

Proceedings of the Estonian Academy of Sciences, 2016, **65**, 2, 159–165 doi: 10.3176/proc.2016.2.11 Available online at www.eap.ee/proceedings

MATERIALS ENGINEERING

# The role of silicon in the hot dip galvanizing process

Sirli Sepper<sup>\*</sup>, Priidu Peetsalu, Priit Kulu, Mart Saarna, and Valdek Mikli

Department of Materials Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

Received 19 October 2015, revised 12 January 2016, accepted 14 January 2016, available online 14 March 2016

**Abstract.** The study focuses on the role of silicon in the hot dip galvanizing process. Coating formation and growth were analysed. Centrifugal casting was used to prepare steel substrates with different silicon concentrations (<0.01%, 0.06%, 0.11%, 0.17%, and 0.30%). Hot dip galvanizing was performed at 450 °C in the industrial galvanizing plant Zincpot (Estonia). The galvanizing time for coating formation was 4–25 s and for coating growth 195 and 1200 s after a longer incubation time. The thickness of the coating was measured and the microstructure of the Zn–Fe coating was examined. Even a very short time contact (4 s) between steel and zinc led to the formation of Fe–Zn intermetallics. The first phase was the  $\zeta$  phase, immediately followed by the  $\delta$  and then, after incubation the  $\Gamma$  phase. The reactions that took place in the galvanizing process during the shorter dipping times (<25 s) were not influenced by silicon concentrations, but the influence of silicon was remarkable after longer dipping times (>25 s). A schematic model of zinc coating formation is presented. Silicon affects hot dip galvanizing reactions by influencing Zn diffusion into the coating.

Key words: hot dip galvanizing, Sandelin effect, role of silicon, coating microstructure, iron-zinc phases.

#### **1. INTRODUCTION**

Structural steels contain a small amount of silicon because it is used as a de-oxidant in the steel making process. Silicon is also a low-cost and very effective strengthening alloying element for steels [1]. Silicon concentration in steel plays a major role in the hot dip galvanizing process. It influences the growth and microstructure of coatings. Steels containing small amounts of silicon (<0.03%) have a compact and continuous zinc coating (galvanizing temperature 450°C), which is composed of  $\Gamma$ ,  $\delta$ ,  $\zeta$ , and  $\eta$  layers. The presence of Si at certain levels, i.e. 0.03–0.14% (Sandelin area) and above 0.3%, produces a coating with excessive thickness, grey appearance, and poor adherence. Steels containing 0.15–0.25% Si also produce a compact and coherent coating (Sebisty effect) [2,3].

The growth of the alloy layer may be controlled by both the chemical composition of the molten zinc and the physical operating parameters: immersion time and the speed of withdrawal. The addition of small amounts of certain elements, such as Al, Pb, Ge, Ti, Bi, Cu, Cd, or Sn, can contribute to the problem resolution by inhibiting the zinc–steel reactivity and/or increasing the bath fluidity [4]. Nickel addition is also considered favourable, because it changes the kinetics, morphology, and thermodynamic equilibrium between the Fe–Zn phases. As a result, Ni at a low concentration (0.06%) inhibits the Sandelin effect [5,6]. However, at a high silicon concentration, the layer thickness might increase if Ni was present in the zinc bath [6].

Most of the studies that describe the effect of silicon during galvanizing use samples that contain many elements. So silicon is not the only variable in their experiments. For example, Kopyciński [7] studied four different steel grades (Si > 0.20%) and two ductile irons. Galvanizing was performed in a Zn–Ni bath at 450°C at the dipping time up to 10 min. The growth rates for the  $\delta$  and  $\zeta$  phases indicated a leading role of the  $\zeta$  phase and a slow growth rate of the  $\delta$  phase [7].

<sup>\*</sup> Corresponding author, sirli.sepper@ttu.ee

Mandal et al. [8] investigated interstitial free steel behaviour, morphology, and the kinetics of the growth of the coatings during galvanizing in pure as well as commercial grade zinc baths at 470 °C. They found no delay in the formation of the  $\zeta$  or  $\delta$  phases in the studied zinc baths [8].

