Effect of precipitations on hydrogen diffusivity coefficient and fishscale resistance of ultra-low carbon vanadium microalloyed steels

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Abstract The relationship of precipitations on hydrogen diffusivity coefficient and fish-scale resistance was studied in the ultra-low carbon vanadium microalloyed steel for enameling. The cold-rolled sheets of 1 mm in thickness were annealed at 750℃ for 5, 6 and 7min, respectively. Results showed that total volume of precipitates has a close relationship with hydrogen diffusivity coefficient and fishsacle resistance. It was found that the annealed sheets contained a large number of fine Ti(C,N), VC and coarse $Ti_4C_2S_2$ precipitates. The total volume fraction of precipitates increased with lengthened annealing time, but the mean phase particle sizes of precipitates was reduced. The hydrogen permeation test showed that the effective diffusion coefficient in sheets was also reduced with lengthened annealing time, and at 25 ℃, the effective diffusion coefficient in the sheet annealed at 750℃ for 5, 6 and 7min is 2.23×10^{-6}, 2.12×10^{-6} and $1.74\times10^{-6}cm^2/s$, respectively, in corresponding with their fishscale resistance enhance.

Keywords: precipitate; hydrogen diffusion, Enameling; texture; fish-scale resistance

1. INTRODUCTION

Ultra-low carbon steels have drawn much attention because of their excellent deep drawability and sufficient fish-scale resistance [1, 2]. Such steels have been widely used as decorative panel in tunnels and subways. Howerver, their strength is general low because of low carbon content in steel. It is known that V, Ti and N elements are added in low carbon steel which can acheive high strength, excellent ductility to satisfy the requirements of forming[3]. It has reported that even small amounts of alloy elements can influence hydrogen diffusivity and solubility in a significant way [4]. This is because Ti form with carbon and sulfur in several kinds of precipitates such as TiC and $Ti_4C_2S_2$. These precipitates can act as an irreversible trap which has a binding energy variable with the degree of coherency of the matrix-precipitate interface[5]. Takahashi et al. have observed that the fine coherent TiC particles(<100μm) are the most effective trapping sites[6]. Xiaomin Yuan have reported that Ti(C,N) and $Ti_4C_2S_2$ precipitates can serve as irreversible traps for hydrogen atoms influenced hydrogen diffusivity[7]. T. Okuyamas et al. have found that hydrogen diffusivity in enameling sheets have an effect on the fishscale resistance[8].In general, the decrease of hydrogen permeability increases the fishscale resistance of the enameling products. G. Papp et al. have derived that the hydrogen diffusion coefficient should be lower than 2.0×10^{-6} cm^2/s for preventing fishscale[9]. R. A. Orianit has deduced that the effective diffusivity is a function of trap density and of the magnitude of the trap depth[10]. R. Valentini et al. have developed a model of hydrogen behaviour in enamelling-grade steels in relation to the fishscale surface defect[11]. However, the study about the relationship of precipitations on hydrogen diffusivity coefficient and fish-scale resistance has not been reported. In this paper, the

relationship of precipitations between hydrogen diffusivity coefficient and fish-scale resistance was studied in the ultra-low carbon vanadium microalloyed steel for enameling.

2. MATERIAL AND EXPERIMENTAL PROCEDURE

2.1 Material

The material used in this study was processed by 50kg vacuum induction furnace and its chemical compositions are listed in Table 1. The ingot was forged into the billets with the size of 30mm in thickness and 150mm in width. Finishing temperature is over 850℃. The ends of billets were saw cut, after then they were cut in the size of 100mm in length. The billets were reheated at 1250℃ for 30 min, and then hot-rolled to strips with a thickness of 4mm under the finishing temperature of 930℃ in Φ500 mm two high mill. The strips were cooled by water after hot-rolling. Then, the strips were reheated at 750℃ for 30min and cooled in furnace in order to simulate coiling. They were then cold-rolled into sheets with a thickness of 1 mm. The cold-rolled sheets were annealed at 750℃ for 5，6 and 7min, respectively, to simulate continuous annealing processes.

