THE MATCH BETWEEN DRAWABILITY AND ENAMELABILITY OF COLD–ROLLED ULTRA LOW CARBON SHEET STEELS

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The Match Between Drawability and Enamelability of Cold-rolled Ultra Low Carbon Sheet Steels

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Abstract The characteristics of chemical composition and production procedure of titanium-bearing ultra low carbon (ULC) steels and rare earth metal-bearing ULC steels are briefly introduced. The types, size and quantity in the steels are analysed by TEM and quantitatively analysis. The hydrogen permeation time and diffusion coefficient are measured by means of electrochemistry experiment. The effects of second phase particle, cold reduction and pre-strain on hydrogen permeation time are studied. The results show that titanium-bearing ULC steel with excessive titanium and RE-Ti-Nb steel exhibit excellent match between drawability and fishscale resistance.

Key words ultra low carbon, enameling, hydrogen permeation, diffusion, drawability, cold-rolled, sheet steel

With the development of metallurgical technology and equipment, it is possible to produce clean sheet steels such as interstitial-free (IF) steel. Generally, the decreasing of carbon and nitrogen in steel, the drawability of final sheet steel goes up. IF steel with excellent drawability has been applied widely for automobile parts. The enameling industry can also need this kind of sheet steels with with excellent drawability to innovate products. However, the conventional ULC steels cannot satisfy the requirement for enameling because of too much purity and thus poor fishscale resistance.

One of the main properties of the enameling steels is the fishscale resistance. It is well known that fishscale is caused by the hydrogen atoms generated during enameling, and it is related to the hydrogen storage ability. Therefore, the fishscale resistance can be prevented by the improvement of hydrogen storage ability, which can be evaluated by hydrogen permeation time and diffusion coefficient by means of electrochemistry experiment. With the permeation time increasing and diffusion coefficient decreasing, the fishscale resistance improved. Okuyamas reported [1] that when the permeation time is over 5 minutes for the steel sheet in 0.8 mm thick, the fishscale can be prevented effectively, that is, for the thickness of 1 mm, the permeation time is 7.8 minutes. Papp studied [2] the relationship of hydrogen permeation time and fishscale resistance and pointed out that the permeation time is at least 6 to 8 minutes for 1 mm thick of steel sheet, which accords with Okuyamas' results.

The hydrogen entrapment sites include vacancies, crystal boundaries, phase boundaries and micro-voids in the vicinity of inclusions and precipitates. As far as ULC steels are concerned, the microstructure is pure ferrite, with the grain sizes mainly at the range of 6 to 8; therefore, the most effective measures to improve hydrogen entrapment in steel is to increase the amount of inclusions and precipitates. It was studied [3] that Ti precipitates and RE sulphides can effectively prevent fishscale, but on the other side, the increment of inclusions and precipitates will impair the drawability of the steel sheet. It is important to add proper amount of alloying elements to meet the requirement of both the drawability and the hydrogen permeability.

1. The characteristics of chemical composition and production procedure

1.1 *The characteristics of chemical composition*

The development of sheet steels is processing from low carbon steel to Al-killed carbon steel, and till now the ULC steel. For enameling use, different alloying elements are added in the steels to form various types of inclusions and precipitates including: (1) cementite, (2) precipitates of titanium, (3) oxides and (4) boron nitride. The aim is to improve obviously the fishscale resistance due to the presence of fine and dispersive particles and inclusions.

The selection of alloying elements depends on the basic chemical composition to a large extent. For the ULC steels, the decisive elements are carbon, nitrogen, sulphur, and the useful alloying elements are titanium, rare earth metals and boron, which can improve remarkably the final properties.

The chemical compositions of ULC sheet steels for porcelain enameling are mainly titanium-bearing ULC steels and rare earth metal containing ULC steels, see Table 1.

Table 1 The chemical composition of cold-rolled ULC steels %

C	Si	Mn	P	S	Al	Alloying elements
⩽0.008	⩽0.03	0.10~0.30	⩽0.020	⩽0.05	⩽0.05	Ti, RE

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

Carbon In titanium-bearing ULC steels, Nilsson et al[4] studied that carbon can influence the mechanical properties. It is necessary to obtain excellent drawability only when carbon decreases below 0.005 percent. With the carbon content going up, the yield strength increases, and the total elongation and also the n value decreases. In this steel, carbon can mainly combine with titanium to form TiC particles, in favor of hydrogen entrapment during enamel firing. High content of carbon will form pinhole defects during enamel firing to impair the surface quality and the adhesion between steel and enamel. The higher the content of carbon, the more pinholes generate. In that case, it is important to decarbonize the steel in order to obtain ultra low carbon steel. The typical carbon content is below 0.004%.