Uchiyama et al. [9] melted electrolytic iron and a given amount of silicon to analyse silicon reactivity in galvanizing. Galvanizing was performed in the temperature range from 440 °C to 600 °C for 600 s in a pure zinc bath. They presented an existence area map of different coating layers depending on the silicon concentration and the immersion temperature [9].

This paper describes the coating formation with different substrate silicon concentrations at 450 °C, which is the common galvanizing temperature. The aim of the study is to describe the role of Si in coating formation and to deploy the know-how to industry.

## 2. MATERIALS AND METHODS

To investigate how silicon affects the reaction between steel and liquid zinc, centrifugal casting was used to prepare specimens with different silicon concentrations. Steel powder (ATOMET 1001) and a calculated amount of Fe–Si powder (Si 46.10%) were melted in a vacuum induction furnace and cast into a copper mould.

The diameter of the cast samples was 35 mm at the thickness of 3 mm. The chemical composition of each specimen was measured using Spectrolab M. The results are presented in Table 1. Sample 1 in Table 1 is steel powder ATOMET 1001 without Fe–Si powder addition. The specimens were annealed at 730 °C for one hour and then air cooled. The oxidation layer was removed by mechanical grinding (80 grit). A small hole was drilled near the edge of each sample to help hang the specimens during the galvanizing process.

A batch-type hot dip galvanizing process was used. The zinc bath temperature was 450 °C. Galvanizing was performed in the industrial galvanizing plant AS Paldiski Tsingipada (Zincpot). According to common practice of the hot dip galvanizing process, which includes degreasing, pickling in HCl, rinsing, and fluxing, the samples were subjected to pre-treatment. The zinc bath consisted of 99.3% Zn, 0.055% Ni, and Al, Bi, Fe, and Sn in balance. The dipping times in the liquid zinc were from 4 s up to 1200 s.

Table 1. Chemical composition of the specimens, %

Sample	С	Si	Mn	Р	Fe
1	< 0.01	< 0.01	0.04	0.005	99.72
2	< 0.01	0.06	0.04	0.007	99.66
3	< 0.01	0.11	0.05	0.006	99.60
4	< 0.01	0.17	0.05	0.006	99.54
5	< 0.01	0.30	0.05	0.007	99.40



Fig. 1. Temperature change inside the specimens.

After galvanizing, the specimens were quenched in water to prevent further diffusion reaction during air cooling. For the examination of the microstructure, hot dip galvanized specimens were cross-sectioned, hot mounted, ground, and polished. A nital etchant was used to reveal the microstructures of the specimens and observations were made with optical microscope Zeiss Axiovert 25 and scanning electron microscopy EVO MA-15 (Carl Zeiss).

To study temperature changes in the wall of a specimen during dipping in the molten zinc, a Vernier Software thermocouple was used. Figure 1 shows the heating curve of the specimens during dipping in the molten zinc at 450 °C. It took approximately 20 s to establish the melting temperature of zinc (419.5 °C) with the investigated specimens.

#### **3. RESULTS AND DISCUSSION**

#### 3.1. Coating growth with dipping time up to 25 s

Dipping time (4, 7, 12, 25 s) was short in the investigation of coating formation on top of the substrates shown in Table 1. After dipping cold steel into the zinc bath, zinc will freeze in the contact surface of steel. Even a very short time contact between steel and zinc leads to the formation of Fe–Zn intermetallics, which are in solid state. After 4 s of dipping in the molten zinc, a thin layer of intermetallic phases ( $\zeta$  and  $\delta$ ) was observed with all tested silicon concentrations (Si <0.01%, 0.06%, 0.11%, 0.17%, 0.30%). Poor adhesion between the steel and the coating could be observed at a dipping time of 4 s.

