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Effects of aluminum concentration on the formation of inhibition layer during hot-dip galvanizing

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The formation of inhibition layer (IL) during hot-dip galvanizing with Al concentration varying from 0.0 to 0.8 wt pct. is studied by both experiments and numerical simulations. Using EDS and XRD, the IL is identified mainly as Zn-bearing Fe_2Al_5. SEM results reveal that the IL thickness increases with Al concentration in zinc bath, and the particles of Fe_2Al_5 on the surface of IL formed in 0.8 wt pct. Al bath are smaller than those formed in 0.2 wt pct. Al bath. On the surface of IL generated in 0.8 wt pct. Al bath there are some tiny particles with size about tens of nanometers randomly dispersing on the larger ones, indicating that the growth of IL is so fast that the growth mode changes and nucleation occurs at the IL/zinc interface. Using a mesoscopic model based on the lattice Boltzmann method, numerical simulations are also performed to study the reactive transport phenomena during IL formation under different Al concentrations. The simulations reveal complex coupled mechanisms between Fe and Al diffusion, Fe dissolution, as well as nucleation and growth of Fe_2Al_5 and the results agree with the experiments.

1. Introduction

During hot-dip galvanizing process, an extremely thin layer of Fe-Al compound with size about tens to hundreds of nanometers, called inhibition layer (IL), forms between the steel substrate and the zinc overlay. This layer serves as a barrier to retard or inhibit the formation of brittle Fe-Zn compounds between steel and molten zinc [1]. Therefore, IL has a critical influence on the microstructure and properties of zinc coating. When Al concentration in the zinc bath is lower than 0.14 wt pct., no Fe-Al compound forms and reaction between Fe and Zn occurs, while when Al concentration is higher than this threshold, the Fe-Al compound forms IL and hinders the formation of Fe-Zn compound [2–4]. The IL formation occurs quickly in only a few seconds, which is affected by various factors including chemical constituent, temperature of molten zinc, substrate material and so on [1,4–10]. Moreover, multiple subprocesses are involved in the IL formation process, including dissolution of Fe, diffusion of Fe and Al in liquid zinc and solid IL, reaction between Fe and Al as well as competition with Fe-Zn reaction [1–5,11]. Thus, study of IL formation is a challenging topic for experimental and theoretical researchers and has drawn great attention [1–18].

The concentration of Al in zinc bath is about 0.13 wt pct. for galvannealing process and about 0.2 wt pct. for galvanizing process, so most of the experiments in the literature focused on the formation and morphologies of IL in bath with Al concentration varying from 0.1 to 0.3 wt pct. at about 460 °C [1–4,11–15]. The typical morphology of IL formed during galvanizing is a double-layer structure, with the lower layer next to substrate containing continuous, compact, roughly equiaxed grains with size about tens of nanometers, and the upper layer adjacent to liquid zinc comprising coarser, larger, elongated grains with size about hundreds of nanometers [1,2,4,6,11–14,18]. To develop more environment friendly galvanizing method, galvanizing steel with scale reduced by heating hydrogen or carbon was suggested by researchers to replace conventional acid pickling [19–22]. The surface of steel with reduced scale is rough and porous [23,24], and a higher Al concentration (0.7 wt pct.) in zinc bath has been proved to be necessary to form a complete IL on such special substrate surfaces [19]. However, to the best of the authors' knowledge, there are few articles focusing on the IL formation in Zn bath containing Al concentration higher than 0.3 wt pct. in the past two decades [25]. Besides, as a vital process during galvanizing, the formation of IL is affected by Al concentration significantly. It is therefore theoretically and industrially meaningful to explore the influence of Al concentration on the IL formation.

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As a complementary method to experiments, numerical simulation has been developed not only to predict galvanizing processes at bath scale to capture the fluid flow and transport processes [26–31], but also at atomic scale to explore the intrinsic properties of compounds forming in zinc bath [32–38]. In the bath-scale simulations, emphasis was put on the evolutions of velocity, temperature and concentration in the whole bath, while the complex reactive transport processes occurring at the surface of steel were simply set as source terms or boundary conditions [26–30]. In atomic-scale calculation using first principle or molecular dynamics, some useful physical parameters, such as crystal structure [36], heat capacity [35,37], diffusivity [38] and formation energy [32] were obtained. However, the size of the atomic-scale simulations is limited to a few nanometers. Thus, there is a gap between bath-scale and atomic-scale simulations. A mesoscale model is a bridge which can connect the galvanizing process parameters, variable surface state and the intrinsic properties of involved compounds together. Recently, Min et al. [39] developed a mesoscale model based on lattice Boltzmann method (LBM) [40–42] to numerically investigate the reactive transport processes during IL formation down to nanoscale. This model not only can take into account the multiple physicochemical processes, but also can capture the dynamic evolutions of IL structure, which is difficult to realize using current experimental techniques [39]. In this paper, this model was also used to explore the effects of Al concentration on the IL formation.

