Original article

A novel iron enrichment isothermal kinetic model proposal for galvanneal coatings

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ABSTRACT

Galvanneal (GA) coatings are extensively used in the automotive industry in car bodies and for exposed parts to enhance corrosion protection. GA coatings are produced in Continuous Galvanizing Lines (CGL) by carrying out a heat treatment immediately after the Zn deposition in the liquid state, where the liquid is constitutionally solidified and transformed into Fe–Zn alloy (composed by its intermetallic compounds (IMCs)). IMCs nucleation and growth kinetics control allows one optimize the coating mechanical performance during steel drawing operations. This work proposes a new kinetic model to describe the GA coating Fe enrichment. Based on the hypothesis that each IMC will be nucleated, Fe enriched, saturated and consumed by an Fe richer IMC, the model was able to describe the Gleeble simulated isothermal Fe enrichment kinetics for unalloyed industrially produced interstitial free (IF) and dual-phase (DP) GA coating steels.

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1. Introduction

GA or Fe–Zn alloy coatings are widely used in the automotive industry in car bodies and for closure parts to offer corrosion protection [1,2]. This coating is composed of fragile Fe–Zn intermetallic compounds (IMCs), namely zeta-ζ (FeZn_{13}: 5.8–6.5 wt.% Fe), palisade delta-δp (FeZn_{10}: 7.0–8.3 wt.% Fe), compact delta-δc (FeZn_{7}: 10.3–11.7 wt.% Fe), gamma-1-Γ₁ (FeZn_{21}: 16.3–18.5 wt.% Fe) and gamma-Γ (FeZn_{10}: 22.2–28.2 wt.% Fe) [3]. IMCs volume fraction distribution defines the coating drawability [4] and its main failure mode is the powdering, where particles with a mean size smaller than the coating thickness are produced and powdered [5]. Powdering may be mitigated by controlling the Fe enrichment kinetics during the coating production [6–9].

For GA coatings exhibiting Fe content levels between 10 and 11 wt.% their microstructures are composed by Γ (∼15 vol. %) and δc (∼85 vol.%), assuring low powdering [10]. Hence, a direct correlation among annealing cycle, microstructure, coating mechanical behavior and powdering exists. Consequently, it is worth studying the IMCs nucleation and growth [11,12] and coating Fe enrichment [13–17] kinetics.

However, by performing an evaluation of the referred works one can see that they do not describe quantitatively the correlation between the IMCs kinetics and GA coating Fe enrichment. As a result, it is not possible to evaluate the effect of each IMC volume fraction and its Fe saturation level on the GA coating Fe content and powdering.

In the present study, a new kinetic model is proposed to describe the GA coating Fe content (W) as a function of the
IMCs Fe content ($W_i$). Hence, the coating Fe content can be defined as follows:

$$W = \sum_{i=n}^{\infty} W_i = W(i_0) + W(k_1) + W(t_1) + W(t)$$

(1)

Taking into account the IMCs volume fraction ($V_{v,i}$) and their Fe saturation content ($Fe_i$), their Fe contents ($W_i$) can be written:

$$W_i = V_{v,i}Fe_i$$

(2)

IMCs volume fraction ($V_{v,i}$) can be experimentally obtained by microstructural analysis (image analysis) or X-ray measurements. Differently, IMCs Fe saturation contents ($Fe_i$) are tricky to be assessed. Due to this fact, it is proposed that the Fe saturation content term could be described by the GA coating Fe content equation proposed by Rios [14]. Rios demonstrated that the rate of the increase in the coating Fe content ($dW/dt$) is proportional to the difference between a certain saturation Fe content ($W_i$) and the coating Fe content ($W$). Applying this equation to each IMC and carrying out proper variable adaptations required by the new approach, one can write:

$$\frac{dFe_i}{dt} = k_i(Fe_{s,i} - Fe_i)$$

(3)

where $k_i$ is a fitting parameter, $Fe_{s,i}$ is the IMC Fe saturated and $Fe_i$ is the IMC Fe saturation content. Eq. (3) can be integrated to each IMC when it nucleates in the time $t_n$. When $t_1 = t_n$, imply that $Fe_1 = Fe_{s,n}$. For longer times, on the other hand, when $t_1 > t_n$, $Fe_1 \to Fe_{s}$, $Fe_1 \to Fe_{s}$. In this case, one can consider $Fe_{s,n}$ and $Fe_{s,i}$ equal or close to the Fe contents found in the Fe–Zn binary phase diagram, respectively. Otherwise, when the GA coating Fe content and IMCs volume fraction are known, it is also possible to calculate $Fe_{s,n}$ and $Fe_{s,i}$ by a error minimization method. Eq. (3) becomes:

$$Fe_1 = Fe_{s,n} + (Fe_{s,i} - Fe_{s,n})(1 - \exp(-k_i(t_1 - t_n)))$$

(4)

