



Effect of Hot Rolled Substrate of Hydrogen Reduction on Interfacial Reaction Layer of Hot-dip Galvanizing



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ARTICLE INFO

Keywords:

Porous and dense surface
Galvanizing
Inhibition layer
Hydrogen reduction

ABSTRACT

The effect of morphology of substrate on intermetallic layer is studied in this work by combining the hydrogen reduction descaling of hot rolled steel and galvanizing process. The results show that the morphology of iron reduced at different temperatures can be divided into porous and dense iron surface. The interfacial reaction layer on steel strip with porous iron is composed of ξ phase and δ phase, and the phase in coating is invariable with the increasing of soaking time. However, the interfacial reaction layer on steel strip with dense iron is considered to be $\text{Fe}_2\text{Al}_5\text{Zn}_x$ intermetallic layer. As the time goes up, a columnar ξ phase forms on the intermetallic layer of steel strip reduced at 700 °C and the Fe-Al intermetallic layer disappears gradually. In addition, the bursting phenomenon of intermetallic layer occurs after dipping for 10s on steel strip reduced at 800 °C, and the δ phase forms on the interface between the “outburst” Fe-Al phase and substrate. The possible mechanisms involved in the formation of Fe-Al and Fe-Zn alloys were also discussed.

1. Introduction

An oxide layer will be generated during the final rolling, curling and cooling process for hot-rolled steels. The presence of the oxide layer leads to a serious deterioration of adhesion between the intercritically annealed strip and the molten Zn during hot-dip galvanizing process, therefore, it must be removed before the strip enters into the annealing furnace. At present, the layer of scale is mainly removed by pickling, with a widely acceptable surface quality. However, the acid mist and the waste acid generated during the pickling process can seriously pollute the environment (Hudson, 1985).

In recent years, with the implementation of energy-saving emission reduction strategy in steel industry and the state's efforts to punish waste acid emissions increases, many steel companies urgently develop environmentally-friendly non-pollution pickling free technology that can replace the common acid pickling method. It is well known that the oxide scale pickling process mainly includes mechanical crushing and gas reduction methods. Due to the rough substrate surface after treatment and high costs of additional equipment, the application of mechanical crushing is limited in the field of hot-dip galvanizing. In the other hand, gas reduction method mainly uses CO and H₂ gas to directly reduce the steel sheet oxides to pure iron, as reported by Tan et al.

(2013), thereby eliminating the pickling process, reducing environmental pollution and improving the continuity of the hot-dip galvanizing process, thus it has been widely studied.

Up to now, many studies on the effect of process parameters, including temperature (Chen and Yuen, 2001), gas composition (Guan et al., 2014) and cold rolling treatment (Jing et al., 2015), on the scale reduction process have been reported in the literature. For example, Shi et al. (2008) reduced the oxide scale on a hot-rolled steel strip by monoxide. The results showed that all of the oxide scales were reduced by carbon monoxide and were completely transformed into a white porous iron. Primavera et al. (2007) reported that the minimal temperature that could be of interest for H₂ treatment of low carbon scale is 500 °C, but during laboratory tests, low-rate reaction starting from 350 °C was evaluated. And the kinetics indicates the dramatic effect of H₂ purity on the rate of reaction. In our previous publication (Ding et al., 2017), it is shown that below 600 °C, the oxide scale is directly reduced into porous iron and the size of the porous iron increases with increasing temperature. Above 700 °C, a dense iron layer forms on oxide scale surface, and a “minimum reduction ratio” is observed at 700 °C as a result of the hindered diffusion of hydrogen by dense iron layer. All the previous studies have showed that gas reduction technology has the feasibility of replacing pickling process and thus will have a better

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<https://doi.org/10.1016/j.jmatprotec.2018.04.027>

Received 6 January 2018; Received in revised form 17 April 2018; Accepted 17 April 2018

Available online 18 April 2018

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application prospects with the subsequent combination of hot-dip galvanizing process. Moreover, compared with the surface condition of the pickled sheet, the surface of the strip appears thicker porous or dense layer after hydrogen reduction, which may affect the subsequent interfacial reaction with the bath.

