Effect of the silicon content in steel on the hot-dip zinc coating microstructure formation

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Abstract. The aim of this study was to clarify the effect of the silicon content in steel on the structure of hot-dip galvanized zinc coating. It was found that in steel samples containing the silicon in an amount of about 0.1% and 0.5% the increased thickness coating was formed. This fact was associated with structural features of the \( \zeta \)-phase. Energy dispersive microanalysis had shown the maximum concentration of silicon in the coating was observed in \( \zeta \)-phase on St3 steel (Si = 0.1%) and in the fine mixture of \( \delta \) and \( \zeta \)-phase on 09G2S steel (Si>0.5%). This phenomenon was analyzed using a Zn-Fe-Si system diagram and its polytermic sections. It was found that there were eutectic reactions of decomposition the liquid to mixture (\( \zeta + \eta + \text{FeSi} \)) phases at the content of silicon in steel about 0.1% and more than 0.5%. Particles of FeSi-phase were involved in the dissolution of \( \Gamma \) and \( \delta \) phases, which led to a direct contact of the melt and the steel substrate. This process was accompanied by the intensive \( \zeta \)-phase formation and the rapid growth of coating thickness.

1. Introduction
The zinc coating structure consists of several intermetallic layers forming by interdiffusion of zinc and iron. The formation of the coating is directly related to the main production parameters: temperature and chemical composition of the melt, the holding time in the melt, the chemical composition of galvanized steel, especially of silicon content in steel [1].

Silicon is a cheap and very effective reinforcing alloying element in steel. Many sheets of construction steel contain small quantities of silicon because it is used in them as a deoxidizing component in production. The sudden forcing of the reaction between the steel with silicon content about 0.06-0.10% and molten zinc was described by Sandelin in the last century [2, 3]. This reaction leads to the abnormal growth of zinc coating thickness and is called in the literature "Sandelin effect". Furthermore, low-alloy steels containing silicon as a cheap alloying element in an amount up to 1% are widely used in reliable constructions. It is known that the presence of silicon in the steel in amounts more than 0.5% can impact negatively on the quality of the zinc coating and leads to its discontinuity, increasing the thickness and impairing the adhesion to the base metal. [4-7]. Despite the great number of studies, the mechanism of the silicon effect on the interdiffusion processes between Fe and Zn in the coating formation is still not completely clear.

Thus, the main aim of this work was research the influence of silicon in the steel on the phase transformations taking place during the zinc coating formation.
2. Materials and methods

Samples for the study were steel plates with different contents of silicon. The chemical composition of the samples was determined on the optical emission analyzer Foundry-Master XPR and was presented in Table 1.

| Grade of steel | C   | Si  | Mn  | P   | S   | Cr  | Ni  |
|----------------|-----|-----|-----|-----|-----|-----|-----|
| St3            | 0.176 | 0.028 | 0.327 | 0.0037 | 0.0140 | 0.089 | 0.0560 |
| St3            | 0.172 | 0.085 | 0.339 | 0.0070 | 0.0073 | 0.040 | 0.0226 |
| St3            | 0.175 | 0.227 | 0.406 | 0.0070 | 0.0026 | 0.038 | 0.0276 |
| 09G2S         | 0.122 | 0.767 | 1.530 | 0.0094 | 0.0094 | 0.033 | 0.0569 |

Before galvanizing samples were subjected to degreasing, pickling, fluxing and drying. Galvanizing was carried out in an experimental bath in the temperature range from 438°C to 468°C with steps of 5°C. The holding time in zinc melt was 4 minutes. Lowering speed and lifting speed from the bath were the same for all parts of samples. Melt in the bath was alloyed with 0.002-0.005% aluminum and 0.028-0.031% nickel. The measurement of the coating thickness was carried out by magnetic and metallographic methods using the Axiovert 40 MAT microscope. The study of the coating microstructure was carried out by TESCAN Vega SB scanning electron microscope. The zinc coating phase composition was determined in monochromatic CuKα radiation on the automated ARL XTRA X-ray diffractometer. The identification of the coating microstructural parts were conducted by determining their local elemental composition using INCAx-act energy dispersive microanalysis detector.

3. Results

Studies have shown that the thickness of the coating depends on the silicon content in the steel. Coatings with maximum thickness are formed on the steels with a silicon content of about 0.1% (Sandelin’s steel) and 0.5% (high-silicon steels). This effect depends on temperature (Figure 1).

Figure 1. The dependence coating thickness (micrometers) of silicon content in the steel (%)

![Graph showing the dependence of coating thickness on silicon content at different temperatures](image-url)
On St3 with silicon content 0.028% and 0.227% at galvanizing temperature in the range of 438-468°C, coating with a constant thickness less 100 μk are formed. On the high-silicon steel with a silicon content about 0.767% coating thickness sharply increases with increasing temperature and is reached 200 μk at 468°C (Figure 2).

![Figure 2](image-url)  
**Figure 2.** The dependence coating thickness (μk) of the galvanizing temperature (°C)

On "Sandelin’s steel" St3 (Si=0.085%) coating with a polythickness from 40 to 180 microns are formed. The difference between the maximum and the minimum coating thickness increases with the growth of galvanizing temperature (Figure 3).

![Figure 3](image-url)
Figure 3. The influence of galvanizing temperature on the polythickness of coatings on steel St3 (Si = 0.085%)

Increasing the coating thickness is undesirable because it leads to increasing zinc consumption and deterioration of the surface quality.