Nitrogen The role of nitrogen is the same as carbon, i.e., to impair drawability of steel. In a traditional IF steel, the nitrogen content can be controlled as low as possible. With the adding of titanium ULC steel, titanium can form the compound with carbon and nitrogen TiN or Ti(CN) particles. They can also combine with boron to form boron nitride in boron-bearing steel. From one hand, the interstitial atoms, carbon and nitrogen, are fully fixed by excessive amount of titanium and boron to extinguish aging of steel, from the other hand, the dispersive particles improve the hydrogen permeation to prevent fishscale.

Sulphur Sulphur and carbon are able to 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 carbonitride.

Titanium and RE In ULC steel, titanium and RE combine with one or more of carbon, nitrogen and sulphur to form inclusions and precipitates. The possible types of particles are shown in Table 2.

Table 2 The types of second phase particles in titanium and RE -bearing ULC steels

Alloys added in ULC steel	Types of second phase particles
Titanium	TiC, TiN, Ti (CN), TiS and $Ti_4C_2S_2$
Rare earth metal	RE sulphide

Although these particles act as useful sites to entrap hydrogen during the enamel firing, they impair seriously the drawability especially the coarse inclusions.

1.2 *Production procedure*

The production procedure of ULC steel is as follows:

Steelmaking in LD →vacuum degassing in RH system→continuous casting→hot-rolled by hot strip tandem mill →pickling →cold-rolling by cold strip tandem mill →annealed by batch annealing furnace or continuous annealing furnace →skin tempering, oiling and packaging.

2. The microstructure and mechanical properties

2.1 *Ti-bearing ULC steels*

The typical chemical compositions of cold-rolled steels are shown in Table 3.

Table 3 Chemical compositions of steels examined (%)

Steel	C	Si	Mn	P	S	Al	Ti
ULC steel for enameling	0.0030	0.02	0.15	<0.015	<0.035	0.022	0.071
Traditional IF steel	0.0027	0.02	0.15	<0.015	<0.035	0.027	0.043

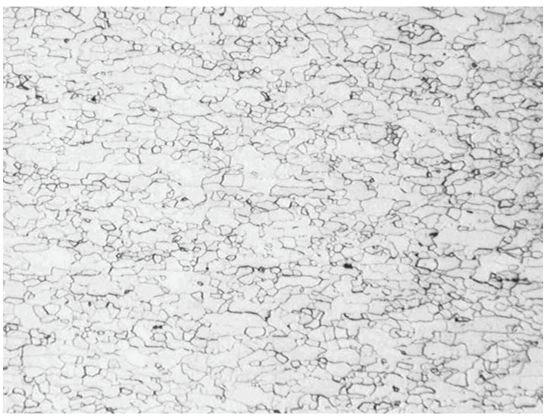
The specimens for tensile tests were taken from the steel sheets in three different directions, longitudinal, diagonal and transverse according to the rolling direction. The specimens were machined to JIS No.5 (width: 25mm, gauge length: 50mm). The average strength, total elongation, n value and r-value are calculated according to the following formula.

$$m=(m_{0^\circ}+2m_{45^\circ}+m_{90^\circ})/4 \tag{1}$$

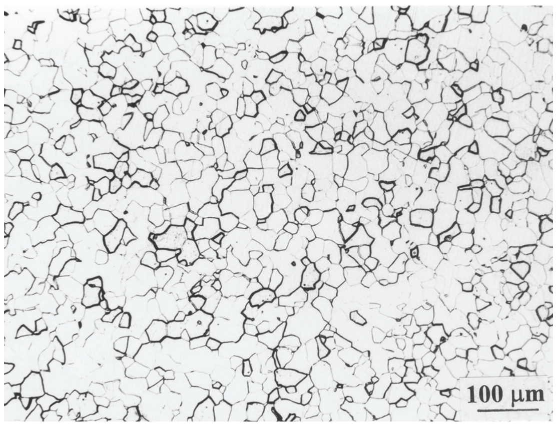
The mechanical properties of both steel sheets with different Ti added are shown in Table 4.

Table 4 Mechanical properties of steel sheets

Steel	$R_{p0.2}$ MPa	R_m MPa	A_{50} %	n_m	r_m
ULC steel for enameling	140	287	51	0.25	2.24
Traditional IF steel	142	299	50	0.24	2.21



(a) enameling steel



(b) traditional IF steel

Fig. 1 The microstructures of Ti-bearing ULC steels

The total elongations and r-values of both steels exceed 50 percent and 1.8, respectively. This demonstrates that the steel sheets examined have extra-deep drawable quality (EDDQ).

The microstructures were obsevded by optical microscopy, shown in Figure 1, which are composed of full ferrite, and the grain size is about ASTM 6~8.

2.2 *RE-bearing steels*

Table 5 Chemical composition of tested steels (%)

Steel	C	Mn	S	Ti	RE	Al	Nb	N
Steel RE-Ti-Nb	0.0009	0.18	0.036	0.056	0.023	0.03	0.014	0.0032
Steel RE-Ti	0.0026	0.18	0.028	0.047	0.035	0.02	–	0.0050
Steel RE	0.0012	0.20	0.026	–	0.021	0.03	–	0.0045

The chemical compositions of RE-bearing cold-rolled steels tested are shown in Table 5.

