Mechanism of Hydrogen Content on the Selective Oxidation of 1.49 Si-1.55 Mn High Strength QP Steel

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Abstract: The galvanizing experiment of QP steel was carried out in two different concentrations of hydrogen content (5% and 15%) with the aim of revealing the mechanism of different hydrogen content on the selective oxidation of high strength QP steel. The morphology of oxide and inhibitory layer on the surface of steel plate was observed by SEM, and the distribution of alloying elements on the surface and coating was characterized by GDOES. The results show that higher hydrogen content makes the environment more reductive, changing the iron oxide on the surface into active iron that can react with liquid zinc. As a result, the enrichment of Si and Mn on the surface is generally reduced, the compactness of the inhibition layer is reduced, the exposed area of the steel plate surface becomes larger, and the amount of leakage decreases.

1. Introduction
Hot dip galvanizing is the most important method of corrosion resistance of high strength steel, and it is no exception for high strength QP (Quenching and Partitioning) steel. However, the selective oxidation of the alloy elements makes Galvanizing of high strength steel is a kind of difficult thing to overcome, and the wettability of galvanized steel can be partially improved by reasonably adjusting of the zinc parameters in the annealing furnace before galvanizing. These parameters mainly include dew point temperature[1-3], annealing parameters[4] and hydrogen content. Among them, there is few researches focus on the selective oxidation of alloying elements by hydrogen content. The gas in the annealing furnace of continuous hot dip galvanizing line is generally a mixture of H₂ and N₂. Cvijovic[5] studied the growth of oxides on the surface of mild steel with two kinds of hydrogen content. When in a 5%H₂+95%N₂ atmosphere, the oxides on the surface are mainly Mn and Cr, including MnO, MnSiO₃, Cr₂O₃, and a small amount of aluminum oxides. There are a lot of MnO in the grain interior and MnSiO₃ in the grain boundary. While the atmosphere changed to 15%H₂+85%N₂, the increase of hydrogen content makes the partial pressure of oxygen decrease and the surface oxides decrease. There is almost no trace of MnSiO₃, and most of the area is metal iron. However, in the study of selective oxidation of Ti-Nb stabilized IF steels during recrystallization annealing, Drillet[6] found that increasing the hydrogen content from 5% to 15% could not reduce Si and Mn oxides.

In summary, opinions on the selective oxidation of HSS by hydrogen content are not consistent, and there is little research on QP steel at present. Compared with other HSS, the addition amount of alloying elements in QP steel is relatively low, which makes the selective oxidation in QP steel
different from that in other HSS. Therefore, in this paper, QP steel was galvanized under two different hydrogen content environments, to explore the influence of different hydrogen content on the selective oxidation of the surface of the steel plate and the internal mechanism of such influence, as a reference for industrial hot dip galvanizing of QP steel.

2. Experimental procedures
The chemical elements of QP steel are: 0.18 C, 1.49 Si, 1.55 Mn, 0.046 Al (mass fraction/%). The used coupon size is 220*110mm, which were wiped with alcohol and acetone respectively before galvanizing. The simulated galvanizing experiment was carried out on the IWATANI hot dip galvanizing simulator at two different N2-H2 mixed atmosphere (15%H2 and 5%H2).

The macroscopic morphology after galvanizing was photographed with a camera. After the zinc layer was removed with 10% nitric acid alcohol, the exposed inhibition layer was characterized by mapping scanning with Zeiss field scanning electron microscope. Meanwhile, the distribution of surface oxides was observed. GDOES was used to characterize the distribution of alloying elements in the zinc layer and the substrate surface with the direction of depth.

3. Results

![Fig.1 Macroscopic morphology of galvanized coupons under different conditions](image)

(a) 15% (b) 5%

Different hydrogen content galvanized macro photos as shown in the Fig1. From the macro photos can be clearly seen, with the less hydrogen content, the surface of the leakage plating situation is more and more serious, the central part of the leakage plating gradually increased, among them, 5% hydrogen content galvanized steel plate in the middle of the leakage plating serious, zinc liquid is liquid droplets on the surface of the steel plate.
Fig. 2 GDOES diagram of zinc coating with different hydrogen content
(a) 15%; (b) 5%; (c) Aluminum content

The GDOES diagram under two conditions is shown in the Fig. 2. The left side is the zinc layer and the right side is the matrix, the junction point is the thickness of the coating. It is obvious that the enrichment of alloying elements can be seen at the cross section, especially Mn and Al. As can be seen from the content curve of aluminum (Fig. 2c), when 15% hydrogen content is present, the value of aluminum content and the width are both larger, which is an important factor for good inhibition of formation of layers. [7]

Fig. 3 Morphology of inhibition layer and surface element distribution formed under different conditions (a) 15% (b) 5%

The inhibitory layer on the galvanized surface with two hydrogen contents is shown in the Fig. 3, and the corresponding alloying element plane are shown on the right of the figure. Inhibitor layers have significantly different compactness and show good consistency with macroscopic coatings. Among them, the inhibitor layers of 5% hydrogen content has more leakage plating, the suppression layer is only sporadically grown on the surface of the steel plate. According to the surface element
distribution map of alloy elements, the surface of rice granular particles is the main component of the inhibition layer, its main element is aluminum element, is an iron - aluminum - zinc intermetallic compound, 5% hydrogen content on the surface of the inhibition layer particles are rare, which is also the direct reason for the 5% macroscopic coating surface leakage plating more.

