Study on the enameling properties of cold-rolled sheet steels contained different alloyed elements

SUN Quanshe[1], XU Chun[2]
1) R & D Center, Baoshan Iron and Steel Co. Ltd., Shanghai 201900, China
2) School of Material Science and Engineering, Shanghai Institute of Technology, Shanghai 201418, China

Abstract The alloyed elements titanium and boron are added in ultra low carbon steels. And the microstructure, mechanical properties, inclusions and precipitates of these steel sheets have been analyzed after cold rolling. The hydrogen permeation time of the steel sheets including annealed steel sheet and after skin-passed or cold-rolled at different reductions were measured. It is shown that the sheet steels possess the different features of enameling properties in the aspect of fishscale resistance, and pinhole resistance.
Keywords: cold-rolled, sheet steel, inclusion, precipitate, enameling property

1. Introduction

To achieve high performance of enameled products, and for the sake of saving energy and simplifying the pretreatment processes before and during enameling process, it is, of course, essential to improve the internal quality and the surface structure of steels. As far as steel be concerned, the chemical compositions such as different alloyed elements added and carbon content, the microstructures, inclusions and even the surface structure of steels, all of the changes in steels develop to suit for vitreous enameling applications. Thus, to satisfy the requirements of various enameling process and final products, the steels diversify with different chemical composition, alloy-addition, microstructure and even surface structure. The typical steel grades include Ti-bearing ULC interstitial-free (IF) steels, decarbonized (de-C) steels and etc., which have all to focus on the achievement of excellent match of drawability and enamelability. The suitability of enameling for the alloy-added steels is investigated in this paper .

2. Materials and experimental procedures

The experimental specimens are cut from hot-rolled sheet and cold-rolled after annealing by industrial production, respectively, which the chemical compositions are listed in Table 1. Among them, Ti-IF steel for enameling (same to DC06EK according to EN 10209) is titanium-contained ultra-low carbon steel, De-C (like DC04ED according to EN 10209) is one kind of decarbonized steels with extra-low carbon steel, SPHC and SPCC are low carbon aluminum-killed steels with different processes, which the former is as hot-rolled and the later is as annealed.

Table1 chemical compositions of tested steels (in weight, %)

Steels	C	Si	Mn	P	S	Al	Ti	N	B	O
Ti-IF	0.003	0.010	0.15	0.013	0.025	0.035	0.08	0.002	0.001	0.004
De-C	0.002	0.003	0.25	0.008	0.020	0.001	0.001	0.002	-	0.040
SPCC/ SPHC	0.042	0.015	0.25	0.001	0.009	0.050	0.002	0.003	-	0.005

The specimen of tensile test is taken in transverse direction at 80mm in gauge length. The metallographic observation of longitudinal section along the rolling direction is undertaken by optical microscopy. The inclusions and precipitates are observed by TEM and SEM with EDAX. Hydrogen permeation time is measured according to ISO 17081, and converted into 1 mm in thickness. The steel sheets after annealing were cold-rolled again at various reductions of 18.7, 38.7 and 58.7 percent, respectively, to measure the change of hydrogen permeation time.