The mechanical properties of final products after cold-rolling and annealing are listed in Table 6.

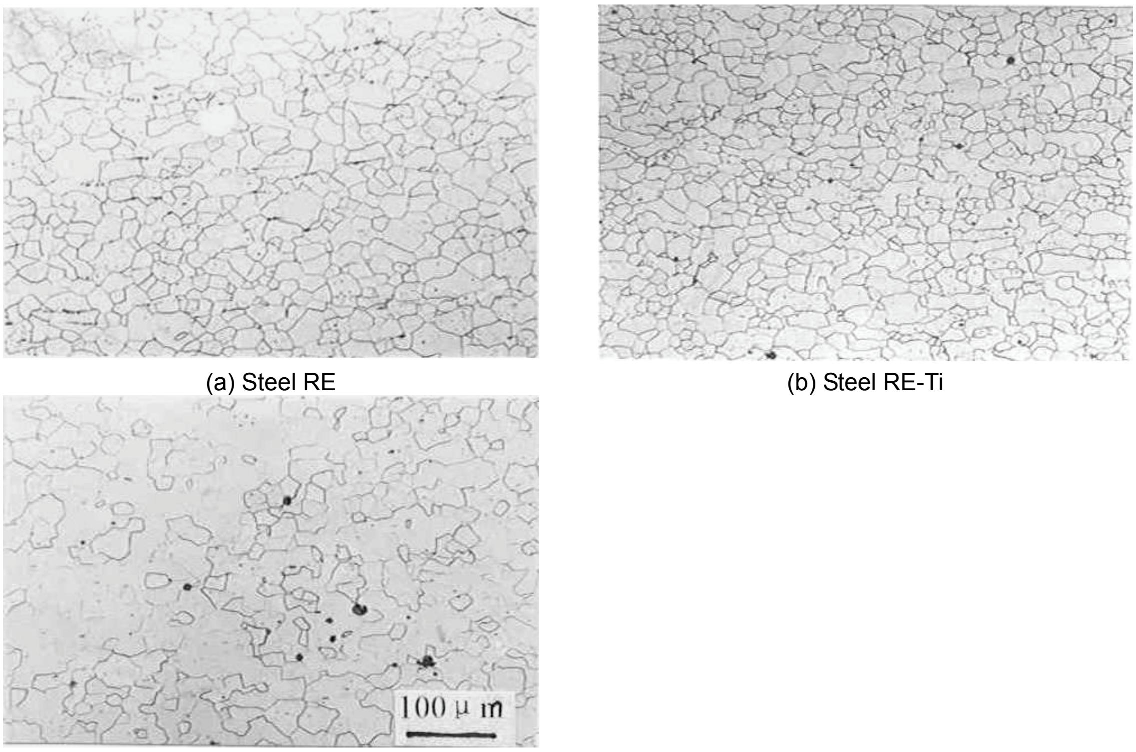
Table 6 Mechanical properties of annealed steel sheets

Steel	$R_{p0.2}$ MPa	R_m MPa	A_{50} %	n_m	r_m
Steel RE-Ti-Nb	112	302	50	0.27	1.88
Steel RE-Ti	252/234	313	48	0.27	1.73
Steel RE	227/221	311	46	0.27	1.49

Table 6 shows that Steel RE and Steel RE-Ti have upper and lower yield strengths, which means the occurrence of yield elongation. Steel RE-Ti-Nb has no yield elongation, and the yield strength is the lowest. It is will be certain that after skin tempered, the yield strength will increase sligthly. The tensile strength of the three steel grades are almost in the same level. The obvious difference is that the elongation and r-value. Steel RE-Ti-Nb exhibits the highest elongation, 50%, and r-value, 1.88, which reaches the EDDQ level.

The RE-only ULC steel has lowest drawability because there is no addition of titanium, the RE can only form RE sulphide in the steel. Therefore, the interstitial atoms of carbon and nitrogen can not be fixed by alloying elements, and the steel generates yield elongation during tensile test. Meanwhile, the addition of titanium in the steel can improve the drawability, but if there is not enough stoichiometrically alloying element such as titanium, the yield elongation can also occur (for example of Steel RE-Ti). Alloying element titanium is useful in the ULC steel because it can combine with carbon, nitrogen and sulphur.

The microstructure is observed by optical microscopy, shown in Figure 2. The microstructure is fully composed of ferrite, and the grain size is about ASTM 6~8.



