Intermetallics formation during hot dip galvanizing of high carbon steel

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Abstract. From the moment of immersion, the reaction between molten zinc and solid steel starts forming intermetallic phases. This diffusion-controlled process is largely responsible for the final phase composition of zinc coatings. Several literature sources describe this phenomenon for interstitial free steels, but high-carbon steels are rarely being used as substrates. Therefore, in this work high-carbon steel substrates were used. Multiple samples were created by hot-dipping at various immersion temperatures ranging from 450 to 490 °C and times from 24 to 60 s to investigate mainly the morphology of the obtained intermetallic phase layers. Investigation was carried out mainly by SEM on 20 condition, where several hundred sites were investigated in total to achieve statistically relevant information. It was found that while increasing the immersion time influences mainly the thickness of individual intermetallic phase layers, the temperature influenced mainly their morphology. It was also observed that these results are significantly different compared to ones found in literature for interstitial free steels.

Keywords: zinc, iron, intermetallic phases, high-carbon steel

1. Introduction
For specific applications high-carbon / high-strength steels are required [1, 2]. Hot-dip Zn coatings are applied for sufficient corrosion protection [3, 4]. Pure Zn is used to enable the formation of intermetallic layers as these are also adding to the corrosion protection and mechanical properties of the coating [3-6]. Many applications of hot-dip Zn coatings utilize alloying with Al. However, Zn coatings with as low as 0.2 wt.% Al are not forming a Fe-Zn based, but rather a very thin Fe-Al based intermetallic layer [3, 7].

Various hot-dip coating procedures may require different coating temperatures. These may be caused for example by heat capacity requirements on the hot-dip bath, or time constrains given by the production planning. This may cause that for various cases, the hot-dip temperature can vary between 450 up to 490 °C.

Due to these considerations it was decided to observe the formation of intermetallic layers at different hot-dip temperatures.

Similar research considering different temperatures and dipping times are usually found in the literature. However, these are mainly focused on low-carbon steels and give only a limited insight into the problematic of high carbon steels [3, 4, 8-11].
Based on the results summarized by Smirnov [3], both Si and C present in the steel substrate have the tendency to change both thickness and morphology of the Fe-Zn intermetallic layers.

2. Experimental procedure

A small hot-dip bath with about 5 kg of pure Zn melt was prepared in a vertical muffle furnace. In total 20 conditions were planned and executed. Hot-dipping was performed at various immersion temperatures ranging from 450 to 490 °C and immersion times were ranging from 24 to 60 s. Temperature of the melt was constantly monitored by a K-type thermocouple inserted directly into the melt.

Substrates of high-carbon steel (main alloying elements in wt.%; 0.92 C + 0.21 Si + 0.3 Mn + 0.2 Cr) with a thickness of 4 mm were cleaned by pickling in 20 vol.% aqueous solution of HCl acid for one minute followed by mechanical wiping and dipping in an aqueous solution of 150 g “double-salt” flux (ZnCl₂·2NH₄Cl) in 1000 ml of demineralized water for about 30 s. Samples were removed from the flux bath and left to dry on air.

As soon as the substrate was dry, it was dipped into the Zn melt. The sample was held in the Zn bath for the required amount of time while it was agitated to allow constantly fresh Zn melt to be in contact with its surface.

Samples were cooled in water immediately after withdrawal from the Zn-bath.

The procedure was repeated until two individual samples for each of the twenty conditions were available.

Microstructural analysis was performed by scanning electron microscopy (SEM) on cross sections of hot-dip samples. Samples were prepared using standard metallographic techniques including grinding on SiC papers, polishing on diamond paste and etching in a reagent of 0.5 vol.% Nital. Final grinding steps and complete polishing procedure had to be done using alcohol-based coolants and diamond pastes. Quantitative metallographic analysis including thickness measurements and determining the volume fraction of coexisting phases was performed by computerised image analysis using ImageJ 1.52 [12] and Gimp 2.10 software.

Only the total thickness of the intermetallic layers was measured. Thickness of the η layer was not investigated. Thickness of this layer is not controlled by diffusion (as in case of Γ, δ and ζ phases), but rather by dynamic forces acting on the coated steel substrate during raising from the Zn bath. This was out of scope for the current research.

Due to the rather uneven nature of the individual intermetallic layers observed, it was decided to follow up their area fraction instead of thickness. Three main microstructure features were distinguished as shown in figure 1.

Grains and areas correlated to individual phases or their morphological variations were manually traced out and filled in with corresponding colours as seen in figure 1. This enabled to calculate their corresponding area fraction and hence volume fraction. Such measurements were carried out on approx. 600 images in total as several sites were investigated on each sample.
Figure 1. Example of an image processed for area measurement; gray: $\eta$ – $\eta$ phase layer, blue: $\zeta$ – particles and areas formed by $\zeta$ phase, green: $\delta_{\text{mix}}$ – areas formed by $\delta$ phase, but with a significantly different morphology, red: $\delta$ – compact $\delta$ layer.