After galvanizing for 4 s, the microstructure and thickness of the Zn–Fe layer were similar regardless of the content of silicon in the substrate. This is also confirmed by experiments reported in [10]. Figure 2 presents the microstructure of the zinc coating (Si 0.30%) after a dipping time of 4 s. First, the  $\zeta$  phase occurred, which was immediately followed by the  $\delta$  and then, after incubation, by the  $\Gamma$  phase. The same test results were reported by Mandal et al. at the galvanizing temperature of 470 °C [8]. It is frequently admitted that the first intermetallic compound that appears during hot dip galvanizing is the  $\zeta$  phase nucleates first, followed by the



**Fig. 2.** Microstructure of the zinc coating after the dipping time 4 s (Si 0.30%).

 $\delta$  and  $\zeta$  phases in a Zn–Ni bath at 450 °C [7]. It is difficult to evaluate the  $\Gamma$  phase because of its small thickness.

Furthermore, with a dipping time of 4 s, a thick  $\eta$  layer was present in the coating (ca 800 µm). It is hypothesized that as the specimen's inside temperature after the galvanizing time of 4 s is low (less than 300 °C, Fig. 1) and probably the temperature in the contact surface of steel and zinc is below the melting temperature of zinc, the nucleation of intermetallic phases takes place in solid state and therefore a thick  $\eta$  layer is present in the coating with the dipping time of 4 s. However, other authors [10,12] claim that nucleation of the phases takes place in the solid–liquid border. Therefore, further research is needed to understand if zinc is completely melted in the contact surface of the specimen when nucleation of the phases takes place.

With an increase in the dipping time, the thickness of the Fe-Zn intermetallic phase increased. Until 25 s, only minor differences occurred in the thicknesses of the intermetallic coating and in the microstructure of specimens with different silicon contents, although a small Sandelin curve appeared with the dipping time of 25 s (Fig. 3). The thickness of the  $\eta$  phase was not taken into consideration because the  $\eta$  phase appeared when a specimen was pulled out from the zinc pot and at the beginning of the reaction the zinc was in solid state. The reactions that took place in the galvanizing process during the dipping time of <25 s were not influenced by silicon concentrations. This is also confirmed by other authors [10,12,13]. The reason might lie in the substrate steel temperature, which in this experiment was below the melting temperature of zinc until 20 s (Fig. 1).

During the first 25 s, the total thickness of the coating was related to the  $\zeta$  phase and the  $\delta$  phase was very narrow. Figure 4 shows the difference in the microstructure and the  $\zeta$  phase thickness at silicon content <0.01% and 0.06%. During the first 25 s, the  $\zeta$  phase



**Fig. 3.** Sum of the thicknesses of the  $\delta$  and  $\zeta$  layers at different dipping times.



**Fig. 4.** Microstructure of the zinc coating after the dipping time of 25 s.

dominated in the coating while the  $\delta$  phase was growing very slowly. The influence of silicon was remarkable after longer dipping times (>25 s).

# 3.2. Coating growth with dipping times 195 and 1200 s

The dipping time of 195 s was chosen because it is the common galvanizing time. In addition, 1200 s was used to investigate the coating growth at a longer incubation time.

Coating growth with the dipping times 195 and 1200 s was strongly influenced by the silicon content of the steel (Fig. 5). The Sandelin curve at about Si content of 0.08-0.15% reflects the thickness of the coating.

Each phase layer has its own growth kinetics, which depends on the silicon content and the dipping time. On the sample with silicon content <0.01%, a compact and continuous zinc coating is visible with the  $\Gamma$ ,  $\delta$ ,  $\zeta$ , and  $\eta$  layers (Fig. 6a). There was a large difference in the



Fig. 5. Coating thicknesses at different substrate silicon contents. Dipping time 195 and 1200 s.







(c)



microstructure of the zinc coating and the thickness of the  $\delta$  layer between the dipping times of 195 and 1200 s (Table 2). After 195 s, the growth of the  $\zeta$  phase was impeded while the growth of the  $\delta$  phase dominated. The  $\delta$  layer of the coating with an immersing time of 1200 s has a greater thickness than the  $\zeta$  layer. The silicon content in the Sandelin range (Si 0.06% and 0.11%) resulted in a thick coating at the dipping times of 195 and 1200 s (Figs 6b and 6c). The coating consists of a thin  $\delta$  layer and a thick  $\zeta$  layer (Table 2).