(a) Steel RE (b) Steel RE-Ti

(c) Steel RE-Ti-Nb

Fig. 2 The microstructure of RE-bearing ULC steels

3 Hydrogen permeability in ULC steels

3.1 *Effect of precipitates on hydrogen permeability*

Precipitates in the steel are excellent irreversible traps to hold hydrogen. It was studied [5] that precipitates such as TiC and TiN particles can improve the hydrogen entrapment and suppress the hydrogen diffusion in the steel.

The morphology of precipitates was observed by transmission electron microscope (TEM). The TEM photographs were used to determine quantitatively the volume fraction, V_f and numbers of particles, N_v according to the following Fullman's formula[6].

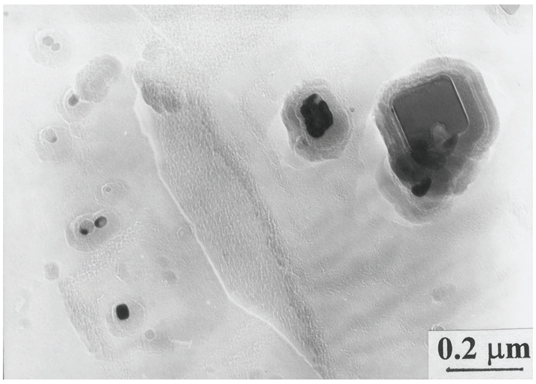
$$V_f=\pi/6\cdot N_s\cdot d^2 \qquad (2)$$

$$N_v=N_s/d \qquad (3)$$

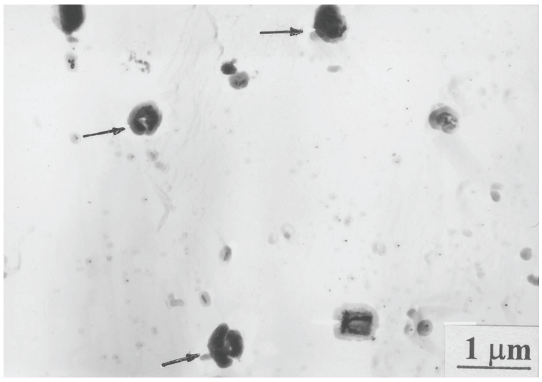
The hydrogen diffusion coefficient, D_{eff} and permeation time, t_b are measured by hydrogen permeation experiment.

3.1.1 *Ti-bearing ULC steels*

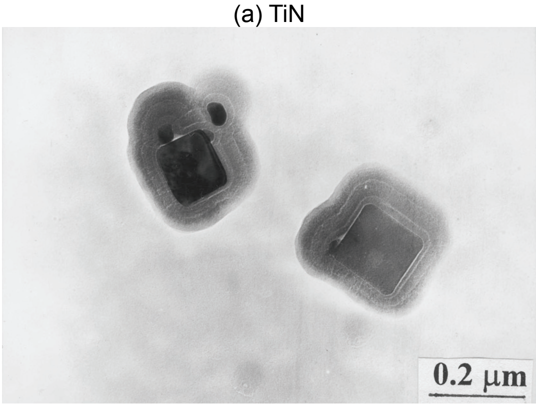
TEM examinations show that the types of precipitates are mainly TiN (or TiCN) and $Ti_4C_2S_2$ in the examined steels, and the typical examples of precipitates are shown in Figure 3.



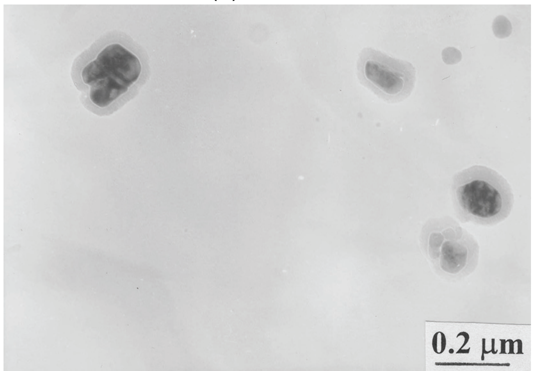
(a) TiN



(b) $Ti_4C_2S_2$



(c) TiN



(d) $Ti_4C_2S_2$

Fig. 3 TEM morphology of precipitates in sheet steels
(a) and (b)Steel (0.043%Ti), (c) and (d)Steel (0.071%Ti)

The average diameters, particle numbers in every cubic meter and volume fraction of TiN (TiCN) and $Ti_4C_2S_2$ are calculated, as shown in Table 7.

Table 7 Results of quantitative analysis of precipitates

Steel	Type of precipitates	Average diameter, d nm	Particle number in m^3, N_v $\times10^{20}$ /m^3	Volume ratio of precipitate, V_f $\times10^{-3}$ m^3/ m^3
ULC steel for enameling	TiN+Ti (CN)	39	1.90	0.59
	$Ti_4C_2S_2$	79	0.35	0.90
Traditional IF steel	TiN+Ti (CN)	24	3.50	0.25
	$Ti_4C_2S_2$	64	0.27	0.37

It is confirmed that titanium will combine with C, N and S to form precipitates. The particles in higher Ti-bearing steel are coarser than those in lower Ti steel. Accordingly, in higher Ti steel, the volume fraction of particles is greater although the particles number per unit is lower.