The formation of IL can be divided into three steps: (1) dissolution of Fe from substrate into zinc bath, (2) rapid growth of IL by nucleation and growth of Fe-Al until surface is completely covered and (3) diffusion-controlled growth of IL [1,5–10]. A widely used model of IL formation was proposed by Tang [5] in which he applied classic nucleation theory considering the influence of temperature of bath and strip, thickness of strip, immersion time, heat transfer as well as fluid flow on IL formation process. The IL formation was divided into two stages, high rate of IL formation by continuous nucleation of Fe_2Al_5 and the growth of the Fe_2Al_5 limited by the supply of Al through liquid diffusion [5]. This model was elaborated by Giorgi [8] combining the dissolution of Fe and growth kinetics of Fe_2Al_5. In this model the surface of substrate is covered by the nucleation and lateral growth of Fe_2Al_5. Several physical parameters were artificially adjusted because of the lack of experimental and simulated values. Until now, the three stages of IL formation are widely accepted but different mechanisms about each stage are continuously proposed by researchers. Some researchers pointed out the second stage was completed by nucleation [5,7] and others believe that the substrate surface was covered by initial nuclei and their fast growth [8,10]. Some experiments indicate that the initial nucleation is $FeAl_3$ which then transforms to Fe_2Al_5 [4]. Different factors controlling the IL growth in the third stage have also been proposed in different models including diffusion of Al in the liquid zinc in Refs. [5,7,10] and solid diffusion of Fe in IL in Refs. [4,6,8]. In our previous model, the surface is treated as being covered by nucleation and fast growth of these nuclei; the third stage is controlled by Al diffusion in liquid zinc first and then by Fe diffusion in IL [39].

In the present study, the IL formation in liquid zinc is explored by both experiment and mesoscale simulations. The emphasis is put on the effects of Al concentration. The rest of the paper is arranged as follows. In Section 2, experiment methodology for IL formation is introduced, and then the IL is analyzed using SEM, EDS and XRD. In Section 3, mesoscopic numerical simulations are performed, and time evolutions of IL structure, concentration fields and IL thickness are displayed. In Section 4, the experimental and simulated results are combined with each other and discussed. Finally, a main conclusion is drawn in Section 5.

2. Experiments

2.1. Experimental method

The specimens used in this study were polycrystalline pure iron. All of them were cut into 70 mm × 10 mm × 4 mm and degreased in a 2.0 wt pct. alkaline solution at 80 °C for 15 min, which were rinsed first and then pickled in 15 vol pct. hydrochloric acid for 3 min to remove oxide and rinsed. Next the specimens were prefluxed in a solution of NH_4Cl and $ZnCl_2$ for 3 min at 60 °C, and then were dried in heater immediately before immersion in zinc bath. The solution of NH_4Cl and $ZnCl_2$ is a traditional activating agent in galvanizing, which can clean the surface further and maintain an un-oxidized surface before immersion in zinc bath. Pure zinc ingots were melted in a graphite crucible first and then pure Al wire and pure iron was added after zinc ingots totally melted. Four zinc baths saturated with Fe and Al were prepared with Al concentration as 0.0, 0.1, 0.2, 0.5, 0.8 wt pct., respectively, and for each bath three specimens were immersed for about 10 s at 460 °C one by one after Al wire was completely dissolved.

The cross sections of galvanized samples were cut from the middle of galvanized specimens, grinded and polished for observation using SEM and EDS. A mixture of glacial acetic acid and hydrogen peroxide with volume ratio 4:1 was used to expose the top view of IL by stripping off the zinc layer. The etching solution can remove zinc and leave the Fe-Al intermetallic phases [15]. The proceeding solution was also used to extract the particles of IL. X-ray diffraction analysis was performed on top view after the Zn layer was removed using Bruker D8AA25X with Cu Kα radiation and the monochromatic operated at 40 kV and 40 mA. The diffraction scans were performed using a parallel beam geometry X-ray diffractometer with an incident angle of 1.0°. The speed was set as 30 s/degree and the step as 0.02°.

2.2. Results

Fig. 1(a) and (b) shows the top-view morphology and EDS spectrum of IL after stripping the overlying zinc obtained in a 0.20 wt pct. Al bath at 460 °C. The typical double-layer structure of IL [4] was observed from top-view (Fig. 1(a)), where some larger grains disperse on the top of compact and fine ones. The EDS result further proves that this layer is rich in Fe, Al and Zn (Fig. 1(b)).

The phase identification was implemented using GIXRD from top-view after stripping the overlying zinc. As shown in Fig. 1(c), except the substrate iron, only Fe_2Al_5 was detected, indicating that the dominant phase in IL should be Fe_2Al_5. Combing with EDS results, IL mainly consists of Zn-bearing Fe_2Al_5 compound. Fig. 1 (d) displays the extracted particles of IL formed in 0.2 wt pct. Al bath, most of which are irregular polygon particles and the size varies in the range of tens to hundreds of nanometers.

The SEM BES images and elemental distributions of Al in cross-section of ILs formed in Zn baths containing 0.0, 0.1, 0.2, 0.5 and 0.8 wt pct. Al are shown in Fig. 2. Al-rich area is hardly examined when the Al concentration is 0.0 or 0.1 wt pct., and thus no elemental distribution is given for these two cases. When the Al concentration is 0.2 wt pct. or higher, there is a band of dark contrast between substrate and coating zinc because of the formation of IL. This dark band is confirmed to be an Al-rich layer as shown in the EDS mapping (Fig. 2(d, f, h)). According to the Fe-Al-Zn ternary phase diagram [3], Fe_2Al_5 can form when the Al concentration is higher than about 0.14 wt pct. The results obtained here are in coincidence with the ternary phase diagram [3]. Moreover, as shown in Fig. 2(c, e, g), when the Al concentration increases the Al-rich layer becomes thicker. Limited by the resolution of BES in SEM, it is hard to measure the IL thickness quantitatively.