



Effect of bath aluminum concentration on the galvanizing of hydrogen reduced hot rolled steel without acid pickling

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ABSTRACT

An environmental friendly hot-rolled galvanizing process without acid pickling was provided via hydrogen reduction of hot mill scale. After reduction, the reduced specimens were directly galvanized in zinc melts with different dissolved Al contents ranging between 0.2 and 0.7 wt.%. It was found that the reduced scale exhibited superior coating wettability during galvanizing. However, the coating surface appearance varied significantly. The specimens galvanized in 0.2 wt.% and 0.4 wt.% Al melts are extremely rough caused by the formation of Fe–Zn alloys in the coating. Al depletion was observed in the zinc overlayer of these specimens. A full inhibition was obtained for specimen galvanized in the 0.7 wt.% Al bath. The coating structure was examined by scanning electron microscope (SEM) and the element distribution in the coating was studied by glow discharge optical emission spectrometry (GDOES). The possible mechanisms involved in the formation of Fe–Zn alloys were also discussed.

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1. Introduction

During hot-rolling of strip steel, a thin oxide film, also known as hot mill scale (HMS), inevitably forms on the steel. To produce a desirable surface, the scales are usually removed by pickling with chloric acid or sulfonic acid prior to the downstream processes. However, acid pickling also creates serious environmental problems, such as acid fog and hazardous sewage and residue [1].

Initiative exploration for more clean descaling technology has drawn great concern from steel companies and research institutes. Several alternative methods have been developed and one substitution is the reduction of oxides using gaseous reductant like hydrogen or carbon monoxide. Considerable work has been done on the gaseous reduction of iron oxides [2–5]. Several researches have also experimentally showed the effect of process parameters on the reduction of HMS [1,6–8]. All these studies suggested that gaseous reduction is a feasible way to replace traditional acid pickling process. The reduction product of HMS, porous spongy iron, can be swept mechanically as well as retained on the substrate to the following processes, like galvanizing. Recently, He et al. [9] and Tan et al. [10] reported the galvanizing of hydrogen reduced scale in Zn–Al and Zn–Al–Mg melts, respectively. In both investigations, hot dipped coatings on reduced scale exhibited excellent adherence.

In commercial galvanizing, most zinc baths contain 0.15–0.2 wt.% aluminum in the melt. Small amount of aluminum addition can brighten the coating surface [11]. More importantly, aluminum addition suppresses the unstable Fe–Zn reactions by creating a thin layer of Fe–Al intermetallics at the steel/melt interface [12]. Many brilliant works have been done on the morphology and kinetics of Fe–Al or Fe–Zn growth on steel substrate [13–18]. However, the influence of the particular substrate surface, like the porous reduced scale, on the Fe–Zn–Al ternary reaction, had not received much attention.

It was the aim of the present work to evaluate the galvanized coating on hydrogen reduced HMS and reveal the effect of bath Al content on the coating structure. The Al addition in the bath was modified in the range of 0.2–0.7 wt.%. Galvanizing samples were prepared by laboratory simulation. Coating structures were examined by scanning electron microscope (SEM) and element distribution in the coating was studied by glow discharge optical emission spectrometry (GDOES) analysis. The possible mechanisms of coating growth in different Al level baths were also discussed.

2. Material and methods

2.1. Materials

A commercial low carbon hot-rolled steel with a thickness of 2 mm was used in hydrogen reduction annealing and galvanizing. The chemical composition of the steel was examined using spark discharge atomic emission spectrometric (SD-AES) analysis and the result is listed in Table 1. The final rolling and coiling temperatures of the strip were

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Table 1
Chemical composition of substrate steel (all in wt.%).

C	Si	Mn	P	S	Al
0.0371	0.011	0.231	0.0142	0.0153	0.0722

882 °C and 680 °C, respectively. Zinc melt used in this study was obtained from the zinc pot of a commercial continuous galvanizing line (CGL). Al and Fe concentrations in the zinc melt were tested using inductively coupled plasma atomic emission spectroscopy (ICP-AES) method. Aluminum wire with a purity of 99.95% was used to modify Al content of the melt.

2.2. Experimental procedure

The hydrogen reduction and hot dip galvanizing were carried out in a hot dip process simulator (HDPS, IWATANI EU A IV). The details of the simulation facility have been described elsewhere [19]. Steel plates were first sectioned into the dimension of 120 × 200 mm and cleaned in alkaline solution before placing into the simulator. Then the specimens were heated to 550 °C and preserved in reduction atmosphere to fully reduce the scale. The reduction atmosphere consisted of 20 vol.% hydrogen with nitrogen balance at a dew point of −40 °C. After reduction, specimens were cooled down to 465 °C at the rate of −15 °C/s with pure nitrogen and held for 20 s to equalize temperature through the panels. The specimens were then dipped into the zinc melt for 3 s which equals to the typical immersion time of industrial CGLs. Subsequently, specimens were lifted up and passed through a pair of gas jets to wipe the excess melt. The bath temperature was kept consistently at 460 °C in all the experiments. To describe the correlation between the bath aluminum content and the coating structure, Al concentration was modified in the range of 0.2–0.7 wt.%. Al content of each composition was also examined using ICP-AES analysis and the results are shown in Table 2. For convenience, the three baths of melt were designated as LA (0.2 wt.% Al), MA (0.4 wt.% Al) and HA (0.7 wt.% Al) in the following description. For comparison, an acid pickled specimen using the same substrate material was also involved in the study. The acid pickled specimen was galvanized in LA bath with the same galvanizing parameter as the hydrogen reduced ones.