Table 8 shows the permeation times and diffusion coefficients of hydrogen in sheet steels (with the thickness of 1.0mm) at room temperature determined by the method of hydrogen permeation experiment.

Table 8 Hydrogen permeation time and diffusion coefficient in steels

Steel	Permeation time, t_b s	Diffusion coefficient, D_{eff} ×10^{-6} cm^2/s
ULC steel for enameling	580	0.62
Traditional IF steel	282	2.32

It is shown that the permeation time of the steel with higher Ti added is longer than that of the lower Ti steel, on the contrary, the diffusion coefficient becomes lower.

The increasing of particles volume in steel improves the hydrogen permeability remarkably. The increasing amount of precipitates is crucial to improve the hydrogen permeability and prevent fishscale, see Figure 4. With the increasing of product between volume and number of all particles, the hydrogen permeation time prolongs obviously, which reveals that the precipitates as the irreversible trap sites to improve the hydrogen permeability.

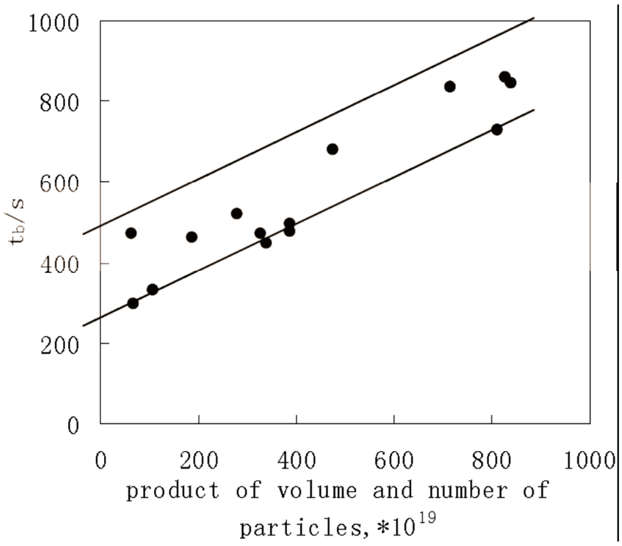


Fig. 4 Relationship of hydrogen permeation time and product of volume and number of particles in Ti-bearing steels

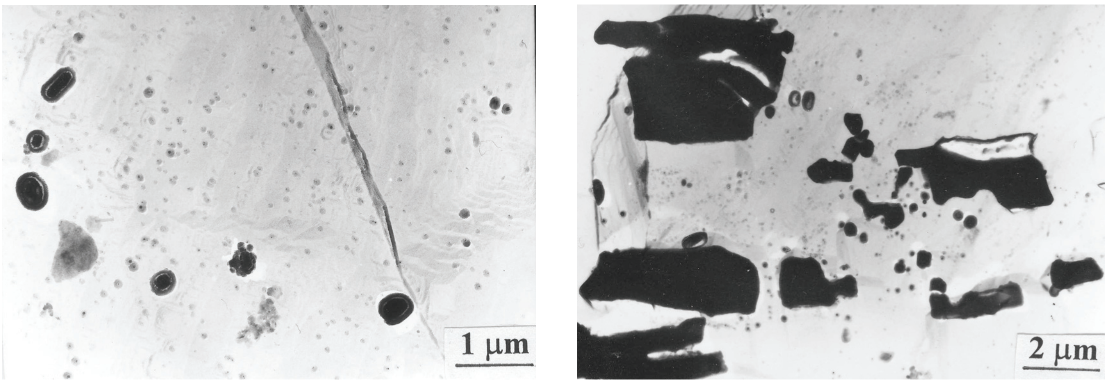
3.1.2 *RE-bearing ULC steels*

The analytical results of precipitates are listed in Table 9.