The substrate with the silicon content of 0.17% (Sebisty range) has larger  $\zeta$  grain size than the low silicon steel (Si <0.01%). The growth in the  $\delta$  layer is





Fig. 6. Microstructure of the zinc coating after different dipping times (195 and 1200 s): (a) Si <0.01%, (b) Si 0.06%, (c) Si 0.11%, (d) Si 0.17%, (e) Si 0.30%.

Si content,	195 s		1200 s				
%	Thickness of layers, µm						
	δ	ζ	δ	ζ			
< 0.01	3	20	44	40			
0.06	3	143	33	168			
0.11	3	151	1	849			
0.17	10	83	26	192			
0.30	30	58	41	467*			

**Table 2.** Thicknesses of the  $\delta$  and  $\zeta$  layers with dipping times 195 s and 1200 s

\* Contains also a  $\delta + \zeta$  mixture phase.

visible at a longer dipping time, but the  $\zeta$  layer still dominates in the coating thickness (Fig. 6d, Table 2).

The coating of the sample with the silicon content of 0.30% is characterized by a thin  $\delta$  layer and a thick  $\delta + \zeta$  layer with a floating  $\zeta$  (Fig. 6e, Table 2).

#### 3.3. Stages of zinc coating formation

When the substrate steel is immersed in a liquid zinc bath, a number of reactions occur depending upon the bath composition, bath temperature, and the impurities of the steel. According to the Fe–Zn phase diagram (Fig. 7), during hot dip galvanizing at 450 °C, an intermetallic layer is formed. It is composed of  $\Gamma$ –Fe<sub>5</sub>Zn<sub>21</sub>,  $\delta$ –FeZn<sub>10</sub>,  $\zeta$ –FeZn<sub>13</sub>, and  $\eta$ –layers. The enthalpies of the formation of all intermetallic compounds are very close to one another and this is why an unstable behaviour of the system might occur with small additions in steel [14].

Based on the experimental results, five stages can be distinguished in zinc coating formation. A schematic model of the stages is shown in Fig. 8.



Fig. 7. Binary Fe-Zn phase diagram (Zn-rich corner) [14].



Fig. 8. A schematic representation of the Fe–Zn layer formation.

Stage 1 is temperature growth of the specimen and the freezing of zinc after dipping the specimen in the molten zinc.

Stage 2 is the nucleation of the  $\zeta$  phase, immediately followed by the  $\delta$  phase. The formation of  $\zeta$  and  $\delta$  phases occurs probably by solid-state diffusion during the dipping time 4 s.

Stage 3 (hot dip galvanizing time between 4 and 25 s) is the growth of the  $\delta$  and  $\zeta$  phases and the formation of the  $\Gamma$  phase. During this stage, the temperature of the substrate is higher than the melting temperature of zinc, and the frozen zinc is completely melted. Stages 1–3 are not influenced by the silicon content of the steel.

Stage 4 is influenced by the silicon content. The growth rate of the  $\delta$  phase is higher than that of the  $\zeta$  phase with the low silicon steel (Si <0.03%). In this stage, Sandelin steel is characterized by a high reaction rate of the  $\zeta$  phase formation. The growth of the  $\delta$  phase is restrained. The coating growth of Sebisty steel is related to the growth of the  $\delta$  and  $\zeta$  phases, although the  $\zeta$  phase dominates in the coating. With the high silicon steel (Si 0.30%), a  $\delta + \zeta$  mixture phase appears in the coating.

The final, fifth stage is the formation of the  $\eta$  layer while pulling the specimen out of the zinc bath. In the case of Sandelin steel, the Fe diffuses into the  $\eta$  layer during air cooling and as a result, the final layer is the  $\zeta$  phase. In this experiment, the specimens were quenched in water after galvanizing to prevent further diffusion reaction; as a result, the  $\eta$  layer can be seen in Figs 6b and 6c.

