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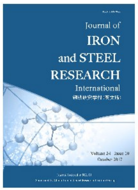

Effects of Al contents on microstructure and properties of hot-dip Zn-Al alloy coatings on hydrogen reduced hot-rolled steel without acid pickling

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ABSTRACT

A new hot-dip galvanizing method was employed on hot-rolled low carbon steel. The effects of Al contents on microstructure, micro-hardness and corrosion resistance of Zn-Al alloy coatings were systematically investigated. Phase composition, microstructure and element distribution in Zn-Al alloy coatings were analyzed using X-ray diffraction (XRD) and electron probe micro analysis (EPMA), respectively. It is found that Al content (0.6—6.0 wt.%) in galvanizing zinc affects surface quality and adhesion between coatings and matrix in the newly developed method. In addition, with increasing Al content, micro-hardness significantly increased due to the increase in Zn-Al eutectoid phases. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) also revealed that increase in Al plays a noticeable role in improving the corrosion resistance of Zn-Al alloy coatings.

1. Introduction

Hot-dip galvanizing is an effective method to improve the corrosion resistance of steels. Traditionally, acid pickling is used to remove the oxide scale on the surface of hot-rolled steel strips in hot-dip galvanizing[1,2]. However, the acid pickling process and subsequent discharge of waste acid can result in serious health problem and environmental pollution. Recently, a clean descaling technology for reducing the oxide scale on the surface of hot-rolled strips under hydrogen or hydrogen-rich atmosphere has been proposed[3-5]. This new procedure not only enhances the wettability of coatings but also suppresses the formation of Fe-Zn brittle phase in hot-dip galvanizing[6-8]. Therefore, this new technique was used in this study.

Generally, hot-dip galvanized steels are widely used in civil constructions and housing[9]. Therefore, the surface of galvanized steel strips gets scratched and corroded when it is exposed in service environments. Hence, micro-hardness and corrosion resistance of Zn coatings are two main parameters which need to improve urgently. Several studies[10-16] showed or proved that the addition of Al in Zn bath can crucially influence micro-hardness and corrosion resistance of Zn coatings through the formation of Zn-Al intermetallic compounds.

In this paper, Zn-Al alloy coatings with varying Al contents of 0.6, 1.5, 3.0 and 6.0 wt.% were prepared using the newly developed hot-dip galvanizing technique where hydrogen reduction of oxide scale was performed without acid pickling. Then, the wettability, adhesion, microstructure, micro-hardness and corrosion resistance of Zn-Al alloy coatings were systematically examined. Consequently, the obtained result can be adopted to optimize the zinc bath composition in commercial galvanizing.

2. Experimental Procedure

2.1. Material and galvanizing bath

The hot-rolled low carbon steel strips with a thickness of 1.8 mm were used in the research. The chemical composition of the steel was composed of C 0.037 wt.%, Mn 0.231 wt.%, Si 0.015 wt.%, S 0.0153 wt.%, P 0.014 wt.% and Fe balance. The thickness of oxide scale on surface of hot-rolled

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steel strip was 6−7 μm. The steel strips were cut into the dimensions of 100 mm×200 mm and cleaned in alkaline cleaning solution for hot-dip galvanizing tests.

Zn ingots were smelted in a crucible and subsequently added with various proportions of Al ingots in order to obtain the expected Al contents in the zinc bath. Therefore, four types of coating baths were designated (Zn-0.6 wt.% Al, Zn-1.5 wt.% Al, Zn-3.0 wt.% Al and Zn-6.0 wt.% Al). For convenience, the four categories of Zn-Al alloy coatings were named as Zn-0.6Al, Zn-1.5Al, Zn-3Al and Zn-6Al in the following description.

