2.

Table 2 Mechanical Property of the Steel Plates for Enamel Glass Vessel

| | | | | | | |
|----------|----------|------------------|------------------|----------------|-------------------------|------------------------|
| 09MnTi | Size, mm | σ_s , MPa | σ_b , MPa | δ_5 , % | Cold bend | Normal temp. Akv, J |
| | Required | ≥235 | ≥360 | ≥22 | d=a, $\alpha=180^\circ$ | ≥60 |
| | 10~24 | 265-395 | 375-470 | 26.0-37.0 | Conforming | 228-364 |
| 09MnTiNb | Size, mm | σ_s , MPa | σ_b , MPa | δ_5 , % | Cold bend | -20℃ Akv, J |
| | Required | ≥355 | ≥440 | ≥21 | d=a, $\alpha=180^\circ$ | ≥27 |
| | 10~18 | 370-460 | 490-570 | 26.0-36.0 | Conforming | 96-192 |

After testing the diffusion coefficient of hydrogen in both kinds of plates and comparing it with Q235B (See Table 3), it is found that the diffusion coefficient of hydrogen is decreased greatly.

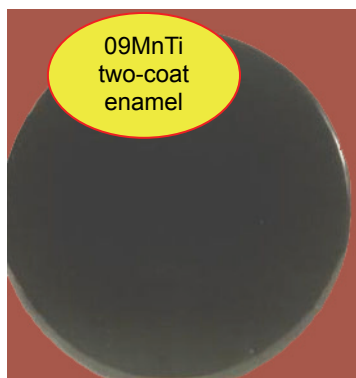
Table 3 Comparison of Diffusion Coefficients of Hydrogen in As-normalized 09MnTi, 09MnTiNb and Q235B

| Steel grade | Q235B | 09MnTi | 09MnTiNb |
|--|-------|--------|----------|
| Diffusion coefficient of hydrogen ($\times 10^{-11} \text{m}^2/\text{S}$) | 135.4 | 24.74 | 11.3 |

The enamel tests of 09MnTi and 09MnTiNb show that both steel grades have the excellent enameling property. **Figure 1** shows the photos of 09MnTi samples of two-coat enamel firing. 09MnTi round cake specimen for two-coat enameling and Q235B specimen were prepared at the same size and in the same conditions. They were placed at the normal temperature and observed after two months. It was found that the former has no fish scaling defect, while the latter has serious fish scaling.

By comparison with 09MnTi, steel grade 09MnTiNb has the better high-temperature resistance and deformation resistance. After enamel firing once, the amount of deformation of a 10000L reaction vessel of 09MnTiNb is only a half of that of Q235B. After the addition of Nb and normalization, the

change in property is obviously decreased.



(a) Two-coat enamel specimen of 09MnTi



(b) Two-coat enamel specimen of Q235B



(c) Two-coat enamel cylindrical specimen of 09MnTi



(d) Two-coat enamel blade of 09MnTi

Fig. 1 Photos of 09MnTi Two-coat Enameling Specimens

After Ansteel realized the total continuous casting, the supply of such the products has been stopped for a time because the problem of Ti affecting the quality of continuous cast slab could not be overcome. Now Ansteel has made the improvement in the design according to the actual conditions in the use of such steel grade and completed the commercial trail of continuous casting.

2.2 Hot-rolled coil for two-coat enameling for **bolted tank**

In order to meet the demands for the hot-rolled coils for two-coat enameling in the environment protection, Ansteel has developed the special coil of steel grade ART310. The chemical composition is shown in Table 4. The delivery condition is the as-rolled sheet. The product property is shown in Table 5.

Table 4 Chemical Composition of ART310 (%)

| C | Si | Mn | P | S | Ti | Als | Ti/C |
|-------|-------|-------|--------|--------|-----------|--------|------|
| ≤0.06 | ≤0.10 | ≤0.35 | ≤0.020 | ≤0.015 | 0.06~0.20 | ≤0.055 | ≥2.5 |

Table 5 Mechanical Property of ART310 Steel Sheet

| Size, mm | Rel, MPa | Rm, MPa | A, % |
|----------|----------|---------|------|
| 2.0~8.0 | ≥300 | ≥350 | ≥19 |

The sheet is produced by continuous casting and rolled by hot continuous rolling mill and then coiled after laminar cooling.