Eq. (4) is only valid when $t_1 \geq t_n$, or the IMCs will enrich only after their nucleations. In this work, the IMCs volume fraction ($V_{v,n}$) and their Fe saturation contents ($Fe_{s,i}$) will be determined experimentally in order to assess the IMCs Fe saturation hypothesis.

### 2. Experimental procedure

The experimental procedure was performed in two steps, unalloyed GA coating samples industrial production (coils) and Gleeble galvannealing simulation. Two steel grades were used aiming the Fe enrichment study with quite distinctive chemistries by the need to assess all the hypothesis described for a fast (IF-Ti) and a slow (DP800) Fe enrichment kinetics [5]. Table 1 describes the chemistries to the above mentioned steel grades.

The steels were hot and cold rolled in a conventional six stand-hot strip and a four stand-cold rolling mill. The full hard coil thickness was 1.00 mm for the IF-Ti steel and 1.20 mm for the DP800 steel. Both steels were galvanized in a Continuous Galvanizing Line (CGL) with a special setup to solidify the deposited Zn coating quickly. The GA furnace was removed from the strip pass line (electromagnetic inductor) and the electrical resistance zone turned off. In addition, all the fans were adjusted at the maximum power to cool as fast as possible the steel sheet to avoid any Fe–Zn IMC nucleation. It is worth stating that the Zn bath Al content was kept at 0.13 wt.%. This Al level is well known as a standard for the GA coating production [5]. The remaining CGL process variables were not changed and all the important parameters are as follows: coating weight (IF-Ti: 70 g/m² and DP800: 80 g/m²), coating thickness (IF-Ti 5.00 μm and DP800 5.71 μm), Zn bath Fe content (0.031 wt.%) and bath temperature (460 °C).

Table 1 – IF-Ti and DP800 steel chemistries, wt.%.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ti</th>
<th>Cr</th>
<th>Mo</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF-Ti</td>
<td>0.0018</td>
<td>0.128</td>
<td>–</td>
<td>0.038</td>
<td>–</td>
<td>–</td>
<td>0.0013</td>
</tr>
<tr>
<td>DP800</td>
<td>0.1350</td>
<td>1.950</td>
<td>0.229</td>
<td>0.022</td>
<td>0.255</td>
<td>0.097</td>
<td>0.0034</td>
</tr>
</tbody>
</table>

Fig. 1 shows for both steels the coating microstructures obtained by the JEOL JSM 6360 15 kV Scanning Electron Microscope (SEM) equipped with the Noran System Six Energy Dispersive Spectrometry (EDS) detector. The specimens preparation involved mechanical sectioning, cold mounting, grounding (320, 800 and 1200 grit) and polishing (3–6 μm diamond). Afterwards, they were cleaned and etched in Nitral [2 mL nitric acid (HNO₃) and 98 mL ethyl alcohol (C₂H₅OH)] for the observation of the unalloyed industrially produced GA coatings.

Fig. 1 also shows that the deployed CGL configuration was able to retard the IMCs nucleation and growth and both transformed volume fractions were lower than 12 vol.%. The image analysis applied to calculate the IMCs volume fraction will be described thereafter. In order to confirm the low GA coating Fe enrichment (unalloyed condition), chemical analyses were performed with the aid of the Varian Spectra A 55B Atomic Absorption Spectrometer (AAS). The chemical analysis was repeated three times to each sample since the Fe content variability across the strip width and surface was minimal of 0.81–0.93 and 1.19–1.50 wt.% for IF-Ti and DP800 steel, respectively. These results show that the unalloyed industrially produced GA coatings were proper to be heat treated by Gleeble to simulate the Fe enrichment process. It is worth pointing out that to the best of authors’ knowledge the GA coating Fe enrichment procedure used in this work (unalloyed GA coating industrial production and Gleeble Fe enrichment) has not been reported.