Table 1 Chemical composition (wt.%) of the steel investigated

C	Si	Mn	S	P	Al	Ti	V	Nppm	Fe
0.025	0.33	1.43	0.006	0.010	0.010	0.030	0.040	50	Balance

2.2 Experimental procedure

The steel sheets after annealing were cut into pieces for several samples using OM，TEM，hydrogen permeation experiment and enamel test, respectively. For optical microscopy, samples were etched in a 2% nital solution after polishing. For transmission electron microscopy, carbon extraction replicas were prepared in a four-step procedure by etching the polished specimen surface in 2% nital, coating the surface with a thin film of carbon, stripping the thin film in 5% nital and then cleaning the film in both alcohol and distilled water. The precipitates in samples were extracted on carbon replicas and examined by an H-800 transmission electron microscope (TEM) equipped with a TN5500 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 precipitated particles was carried out using the standard quantitative metallographic methods[12].

For enameling test, samples were carried out using a standard for determination of the susceptibility of a steel to the fishscaling (preliminary classification: UNI E14.07.994). Samples were used as the enamel substrate and subjected to the following procedures on both sides: (i) Pretreatment of samples. Place the samples in a hot (90-95℃) alkaline degreasing solution for 25 min. Rinse well in running water at 30℃ and then in distilled water; after rinsing the film of water on the samples must be continuous. Dry in oven at 100-105 ℃ for 10 min. Spray the enamel on both sides of the samples; spray so as to obtain a 0.1 mm thick uniform layer of enamel after firing. Dry in oven at 105℃ for 10 min. (ii) Firing. The samples are placed in the firing chamber and are fired at 830 ℃±10℃ for 3 min to 5 min

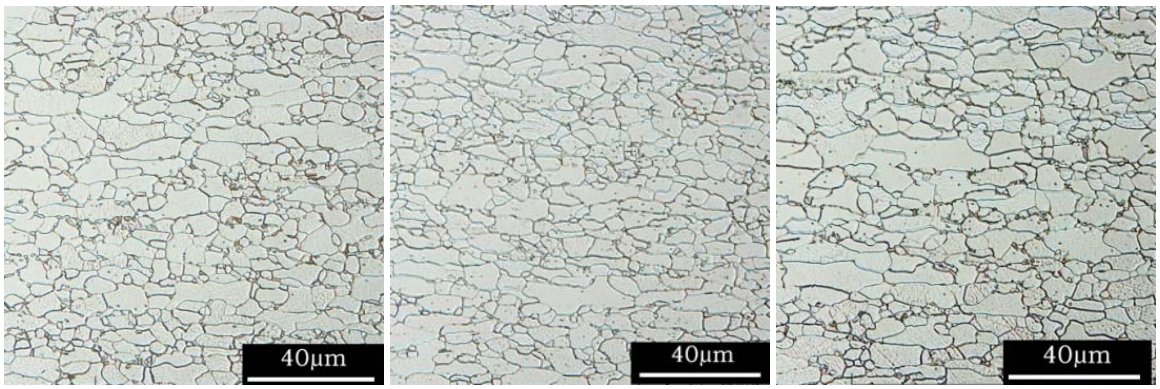
allowing the fusion process to take place. (iii) Results. 24h after firing see whether appreciable fishscales are visible to the naked eye.

After the firing of enamel, the specimens were placed in the furnace of the instrument and held at 150℃ until all the hydrogen had been desorbed. Measurements were also made on the same specimens in the as-supplied state and after the pickling before enamelling.

Hydrogen permeation experiments were carried out using an electrochemical method developed by Devanathan and Stachurki [13]. Square samples were cut from the annealed sheets, mechanically ground to 1.0 mm in thickness using emery paper from 400 to 1200. The samples were then electrolytically polished in a solution of perchloric acid, washed several times in distillated water and degreased with acetone. After that, Both sides of the samples were electroplated with Pd. Each sample was used as a membrane separating an electrochemical cell into two halves. In the left half, hydrogen was introduced by cathodic charging on the left side of the membrane. Hydrogen coming through the right side of the membrane was ionized while the output flux of hydrogen was measured by monitoring the current in the right half of the electrochemical cell. Both cathodic and anodic solutions were 0.1N NaOH, which were deaerated with N_2 to reduce the background current caused by oxygen reduction [14]. The charging current density was maintained at 0.8mA/cm^2, which was low enough to avoid damage to the membrane [5]. All hydrogen permeation curves were measured for the first permeation transient. Thus, each sample was used only for measurement of one curve. The effective diffusion coefficient of hydrogen D_{eff} can be calculated from the hydrogen permeation curves by the time lag method[13]:

$$D_{eff} = L^2/6t_L \qquad (1)$$

Where L is the sample thickness and t_L is 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 $J_t/J_\infty = 0.63$[13].