The surface and cross-section morphology of the scale and galvanized specimens were examined by SEM (Zeiss EVO MA25) with the assistance of energy dispersive spectrometer (EDS) analysis. The cross-section samples were etched with 1% amyl nital before SEM observation to give a clear view of the coating structure. Furthermore, to have a direct observation of the steel/coating interface, Zn coatings were selectively stripped using 5 wt.% hydrochloric acid solution with 10 g/L methenamine ($C_6H_{12}N_4$) as corrosion inhibitor. The preceding acid solution dissolves the η -Zn overlayer while retaining the Fe–Zn and Fe–Al alloys. Depth profiles of element distribution through the coatings were measured using GDOES (Leco, GDS850A). The glow discharge area was 4 mm in diameter and operated at a power of 28 W. The sputter rate was set at 0.2 $\mu\text{m/s}$ and the light emission was monitored with a time interval of 0.01 s.

Table 2
Chemical composition of zinc bath.

Melt	Designed Al content (wt.%)	Measured Al content (wt.%)
LA	0.2	0.19
MA	0.4	0.41
HA	0.7	0.71

3. Results

3.1. Scale structure

The cross-section microstructure and phase composition of the studied HMS have been examined previously [20]. The formation mechanisms of HMS were also systematically discussed by Chen and Yuen [21]. Here, as we concentrate on the galvanizing properties, the surface morphology of the HMS before and after reduction was discussed.

Fig. 1 presents the surface morphology of the examined scale. The as-received scale (Fig. 1a) is dense and uniform, which is composed of extremely fine equiaxial grains with a size of 0.1–1 μm . XRD analysis [20] suggested that these crystals are ferroferric oxide (magnetite, Fe_3O_4). The bright spots were identified as iron oxide (hematite, Fe_2O_3) which was introduced by slight oxidation at room temperature. While after reduction, the surface morphology changed significantly. As can be seen from Fig. 1b, the reduced scale is composed of granular grains with round and smooth profile. A large number of micro pores, ranging between 0.1 and 0.5 μm in diameter, were observed in the scale. Meanwhile, a characteristic of sintering produced by the long time preservation at high temperature was also observed. Fig. 2 shows the cross-section structure of the reduced scale. As can be seen from this micrograph, the scale was completely reduced into metallic iron and residual oxide was not observed. Micro pores penetrate through the whole thickness of the scale and several large voids are present at the substrate/scale interface.

Different from the traditional strip steel surface after acid pickling or cold rolling, the reduced one was characterized by (1) large specific surface area and (2) large quantity of micro pores. The effect of the porous substrate on the galvanizing reaction will be discussed later.

3.2. Appearance of the galvanized steel

The as-reduced specimens were galvanized in LA, MA and HA zinc baths, respectively, and their typical appearance is shown in Fig. 3. In all cases, bare spot was not observed which indicates that the reduced scale exhibited superior wettability to the zinc melt. However, there are significant differences in the surface roughness and lustrousness between the three specimens. The surface of LA specimen is extremely rough, which exhibited a “write” appearance in most surface area. For MA specimen, the surface is brighter than the LA specimen but still exhibits massive convex points. While the surface of HA specimen is much smoother and free of visible defect. It should be mentioned that the transverse stripes on the high Al content specimens were induced by gas blow of the wiping nozzle.

3.3. Microstructure of galvanized coating

A more elaborate and convictive observation of the coating structure was carried out using SEM. Fig. 4 shows the typical surface morphology of the galvanized coatings. The surface of LA coating (Fig. 4a) is rugged and of considerable heterogeneity. It is almost entirely covered by pillar-like crystals which contain 4–6 wt.% iron indicated by EDS analysis. Meanwhile, a great number of “outburst” structure developed on the surface. The surface of MA specimen is much more even and clean. As shown in Fig. 4b, although convex lumps are still present on the surface, pure η -zinc takes up most of the surface area instead of ζ - FeZn_{13} crystals, which is reflected in a brighter surface appearance. The surface of HA specimen (Fig. 4c) is composed of homogeneous equiaxial η -zinc, where neither Fe–Zn intermetallic phase nor convex points were observed.

The cross-section morphology of the coatings was investigated and shown in Fig. 5. In order to clearly identify the phase composition, specimens were etched using 1% amyl nital before observation. As can be seen from Fig. 5a, a thick layer of intermetallic compounds developed in the LA coating. Obviously, the alloy layer consists of two sub-layers,

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