It is widely accepted that a small amount of aluminum with a value about 0.15–0.20 wt.% will be added to zinc pot during conventional continuous hot-dip galvanizing process to form a Fe–Al intermetallic layer, which is also named inhibition layer, at the substrate and over-layer interface to inhibit the formation of Fe–Zn reaction as reported by Baril and L'Espérance (1999). A large number of works have been done to describe the formation and growth of Fe–Al and Fe–Zn intermetallic phases during hot-dip galvanizing of pickled sheets. According to Chen et al. (2008), for a 0.20 wt.% dissolved Al bath, FeAl₃ nucleates and grows during the initial stages of interfacial layer formation followed by Fe₂Al₅Zn_x formation by diffusion-controlled transformation and growth. The final microstructure of the interfacial layer consisted of Fe₂Al₅Zn_x in a two-layer arrangement comprising a fine-grained, compact lower layer and a coarser, noncompact upper layer. Wang et al. (2010) presented characterization results on inhibition layers formed on a TiNb-stabilized interstitial-free steel after short time galvanizing. The epitaxially nucleated Fe₂Al₅ grains on Fe substrate had very small grain size, 20 nm or less, and several variants were intimately mixed.

However, few publications focus on the interfacial layer growth of hot-dip molten zinc with hydrogen reduction hot-rolled steel. Especially, the pure porous iron surface produced by gas reduction has a great difference from the surface condition of the pickled plate, therefore, it is necessary to re-understand the hot-dip galvanizing process when the oxide scale is removed by gas reduction method. The works of He et al. (2016) showed that the rough surface obtained from the hydrogen reduction can improve the adhesion of the coating during hot-dipping in Zn-0.17 wt.%Al, where the Fe–Al inhibition layer does not appear obviously at interface. Moreover, publication reported by Guan et al. (2015) indicated that plates with different surface condition after acid pickling and hydrogen reduction at 550 °C, Fe–Al inhibition layer did not formed at the interface in the second ones, which possess a porous surface, after hot-dip 0.2 ~ 0.7 wt.%Al galvanizing with the same soaking times. Li et al. (2017) studied the effects of Al contents on microstructure, micro-hardness and corrosion resistance of Zn–Al alloy coatings. It is found that Al content ranging from 0.6 to 6.0 wt% in galvanizing zinc affects surface quality and adhesion between coatings and matrix in the newly developed method

From the above summary of the literature, it can be concluded that it works to combine the hydrogen reduction and hot-dip galvanizing process. Furthermore, it is also found from industrial trial that the surface morphology obtained through hydrogen reduction has a great impact on the interfacial reaction of the hot-dip galvanizing (Tan et al., 2016). However, the mechanism of the impact, especially how the porous iron affects the formation of the inhibition layer in the galvanizing process, is still poorly understood.

The aim of this paper is to systematically investigate the evolution of the interfacial reaction layer of the hot-rolled steel hot-dipped in Zn-0.2 wt.%Al when the steel strip is pre-reduced at different temperatures ranging from 500 °C to 800 °C and with different surface morphologies. And the possible mechanisms of Fe–Al and Fe–Zn growth on the different substrates will also be discussed.

2. Experimental method

Coupons of a hot-rolled low carbon steel (containing 0.037 C-0.263 Mn-0.01S-0.009Si-0.011 P -0.0724 Al, all in mass percentage) supplied by Baosteel Company in sheet form, were used in the as-received condition. The final rolling temperature was 874 °C, and coiling temperature was 707 °C. The size of the sample for each experiment was 40 mm × 20 mm × 2 mm. Zinc ingots for experiments were taken from

the industrial continuous hot-dip galvanizing line. The zinc ingots tested by ICP showed that the composition was Zn-0.2 wt.%Al.