Corelating these data with the overall intermetallic layer thickness enabled to calculate a geometrically idealized thickness for the individual microstructure features neglecting their uneven nature. These values were calculated simply by dividing the total thickness of the intermetallic layers into sections corresponding to the volume fraction of each microstructure feature. This way it was possible to visualise the influence of both immersion time and temperature much more clearly (as will be shown later in figure 8 and figure 10).

3. Results
A typical microstructure observed during our experiments is shown in figure 2. Main point of interest for this article was to observe the construction of the Fe-Zn intermetallic layers formed on a high-carbon steel substrate during the hot-dip process. EDX measurements were performed to confirm the composition of the individual phases observed (figure 2, table 1). Following phases were distinguished based on inputs from literature: $\eta$ (0.03 wt.% Fe), $\zeta$ (5.7-6.3 wt.% Fe) and $\delta$ (7.0-11.0 wt.% Fe) while the $\Gamma$ phase (20.0-27.0 wt.% Fe) was not identified during our measurements. Basic properties of the investigated phases are listed in table 2 [6]. Based on this information, increasing the $\delta$ phase content should be preferred from a mechanical point of view.

Figure 2. SEM image from the sample produced at 470 °C and 60 s; including EDX measurement points marked in the image.
Table 1. Chemical composition of the individual layers as measured by SEM/EDX.

| Spectrum | Fe [wt.%] | Zn [wt.%] | Identified phase |
|----------|-----------|-----------|-----------------|
| 1        | 0.42      | 99.58     | η               |
| 2        | 6.92      | 93.08     | ζ               |
| 3        | 6.65      | 93.35     | ζ               |
| 4        | 6.17      | 93.83     | ζ               |
| 5        | 6.55      | 93.45     | ζ               |
| 6        | 7.93      | 92.07     | δ               |
| 7        | 8.35      | 91.65     | δ               |
| 8        | 10.59     | 89.41     | δ               |
| 9        | 11.39     | 88.61     | δ               |

Table 2. Basic properties of phases observed

| Phase | Fe content [wt.%] | Melting point [°C] | Crystal Structure | micro HV | Characteristic mechanical property |
|-------|-------------------|--------------------|------------------|----------|-----------------------------------|
| η     | Zinc <0.03        | 419                | hexagonal        | 70-72    | soft, ductile                     |
| ζ     | FeZn₁₃            | 5.7-6.3            | 530              | 175-185  | hard, brittle                     |
| δ     | FeZn₇             | 7.0-11.0           | 530              | 240-300  | ductile                          |
| Γ     | Fe₅Zn₁₀           | 20.0-27.0          | 670-780          | ---      | hard, brittle                     |

3.1. Hot-dip galvanizing at 450°C
For all conditions prepared at 450 °C (figure 3) the compact δ layer and a rather constant ζ layer is visible. The δ layer is only locally interrupted as seen in figure 3b and d. ζ layer seems to have particles “floating” into the η layer (molten Zn during the experiment) as seen in figure 3b - d. Areas labelled δ_{mix} are only rarely observed. About 3 vol.% were measured at 60 s (figure 3d).
3.2. Hot-dip galvanizing at 460°C
The conditions prepared at 460 °C (figure 4) are very similar to the ones prepared at 450 °C (figure 3). There was a slight increase in the volume fraction of δ\text{mix} areas (as shown later in figure 9). Also, the ζ layer seems to be less compact. More individual particles are observed “floating” in the area of η phase (figure 4).
3.3. **Hot-dip galvanizing at 470°C**

At 470 °C (figure 5) the fraction of $\delta_{\text{mix}}$ grew significantly. It is now clearly growing in between individual particles of $\zeta$. On the other hand, no more “floating” $\zeta$ particles are observed compared to lower temperatures. The compact $\delta$ layer seems to be unchanged compared to previous conditions.

![Cross section of samples produced at 470 °C: a) 24 s; b) 30 s; c) 40 s; d) 60 s.](image)

**Figure 5.** Cross section of samples produced at 470 °C: a) 24 s; b) 30 s; c) 40 s; d) 60 s.

3.4. **Hot-dip galvanizing at 480°C**

Conditions prepared at 480 °C (figure 6) are very similar to the ones prepared at 470 °C (figure 5). Volume fraction of $\delta_{\text{mix}}$ grew again mainly at the expense of $\zeta$ particles. Volume fraction of $\zeta$ particles in now only less than 30 % for the conditions prepared at 24, 30 and 40 s (figure 6a - c).
Figure 6. Cross section of samples produced at 480 °C: a) 24 s; b) 30 s; c) 40 s; d) 60 s.

3.5. Hot-dip galvanizing at 490°C

At 490 °C (figure 7) ζ particles were not observed at all for immersion times from 24 to 40 s (figure 7a - c). Most probably due to this fact also areas of δ mix could not be distinguished. Only the compact δ layer was observed. At 60 s (figure 7d) all previously identified microstructure features were observed again.
Figure 7. Cross section of samples produced at 490 °C: a) 24 s; b) 30 s; c) 40 s; d) 60 s.

