INTERMETALLIC PHASE FORMATION IN GALVANNEALED STEEL COATINGS WITH VARYING ALUMINUM CONTENT

Trevor Q. Coddington and Desmond C. Cook
Department of Physics, Old Dominion University, Norfolk, VA 23529, U.S.A.

Aluminum added to the galvanizing bath before annealing is believed to modify the formation of iron-zinc phases and to some extent control the coating characteristics of commercially produced galvannealed steel sheet. The microstructure of commercially simulated galvanneal steel coatings was studied with aluminum contents of 0.11 and 0.15 weight percent, an anneal temperature of \(482^\circ\text{C}\), and varying anneal hold times between 0 and 25 seconds. Scattering Mössbauer spectroscopy and scanning electron microscopy (SEM) were used to identify all iron-zinc phases in the 10 \(\mu\text{m}\) thick coatings. Phase formation as a function of aluminum content in the galvanizing bath and anneal time will be investigated.

1. Introduction

Galvannealed steel is widely used within the international automotive industry to increase corrosion resistance, paintability, and weldability of automobile body paneling. By allowing steel to anneal after hot-dip galvanizing, iron-zinc intermetallic phases form within the coating. 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. These four phases correlate with the most widely accepted Fe-Zn binary phase diagram [1]. 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 [2,3,4].

Aluminum added to the galvanizing bath before annealing is believed to modify the formation of iron-zinc phases and to some extent control the coating characteristics of commercially produced galvanneal steel sheet. 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 present within the coating during galvannealing.

The ability to identify the phases formed within a coating during galvannealing is required to produce galvannealed coatings for specific applications. The present investigation identifies the four Fe-Zn intermetallic phases present within a galvannealed coating containing two different amounts of aluminum additives as a function of anneal time. Scattering Mössbauer spectroscopy as well as scanning electron microscopy have been used to examine the microstructure of the galvannealed coatings.

2. Experimental Procedure

Galvannealed coatings were produced using a hot-dip galvanneal simulator at Homer Research Laboratories operated by Bethlehem Steel Corporation in Bethlehem, PA, USA. 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 baths containing 0.11 and 0.15 weight percent aluminum and then annealing at 482°C for 0, 4, 10, 15, and 25 seconds.

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. Phase formation in each coating was analyzed in-situ using scattering Mössbauer spectroscopy. 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 with a flow rate of approximately 5 cm³ min⁻¹ [5]. 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 analysis, 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. 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 Γ and δ phases to vary [2,3].

Scanning electron microscopy (SEM) was completed at Homer Research Laboratories on an AMRAY 1600 Turbo SEM. Samples were polished and mounted in epoxy for desired experimental geometry. Photos of the secondary electron image were taken at magnifications between 7000X and 12000X with electron energies of 20 keV. The SEM was equipped with an energy dispersive spectroscopic (EDS) system with a resolution of approximately 2 microns.

3. Results and Discussion

The percentage of Mössbauer areas for each phase, coating weight, and iron concentration of the δ phase as a function of galvanneal times and aluminum content are shown in table I. Mössbauer relative areas are determined from fitting after the substrate signal in the spectrum has been subtracted.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Time (s)</th>
<th>Al Conc. (%)</th>
<th>Coating Wt. (g/m²)</th>
<th>Mössbauer Relative Area</th>
<th>δ Fe Conc.</th>
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<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.11</td>
<td>54.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>0.11</td>
<td>54.3</td>
<td>39 42</td>
<td>15 4</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.11</td>
<td>60.8</td>
<td>2 75</td>
<td>17 6</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>0.11</td>
<td>52.2</td>
<td>- 81</td>
<td>2 16</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>0.11</td>
<td>56.7</td>
<td>- 76</td>
<td>10 14</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0.15</td>
<td>62.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>0.15</td>
<td>56.9</td>
<td>74 26</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>0.15</td>
<td>56.8</td>
<td>48 52</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>15</td>
<td>0.15</td>
<td>51.8</td>
<td>24 60</td>
<td>11 5</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>0.15</td>
<td>64.0</td>
<td>7 74</td>
<td>12 6</td>
</tr>
</tbody>
</table>

Table I: Summary of iron-zinc phases formed at different anneal times and aluminum contents.