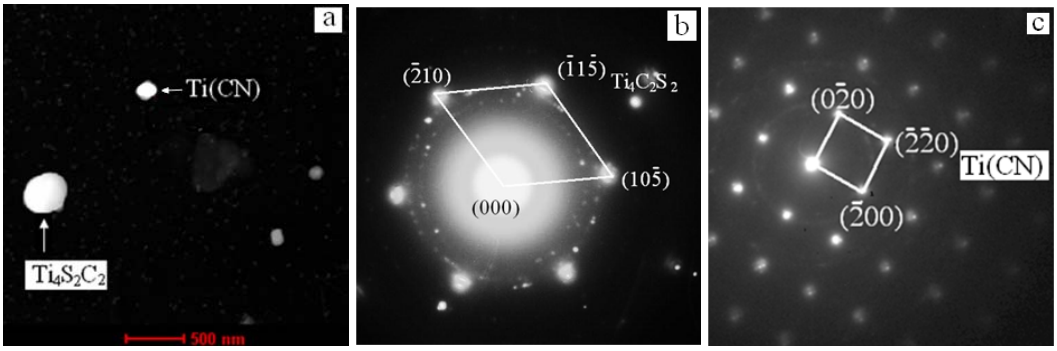
(a) 5min (b) 6 min (c) 7min

Fig.1 Microstructure of the steels annealed at 750℃ with different annealing time

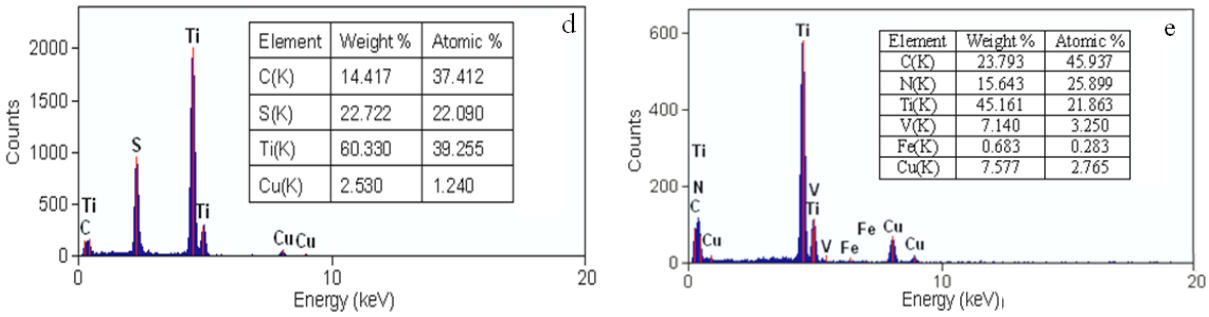
3. RESULTS

3.1 Microstructure and precipitate characterization

The microstructures of the steels using different annealed routes are shown in Fig. 1. The annealed microstructures consisted of elongated ferrite grains. Some golden color particles containing titanium can be observed in optical microscopy. But there are slightly different in quantity and sizes of the particles among the steels in different annealing time. A large number of small particles can be found in the steels after annealed at 750℃for 7minutes.