The property of the as-rolled sheet and after enameling treatment is shown in Table 6.

Table 6 Tensile Strength of the Steel Sheet before and after Enameling

| Size mm | As-rolled | | | After simulated enameling treatment | | |
|------------|-----------|---------|-------|-------------------------------------|---------|------|
| | Rel, MPa | Rm, MPa | A, % | Rel, MPa | Rm, MPa | A, % |
| 3.0 | 460~480 | 580~610 | 26~29 | 265~320 | 320~370 | 37 |
| 5.0 | 400~440 | 510~550 | 27~32 | 270~310 | 330~390 | 38 |
| 6.0 | 350~390 | 440~470 | 29~33 | 280~300 | 340~370 | 39 |
| 7.0 | 340~380 | 440~465 | 29~33 | 285~310 | 355~410 | 35 |

The comparison of the impact toughness of 7mm thick plate before and after enameling is shown in Table 7. It can be seen in Table 7 that the plate has the good impact toughness, no matter before and after enameling. However, for the plate after enameling, the impact toughness value is slightly smaller.

Table 7 Results of Impact Toughness Test of Steel Sheet

| Cross section Mm | As-hot-rolled | | After simulated enameling treatment | |
|---------------------|--------------------|--------------------|-------------------------------------|--------------------|
| | -20AKv(Lateral), J | -40AKv(Lateral), J | -20AKv(Lateral), J | -40AKv(Lateral), J |
| 5.0×10 | 165, 173, 170 | 156, 178, 175 | 158, 154, 152 | 141, 144, 150 |

Figure 2 shows the structure of the sheet/plate at different thickness before and after enameling. It can be seen in the figure that the sheet/plate before and after enameling has the ferrite structure. However the grain of the sheet/plate after enameling is obviously coarse, approx. Class 7 in grain size. Figure 8 shows the precipitate structure of 4mm thick plate before and after enameling. It can be seen in the Figure that the precipitate of Ti is obviously grown and the volume fraction of the precipitates is obviously increased. It has proved by energy spectrum analysis that those grown precipitates are mainly TiC.

Figure 3 shows the appearance in the enamel surface of the test sheet/plate after two-coat enameling and the enamel layer and base metal interface observed through scanning electron microscopy. The test results show that the test sheet/plate has no fish scaling spot, no bubbling, tight steel/enamel interface and that the sheet/plate has the excellent two-coat enameling property.

The developed products have been supplied at first to Beijing United Innovation Environment Protection Equipment CO., Ltd. for trail use, and also used for the water treatment system of Jiuquan Satellite Launching Center and the sewage treatment system for Beijing Olympic Game 2008. Recently the batch trail products have been supplied to Xisen Sanhe Group, Linyi Shengneng Group

in Shandong, Beijing Weilun Chemical Environment Protection Science and Technology Co., Ltd.. It shows that the developed products can meet completely the design requirements of those projects. The **bolted tank** made of two-coat enamel plate have many advantages such as beauty, duration, low-cost construction, etc..