Table 9 Quantitative analyses of second phase particles in the steels

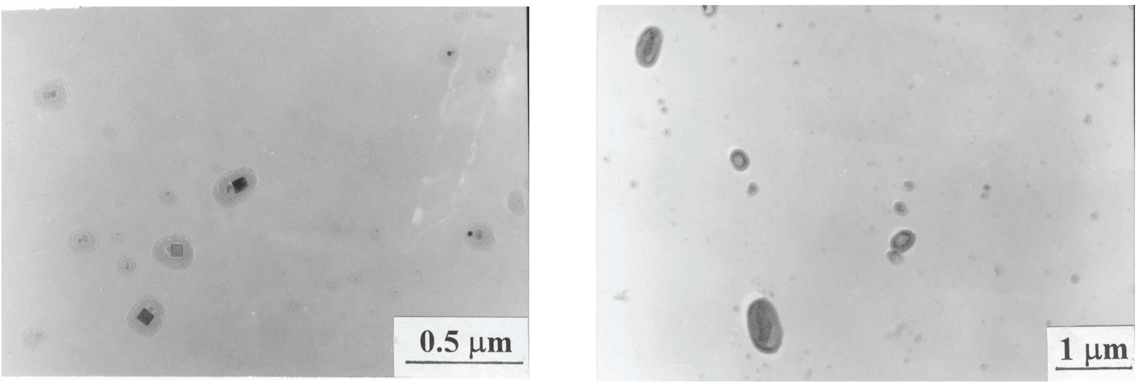
Steel	Types of particles	Average diameter, d nm	Particle number in m^3, N_v ×10^{20} /m^3	Volume ratio of precipitate, V_f ×10^{-3} m^3/m^3
Steel RE	MnS	45	1.8	8.6
Steel RE-Ti	Ti(CN)	32	1.5	2.6
	MnS	64	0.39	5.4
Steel RE-Ti-Nb	Ti(CN)	27	3.1	3.2
	MnS	58	0.57	5.8

In RE-only steel, the precipitate is mainly observed manganese sulphide (as shown in Figure 5(a)), and a few RE sulphide and its compound, see Figure 5(b). In Steel RE-Ti and Steel RE-Ti-Nb, a large amount of dispersive and fine particles are observed, as shown in Figure 6 and Figure 7, which are identified as Ti(CN). Meanwhile, there are inclusions, which are identified as the sulphide of titanium and manganese, and RE sulphide.

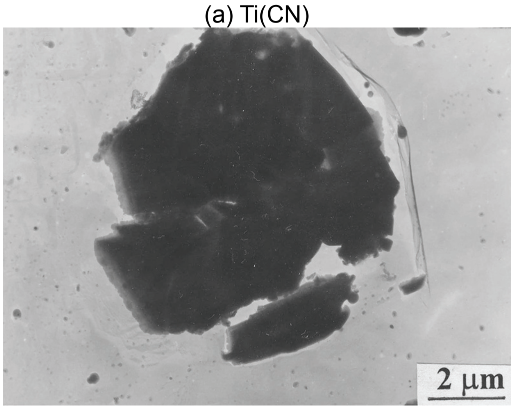


(a) MnS (b) RE sulphide

Fig. 5 Morphology of precipitates in Steel RE

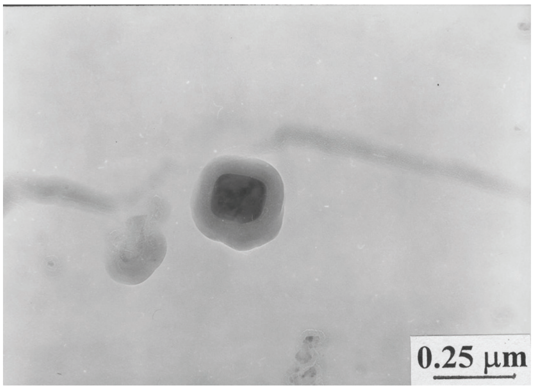


(a) Ti(CN) (b) (Mn,Ti)S

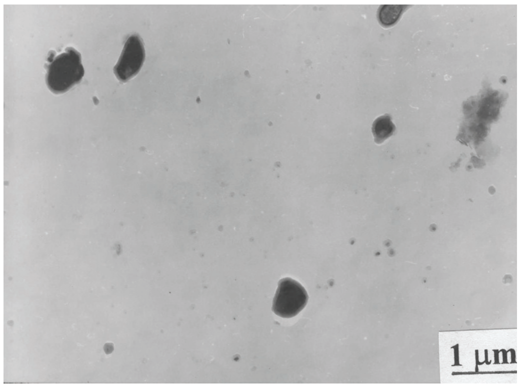


(c) (RE, Ti)S

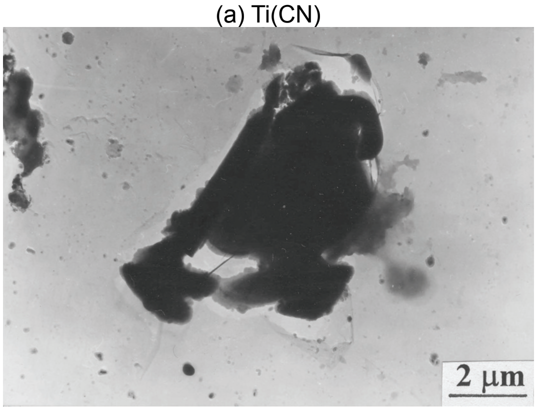
Fig. 6 Morphology of precipitates in Steel RE-Ti



(a) Ti(CN)



(b) (Mn,Ti)S



(c) (RE,Ti)S

Fig. 7 Morphology of precipitates in Steel RE-Ti-Nb

Table 10 Permeation time and diffusion coefficient of hydrogen in sheet steel at room temperature