3. Results and discussions

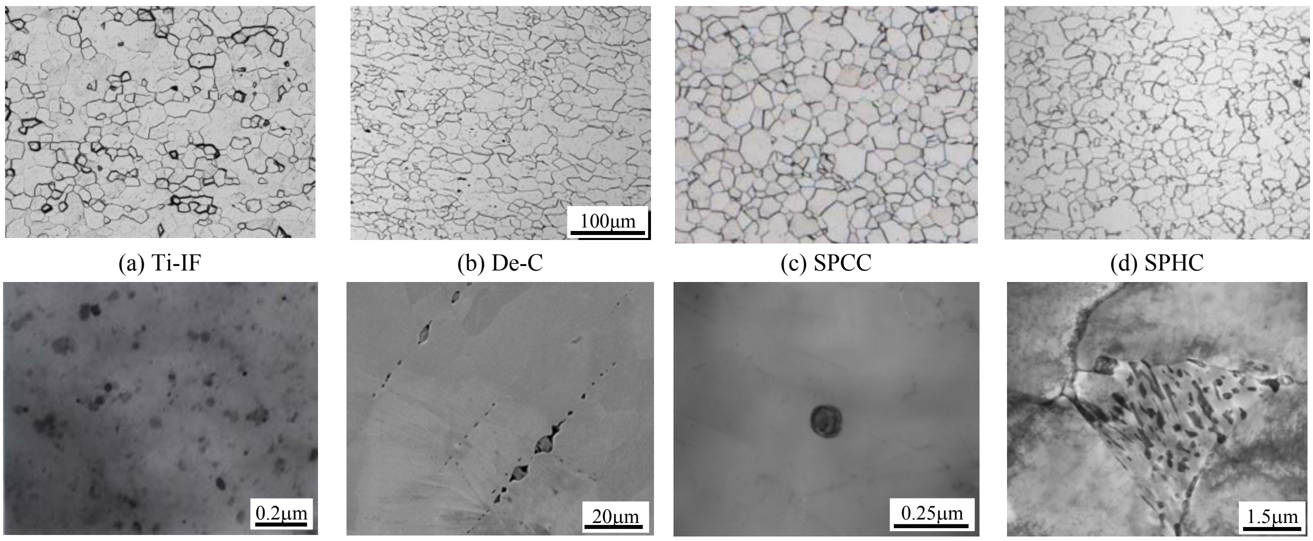
3.1 Tensile properties, microstructures and second phase particles of different steels

Ti-IF and De-C steels both possess excellent deep drawability because of very low carbon contained, especially for IF steel, which excessive Ti added to stablize all of the carbon and nitrogen atoms eliminates ageing phonomena and improves the elongation in diagonal direction. The typical tensile properties are shown in Table 2. Compared to the ULC steels, both of the low carbon steels, SPCC and SPHC, are provided with higher yield strength and thus lower total elongation.

Table 2 Typical tensile properties of tested steels

Steels	Thickness, t mm	Yield strength, Rp0.2 MPa	Tensile strength, Rm MPa	Total elongation, A(gauge length: 80mm) %
Ti-IF	0.8	140	302	45
De-C	0.8	170	305	42
SPCC	1.8	220	341	41
SPHC	1.8	224	347	40

The optical microstructures and morphology of second phase particles of different steels, observed by TEM and SEM are shown in Figure 1. The microstructures are composed of pure ferrite for both Ti-IF steel and De-C steel, and ferrite plus very few pearlite or cementite for SPCC and SPHC, which depends on carbon concentration.



(a) Ti-IF (b) De-C (c) SPCC (d) SPHC

(e) Ti-IF (f) De-C (g) SPCC and SPHC

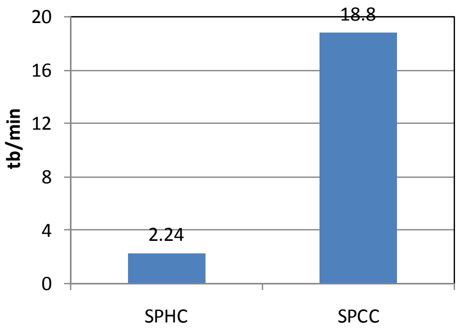
Figure 1 Optical microstructures from (a) to (d) and morphology of second phase particles from (e) to (g) in different steels

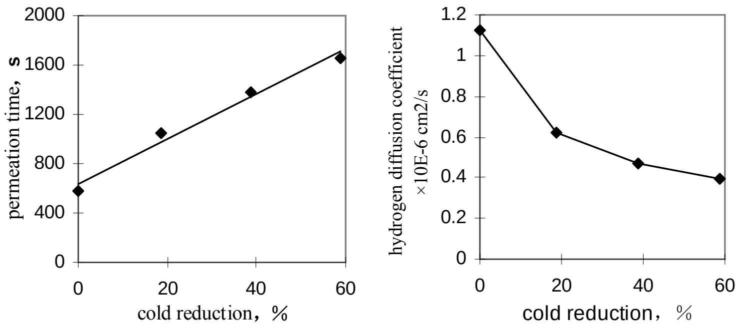
In Ti-IF steel, the second particles consisted of coarser TiN inclusions and finer dispersively-distributed compunds of Ti with C, N and S, mainly are TiN and Ti(CN), $Ti_4C_2S_2$ particles. In De-C steel, the main inclusions are MnO and MnS and their compunds at larger size. However, in low carbon steels, SPCC and SPHC, because of no additon of Ti alloy elements, there are only cementites and also AlN particle exists, the less carbon content, the fewer cementite contains.

