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Analysis of Fishscaling Resistance of Low Carbon Heavy Plate Steels

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Abstract: The precipitates and hydrogen permeation behavior in three kinds of hot rolled low carbon heavy plate steels for enameling were analyzed; then, both sides of the steels were enameled. The experimental results show that a large amount of coarse $Ti_4C_2S_2$ and fine Ti(C,N) particles exist in the optimized Ti-bearing steel, quite a lot of fine Ti(C,N) particles exist in the optimized carbon steel, but only a little bit fine Ti(C,N) particles exist in the carbon steel. The fishscaling resistance of the steels can be correlated to the effective hydrogen diffusion coefficient, and a model of correlation between the effective hydrogen diffusion coefficient and the volume fraction of the precipitates was established and verified. The effective hydrogen diffusion coefficient should be lower than 3.96×10^{-6} cm^2/s to avoid fishscaling in heavy plate steels.

Key words: fishscaling resistance; hydrogen permeation; precipitate; enameling

Fishscale is one of the worst defects in the production of enameled steel products[1]. It is caused by an excess of hydrogen which dissolves into the steel during the enameling process, especially during the enamel firing at the temperature of 800—850 ℃. Since its solubility steeply decreases during subsequent cooling, hydrogen moves toward the steel-enamel interface in quantities that can cause fishscaling even after a lapse of time. When the steel is enameled, whether the fishscaling happens or not depends on the chemical compositions, the trapping sites, such as microvoids, dislocations and precipitates, and eventually the hydrogen permeation behavior in the steel. The hydrogen diffusivity in steel has an obvious effect on the fishscaling resistance[2]. The lower the hydrogen permeability, the lower the fishscaling susceptibility. It is reported that the hydrogen diffusion coefficient should be lower than 2.0×10^{-6} cm^2/s to avoid fishscaling when the sheet steels were enameled[3], and the trapping sites significantly influence the hydrogen solubility and diffusivity[4,5].

The trapping sites can be classified into reversible and irreversible types according to the binding energy (E_b in eV) with the hydrogen atoms[6]. Normally, dislocations and grain boundaries, which have a lower E_b of about 0.25—0.27 eV, are reversible sites; inclusions, precipitates and microvoids, on the contrary, with a higher E_b of about 0.80—0.98 eV, are irreversible sites. In the hot rolled steels for enameling, the precipitates or inclusions are main irreversible sites for hydrogen. The effects of these particles on the fishscaling resistance have been studied by many researchers[7-12]. Valentini et al.[13,14] established a model to quantitatively assess the fishscaling susceptibility using the free hydrogen parameter. However, most of the researches on fishscaling resistance have been done on hot or cold rolled sheet steels, fewer on hot rolled heavy plate steels. Nowadays, there are increasingly demands for heavy plate enameling steels, for example, steels used for chemical reaction vessels, silos. These steels, which are normally in thickness of about 12—25 mm, will be enameled one side or both sides, then fishscaling may occur and a different susceptibility from the sheet steels is shown. So, this paper focuses on the fishscaling resistance of hot rolled low carbon heavy plate steels for enameling, and the precipitates, hydrogen permeation behavior and enameling process are all studied.

1 Experimental

A carbon steel (named CB), an optimized car-

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bon steel (named OCB) and an optimized Ti-bearing steel (named OTB) were designed in laboratory, and then vacuum-melting, ingot casting, forging and slab hot rolling process were carried out. The slabs were reheated at 1200 ℃, and then hot rolled to heavy plates with a thickness of 16 mm at the finishing temperature of 880 ℃, and then air cooled to the room temperature. The yield strengths of the three steels were between 265 to 290 MPa. The CB steel did not contain vanadium and just had a little bit titanium. Vanadium was added in the OCB steel but the carbon content was decreased. The OTB steel had a higher content of titanium but a lower carbon content than that of the OCB steel. The variation of such elements content is to maintain the yield strength and to modify the fishscaling resistance of the steels. The chemical compositions for the three developed steels are shown in Table 1.

Table 1 Chemical compositions of the developed steels

mass%

Steel	C	Mn	S	Al	Ti	V	N
CB	0.144	0.85	0.004	0.046	0.015		0.0048
OCB	0.092	0.84	0.004	0.041	0.016	0.047	0.0056
OTB	0.069	0.70	0.010	0.040	0.050	0.052	0.0087

The precipitates in the steels were extracted on carbon replicas and examined by an FEI Tecnai G^2 high resolution transmission electron microscope (HRTEM) equipped with an energy dispersive spectrometer (EDS). Selected area electron diffraction (SAD) patterns combined with EDS analysis were used to identify the precipitates. The quantitative analysis of the precipitates was carried out using the ordinary quantitative metallographic methods, that is to measure the average diameter d and the number of the particles per unit area N_s from the electron micrograph. The relative error of the particle diameter is less than 8% under 95% confidence level. The particle volume fraction V_f and the number of particles per unit volume N_v can be calculated by the Fullman formula

$$V_f = \pi/6 \cdot N_s \cdot d^2 \quad (1)$$

$$N_v = N_s/d \quad (2)$$

Hydrogen permeation was measured using an electrochemical method developed by Devanathan and Stachurki[6]. Square samples of 1.2 mm×50 mm×50 mm were cut from different locations in the thickness of the heavy plates, ground to 1 mm in thickness and then electrolytically polished. Put the samples into 20% HCl electrolyte and made a cathodic polarization treatment for 10 to 20 s with current density of 21.5 mA/cm^2. After immersed and washed by anhydrous ethanol and toluene, the samples were then immediately one-side electroplated with 0.05 to 0.10 μm Pd layer. The prepared specimen was installed in a CS-330 electrochemistry workstation. European standard (NF EN ISO 17081) was adopted for measurement. The bare face of the specimen is for charging the hydrogen, and the Pd electroplated face is diffusion face. Both cathodic and anodic solutions were 0.1 mol/L NaOH, which were deaerated with N_2 to avoid the cathodic reaction due to O_2. The charging current density was maintained at 1.8 mA/cm^2, and then began to record the anode current with different times on the diffusion face, until the anode current reaches a steady state (the maximum value).

The effective diffusion coefficient of hydrogen D_{eff} can be calculated from the hydrogen permeation curves by the time lag method[4,6]

$$D_{eff} = L^2/6t_T \quad (3)$$

where L denotes the specimen thickness and t_T denotes the lag time. The lag time can be obtained by spotting the time at which the permeation rate is 0.63 times the steady-state value, namely normalized output flux $J_t/J_\infty = 0.63$[6]. Hydrogen trap parameter α is also calculated using the following equation for assessing the fishscaling resistance of steel

$$\alpha = -1 + t_T/t_L \quad (4)$$

where

$$t_L = L^2/6D_L$$

$$D_L = D_0 \exp(-Q/RT)$$

t_L is the lag time of hydrogen in metal lattice without trapping sites; D_L is the hydrogen diffusion coefficient in metal lattice without trapping sites. D_0 and Q are 0.78×10^{-3} cm^2/s and 7950 J/mol, respectively[5]. $D_L = 2.9843\times10^{-5}$ cm^2/s when temperature is 293 K.

The both sides of the steels were enameled, and the enamel frit consists of more than 60% of SiO_2 and the other oxides. The ground coat and six overglazes were sprayed and fired in turn. The firing temperatures are between 870 and 920 ℃. The thickness of the enamel layer is about 1 mm. The enameled heavy plates were observed by the naked eyes for fishscales. The small cross-sectional samples cut from the enameled heavy plates were mounted, ground and polished, and then the samples were examined by a Leica DMR-HC optical microscope (OM) for traces of fishscaling.