Steel	Permeation time, t_b s	Diffusion coefficient, D_{eff} $\times10^{-6}cm^2/s$
RE	165	3.968
RE-Ti	259	2.525
RE-Ti-Nb	353	1.851

The permeation time and effective diffusion coefficient of hydrogen in sheet steel at room temperature are shown in Table 10. From Table 10, three grades of the steels have different permeation time and diffusion coefficient of hydrogen. With the increasing addition of alloying element such as RE, Ti and Nb, the permeation time goes up and diffusion coefficient goes down. The permeation time and effective diffusion coefficient of hydrogen represents the hydrogen entrapment ability, which can qualitatively reflect the fishscale resistance of the steels during enameling and firing, i.e., the longer the permeation time, the stronger ability to store hydrogen and the better to resist fishscale. Therefore, the steel co-added with RE, Ti and Nb features the best fishscale resistance.

Figure 8 shows the test temperature can also affect the permeation time and diffusion coefficient of hydrogen in steels. With the temperature going up, the permeation time decreases and diffusion coefficient increases. The reason is that with the temperature goes up, the diffusion of hydrogen atoms in steels will be accelerated.

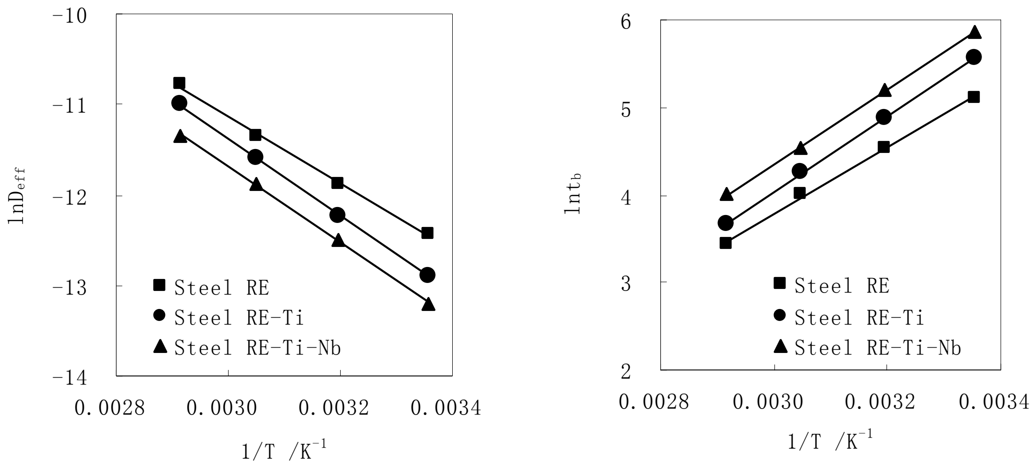
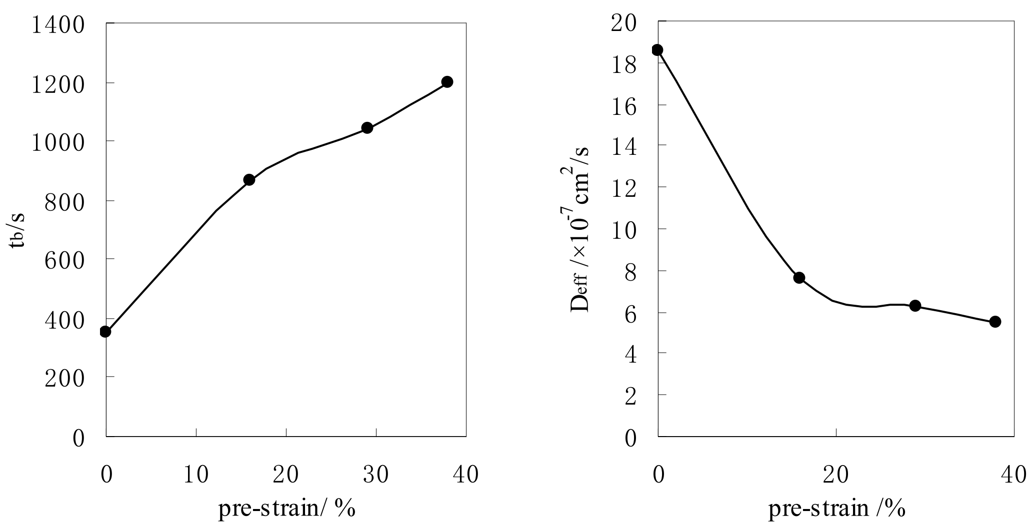


Fig. 8 The permeation time and diffusion coefficient of hydrogen in steels at different temperatures

3.2 *Effect of pre-strain on hydrogen permeability*

The tensile examples taken from Steel RE-Ti-Nb were strained by uniaxial tensile, and the strains are 0, 16, 29 and 38 percent, respectively. The permeation time and effective diffusion coefficient of hydrogen in the strained steels are measured at room temperature, as shown in Figure 9. For the convenience of comparation, all the data are computed to be at the same thickness, i.e., 1mm. With the pre-strain increasing, the permeation time goes up obviously, and the effective diffusion coefficient decreases.