#### 2.1. Offline isothermal Fe enrichment simulation

The isothermal annealing cycles were carried out using a Gleeble 3500 and the specimens size were set with dimensions...
of 125 mm × 50 mm × thickness. Three soaking temperatures were used according to the industrial practice: 450 °C, 500 °C and 550 °C and the soaking times were 3, 6, 9, 25, 50, 90 and 180 s.

Each annealing cycle was repeated two times due to the high thermal stability imposed by Gleeble, where Fe content variability for all samples remained lower than 2 wt.% (worst case). The heating rates were set for all annealing cycles equal to 50 °C/s for simulating the GA furnace inductor heating zone. The cooling rates were not lower than 6 °C/s.

2.2. GA coating characterization

2.2.1. SEM analysis

The metallic coatings were characterized by a SEM coupled with an EDS system as already mentioned. The metallographic characterization was carried out on the upper surface of the coil to eliminate any coating scratch effect. The cross-section secondary electron (SE) characterization was followed by the EDS analysis in the same region to determine the IMCs Fe saturation content. Each IMC was analyzed three times in different fields as schematically shown in Fig. 3a. The electron-beam spot size was not higher than 1.0 μm.

2.2.2. Image analysis procedure – IMCs volume fraction calculation

GA coatings have a microstructure that does not allow a direct phase quantification by the image analyzer since it is not able to detect automatically the Fe–Zn IMCs color threshold even when special etching techniques are applied (such as color etching). Therefore, a semiautomatic image analysis procedure was developed and applied in this work to allow the IMCs volume fraction calculation.

According to the developed procedure, the SEM microstructure is subjected to an image filter to enhance its contrast. In this step, the software Image J 1.45 was used along with the additive CLAHE (Contrast Limited Adaptive Histogram Equalization) which has three parameters: block size, histogram bins and maximum slope. All the images were treated with the same parameter values of 49, 499 and 2.50, respectively. Next, a contour tracing process to identify all IMCs boundaries is needed. This treatment was carried out semi-automatically by using the Corel Draw X5 (trace tool). Finally, the mapped microstructure could be analyzed by the Image J and the area fraction to each IMC calculated accurately. All the steps of this procedure were repeated three times to each sample in different fields. Fig. 2 shows the procedure steps.

Fig. 2 – Main steps of the developed procedure to quantify the IMCs volume fraction: (a) SEM microstructure after CLAHE, (b) traced microstructure, (c) mapped microstructure and (d) treated microstructure for image analysis.
3. Results and discussion

Fig. 3 shows the microstructures of the GA coatings obtained at 450 °C, 500 °C and 550 °C soaking temperatures for the IF-Ti steel. The microstructural changes after coating solidification at all temperatures are characterized by phase growth or shrink where the IMCs Fe richer will consume the poorer ones. The microstructure of the GA coating at 450 °C is composed by $\delta_{P}$, $\delta_{C}$ and $\Gamma$ after its solidification ($t = 3$ s). It is worthy stating that $\delta$ phase may exhibit two dissimilar morphologies as a function of the Fe content, namely palisade $\delta_{P}$ (7.0–8.3 wt.% Fe) and compact $\delta_{C}$ (10.3–11.7 wt.% Fe) [18–20]. When this microstructure is further Fe enriched $\delta_{C}$ phase consumes $\delta_{P}$ progressively. This remark indicates that the Fe enrichment process is taking place by IMC change and not only by IMC Fe saturation. At the time when $\delta_{P}$ volume fraction is zero, $\delta_{C}$ starts its Fe saturation. This cooperative kinetics was only noticed owing to the individual IMC Fe saturation study. For those samples galvannealed at 500 °C and 550 °C the IMCs evolution during the GA coating Fe enrichment was quite similar. Since $\delta_{P}$ was not found, the Fe enrichment took place by $\delta_{C}$ phase saturation up to a certain saturated level. Based on EDS Fe contents, $\Gamma$ phase grows and consumes a saturated $\delta_{C}$ while it remains Fe-poor (~22.2 wt.% Fe). At all temperatures $\Gamma_1$ phase exhibited the same behavior and remained over $\Gamma$ phase with a constant volume fraction. It was also noticed that $\Gamma_1$ phase may act as substrate to the nucleation and growth of $\Gamma$ phase, as reported by Lin et al. [12].

