Modification of galvannealed steel through aluminum addition

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Aluminum is believed to modify and to some extent control the coating characteristics of commercially produced galvanneal sheet steel. These include mechanical, chemical, and aesthetic properties. Whereas the aluminum added to the molten zinc bath is known to form intermetallics before the steel is annealed, our research is primarily concerned with the effect aluminum has on suppression or enhancement of the particular iron–zinc alloy phases in the coating during galvannealing. The microstructure of four commercially important iron–zinc intermetallic phases containing varying aluminum content between 0–1.5 weight percent has been studied. It is also believed that an iron–aluminum alloy, known as the inhibition layer, forms on the steel surface following hot dipping and prior to annealing. Transmission and scattering Mössbauer spectroscopy as well as X-ray diffraction have been used to identify iron–zinc and iron–aluminum alloys present in the coatings. Discussion will be presented on the effect aluminum has on phase suppression for Fe–Zn alloys prepared in commercially produced galvanneal.

1. Introduction

Galvanneal steel coatings are widely used, specifically within the automotive industry, as a means to enhance corrosion resistance, paintability, and weldability. These coatings are produced by allowing the steel to anneal in an oven immediately after hot-dip galvanizing.

Annealing allows the zinc and iron to diffuse and form intermetallic phases within the coatings. The iron content in the coating depends primarily on the anneal temperature and time, with up to four iron–zinc intermetallic phases able to form. They range from the zinc rich Zeta, $\zeta$, phase which forms at the coating surface, to the Delta, $\delta$, and Gamma-1, $\Gamma_1$ phases which appear generally as thicker layers, and finally to the iron rich Gamma, $\Gamma$ phase which forms a thin layer at the steel substrate surface. The presence of each phase in the coating controls the performance of the material in different ways. Previous research completed in our laboratories has successfully identified all iron atomic sites in the four pure Fe–Zn intermetallic phases [1–3]. Aluminum added to the galvanizing bath is believed to modify and to some extent control galvanneal coating properties. This includes mechanical, chemical, and aesthetic properties.

Successful application of galvanneal coatings has provided a means by which steel companies can economically meet the environmental demand to improve the
corrosion resistance of sheet steel. The ability to identify the phases formed within a coating during galvannealing is required to produce galvanneal coatings for specific applications. The present investigation identifies the four Fe–Zn intermetallic phases present within a galvanneal coating containing aluminum additives as a function of anneal time. Scattering Mössbauer spectroscopy and X-ray diffraction have been used to examine the microstructure of the galvanneal coatings.

2. Experimental procedure

Galvanneal coatings were produced using a hot-dip galvanneal simulator at a commercial site. A commercially popular low carbon steel was selected as the base for this study. The base steel has a composition as follows: 0.006% C, 0.17% Mn, 0.01% P, 0.004% S, 0.042% Al, 0.0051% N, 0.053% Ti, and 0.023% Cr. Coatings were formed by galvanizing the steel substrate in a bath containing 0.11% Al and then annealing at 900°F (482°C).

Prior to analysis, each sample was rinsed with acetone to remove any dirt or oil from the coating surface. Sections of each sample which were free from scratches or obvious defects were selected for analysis. Each coating was analyzed in-situ using scattering Mössbauer spectroscopy. The coatings were also studied intact using X-ray diffraction, which permits identification of small amounts of the Zeta and Delta phases. Furthermore, as with Mössbauer spectroscopy, X-ray diffraction analysis is able to determine the relative iron concentration of the Delta phase present in the coatings [2,3]. This provides a convenient cross reference for the Mössbauer analysis.

Crystal structure of the galvanneal coatings was studied non-destructively using a Philips model APD3720 automated powder X-ray diffractometer. Small strips of the galvannealed sheet were mounted directly into the X-ray diffractometer without the need for the standard holder used for powder samples. Data were recorded using a Cu anode X-ray tube operating at 40 kV and 25 mA. General goniometer scans between the angles of 35° and 50° two-theta were used with a resolution of 0.01 degrees and a count time of 1 second.