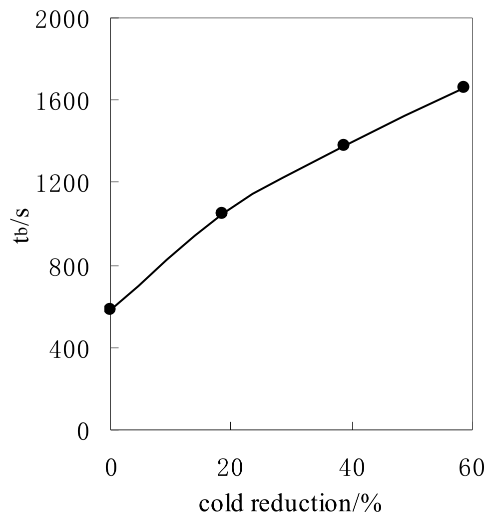
(a) (b)

Fig. 9 The permeation time and effective diffusion coefficient of hydrogen in the strained steels at room temperature

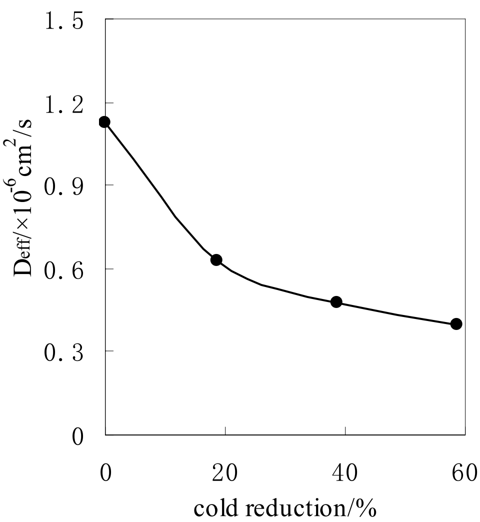
As we know, the hydrogen entrapment traps are divided two types: reversible and irreversible. The steel sheets generate large amount of dislocation after drawing, and also micro voids. The dislocation is regarded as reversible trap, and void as irreversible trap. These hydrogen traps can be helpful to store hydrogen during enameling and firing [6].

3.3 *Effect of cold reductions on hydrogen permeability*

The annealed steel sheets were cold-rolled with reductions of 18.7, 38.7 and 58.7 percent, respectively. The cold-rolled steel sheets were used to examine the hydrogen permeation time and diffusion coefficient, as shown in Figure 10.



(a)



(b)

Fig. 10 Hydrogen permeation time (a), and effective diffusion coefficient (b) in steel sheet with different cold reductions.

It is shown that the hydrogen permeability in sheet steels is affected by the cold reductions to a great extent. With the increasing of cold reductions, the permeation time prolongs, but the diffusion coefficient decreases. When the cold reduction goes up to 58.7 percent, the permeation time of hydrogen in sheet steels gets to as long as 27.7 minutes.

It was reported [7] that both dislocation and grain boundary are reversible hydrogen traps. The effect of dislocations on hydrogen permeability depends on the density of dislocations. The permeation time increases and the diffusion coefficient decreases by the increment of the density of dislocations resulted from cold deforming, as shown in Figure 10. It can be predicted that the steel sheet will have better hydrogen permeability after forming such as punching, bulging, etc. Therefore, cold deformation creates the hydrogen entrapping areas in the steel and improves the hydrogen permeability of steel sheets.

4. Conclusions

The ULC steels for enameling use are different from the traditional ULC steels. In order to improve the drawability and fishscale resistance of enameling steels, it is necessary to add adequate amount of titanium and rare earth metal. Titanium and RE combine with one or more of carbon, nitrogen and sulphur to form second phase particles.

(1) The types of precipitates in Ti-bearing ULC steels are mainly TiN, TiCN and $Ti_4C_2S_2$. With the increasing of Ti content the fraction of precipitates in the steel increases. In RE-bearing ULC steels, RE mainly combines with sulphur to form inclusions of RE sulphide and compound of RE and manganese sulphide, and titanium to form dispersive and fine particles of titanium nitride and carbonitride.

(2) Ti-bearing ULC steel and RE-Ti-Nb steel both exhibit extra deep drawability.

(3) Precipitates as irreversible traps in the steels affect greatly the permeation time. With the product of volume and number of particles the permeation time prolongs.

(4) The pre-strain and cold deformation generate dislocation and micro voids to be the reversible traps to hold hydrogen. With the increment of cold reduction and pre-strain, the permeation time prolongs and the diffusion coefficient decreases.

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