2.2. *Hot-dip galvanizing simulation*

The hydrogen reduction and hot-dip galvanizing were carried out in a hot-dip galvanizing simulator (IWATANI SURTEC). Fig. 1 shows the experimental procedure of hot-dip Zn-Al alloy coatings on hot-rolled low carbon steel strip by using hydrogen reduction of oxide scale without acid pickling, based on the previous studies of the authors′ working group[4,7,17]. The following procedure was used for each hot-dip galvanizing process: (1) the specimen was placed inside the furnace and the furnace chamber was filled with Ar after evacuation; (2) the specimen was heated to 800 ℃ at a rate of 20 ℃/s in Ar atmosphere; (3) Ar was immediately replaced by a mixture of Ar+20 vol.% H_2 and the specimen was exposed for 300 s after reaching 800 ℃, and the oxide scale on the surface of steel plates was reduced; (4) the atmosphere was reverted back to Ar and the specimen was cooled from 800 to 480 ℃ at a rate of 30 ℃/min, and then dipped for 3 s in a 480 ℃ zinc bath; (5) the specimen was lifted up and rapidly cooled to room temperature. The reduction atmosphere consisted of 20 vol.% hydrogen with nitrogen balance at a dew point of −50 ℃.

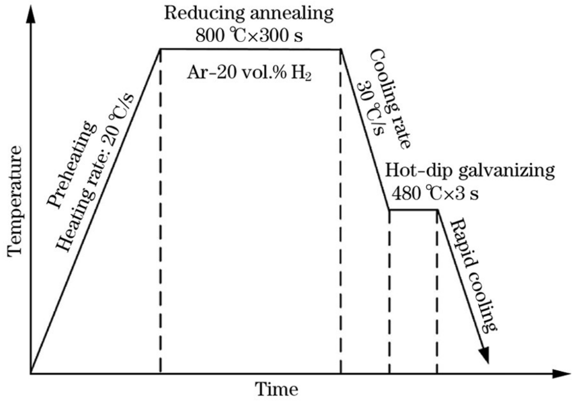

Fig. 1. Schematic of reduction and galvanizing process used in present study.

2.3. *Characterization*

The adhesion of coatings were examined by 180° bending test (universal testing machine) and the bending surface was observed by Olympus optical microscopy. Moreover, surface morphology, cross-section microstructure and element distribution of the oxide scale, reduced scale and coatings were studied using electron probe microanalysis (EPMA) and energy dispersive spectrometer (EDS). The X-ray diffraction (XRD) was performed to identify the compositions of different phases in the oxide scale, reduced scale and Zn-Al alloy coatings. The XRD data of diffraction peak were collected with angular resolution of 0.05° over the angular range of 20°−80° (2θ) and with a counting time of 0.5 s/step.

The micro-hardness of coatings was measured by using a micro-hardness tester. The applied loading was 0.5 N and the holding time was 10 s. At least 7 measurements were performed for each sample under the same condition. The average value was seen as the Vickers hardness (HV) of the coatings.

The specimens for electrochemical experiments in square shape with the size of 15 mm×15 mm were cut from the galvanized steel strips. Each specimen was mounted by using epoxy resin, leaving the surface area in the size of 1 cm^2 exposed to electrolyte solution. All the electrochemical tests were performed using three electrodes electrochemical flat cell (model: CS2350-CorrTest4 made in China) under quiescent condition at the constant temperature (25 ℃) and open to the air. The counter electrode, reference electrode and working electrode were platinum foil, saturated calomel electrode (SCE) and specimens, respectively. The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were employed for comparison of the corrosion resistance of Zn-Al alloy coatings with different Al contents in 3.5 wt.% NaCl solution. Potentiodynamic polarization curve was performed at a scanning rate of 1 mV/s from −0.10 V to 0.15 V relative to the open circuit potential. Additionally, the EIS was obtained with amplitude of 10 mV close to the open circuit potential and frequency ranging from 10^{-1} to 10^5 Hz.

3. Results and Discussion

3.1. *Oxide scale and reduced scale*

Fig. 2 presents the evolution of microstructure and phase composition of the oxide scale before and after reduction. It is worth noting that before reduction, the surface morphology of the oxide scale was integrality and compactness, as shown in Fig. 2(a). Moreover, combining Fig. 2(c) with Fig. 2(e), it can be observed that the thickness of the oxide scale in cross-section was 6−7 μm and the oxide scale of hot-rolled steel strip mainly contained two distinguishable layers: (1) a thin outer layer of Fe_3O_4 and (2) a thick layer

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