The Mössbauer spectra were recorded at low velocities ranging from ±1.5 mm/s and at room temperature using a 50 mCi ⁵⁷Co in Rh source. The spectra were recorded using a toroidal detector using a gas mixture of 90% Kr + 10% CH₄ and a flow rate of approximately 5 cm³ min⁻¹ [4]. The 1.8 keV Kr escape peak and 14.4 keV pulses were simultaneously acquired to improve the count rate and reduce collection time. Spectra were analyzed on an IBM3090 mainframe computer using standard fitting routines. During analyses, spectral fits showed that the Mössbauer parameters of the phases in the coatings agreed well with those of the pure phases described in previous research [3]. As fitting proceeded, we found we could constrain the hyperfine parameters to those found in the pure phases and allow only the relative fraction of each phase and the iron concentration of the Gamma and Delta phases to vary.
3. Results and discussion

The percentage of Mössbauer area, coating weight, and iron concentration of the Delta phase as a function of galvannealing time are shown in table 1.

Figure 1 displays the scattering Mössbauer spectrum for Sample #1.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>GA time (s)</th>
<th>Coating wt. (g/m²)</th>
<th>Relative Area</th>
<th>Fe conc.</th>
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<tr>
<td>1</td>
<td>0</td>
<td>54.1</td>
<td>-</td>
<td>Low</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>54.3</td>
<td>39 42 15 4</td>
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<tr>
<td>3</td>
<td>10</td>
<td>60.8</td>
<td>2 75 17 6</td>
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<tr>
<td>4</td>
<td>15</td>
<td>52.2</td>
<td>- 81 2 16</td>
<td>Medium</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>56.7</td>
<td>- 76 10 14</td>
<td>Medium</td>
</tr>
</tbody>
</table>

Figure 1. Mössbauer spectrum of Sample #1.
Mössbauer spectrum of Sample #1 showed no formation of any Fe–Zn intermetallics. The signal generated from the scattering geometry is that of the iron substrate and possibly some free iron within the zinc coating. From this spectrum we could not identify any inhibition layer consisting of an Fe–Al intermetallic. Further research, comprising of conversion electron Mössbauer spectroscopy on the bottom of the coating once fractured off the substrate, will identify conclusively whether there is an Fe–Al intermetallic formed in the early stage of galvannealing between coating and substrate.

After 4 seconds, the Mössbauer spectra of Samples #2–5 show the formation of the four Fe–Zn intermetallic phases. Figure 2 displays as a function of anneal time spectra with the iron substrate signal of Sample #1 subtracted away. The Mössbauer spectrum, along with the X-ray diffraction pattern, of Sample #2 exhibits a large concentration of the zinc rich Zeta phase along with a low iron concentration Delta phase. The spectral fit gives relative areas of the Zeta and Delta phases at 39% and 42%, respectively with an error of ±5%. Summation of the relative areas of the Gamma and Gamma-1 phases produces 19% of the total area with an error of ±10%. As table 1 shows the summation of the Gamma and Gamma-1 phases remains fairly
constant as galvanneal time increases. At a galvanneal time of 10 seconds the Zeta phase is almost undetectable while the Delta phase dominates 75% of the Mössbauer signal. This result demonstrates that with increasing galvanneal time the Zeta phase breaks down while the Delta phase increases.

At times greater than 10 seconds, as shown by Samples #4 and #5, the Zeta phase is nonexistent. At these times the Delta phase signal remains constant. However, we were able to determine the iron concentration in the Delta phase increased from a low to medium concentration. Also, Samples #4 and #5, show a greater presence of the Gamma phase and lesser presence of the Gamma-1 with the sum remaining approximately the same.

4. Conclusion

From our results we conclude that for the given steel substrate galvanized in a 0.11% Al bath, the Zeta phase forms at early galvanneal times less than 10 seconds. At galvanneal times greater than 10 seconds the Zeta phase has completely disappeared. We are also able to conclude that the iron concentration of the Delta phase increases as a function of galvanneal time. Finally from our scattering Mössbauer geometry results we were unable to identify any iron–aluminum intermetallics formed at any stage of the galvanneal process.

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References