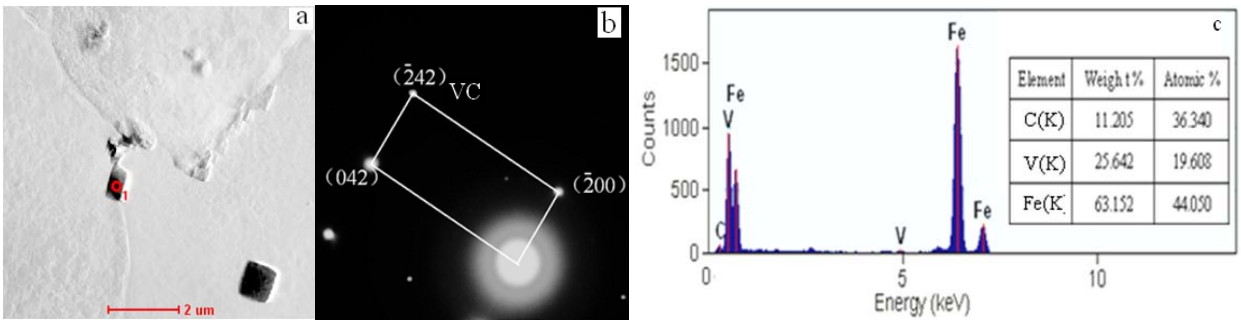
(a) $Ti_4C_2S_2$ and Ti(C,N) precipitates (b) SAD pattern of $Ti_4C_2S_2$ (c) SAD pattern of Ti(C,N)



(d)EDS spectrum of $Ti_4C_2S_2$ (e) EDS spectrum of Ti(C,N)

Fig. 2 TEM micrographs showing precipitate in the sample annealed at 750℃ for 5min

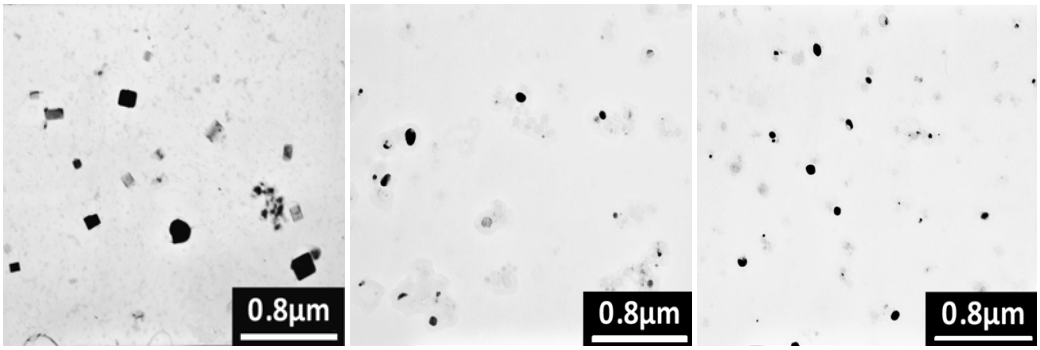
Fig. 2a shows a TEM image of typical precipitates in the sample annealed at 750℃ for 5min. Fig. 2b and 2d, respectively, show the SAD pattern and EDS spectrum of the coarse particle marked by a long arrow in Fig. 2a. These results indicate that the coarse particle is $Ti_4C_2S_2$.The EDS spectrum of $Ti_4C_2S_2$ shows an atomic ration Ti/S≈2 (as shown in Fig. 2d)[15]. Fig.3c presents the SAD pattern of the fine particle marked by a short arrow in Fig. 2a. Its EDS spectrum shows an atomic ration Ti/C/N≈1:2:1(as shown in Fig. 2e). Since precipitates were extracted on carbon replicas, the carbon atomic number of the precipitates should be more than other atoms. From the SAD pattern and EDS spectrum, the coarse particle can be identified as Ti(C,N).



(a) VC precipitate (b) SAD pattern of VC (c) EDS spectrum of VC

Fig. 3 TEM image showing VC precipitate in the sample annealed at 750℃ for 5min

Fig. 3a shows a TEM image of rectangular precipitates in the sample annealed at 750℃ for 5min. Fig. 3b presents the SAD pattern of the rectangular particle marked by a red circle in Fig. 3a. The EDS spectrum shows that it contained V and C, which isshown in Fig. 3c . From the SAD pattern, the black particles can be identified as VC.



