The Reaction between Solid Iron and Liquid Al-Zn Baths

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The reaction which occurred between iron panels and Al-Zn baths during hot dipping was investigated. Three baths were studied: 45Al-55Zn, 55Al-45Zn, and 75Al-25Zn (in wt pct) in the temperature range of 570 to 655 °C. The reaction between the iron panel and the Al-Zn bath was very severe and in all cases the iron panel was totally consumed by the bath in less than two minutes. The rapid attack of the iron panels by the Al-Zn baths was attributed to two separate causes depending on growth conditions. First, in some panels the intermediate layer which formed between the iron panel and the molten bath was nonadherent. This resulted in the direct contact of the molten bath with the iron panel at a nonequilibrium interface, which presented a large driving force and little inhibition for the reaction. Second, in panels containing an adherent alloy layer, the layer had channels of liquid Zn which extended from the molten bath to the iron panel. These channels allowed rapid transport of Zn and Al to the iron panel which resulted in a very high reaction rate. The controlling step in the reaction between the iron panel and molten Al-Zn bath was the diffusion rate of Al in the molten bath to the surface of the iron panel. The diffusion coefficient of Al in the molten bath was found to be in the range of 1 × 10^{-5} to 5 × 10^{-5} cm²/s. Microstructural, electron microprobe, and X-ray diffraction data are presented to support the above-mentioned mechanisms and conclusions.

I. INTRODUCTION

The effects of aluminum additions to galvanizing baths have been the subject of many studies.1,2 These studies have all dealt with aluminum additions of 10 wt pct or less. Ghuman and Goldstein3 studied aluminum additions to zinc baths in the range of 0 to 10 wt pct over the temperature interval of 450 to 700 °C. They stated that at temperatures below 600 °C aluminum sharply reduces the reaction between molten zinc and the iron panel. At temperatures above 600 °C in Zn baths with 1 to 10 wt pct Al the reaction between the bath and the iron panel was very violent and exothermic. It was proposed that a reaction between aluminum containing Fe₂Zn₇ and the Al-Zn bath forms Fe₃(Al, Zn)₅ which was hypothesized to be a Brewer-Engel compound.3 The formation of a Brewer-Engel compound is accompanied by a large heat of formation which was proposed to account for the violent and exothermic reaction observed by Ghuman and Goldstein.3 Gualtieri and Ficalora4 measured the heat of formation of FeAl₁₋xZnₓ as a function of Zn concentration. They found a large peak in the heat of formation near 13 wt pct Zn and attributed this to an electron transfer process similar to that expected in Brewer-Engel type compounds.

The goals of this work were to determine if the reaction kinetics were diffusion or interface controlled and to explain the mechanism by which the rapid reaction between Al-Zn baths and iron sheet occurred.

II. EXPERIMENTAL PROCEDURE

High purity Fe, Al, and Zn were used throughout this study.5 The Si content of the Fe and Al was especially important due to its strong effect upon growth kinetics when present.6,7 Alloys were saturated with iron. This was done to prevent the iron had a grain size of 20 m and was also used to saturate the Al-Zn baths prior to dipping.

Three different bath compositions were investigated: 45Al-55Zn, 55Al-45Zn, and 75Al-25Zn, and all compositions are given in wt pct. Each bath consisted of 1000 cm³ of material, and was studied at two different dipping temperatures. The compositions and temperatures of the baths are shown in Table I. Prior to dipping, the baths were saturated with iron. This was done to prevent the iron panel from being dissolved by the molten bath which would have complicated the reaction being studied. To ensure saturation, the amount of iron used was slightly greater than that given by the Fe-Al-Zn ternary diagram of Köster and Godecke.10 A bath was checked for saturation by observing if any dross had collected at the bottom of the pot. This dross was determined by EMPA (electron microprobe analyzer) to be Fe₅Al₁₋ₓ with approximately 2 pct Zn in solid solution.

The baths and panels were prepared in the following manner. A SiC crucible (8.9 cm in diameter and 18.4 cm in height) was used to contain the molten baths. It was experimentally determined that over a period of 20 hours the amount of Si leached out of the crucible by molten Al was insignificant, i.e., total Si less than 0.005 wt pct. The bath materials were melted in a Lindburg resistance heated pot furnace where the temperature was monitored using a chromel-alumel thermocouple in a mullite sheath and was held to ±3 °C. The time required for the panel to reach the bath temperature was measured by spot welding a thermocouple to the surface of a panel and recording the temperature change during the dipping and quenching processes. Iron panels measuring 5 cm by 5 cm with a 6 mm diameter hole in one end were ultrasonically cleaned in acetone for several minutes and stored in a desiccator until needed. When the bath was ready, the panels were held with a stainless steel wire and the following steps were carried out just prior to dipping:

