ZINC-IRON PHASES FORMED ON GALVANNEALED STEEL

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Mössbauer spectroscopy has been used to identify the zinc-iron intermetallic phases present in the coating of three galvannealed steels, two of which were produced on commercial galvanizing lines and one in the laboratory. Both CEMS and XMS have been used in order to determine the depth dependence of each phase. Three main zinc-iron phases have been identified with the proportion of each dependent on the preparation conditions. In the commercially produced coatings, CEMS, probing near the top of the coating, indicates that the zinc rich \( \delta \)-FeZn_{13} and \( \delta \)-FeZn_{10} alloys are present. XMS indicates the presence of some \( \gamma \)-Fe_{5}Zn_{10} closer to the steel. In contrast, the laboratory produced sample contains nearly pure \( \delta \)-FeZn_{13} through the entire coating thickness. Subphases of the delta and gamma alloys were also identified. These subphases appear to be mixed with a preference for the higher zinc subphase of each to form closer to the surface of the coating.

1. Introduction

One method by which steel surfaces are protected from degradation is to produce a metallic coating which is able to protect the steel substrate by isolating it from the hostile medium. One such coating on steel consists of zinc-iron alloys which act as a sacrificial anode to protect the steel. A common way to produce these intermetallic phases is to use a hot-dip process by which the steel is dipped into a bath of molten zinc [1]. If heat is applied to the coated steel before the zinc solidifies, a number of zinc-iron intermetallic phases may form on the surface of the steel. The degree to which the galvannealed steel is protected and the mechanical properties of the surface, are dependent on the zinc-iron phases present. In order to determine the actual phases in the coating and also to correlate these phases with preparation conditions, Mössbauer analysis has been performed on samples of galvanneal.

2. Sample preparation and experimental procedure

Three samples of galvannealed steel, prepared under different conditions which represent a range of possible processing conditions, were studied at 300 K using
the CEMS and XMS methods, [2]. Each coating was about 10 microns thick and had a mass of about 60 gm m\(^{-2}\). Material A was produced on a commercial hot-dip coating line in which the steel sheet was heated in a protective atmosphere before coating, dipped in a molten zinc bath containing 0.1 to 0.2% aluminum, and galvanized in a gas-fired furnace immediately after coating. This material is typical of galvanized sheet produced on a “hot line”. Material B was produced in the laboratory by induction heating steel sheet that had been previously electrogalvanized. The electrogalvanized coating was initially pure zinc, and this material was included for purposes of comparing to the aluminum-containing commercially produced material. Material C was produced on a commercial hot-dip line as with A, except that instead of being heated in a protective atmosphere prior to hot-dipping, the sheet was first batch annealed in a separate operation, then cleaned and fluxed with zinc-ammonium chloride in-line prior to coating. This material is typical of galvannealed sheet produced on a “cold line”.

3. Results

Spectra recorded at high velocity quickly confirmed that XMS probed the entire coating thickness and into the steel substrate, whereas CEMS showed no indication of the substrate. Low velocity CEMS and XMS spectra were recorded to allow more accurate analysis. These are shown in fig. 1. Fitting the six spectra indicated that the three main intermetallic phases, zeta, delta and gamma were present and in different amounts for each sample. Also detected were the two common delta phases and two common gamma phases. The CEMS and XMS spectra indicate different intermetallic alloys form as a function of depth into the coating.

Fig. 1. Mössbauer spectra of 1) Material A, 2) Material B and 3) Material C, recorded at 300 K using (a) CEMS and (b) XMS.
Table 1
Mössbauer parameters obtained for the zinc-iron intermetallic phases from the fits to the three pairs of spectra shown in fig. 1

<table>
<thead>
<tr>
<th>Phase</th>
<th>Isomer shift (mm/s)</th>
<th>Quadrupole splitting (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi$</td>
<td>0.484</td>
<td>0.148</td>
</tr>
<tr>
<td>$\delta_{1p}$</td>
<td>0.477</td>
<td>0.436</td>
</tr>
<tr>
<td>$\delta_{1k}$</td>
<td>0.446</td>
<td>0.650</td>
</tr>
<tr>
<td>$\Gamma_1$</td>
<td>0.085</td>
<td>0.000</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>0.440</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Table 1 gives the Mössbauer parameters resulting from the fits to the six spectra. These parameters are close to those reported in earlier studies [3,4]. The relative area of each subspectrum is recorded in table 2. No correction has yet been made to account for attenuation due to coating thickness.