Fig. 4 shows the microstructures of the GA coatings for the DP800 steel. DP800 GA coating Fe enrichment kinetics is slower than that of IF-Ti steel. This fact is attributed to the solute segregation on the steel grain boundaries that minimizes the diffusivity of these regions [21]. As described by Lin [22], the selective oxidation phenomenon that takes place during the DP800 annealing under a $H_2/N_2$ atmosphere is also able to impair the Fe enrichment due to the formation of a physical oxide barrier between coating and steel. More details about this phenomenon may be found in the work of Mataigne [23], Suzuki [24] or Liu [25].

The constitutional solidification phenomenon was possible to be assessed at 450 °C soaking temperature due to the slow kinetics exhibited by the DP800 steel. In this temperature eta phase ($\eta$) becomes Fe supersaturated ($\eta_{es}$ examples are shown in Figs. 1 and 4a) and regular $\zeta$ crystals are nucleated. $\delta_{C}$ phase
can also be noticed adjacent to the steel substrate (identified by its equiaxed morphology and Fe content) but is quickly consumed, probably by the peritectic reaction $\text{Zn}_{\text{liq}} + \delta_c \rightarrow \zeta$. For longer times, one could expect that the $\zeta$ phase would consume all liquid Zn. However, $\delta_p$ nucleates and not only consumes the remained liquid Zn but also $\zeta$. The $\delta_p$ growth was followed by the formation of a $\delta_c$ continuous layer over the substrate. The microstructural evolution at 500 °C and 550 °C soaking temperatures are once again similar. For these temperatures it can be noticed that $\delta_c$ is nucleated as a result of the constitutional solidification. For longer times the Fe enrichment process will take place by the $\delta_c$ Fe saturation. Moreover, it is confirmed that the $\Gamma$ will consume $\delta_c$ only after its Fe saturation. Fig. 5 shows the EDS results that confirm that each IMC in the coating will be enriched up to a certain Fe saturation content.

The IF-Ti steel GA coating IMCs have also exhibited individual Fe enrichment. However, their Fe saturation curves were less evident due to the faster kinetics to reach the saturated state and they have been omitted. The $\Gamma$ Fe saturation was not noticed for all samples and this fact can be explained by the presence of the saturated $\delta_c$. Each and every IMC Fe saturation can be calculated by Eq. (4) once demonstrated that they are nucleated and subsequently enriched.

Fig. 6 shows the GA coating Fe content ($W$) curves (solid lines) calculated as a function of the IMCs Fe saturation content ($Fe_i$) and volume fraction ($V_{\delta,\Gamma}$). In addition, it is also plotted the GA coating Fe content obtained by AAS for the IF-Ti steel in order to allow a direct comparison.

The GA coating Fe enrichment kinetics was well described by the proposed model. The Fe enrichment rate is high and related to the constitutional solidification ($t < 3 s$) for both temperatures at the beginning of the process. A phase stabilization process will occur for annealing times ranging from 8 up to 25 s, where $\Gamma$ and $\Gamma_1$ volume fractions will be constant. This behavior was also reported by Jordan et al. [26] and the GA coating Fe enrichment rate becomes slower. Subsequently, $\delta_c$ is Fe saturated under microstructural stability. Finally, a Fe-poor $\Gamma$ consumes the rich or saturated $\delta_c$.

According to these remarks one can say that the microstructural changes will define the GA coating Fe enrichment since its constitutional solidification until the $\Gamma$.
thickening. Furthermore, whenever the IMCs Fe saturation content state is given it will be possible to foresee their growth or shrink. In this study it is possible to establish that an Fe-poor IMC will be phase transformed into a richer one only after its own saturation. On the other hand, an Fe-rich IMC will not be Fe saturated until the immediate Fe-poor one has been entirely consumed. This phase transformation that occurs during the GA coating Fe enrichment is called Fe–Zn IMCs cooperative growth.

Fig. 7 shows the obtained results for the DP800 steel and the same remarks made for the IF-Ti steel can be applied. However, one must be aware of the scattered results at 550 °C soaking temperature, probably due to a deleterious effect caused by the selective oxidation phenomenon.
4. Conclusion

This work confirmed the possibility to model the GA coating Fe enrichment kinetics by a novel approach that takes into account the IMCs Fe saturation and its volume fraction during the galvannealing. In addition, it was also demonstrated that each IMC that composes the coating will be Fe enriched up to a certain saturation level. Finally, it was possible to establish that the IMCs growth or shrink is related to their respective Fe saturation level. This assumption is the framework for the introduction of the GA coating Zn–Fe IMCs cooperative growth.

Conflict of interest

The authors declare no conflict of interest.

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