(a) 5min (b) 6 min (c) 7min

Fig. 4 Carbon replica TEM photos showing morphology of precipitates annealed at 750℃with different annealing time

More circular and rectangular particles with homogeneous dispersion in microstructure of the steels annealed at 750℃ were observed under transmission electron microscope, which is shown in Fig.4. However, their shapes, sizes and numbers showed obvious differences. There were large particles in the steels annealed for 7min, but the number of the large particles was small. The results were different from those of steels annealed for 5 and 6min, the number of particles decreased gradually with lengthened annealing time, especially the number of the large particles. Gerenally the size of large particles ranges from 50 to 150nm, which was identified as $Ti_4C_2S_2$ precipitate, and the particles with the size smaller than 50nm were identified as Ti(C,N) or VC precipitates. In order to investigate the effect of annealing time on the precipitates in steels, quantitative analysis of the precipitates was accomplished, which is summarized in Table 2. The results reveal that number per unit volume of particles in steels increased with lengthened annealing time.

Table 2 Quantitative analysis of precipitates in steels annealed at 750℃ with different annealing time

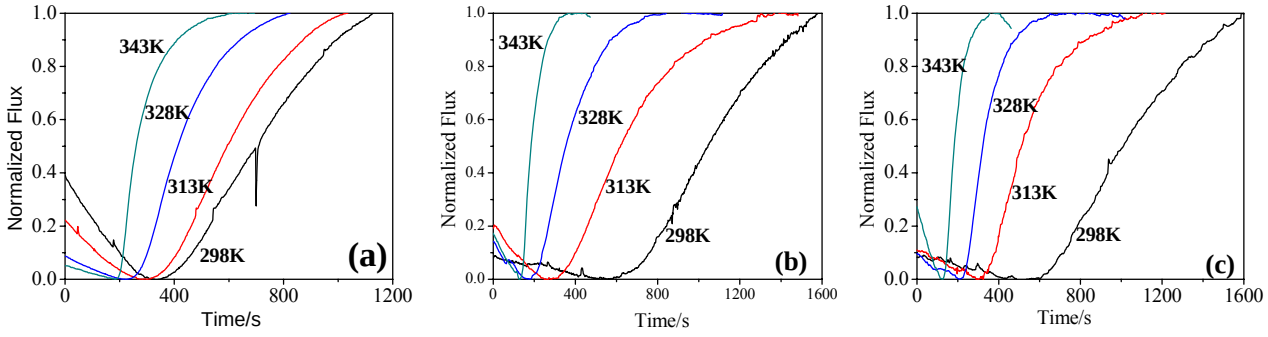
Annealing time	Mean size, d/nm	Volume fraction, V_f/%	Number per unit volume, Nv /particles /m^3
5min	37.7	0.044	0.157×10^{20}
6min	34.3	0.056	0.266×10^{20}
7min	32.7	0.056	0.309×10^{20}

3.2 Enamel test

Fig. 5 shows fishscaling appearance of these enameling steel sheets. Some small and sporadic white holes are visible to the naked eye after finishing firing 24h later in enamel layer of the steels that annealed at 750℃ for 5min, as shown in Fig.5a. And 5~10 white holes can also be observed clearly after finishing firing for 48h on surface of enameling steels that annealed at 750℃ for 6 min. which is shown in Fig. 5b. The white holes are the place where scale peels off, i.e. "fishscales". Furthermore, the quantity of fishscales annealed for 5min is more than that for 6min. However, no fishscale can be found after finishing enameling test 7 days in the steels that annealed at 750℃ for 7min, as shown in Fig.5c, which meant that they have excellent fish-scale resistance. The results of enamel test are also reported in Tables 3, where the following rough classification of fishscaling is suggested: none (no fishscale), light (small, sporadic fishscales), medium (small but widespread fishscales), and heavy (extensive fishscales with breakaway of large pieces of enamel).

(a) 5min (b) 6 min (c) 7min

Fig. 5 Fishscale morphology of enamelled steels annealed at 750℃with different annealing time



(a) 5min (b) 6 min (c) 7min

Fig. 4. Normalized output flux of hydrogen vs. time at different temperaturesfor the samples annealed at 750℃for different time

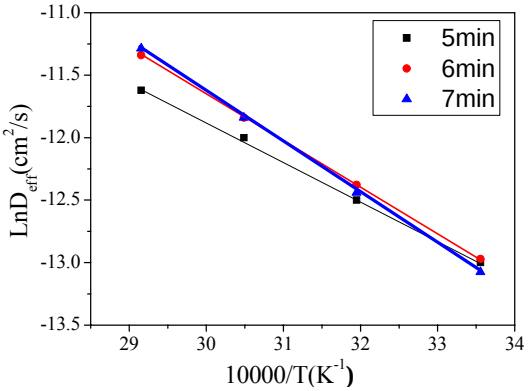


Fig. 5. Effective diffusion coefficient as a function of reciprocal temperature for the samples annealed at 750℃ for different time