3.6. Summary of measured data

Measured data can be summarized rather clearly as shown below in figure 8 and figure 9. In figure 8 it can be observed that for each temperature, geometrically idealized thickness of both δ and ζ phases is increasing with increasing immersion time. While as mentioned earlier, all areas formed by the δ phase were divided into areas of δ and δmix (for example figure 7d).
Figure 8. Geometrically idealized thickness calculated based on volume fraction at different temperatures: a) 450 °C; b) 460 °C; c) 470 °C; d) 480 °C; e) 490 °C.

The immersion time has a very significant influence on the overall intermetallic layer thickness. Therefore, only volume fraction of the individual microstructure features was used to assess the influence of temperature (figure 9). For the immersion times of 24, 30 and 40 s (figure 9a - c), increasing temperature promoted mainly an increase in the volume fraction of $\delta$ and $\delta_{\text{mix}}$ areas. Both increased their volume fraction at the expense of $\zeta$ phase areas. For all these conditions (figure 9a - c) the complete disappearance of $\zeta$ phase areas was observed at 490 °C. On the contrary, at the immersion time of 60 s (figure 9d) volume fraction of the compact $\delta$ layer is slightly decreasing with the increasing immersion temperature. Also, the volume fraction of $\zeta$ phase is decreasing significantly less. Even at 490 °C, over 40 vol.% of the microstructure is still formed by the $\zeta$ phase.
Figure 9. Volume fraction of individual microstructure features: a) 24 s; b) 30 s; c) 40 s; d) 60 s.

4. Discussion

Based on SEM / EDX measurements, it was found that the individual phases can be determined most reliably using BSE images. Their morphologies are clearly recognizable.

There is still lack of information about intermetallic layer’s formation on hot-dip galvanised high-carbon steels. Literature sources deal mostly with low-carbon, or interstitial free steels as substrate [8, 9, 13-15]. Both thickness measurements and microstructures are different compared to our findings. Bakhtiari et.al. [9] identified maximum intermetallic layer thickness to be approx. 37 µm at 480 °C and 60 s immersion. These results were very similar to our measurements at approx. 36 µm, but ours was found already at 460 °C and 60 s. On the other hand, Bicao et.al. [8] found a significantly higher maximum thickness of approx. 60 µm, but again at 480 °C and 60 s similar to Bakhtiari [9].

We suspect, that our findings are influenced by higher Si (0.21 wt.%) as well as increased C (0.92 wt.%) content in our substrate material. Both of these elements are reported to influence the morphology as well as overall thickness of the alloy layer [3, 4].

Results of Kuklik [4] suggest that for interstitial free steels the maximum intermetallic layer thickness should be achieved between 480 to 490 °C. For a steel with over 0.12 wt. % Si this should be observed at 440 °C. These findings would correlate with the differences between our research and the results of both Bicao and Bakhtiari [8, 9].

Our overall morphology of the intermetallic layers was also different compared to those observed on low-carbon steel, or pure iron [4, 9, 8, 13]. Main difference was observed in the presence of the δ_mix areas. Similar microstructures were only observed in the work of Smirnov [3]. Also, rather good overlap was observed with the images taken by Kopyciński et.al. [10, 11] on hot-dip coated cast iron parts. Morphology of the intermetallic phases is comparable to our findings observed at 450 °C. However, overall intermetallic layer thickness is reported to be 42% lower on average. This is most probably caused by the rather different shape of their samples. Even the increased reactivity of their cast iron substrate (over 3 wt.% of C and over 2 wt.% of Si) could not counteract the need to heat the larger bulk.

In the work of Bakhtiari et. al. [9] also significant portion of Γ layer was identified. Thickness of this layer was ranging from 2 to 10 µm at 450 to 480 °C respectively. Similar results were reported by Šumec et. al. [13] with approx. 1.2 µm of Γ layer measured at 450 °C and 60 s. It was not possible to identify any Γ layer in our samples. This was probably caused by the increased carbon content of our steel. As reported by Smirnov [3], carbon can delay the formation of the Γ layer up...
to 7 min at 450 °C in high-carbon steels with 0.9 wt.% of C. As our immersion time was maximum 60 s, Π layer probably did not form yet. In samples prepared at 450 and 460 °C particles of the ζ layer seem to be “floating” away into the melt, hence the overall thickness is hard to measure. This also shows that the overall thickness of the intermetallic layer might be even more, but some parts of the ζ layer got detached and were washed away by the molten Zn. The same phenomena was observed also by other authors [4, 10, 11, 14]. These “floating” particles are not visible for temperatures above 460°C. It can be observed that for each temperature, overall intermetallic layer thickness is increasing with increasing immersion time. On the contrary, overall intermetallic layer thickness is decreasing with increasing temperature as seen in figure 10.

Figure 10. Geometrically idealized, total intermetallic layer thickness for all conditions investigated.

5. Conclusions

- Increasing dipping time from 24 to 60 s increases the intermetallic layer thickness, while raising the Zn-bath temperature from 450 up to 490 °C decreases the volume fraction of ζ phase, while volume fraction of δ phase is increasing.
- The δ phase is reported to be more ductile [3, 6], hence higher volume fraction of δ phase should be beneficiary for overall coating quality. Therefore, hot-dip galvanising at 480 – 490 °C for 24 – 40 s seem to be optimal parameters for industrial use.

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