Hot dip galvanized coating formation can be described as a diffusion process. Zinc diffuses into the steel and iron diffuses into the zinc. As the diffusion coefficient of zinc is higher than that of steel  $(D_{Zn} > D_{Fe})$ , it is believed that zinc readily diffuses into the steel and forms intermetallic compounds [15]. On the other hand, it is known that when solid iron is immersed into liquid zinc, loss of iron weight takes place. The total iron loss consists of iron dissolved into the zinc bath and iron that has remained in the alloy layers. The iron loss of the substrate depends on the silicon concentration of the steel up to 520 °C [9]. According to data from Uchiyama et al. [9], it can be concluded that the zinc coating thickness, which depends on the silicon concentration at 450°C, is related to the total iron loss of the substrate. It is possible to draw the Sandelin curve with the x-axis of Si concentration (%) and the y-axis of the total iron loss of the steel. Thus, it is possible that silicon affects hot dip galvanizing reactions by influencing zinc diffusion into the steel and iron diffusion into the coating.

Many studies have described the influence of silicon on the coating formation, but a fundamental understanding of the phenomenon is still lacking. Most researchers agree that the low solubility of silicon in the  $\zeta$  layer is important. It leads silicon segregation to the grain boundaries and formation of areas of liquid Zn between the  $\zeta$  crystals. However, some theories state that ferrosilicon particles in the coating can act as nucleation sites for the nucleation of the  $\zeta$  phase [16]. This theory seems questionable because many researchers have not found Si particles in the coating (including experiments made in Tallinn University of Technology). In recent investigations it is claimed that the Si content in steel has no direct influence on the galvanizing process but affects it indirectly by influencing the effusion of hydrogen [17]. More research is needed to develop a holistic theory of layer formation.

#### 4. CONCLUSIONS

The focus of the study was on the role of silicon in the hot dip galvanizing process. The following conclusions can be drawn:

 Based on experimental results it is hypothesized that hot dip galvanizing reactions between Fe and Zn take place in solid state. During galvanizing, zinc solidifies in the steel surface and as a result, the coating will grow in the contact surface of steel and solid zinc. There is no contact between Fe and liquid Zn. Further research is needed to confirm the hypothesis.

- Even a very short contact time (4 s) between steel and zinc leads to the formation of Fe–Zn intermetallics.
  First, the ζ phase occurs, immediately followed by the δ, and then, after incubation, by the Γ phase.
- The reactions that take place in the galvanizing process during the dipping time <25 s are not influenced by silicon concentrations. The influence of silicon is remarkable after longer dipping times (>25 s).
- Silicon most probably affects hot dip galvanizing reactions by influencing zinc diffusion into the steel and Fe diffusion into the coating. The higher the Fe diffusion, the thicker the Zn coating is.

## **ACKNOWLEDGEMENTS**

This research was supported by the European Social Fund of Doctoral Studies and the Internationalization Programme DoRa. The authors would like to express their gratitude to the Paldiski Tsingipada AS (Zincpot) for support and cooperation.

#### REFERENCES

- Nai-Yong Tang. Control of silicon reactivity in general galvanizing. *Journal of Phase Equilibria and Diffusion*, 2008, 29(4), 337–344.
- Che, C., Lu, J., Kong, G., and Xu, Q. Role of silicon in steels on galvanized coatings. *Acta Metall. Sin. (Engl. Lett.)*, 2009, 22(2), 138–145.
- Che, C., Lu, J., and Kong, G. Interpretation of Sebisty effect of hot dip galvanized steels. *Trans. Nonferrous Met. Soc. China*, 2005, **15**(6), 1275–1279.
- Jalel Ben nasr, Snoussi, A., Bradai, C., and Halouani, F. Optimization of hot-dip galvanizing process of reactive steels: minimizing zinc consumption without alloy additions. *Mater. Lett.*, 2008, 62, 3328–3330.
- Pistofidis, N., Vourlias, G., Konidaris, S., Pavlidou, El., and Stergioudis, G. The combined effect of nickel and bismuth on the structure of hot-dip zinc coatings. *Mater. Lett.*, 2007, 61, 2007–2010.
- 6. Maass, P. and Peissker, P. (eds). *Handbook of Hot-Dip Galvanization*. Wiley-VCH Verlag, Weinheim, 2011.
- Kopyciński, D. The shaping of zinc coating on surface steels and ductile iron casting. *Arch. Foundry Eng.*, 2010, 10, 463–468.
- Mandal, K. K., Mandal, D., Das, S. K., Balasubramaniam, R., and Mehrotra, S. P. Microstructural study of galvanized coatings formed in pure as well as commercial grade zinc baths. *T. Indian I. Metals*, 2009, 62(1), 35–40.
- Uchiyama, Y., Koga, H., and Inokuchi, H. Reaction between Fe–Si alloys and liquid zinc. *T. Jpn. I. Met.*, 1983, 24(5), 272–280.