3.2 Characteristics of hydrogen storage ability for different steels

3.2.1 Comparison of hydrogen permeation time between hot- and cold-rolled steel sheets

If steels proceeded through different hot- and cold-rolling processings, the hydrogen permeation time in 1 mm thickness, changes remarkably, as shown in Figure 2. The main cause to influence the hydrogen permeation time is that a large number of micro-voids generate after cold-rolling, especially at high cold reduction, and the micro-voids still exist in the steels after annealled. There is the big difference between hot-rolled and cold-rolled steels. In that case, it will be more difficult to increase hydrogen storage traps for hot-rolled steels.





(a) (b)

Figure 2 The comparison of hydrogen permeation time for SPHC and SPCC

Figure 3 Hydrogen permeation time (a), and diffusion coefficient (b) in steel sheet with different cold reductions

3.2.2 Effect of cold reductions on hydrogen permeability

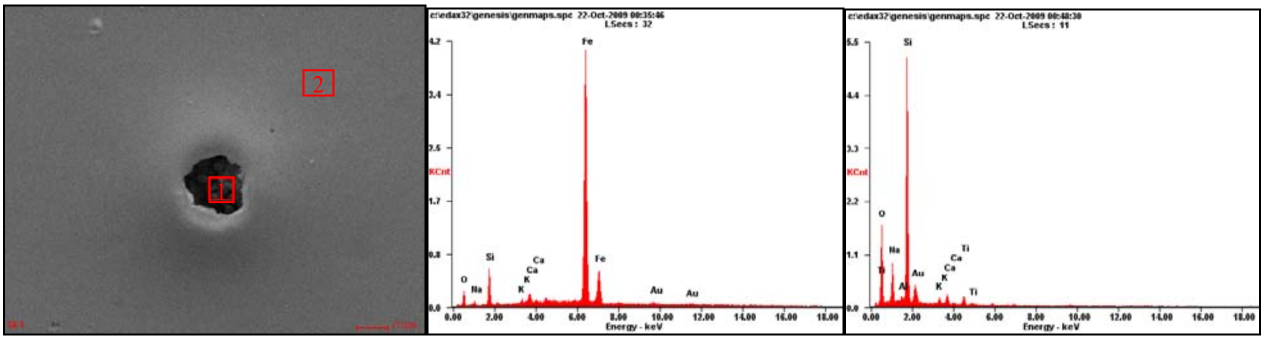
It was studied[1-3] that in Ti-IF steels, Ti precipitate can effectively prevent fishscale. In general, steel sheets will be undertaken cold deformation such as punching and bulging, and the cold reductions will affect the hydrogen permeability of steel sheets.

The steel sheets after cold-rolled and annealed, were processed by skin-passed with different cold reductions of 18.7, 38.7 and 58.7 percent, respectively. The specimens after skin-passeded were prepared to measure the hydrogen permeation time and diffusion coefficient, as shown in Figure 3. The results show 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, and the diffusion coefficient decreases, for example, when the cold reduction goes from 0 up to 58.7 percent, the permeation times of hydrogen in sheet steels increase from 10 minutes to 28 minutes consistentively.

The cold deformation will increases dislocation and generates micro-voids in steel. It was reported [4] that both dislocation and grain boundary are reversible hydrogen traps. The effect of dislocations on hydrogen permeability depends on the density of dislocations, and the micro-voids in generated in the vincity of second particles and steel matrix is inreversible traps to store hydrogen during enameling and firing. Therefore, the permeation time increases and the diffusion coefficient decreases with the increment of the combined effect of dislocations and micro-voids resulted from cold deforming. It can be predicted that the steel sheet will have better hydrogen permeability after deforming, and improves the fishscale resistence.

3.3 Pinhole and its influencing factors

Pinhole is one kind of surface defect occurred on the surface of enamel layer, which the mechanism is caused by the large-sized bubble produced during firing. Figure 4 shows the pinhole produced on the surface of enamel layer, which the steel matrix is SPHC.



(a) (b) area 1 (c) area 2

Figure 4 the pinhole produced on the surface of enamel layer, and the steel matrix is SPHC contained low carbon

The element analyses by EDAX shows that it is composed of many oxides such as SiO_2, and FeO, but for ordinary surface, there is no Fe and Fe oxide detected. It is well-known that the Fe and FeO will impair the corrosion resistance, which is why the pinhole defect has to control at very few number. Figure 5 shows the morphology of pinhole at cross section of enamel layer.