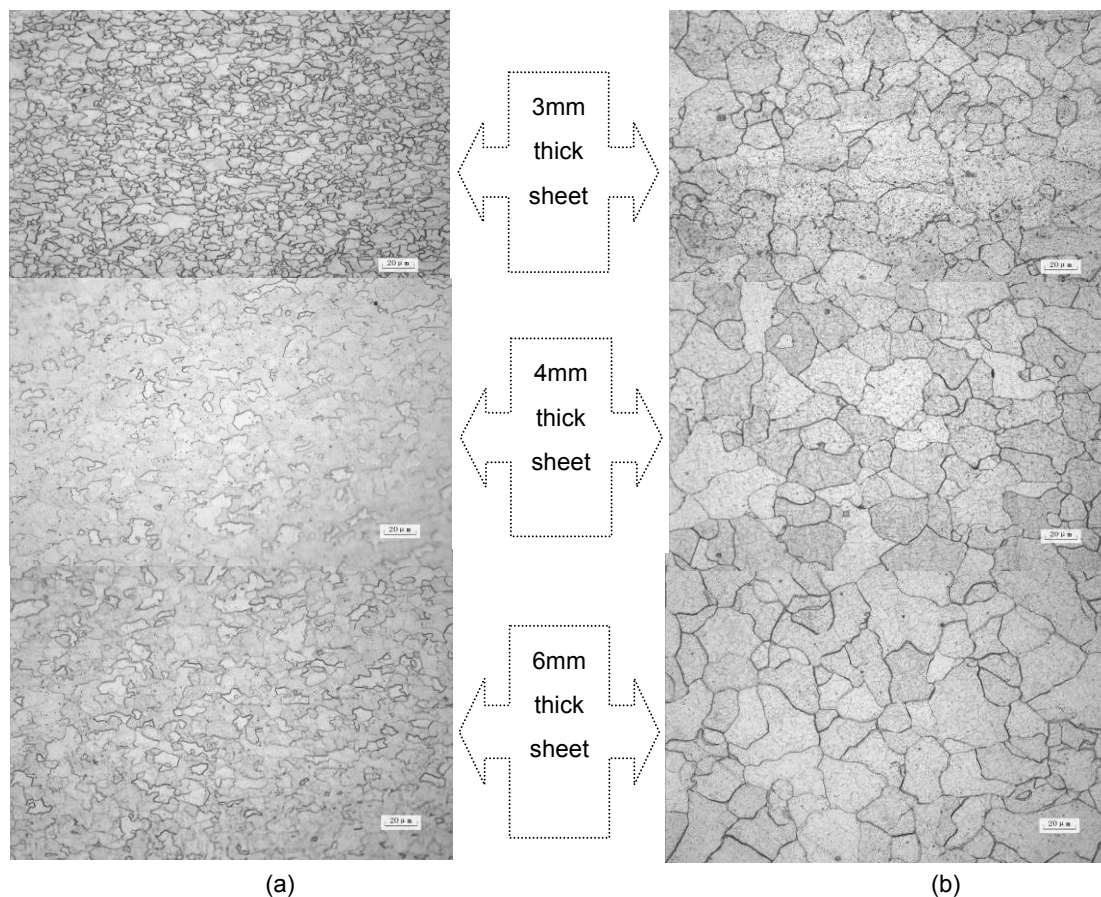


Fig. 2 Comparison of the Structures of ART310 before and after Enameling
(a) As-rolled; (b) As-enameled

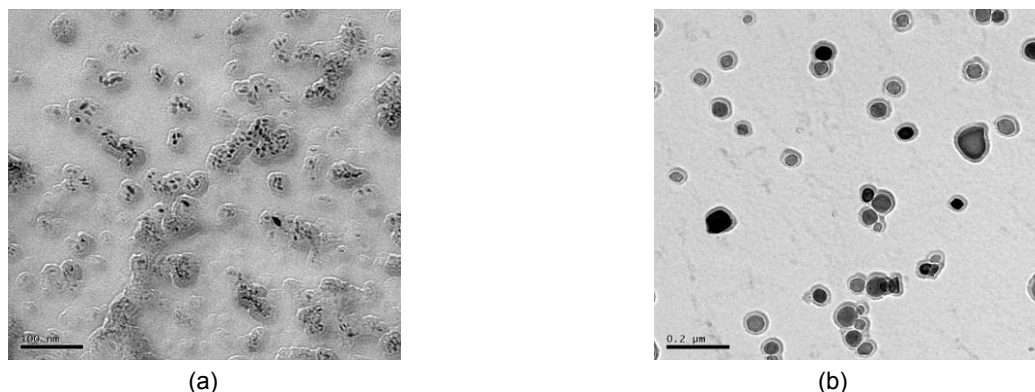


Fig.3 Comparison of the Precipitate Structures of 4mm Thick Plate before and after Enameling
(a) As-rolled; (b) As-enameled