1. Hold in a caustic cleaner at 70 to 80 °C
2. Rinse in hot running water
Table I. Bath Compositions and Temperatures Which Were Used for This Study

<table>
<thead>
<tr>
<th>Bath Composition (Wt Pct)</th>
<th>Temperature, °C</th>
</tr>
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<tbody>
<tr>
<td>Al  Zn  Fe</td>
<td></td>
</tr>
<tr>
<td>45.5  53.1  1.4</td>
<td>570, 590</td>
</tr>
<tr>
<td>54.1  44.4  1.5</td>
<td>590, 610</td>
</tr>
<tr>
<td>73.7  24.5  1.8</td>
<td>635, 655</td>
</tr>
</tbody>
</table>

(3) pickle in 15 pct HCl solution at 80 to 90 °C
(4) rinse in hot running water
(5) hold in liquid flux at 60 to 70 °C
(6) furnace dry in air at 90 to 110 °C

Each of the above steps was carried out for 15 seconds except the drying stage, which took 1.5 to 2 minutes. The caustic cleaning solution was prepared by dissolving 130 grams of sodium hydroxide in one liter of water. The flux was developed by E. I. Du Pont de Nemours and was a standard ZnCl2 galvanizing flux modified to work with high Al baths.

Once the panel was dried, the oxide was scraped off the top of the bath and the panel was dipped and agitated slightly. After the desired time the panel was withdrawn and immediately water quenched to maintain the structure of the panel as it existed in the bath. In most cases three identical panels were made for a given set of dipping conditions, i.e., bath composition, bath temperature, and dip time.

Light optical microscopy of two panels from each set of dipping conditions was used to characterize the microstructures. A polishing fluid with a pH slightly greater than 7 was employed since water caused galvanic corrosion of the coating and was therefore unsuitable. After polishing, the sample was rinsed in ethyl alcohol and etched with 1 pct nitric acid-amyl alcohol for 20 seconds to reveal the microstructure of the overlay. The microstructure of the alloy layer was best revealed by Keller’s etch, 2 ml HF (48 pct), 3 ml HCl (conc.), 5 ml HNO3 (conc.), and 190 ml water.

X-ray diffraction (XRD) was carried out using a Diano 8535A diffractometer with a Cr target at 45 kV, a vanadium filter, and a 2θ scan rate of 2 deg/min. A 2θ range of 10 deg to 157 deg was scanned for each spectrum. A JEOL 733 microprobe with an 18 kV acceleration voltage and a 10 nA beam current was used for quantitative microchemical analysis. Quantitative wavelength dispersive X-ray microanalysis was carried out using a LiF crystal for Fe and Zn X-rays and a TAP crystal for Al X-rays. Pure element standards were used for Fe and Zn while an alloy standard of 31.4Al-68.6Ni was used for Al. Spectral intensities were converted to quantitative compositional values using the Tracor Northern ZAF matrix correction method which is based on the Magic IV program developed by Colby.\[10\]

III. RESULTS

A. Heating and Cooling Rates

Figure 1 is a plot of panel temperature vs time and shows the heating and cooling rates for a typical panel. A chromel-alumel thermocouple was spot welded to the surface of an iron panel so the temperature of the panel could be monitored during the entire dipping procedure. A panel required 2 to 3 seconds to reach the bath temperature, 610 °C, and 0.5 seconds to quench to room temperature. The heat-up time could be reduced by preheating the panel to the bath temperature; however, this was not possible since the flux began to decompose at temperatures in excess of 130 °C. Figure 1 is for a panel dipped for 7 seconds. This panel is thin compared to panels dipped for longer times; the latter cooled more slowly because the coating was correspondingly thicker.

B. Reaction Rates and Kinetics

The reaction between the iron panel and Al-Zn bath was both rapid and severe. Figure 2 shows a panel dipped in the 45Al-55Zn bath at 590 °C for 36 seconds. The coated panel swelled to 20 times its original thickness. The amount of heat released during the reaction was so great that panels dipped for 4 and 9 seconds glowed red a few seconds after being withdrawn from the bath and held in the air. This same reaction was seen in all of the baths.

Reaction kinetics between the Al-Zn baths and iron panels were determined in the following manner. The thickness of the iron panel, measured as a function of time, was subtracted from the initial iron panel thickness of 650 μm and this quantity was divided by two. Each data point plotted in Figures 3(a) and (b) is an average of 96 measurements taken from two panels (48 from each) dipped under the same conditions. These data points were plotted both in terms