Of course, measures must be taken to control the occurrence of pinhole, and what is most important is that the steels contain very low carbon, and also the clean surface. In addition to the carbon content of steel, many other factors can cause the defects of bubbles and pinholes by the continuous processes from steel working, pretreatment, and firing, for example, residual oil, thickness of enamel layer, and firing temperature, and etc. Figure 6 is the effect of thickness of enamel layer and degreasing on the pinhole. The results show that with the increasing of enamel thickness, the average number of pinhole for every square meter increases, and enameling followed by degreasing reduce the pinhole greatly. Therefore, increasing the layer thickness and degreasing will improve obviously the pinhole resistance.

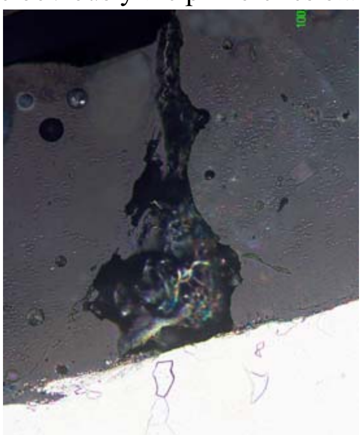


Figure 5 the morphology of pinhole at section

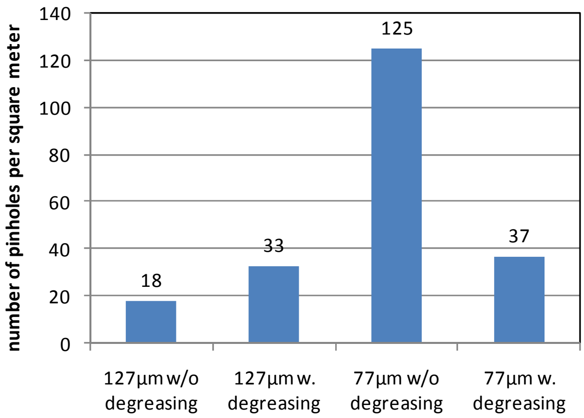


Figure 6 the effect of enamel thickness and degreasing on the pinhole number

4. Conclusions

(1) Compared to the ULC steels, Ti-IF steel and De-C steel both possess excellent deep drawability, the low carbon steels including SPCC and SPHC are provided with higher yield strength and lower total elongation. In Ti-IF steel, the second particles consisted of coarser TiN inclusions and dispersive, finer and Ti(CN), $Ti_4C_2S_2$ particles. In de-C steel, the main inclusions are MnO and MnS and their compunds with larger size. In low-carbon steels, SPCC and SPHC, without additon of Ti alloy elements, there are only cementites and also

AlN particle exists.

(2) There is the big difference between hot-rolled and cold-rolled steels, and the main cause to influence the hydrogen permeation time is that a large number of micro-voids generate after cold-rolling, especially at high cold reduction, and still exist in the steels after annealled. In that case, it will be more difficult to increase hydrogen storage traps for hot-rolled steels.

(3) Before enameling process, the steel sheets have to undertake cold working to influence the hydrogen permeation ability of steels. With the cold reduction increases, the hydrogen permeation times increases consistentively. The effect of dislocations on hydrogen permeability depends on the density of dislocations, and the micro-voids in generated in the vincity of second particles and steel matrix is inreversible traps.

(4) Many factors can cause the defects of bubbles and pinholes in addition to the chemical composition of steels, increasing the layer thickness and degreasing will improve obviously the pinhole resistance.

References

1. SUN Quanshe, JIN Lei, et al., HSLA Steels'2000, Xi'an China, Edited by LIU Guoquan WANG Fuming WANG Zubin ZHANG Hongtao, Organized by THE CHINESE SOCIETY FOR METALS METALLURGICAL INDUSTRY PRESS.
2. XU Chun, LI Xiaojie, Heat Treatment, 3. Vol. 26 , 2011, 16-21.
3. SUN Quanshe, et al., Vol.35, No. 1, January 2000, 39-42.
4. H. H. Johnson, Metall. Trans. A, 1988, 19A: 2371.