![Fig.4 Microstructure of oxide on galvanized coupons under different conditions](image)

Both under the condition of the surface appeared a certain degree of oxidation, from surface oxidation enlarge images can be seen that with the increase of hydrogen content, surface oxidation degree of obvious increase, when hydrogen content is 5%, the surface of the oxide not only divided and crack is bigger, the oxide forms that inhibit the growth of layer can't very good on the surface, the oxide occupied all of the steel plate surface, the oxide in the process of galvanized if cannot be eliminated, then the macro coating will appear obvious plating leakage phenomenon.

4. Discussion

Although the galvanized time is short, its wettability depends on the selective oxidation of the alloying elements on the surface during the annealing. Less oxidation of alloying element is beneficial to the growth of the inhibition layer, which is a necessary condition for a good galvanized surface. In order to better reveal the internal mechanism of selective oxidation of steel plate surface under different hydrogen environment. The following figures list the enrichment of the main alloying elements along the depth direction.

According to the Fig.5, it can be clearly observed that the main enrichment element in both cases is iron. In addition, both Si and Mn are oxidized to a certain extent on the surface. Among them, the enrichment of Si is small, which is marked with a separate coordinate. Either the content of Si and Mn on the surface is relatively high, and then decreases rapidly. An obvious small fluctuation occurs around 0.25um, and then gradually decreases and becomes flat.
Singled out enrichment of Si and Mn in Fig.6, the concentration of Si on the surface of 15%H₂ atmosphere is lower than in the 5%H₂ condition, then it goes a rapid rise and a rapid fall form surface to 30 nm. After that, the Si content of 5%H₂ was obviously higher than that of 15% H₂ conditions with the increase of depth. A small crest appears on both curves at about 0.3 um. The silicon oxides are notoriously difficult to remove in subsequent reactions. For the curve of Mn, the enrichment of Mn in the condition of 15%H₂ is significantly lower than that in the condition of 5%H₂. The trend of both of them presents a parabolic shape with a peak at around 20nm. Although Mn oxide can be eliminated or partial eliminated in the subsequent reaction, high enrichment of manganese is also not conducive to improving the galvanizing performance.

When the dew point temperature is lower than zero, the relationship between different hydrogen content, oxygen partial pressure, dew point and temperature is as follow:

$$\frac{1}{2} \ln P_{O_2} = 9.8DP / (273.5 + DP) - \frac{13088}{T} + lgP_{H_2} + 0.78$$  \hspace{1cm} (1)$$

The T is the temperature in K. The $P_{H_2}$ and the $P_{satH_2O}$ are the partial pressure of hydrogen and the saturation vapor pressure of H₂O in atm, respectively. The $P_{O_2}$ is the partial pressure of oxygen generated by the decomposition of water vapor. According to in formula (1), the partial pressure of oxygen under the two conditions is 4.97E-25(15%H₂) and 4.47E-24(5%H₂), the partial pressure of oxygen with 5% hydrogen content is higher than that with 15% hydrogen content.

With a higher partial pressure, the alloying elements are more likely to undergo internal oxidation.
The internal oxidation of alloying elements is more conducive to the wettability of zinc plating. On the other hand, the gas in the recrystallization annealing furnace of continuous hot dip galvanizing line is generally a mixture of nitrogen and hydrogen. At this atmosphere, the oxide can be reduced, the iron oxide on the surface of the steel plate will be reduced to active iron that can react with liquid zinc. As a reducing agent, the content of hydrogen determines the reducibility of the atmosphere. The higher the hydrogen content, the more reductive it is, and the shorter the time required reducing the iron oxide. Most of the surface area is metal iron, which is the main oxide on the surface. In our experimental conditions, the common result of both mechanisms is a reduction in surface oxides, the oxidation of Si and Mn in 15% hydrogen environment is significantly lower than that in 5% hydrogen environment, and the iron becomes reduced iron, which can significantly improve the wettability of the zinc solution to the steel plate.

5. Conclusion
Q&P steel was galvanized in different hydrogen content, and its surface and inhibition layer were characterized through a series of experiments. The following conclusions were drawn:

(1) With the decrease of hydrogen content from 15% to 5%, the oxidation degree on the surface of the steel plate becomes more serious, leading to the deterioration of the density of the inhibition layer, the exposed area on the surface of the steel plate becomes larger, and the leakage plating increases.

(2) The concentration of Si on the surface of 15%H₂ atmosphere is lower than in the 5%H₂ condition, then it goes a rapid rise and a rapid fall form surface to 30 nm. After that, the Si content of 5%H₂ was obviously higher than that of 15% H₂ conditions with the increase of depth. A small crest appears on both curves at about 0.3 um.

(3) The enrichment of Mn in the case of 15%H₂ is significantly lower than that in the case of 5%H₂. Either trend of Mn present a parabola shape and appears a peak at about 20nm below the surface.

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