3.3 Hydrogen permeation test

The hydrogen permeation curves at different annealing time are shown in Fig. 4. It can be seen that hydrogen diffusion is accelerated with the increase of temperature. From these curves, we obtained the lag times of hydrogen permeations at different temperatures, as shown in Table 3. Thus, the effective diffusion coefficient of hydrogen D_{eff} can be calculated by using formula (1). Table 3 lists the lag times t_L obtained at 25℃, and the corresponding effective diffusion coefficients D_{eff}. The effective diffusion coefficient as a function of reciprocal temperature for the samples is shown in Fig. 5. The activation energies of hydrogen diffusion in the samples annealed at 750℃ for 5min, 6min and 7min were calculated to be 25.23, 32.05 and 33.06kJ/mol, respectively. At 25 ℃, the effective diffusion coefficient in samples is 2.23×10^{-6}, 2.12×10^{-6} and 1.74×10^{-6}cm^2/s, respectively. It was suggested that the hydrogen diffusion coefficient in porcelain enameling steels should be lower than 2.0×10^{-6} cm^2/s for preventing fishscale. Thus, the ultra-low carbon vanadium microalloyed steel whose annealing time for 7min has excellent fish-scale resistance. The enamel experimental results also confirmed this conclusion.

Table 3 Results of quantitaty of precipitates, hydrogen permeation and enamel test

Annealing time	Thinckness of sampl, L/cm	Mean size, d/nm	Number per unit volume, Nv /particles/m^3	Lag time, t_L/s	Diffusion coefficient, D_{eff}/cm^2/s	Enamel test
5 min	0.097	37.7	0.157×10^{20}	703	2.23×10^{-6}	Light
6 min	0.101	34.3	0.266×10^{20}	803	2.12×10^{-6}	Light
7 min	0.101	32.7	0.309×10^{20}	977	1.74×10^{-6}	None

4. DISCUSSION

Table 3 lists the results of quantitaty of precipitates, hydrogen permeation experiment and enamel test. Results showed that number per unit volume of precipitates has a close relationship with hydrogen diffusivity coefficient and fishsacle resistance. It was found that precipitates in steels strongly influence hydrogen solubility and diffusivity. Since the precipitates such as $Ti_4C_2S_2$, Ti(C,N) and VC dispersed in steels are considered as irreversible traps, hydrogen diffusivity coefficient of test steels decreases with the increase of number per unit volume of precipitates, enhanceing to fishsacle resistance of enamel layer. It was reported that the precipitation of fine particles is an effective way to decrease hydrogen diffusivity [14], and large quantities of precipitates in steels can also reduce

hydrogen diffusion coefficient. Becuase hydrogen diffusivity in enameling sheets have an effect on the fishscale resistance[8]. In general, the decrease of hydrogen permeability increases the fishscale resistance of the enameling products. It was reported that the hydrogen diffusion coefficient should be lower than 2.0×10^{-6} cm^2/s for preventing fishscale[9]. Hence the sheets annealed for 7min has lower D_{eff} than those sheets annealed less than 7min, in correspondence with its higher total volume fraction of the $Ti_4C_2S_2$, Ti(C,N) and VC precipitates, and they have no fishscale in enamel test.

5. CONCLUSIONS

1) The total volume of precipitates has a close relationship with hydrogen diffusivity coefficient and fishsacle resistance.

2) The ultra-low carbon vanadium microalloyed steel sheets contained a large number of fine Ti(C,N), VC and coarse $Ti_4C_2S_2$ precipitates after annealed at 750℃ for 5, 6 and 7min. The total volume fraction of precipitates increased with lengthened annealing time, but the mean phase particle sizes of precipitates was reduced.

3) The effective diffusion coefficient in sheets was reduced in corresponding with their fishscale resistance enhance with lengthened annealing time.

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