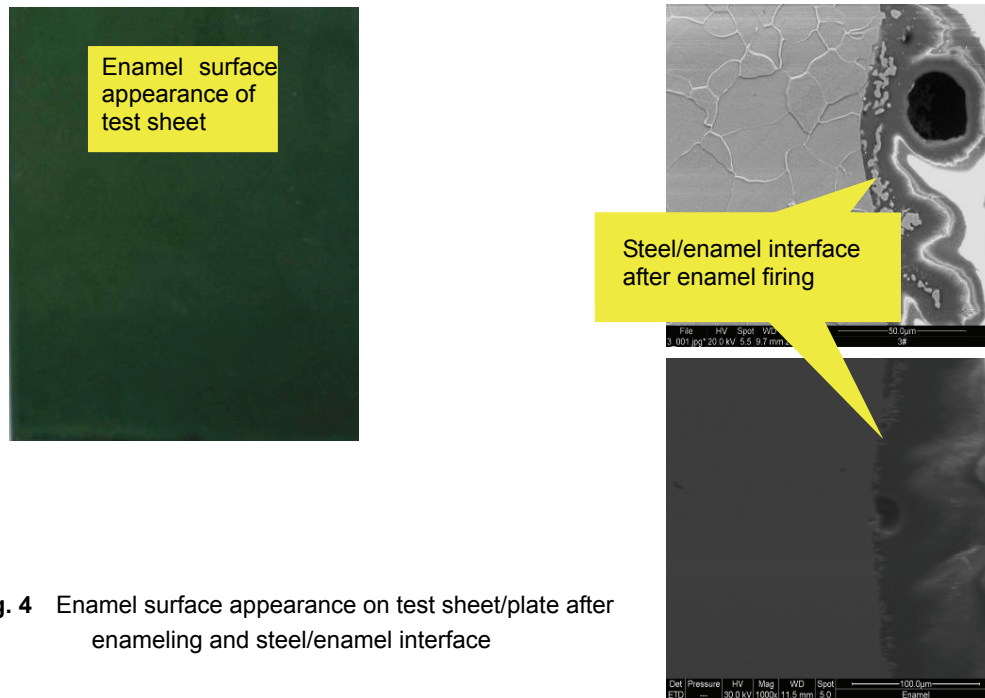


Fig. 4 Enamel surface appearance on test sheet/plate after enameling and steel/enamel interface

Figure 5 ~ Figure 10 are the photos of the heavy-duty sediment tanks and reactors made of the developed products. These examples have proved that the production of the hot-rolled sheet/plate for two-coat enameling with good enameling property and high strength after enameling at Ansteel is a good start for the development of environment protection equipment and biological energy engineering in China.



Fig. 5 Bolted two-coat enamel tank – water treatment system of Jiuquan Satellite Launching Center



Fig. 6 Bolted two-coat enamel cyclone tank – sewage treatment system for Beijing Olympic Game 2008



Fig. 7 Bolted two-coat enamel sediment tank
–Industrial waste water treatment system in
Quanzhou



Fig. 8 Two-coat enamel anaerobic reaction vessel
– biological power plant of Xisen Sanhe Group



Fig. 9 Bolted two-coat enamel reactor or
Garbage Disposal System in Jinjing



Fig. 10 Bolted two-coat enamel
reactor in Tai'an Brewery

3. Conclusions

① The ratio of Ti and C is an important factor to affect the enameling property of hot rolled sheet. The hydrogen permeation time has the correlation of monotone increasing with Ti content and Ti/C. When the Ti/C ratio is more than 2.5, the steel sheet will have more steady ability of hydrogen trapping.

- ② Ti will play a better role of hydrogen trap if it exists in steel in the form of precipitates. During the period of rolling and heat treatment, the precipitate TiC is generated, which is adjustable in the number. Such the precipitates are just the important hydrogen traps. The compound of N, S and Ti will not vary at least in the number of precipitates when the temperature changes.
- ③ Ti is used as the element to form the hydrogen traps. By the control of the Ti/C ratio and the number of precipitates, the hot-rolled sheet/plate with excellent enameling property for two-coat enameling will be produced.
- ④ The hot-rolled coil and sheet containing Ti for two-coat enameling and the medium and heavy plate for enamel glass vessel, developed by Ansteel, have the good mechanical property and enameling property. They have been used for the manufacture of two-coat enamel structural members and show the good performance in the use.

Author:

Wang Dongming (1969-), male, master, Senior engineer, Technical Center of Angang Steel Co., Ltd., China

Add: 63 Wuyi Road, Tiedong, Anshan 114001 P.R.China

Tel: 86-0412-6721014

Email: angangWDM@126.com