The iron concentration in the Delta phase is grouped as follows: Low=8½ - 10 at.% Fe; Medium=10 - 11½ at.% Fe; High= 11½-13 at.% Fe. Error for relative areas is ±5%.

Figure 1 displays SEM photographs of samples #1 and #2 prepared with 0.11% Al. In figure 1(a), sample #1 shows a galvanized coating, or a steel substrate with a pure zinc coating without formation of any iron-zinc phases. Therefore, only the iron signal generated from the substrate was detected in the Mössbauer spectrum [6]. From this spectrum we could not identify any inhibition layer consisting of an Fe-Al intermetallic due to its lack of signal strength or low aluminum content. However, EDS identified a trace of aluminum existing at the interfacial boundary. Further research
will ascertain conclusively whether the aluminum is in the form of a Fe-Al binary intermetallic or a Fe-Zn-Al ternary alloy. As shown in the SEM photo of figure 1(b), all four phases have formed in the coating of sample #2, in agreement with the Mössbauer analysis. Zeta can be distinguished easily by its jagged columnar shape in the top half of the coating. The delta phase appears just underneath and between the ζ and the dark layered band of Γ₁. Gamma is the thin grayish layer between the substrate and Γ₁. The whitish band in the photos is due to a buildup of electrons at the interfacial boundary. EDS was unable to identify any aluminum at the interfacial boundary of sample #2. Mössbauer analysis of samples #2-5 have been previously published [6] and the results are summarized in table I for comparison with the samples produced at the higher aluminum concentration in the current investigation.

Analysis of sample #6 concludes that no Fe-Zn intermetallics have formed which is expected for a zero anneal time sample and looks identical the photo of sample #1. Compared to sample #1, EDS was able to detect a larger amount of aluminum at the interfacial boundary of sample #6 as anticipated by its greater aluminum content in the galvanizing bath.

Scattering Mössbauer spectra for samples #7-10 prepared with 0.15% Al are shown in figure 2. Our analysis of samples #7 and #8, with anneal times of 4 and 10 seconds respectively, show that only ζ and δ form within the coating and there is no formation of Γ₁ or Γ. SEM photographs of these two samples are shown in figure 3 (a) and (b). One can see in sample #7, the Fe-Zn reaction takes place at the interface between molten zinc and the steel substrate and iron appears to diffuse out into the zinc. With the increased amount of aluminum content in the galvanizing bath, from 0.11% to 0.15%, the formation of Fe-Zn intermetallics has been inhibited or delayed. Γ₁ and Γ do not appear until the 15 second anneal time sample for the high, 0.15%, aluminum samples. This is a delay of over 10 seconds compared to the low, 0.11%, aluminum samples. EDS detected small amounts of aluminum at the interfacial boundary of samples #7 and #8. With increased anneal time, iron diffuses toward the outer surface. At 10 seconds, the zeta phase is nearly at this outer surface.

At anneal times of greater than 10 seconds, such as samples #9 and #10, all four intermetallic phases have formed. This is evidenced in the SEM
photographs in figure 3 (c) and (d). However, even in the 25 second annealed sample #10, zeta is still present. Whereas, in the low aluminum samples zeta disappeared within 15 seconds of anneal time.

Figure 3: SEM Photographs of samples (a) #7, (b) #8, (c) #9, and (d) #10.

4. Conclusion

An increase in aluminum content in the galvanizing bath from 0.11% to 0.15% delays the formation of all four phases over 10 seconds. EDS was able to identify aluminum at the interfacial boundary, however a higher resolution is needed to accurately determine the interfacial layer's crystal structure. From our results, \( \Gamma \) and \( \Gamma' \) do not form until the aluminum is undetectable at the interfacial boundary. Finally, \( \zeta \) decreases in amount with increasing anneal time.

References