Studies have shown that the structure of the main phase (\(\Gamma + \Gamma_1, \delta, \zeta, \eta\)) of the zinc coating depends on the silicon content in the steel (Figure 4).

![Image of Figure 4](image-url)

Figure 4. The microstructure of the coatings obtained by \(T=450^\circ\) C, \(\tau=4\) min:
  a - on steel St3 (Si=0.028%); b - on steel St3 (Si=0.085%);
  c - on steel St3 (Si=0.227%); d – on steel 09G2S (Si=0.767%).
In coating on steel with a minimum silicon content (0.028%), all phases according to the diagram Fe-Zn were found by X-ray analysis. The δ-, ζ- and η phase ratio is approximately the same over the entire temperature range. Phases Γ and Γ1 are observed in the form of a thin black stripe. Phase δ is columnar, compact, homogeneous. Phase ζ has the fine structure and the minimum thickness (Figure 4a).

On "Sandelin’s steel" with a silicon content of 0.085% the coating has a maximum thickness and a significant variation in thickness. The sites of coating with maximum thicknesses represent the large ζ-phase dendrites, the size of which is 2-3 times greater than the thickness of this phase at adjacent sites. With increasing galvanizing temperature the ζ-phase dendrites grow through the whole thickness of the coating and are come on its surface, giving it the gray color. In places of the large dendrites, ζ-phase location δ-phase is more thin or absent. There is no pure zinc (η-phase) in those places. (Figure 4b).

The coating on St3 steel with a silicon content of 0.227% Γ and Γ1-phases are not visible. The δ-phase has a columnar structure of constant thickness, the ζ-phase has porous branched dendrites. The main feature of the coating on that steel is the presence of areas with compact structure in the upper part of the ζ-phase dendrites, possibly constituting the additional phase layer. These areas may be an additional phase layer (Figure 4c).

The structure of coating on 09G2S steel with a silicon content of 0.767% Γ and Γ1-phases are not visible. The δ-phase has a columnar structure without clear boundaries. It gradually changes to a fine mixture of phases supposedly eutectic nature. Very wide ζ-phase dominates in the coating. It is represented by large crystals of cubic and rectangular shapes. Close to the coating surface the ζ-phase crystallites become denser and more elongated in the direction of crystallization. (Figure 4d).

4. Discussion
For an understanding of the silicon effect, analysis of its distribution across the coating thickness was carried out. (Figure 4). Studies have shown that the silicon concentrations in the different phases of the coating are very different. The amount of silicon in the steel surface layer (α-phase) is almost three times more than its average content in the steel in all tested samples. Some researchers explain this effect the accumulation of (FeO2*SiO2) double oxides in the surface layer of steel [8]. The coating on St3 silicon concentration reaches its maximum values in ζ-phase. According to the theory of diffusion layers formation, the maximum concentration of the element indicates the formation of a chemical compound (phase). It allows us to assume that silicon integrates into ζ-phase, forming a three-component Zn-Fe-Si compound. As opposed to St3 in the coating on steel 09G2S maximum values of the silicon concentration are observed in the fine mixture of phases δ and ζ, and in the ζ-phase layer near the surface.

Analysis of the Zn-Fe-Si phase diagram has shown that the silicon presence in the steel leads to the appearance of a new phase - FeSi in the zinc coating (Figure 5) [9]. The mechanism of formation of FeSi particles is described by nonvariant reactions that are demonstrated in the polymeric sections of the Zn-Fe-Si system (Figure 6). When the content of silicon of about 0.1% (Sandelin’s steel) eutectic reaction of the liquid phase disintegration to mixture ζ + η + FeSi takes place in the system. FeSi phase is formed in a wide range of compositions less than 9.1 wt.% Fe. When the silicon content of about 1% (high-silicon steel) the FeSi phase amount becomes significantly greater (Figure 6) [9].
Figure 5. The phase structure of Zn-Fe-Si system alloys at ambient temperature

Figure 6. The polymeric sections of the Zn-Fe-Si system:
- a – 95% Zn
- b – 98% Zn [9]

Foreign studies have also confirmed the existence of an equilibrium state between the liquid, the $\zeta$-phase, and FeSi-phase, which prevents the equilibrium between the liquid phase and the $\delta$-phase [10, 11]. This phenomenon destroys the integrity of the coating layers; liquid zinc has the direct contact with the steel base, which accelerates the interdiffusion of iron and zinc. On reaching the surface coating, the iron stream is converted into $\zeta$-phase crystallites in zinc.
5. Conclusion
Metallographic studies have concluded that the maximum thickness of the zinc coating is observed in steel samples with silicon content about 0.1% (Sandelin’s steel) and 0.5% (high-silicon steel). This fact was associated with structural features of the $\zeta$-phase. Energy dispersive microanalysis had shown the maximum concentration of silicon in the coating was observed in $\zeta$-phase on St3 steel ($\text{Si} = 0.1\%$) and in the fine mixture of $\delta$ and $\zeta$-phase on 09G2S steel ($\text{Si} > 0.5\%$). Analysis of Zn-Fe-Si system diagram and its polytermic sections has shown that there are eutectic reactions of decomposition the liquid to mixture ($\zeta + \eta + \text{FeSi}$) phases at the content of silicon in steel about 0.1% and more than 0.5%. Particles of FeSi-phase were involved in the dissolution of $\Gamma$ and $\delta$ phases, which led to a direct contact of the melt and the steel substrate. This process was accompanied by the intensive $\zeta$-phase formation and the rapid coating thickness growth.

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