- Liberski, P., Tatarek, A., and Mendala, J. Investigation of the initial stage of hot dip zinc coatings on iron alloys with various silicon contents. *Solid State Phenom.*, 2013, **212**, 121–126.
- Foct, J., Reumont, G., Dupont, G., and Perrot, P. How does silicon lead the kinetics of the galvanizing reaction to lose its solid–solid character. *J. Phys. IV*, 1993, 3, 961–966.
- Liberski, P., Tatarek, A., Kania, H., and Podolski, P. Coating growth on silicon-containing iron alloys in hot dip galvanizing process. In *Proceedings 22nd International Galvanizing Conference INTERGALVA*. Madrid, 2009, 181–187.
- Lu, J., Che, C., Kong, G., Xu, Q., and Chen, J. Influence of silicon on the α-Fe/Γ interface of hot-dip galvanized steels. *Surf. Coat. Tech.*, 2006, 200, 5277–5281.

- Guttmann, M. Diffusive phase transformations in hot dip galvanizing. *Mater. Sci. Forum*, 1994, 155–156, 527–548.
- Xu, J., Bright, M. A., Liu, X., and Barbero, E. Liquid metal corrosion of 316L stainless steel, 410 stainless steel, and 1015 carbon steel in a molten zinc bath. *Metall. Mater. Trans. A*, 2007, 38(11), 2727–2736.
- 16. Porter, F. C. Zinc Handbook: Properties, Processing, and Use in Design. CRC Press, 1991.
- Schulz, W.-D., Schubert, P., and Thiele, M. An alternative approach to explaining the effect of silicon on the galvanizing reaction. In *Edited Proceedings – Twentieth International Galvanizing Conference*. Amsterdam, 2003, 61–64.

# Räni mõju kuumtsinkimisprotsessis

# Sirli Sepper, Priidu Peetsalu, Priit Kulu, Mart Saarna ja Valdek Mikli

On käsitletud terases sisalduva räni mõju kuumtsinkimisprotsessile. Et katsekehades oleks ainsaks muutujaks ränisisaldus, kasutati katsekehade valmistamiseks tsentrifugaalvalu, kus sulatati omavahel Fe-pulber ja arvutatud kogus Fe-Si-pulbrit. Ränisisalduseks valiti Si <0,01, 0,06, 0,11, 0,17 ja 0,30%. Tsinkimine viidi läbi kuumtsinkimistehases AS Paldiski Tsingipada (Zincpot), kus tsingivanni temperatuur oli 450°C. Kasutati nii lühikest kui ka pikka kastmisaega. Lühike kastmisaeg tsingivanni oli 4–25 sekundit, et uurida kattes erinevate faaside teket. Pika tsingivannis hoidmise aja (195 ja 1200 sekundit) eesmärgiks oli uurida erinevate faaside kasvu ajas.

Kastmisaja 4 sekundi jooksul tekkisid juba esimesed Fe-Zn-faasid terase ja tsingi kokkupuutepinnal. Esimene tekkinud faas oli  $\zeta$  kiht, koheselt järgnes  $\delta$  kiht ja peale inkubatsiooniaega  $\Gamma$  kiht. Kuumtsinkimisreaktsioonid kastmisajaga <25 sekundit ei sõltunud alusmaterjali ränisisaldusest. Räni mõju on suur pikema kastmisajaga (>25 sekundit). Katsetulemuste põhjal loodi skemaatiline mudel, kus kirjeldati katte tekkimist erinevate ränisisalduste korral. Järeldati, et räni mõjutab tsingi difusiooni terasesse ja raua difusiooni kattesse.