The isothermal reduction experiments were performed on the laboratory apparatus shown in our previous publication (Ding et al., 2017). The sample cleaned by hot alkali solution consisted of 2.5 pct NaOH (AR, Batch NO: 20161125, SCRC), 2.5 pct Na₂CO₃ (AR, Batch NO: 20160808, SCRC) and 95 pct H₂O and measured by an electronic balance with 1/100,000 tolerance (Discovery DV215CD, OHAUS) was put into the quartz tube. After evacuation (-0.1 MPa), the quartz tube was filled with high purity nitrogen (99.999%) until the internal pressure reach to 10⁵ Pa and heated up to target temperature (500 °C, 600 °C, 700 °C, 800 °C) at an average rate of 40 °C/min under the protection of nitrogen. In order to achieve thermal equilibrium, 5 min of isothermal hold was applied before reduction. Then, the high purity nitrogen was replaced by 30 pct H₂-N₂ mixture with a gas flow rate of 2 L/min to reduce the oxide scale. After the reduction for 1 min, 3 min, 5 min, 8 min, the samples were cooled down to room temperature at an average rate of 50 °C/min with nitrogen and measured using an electronic balance again.

Then obtained substrates were respectively dipped into the molten Zn-0.2 wt.%Al baths at 460 °C (± 2 °C) for various dipping times (3 s, 10 s). Prior to dipping, the baths were saturated with iron (approximately 2 wt.%). When it reached a desired time, the iron panel withdrawn at a constant velocity and then quenched in cold water immediately to prevent further diffusion reaction during air cooling. All experimental samples were repeated under the same conditions to confirm the reproducibility of the experimental results.

The specimens were prepared in conventional way for microstructure examination (i.e. cross-sectioned, hot mounted, ground, and polished). In order to facilitate the observation of galvanized coating microstructure, the cross-section samples were observed using 1 vol% picric acid (2,4,6-trinitrophenol) + 1 vol% nitric acid + 98 vol% n-amyl alcohol mixed etching solution with etching time about 10s ~ 15s. The surface and cross-section morphology and the chemical composition of samples were observed directly by SEM with a TESCAN VEGA-LMUH scanning electron microscope at 30 kV and energy X-ray spectroscopy (INCA EDS). The specific surface area of different reduction surface with different sample size was tested by a mercury porosimeter (model number: PoreMaster33, 2005 edition).

3. Results

3.1. Surface and cross-sectional morphology of reduction of oxide scale

The top-view and cross-section morphology of oxide scale on sheet surface after reduction at all four temperatures for 5 min were shown in Figs. 1 and 2, respectively. It can be seen that the reduced iron is porous irregularly at 500 °C (Fig. 1(a) and 2(a)). At 600 °C, a sharp drop in density of porous iron occurs (Fig. 1(b)), which may result from sintering (Chen, 2017; Matthew et al., 1990), and a little residual island oxide still exists inside. Furthermore, it is clearly seen that as the temperature increases from 500 °C to 600 °C, the pore size of reduced iron goes up accordingly, by comparing Fig. 2(a) to (b). For the reduction at 700 °C, the wüstite on scale surface and around cracks and holes is reduced into dense iron (Fig. 1(c)) which is different from the porous morphology at 500 °C and 600 °C. In Fig. 2(c), it can be seen that a wüstite layer still exists on the sample surface (Fig. 2(c)). When temperature increases to 800 °C, dense iron layer is also found on the oxide scale surface (Fig. 1(d)). However, the inside iron oxide is reduced into pore iron with a large proportion (Fig. 2(d)), which is different from that at 700 °C.

The reduction process of the oxide scale and the formation mechanism of the surface morphologies after reduction at different temperatures have been illustrated and discussed in detail in previous studies (Ding et al., 2017) and they will not be further explained here. This work mainly continues to investigate the effect of these different

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