For material A, the CEMS spectrum shows that the predominant alloy present is the delta phase which has the largest quadrupole splitting of all the zinc-iron alloys. The fit also shows that more than one quadrupole split phase is present and from the relatively large splittings, it is certain that both are delta phases. However the actual splitting of one component is significantly different to the previously reported value, [4]. The surface region of the coating contains about 82% of the delta phases, $\delta_{1p}$ and $\delta_{1k}$ with nearly twice as much of the $\delta_{1p}$ phase present. Also, 18% of this surface region is comprised of the two gamma phases, $\Gamma_1$ and $\Gamma_2$. The XMS spectrum confirms that only the two delta and two gamma phases are present throughout the entire coating. As expected, the percentage of each phase detected using the X-rays, is different due to the deeper penetration of this radiation. For the spectrum, the percentage of the $\delta_{1p}$ component detected decreases, whereas each of the other three components increases. This indicates that the $\delta_{1p}$ phase forms closer to the surface than the $\delta_{1k}$ phase as is expected from stoichiometry. XMS also samples more of the gamma phase which generally forms close to and at the steel interface. The fraction of each phase present indicates that $\Gamma_1$ is more plentiful. However, it is unclear whether the $\Gamma_1$ or $\Gamma_2$ phases are actually separated and if so, which is closer to the steel substrate.

Table 2
Summary of the relative area under the subspectra of each Zn-Fe phase in the three materials

<table>
<thead>
<tr>
<th>Zn-Fe Phase</th>
<th>A CEMS</th>
<th>A XMS</th>
<th>B CEMS</th>
<th>B XMS</th>
<th>C CEMS</th>
<th>C XMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi$</td>
<td>0.0</td>
<td>0.0</td>
<td>92.2</td>
<td>83.2</td>
<td>72.8</td>
<td>50.6</td>
</tr>
<tr>
<td>$\delta_{1p}$</td>
<td>52.3</td>
<td>48.1</td>
<td>0.0</td>
<td>0.0</td>
<td>15.7</td>
<td>36.4</td>
</tr>
<tr>
<td>$\delta_{1k}$</td>
<td>29.5</td>
<td>30.4</td>
<td>1.1</td>
<td>2.4</td>
<td>11.5</td>
<td>8.9</td>
</tr>
<tr>
<td>$\Gamma_1$</td>
<td>2.0</td>
<td>4.0</td>
<td>4.2</td>
<td>5.6</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>16.2</td>
<td>17.5</td>
<td>2.5</td>
<td>8.8</td>
<td>0.0</td>
<td>2.1</td>
</tr>
</tbody>
</table>
For material B, both the CEMS and XMS spectra indicate that the coating is predominantly the zeta phase, $\xi$-FeZn$_{13}$. This phase is generally found closest to the outer surface of zinc-iron coatings. The fits to the two spectra show that 92% of the near surface region is $\xi$-FeZn$_{13}$ while the XMS spectrum gives a total of 83% for the entire coating. About 14% of the two gamma phases are also detected by the X-rays which again indicate this formation is closer to the surface of the steel. A very small amount of the $\delta_{1k}$ phase is also possibly present. Previous papers, [3,4], have reported that the spectrum of $\xi$-FeZn$_{13}$ is a broadened single line. However, it is clear that in fact a small quadrupole interaction is present in this alloy.

For material C, the CEMS spectrum is similar to that of material B. However the broadening of the spectrum shows that some of the delta phase is present. The dominant phase present close to the surface of the coating is again the zeta phase which comprises about 73% of the material. Analysis also indicates that 27% of this surface region is made up of the two delta phases and possibly a small amount of the gamma phase, $\Gamma_1$. The XMS spectrum on the other hand is more complex. Each of the three main phases, comprising of five identifiable alloys, is present. Once again the zeta and delta phases are most abundant and only a small amount of the gamma phase is present.

4. Discussion

The results clearly identify the phases present within each coating. A comparison of the relative areas for each phase, shows that in general the zeta phase is closer to the surface of the coating than are the delta phases. From each material it is true that the gamma phases form closest to the steel surface. The two delta phases appear to be only slightly layered. This is not in general agreement with other metallographic results, [4], which indicate distinct layering of the two delta phases. Conclusions from the present studies are that although more of the $\delta_{1p}$ phase forms closer to the surface, distinct layering is not present. It is possible however that material preparation are important in controlling the fraction of each of the delta phases that form.

The detection of two subspectra for the gamma phase has lead to discussions, [3,4], as to whether or not the subspectra are due to two sites in the one phase or perhaps two distinct phases. It is concluded from the present results that, since the ratio of the areas of the $\Gamma_1$ to $\Gamma_2$ phases is not constant for the CEMS and XMS spectra, two distinct gamma phases must exist. It could also be suggested that, if the gamma phases form close to or at the steel substrate, the XMS method should detect significantly larger proportions of these phases than would CEMS. The areas given in table 2 do not indicate this to be true. The results would suggest a significant amount of mixing of the gamma phases with the delta and zeta phases throughout the entire thickness of the coating, with only a small
preference for the gamma phases to be more concentrated closer to the steel substrate. Recent metallographic analysis suggests that small voids in the coating may promote some amount of the gamma phase to the surface regions of the coating.

5. Conclusion

Mössbauer analysis of galvannealed materials is able to separately identifying the three main zinc-iron phases that form. Different amounts of each phase form depending on the preparation conditions of the coating. Mössbauer spectroscopy is also able to identify the presence of the subphases of the delta and gamma alloys. It can be concluded that the subphases of the delta and gamma alloys are mixed with a preference for the higher zinc subphase of each to form closer to the surface of the coating. There also appears to be a significant amount of mixing of at least the delta and gamma phases and probably zeta phase as well.

References