

EFFECT OF CHEMICAL COMPOSITION OF STEEL ON THE STRUCTURE OF HOT – DIP GALVANIZED COATING

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This article describes the effect of the content of conventional steel impurity elements on the thickness and composition of the zinc layer. This article is focused primarily on low-temperature, batch hot-dip galvanizing; however, the continuous coating process is also mentioned. The main discussion covers galvanizing from pure zinc melt, and only touches on galvanizing from melts with the usual amounts of aluminium (0,2 wt. %). Silicon, phosphorus, aluminium and sulfur may have an especially negative effect on the mechanical properties of the coating and its final appearance. The content of ballast carbon and manganese has a rather limited effect on composition and coating thickness.

Key words: steel, hot – dip galvanizing, intermetallics Fe – Zn, chemical composition, outburst structure

INTRODUCTION

Low - temperature, batch hot-dip galvanizing ($t \sim 450 \text{ }^\circ\text{C}$) is among the most common, definitive methods of corrosion protection for carbon structural steel. The resulting defect - free coating provides long - term protection against atmospheric corrosion of steel.

During the hot-dip galvanizing process, a system complex metallurgical reactions occur at the interface of the galvanized steel and the molten zinc leading to a coating of intermetallic phases Fe - Zn. The intermetallic phases differ in composition and structure. A layer of pure zinc may stick on the outer surface of the coating. Conversely, the coating layer closest to the original surface is composed of intermetallics with a basic cubic lattice, while the gamma (Γ) phase is of bcc structure and the gamma1 (Γ_1) phase is fcc. Above these phases, a phase grouping known as delta ($\delta_{ik} + \delta_{lp}$) crystallizes; this grouping has a very complicated structure with a basic hexagonal lattice (hcp). Above this phase is the intermetallic zeta (ζ) phase with, at least for metals, an atypical monoclinic structure [1, 2].

The presence and even the thickness of individual intermetallic phases and layers of pure zinc is affected by many factors. The following are of fundamental importance: zinc bath temperature, surface texture of the galvanized zinc is affected by many factors. The following are of fundamental importance: zinc bath temperature, surface texture of the galvanized steel, type of mechanical or heat processing, and even wall thickness of the galvanized steel. For the creation of the coating, however, alloying elements present in the galvanizing

bath (Al, Sn, Ni, Bi), immersion time in the bath, and the method and duration of cooling after galvanizing are also important [1].

Impurities contained in zinc-alloy structural steel are of vital importance to the overall thickness and composition of the coating. The following is a detailed description of the impact of individual common impurities in non-alloyed structural steels to the composition and coating thickness of the hot-dip galvanizing process [3].

DETAILED DESCRIPTION OF THE EFFECT OF INDIVIDUAL ELEMENTS

Effect of Silicon

Oxygen is introduced to the steel during its production to specifically reduce carbon content, but also other impurities. Excess amounts of free oxygen are removed via steel deoxidation, i.e. the addition of elements with a higher overall affinity for oxygen than carbon. For this purpose Si, Al, and Mn are often used, with silicon being the deoxidizer of choice. Such steels are then referred to as silicon-killed steels [1,3].

However, silicon in the steel significantly increases the solubility of iron in the zinc melt. Consequently, coatings may be formed not only of great thickness, but with insufficient adhesion to the substrate, therefore easily descaling. The silicon contained in the steel may also influence the composition of the coating [2].

In terms of the influence of the silicon content in the steel on the creation of the zinc coating, the amount of silicon can be divided into four types. Steel with a low silicon content (killed steel) of $< 0,03 \text{ wt. } \%$ Si, steel with a silicon content in the “Sandelin range” (according to RW Sandelin), i.e. (0,03 to 0,12 wt. %), steel in the “Sebisty range” (according to JJ Sebisty), i.e. (\sim

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0,15 to 0,25 wt. %) and, lastly, steels with high silicon content (> 0,25 wt. %) [1, 3].

Low-silicon steel (non-silicon-rimmed) (< 0,03 wt.% Si) is clearly the best for creating quality coatings in the hot - dip galvanizing process. The coatings on these steels are characterized by good mechanical properties, cohesive alloy layers and excellent adhesion of the coating to the steel substrate. When galvanizing steel with this content of silicon, a substantial portion of delta phase ($\delta_{ik} + \delta_{ip}$) is formed, which in this case consists of extremely closely spaced hexagonal columnar crystals. This phase effectively prevents the diffusion of iron atoms; therefore, the rising phase zeta (ζ) has a limited thickness. When galvanizing this kind of steel, the zeta (ζ) phase is very fine, and its upper part is often imbued with an adherent layer of pure zinc (eta (η) phase). When the steel is left longer in the galvanizing bath, only the delta phase ($\delta_{ik} + \delta_{ip}$) grows [2,3].

If the amount of silicon in the steel is increased (> 0,03 wt. % Si), i.e. silicon steel is "rimmed", then there is a fundamental change in the structure of the coating and also its overall thickness. The coating of steel with a silicon content in the "Sandelin range" (0,03 to 0,12 wt. %) is 600 micron thick, but only after the normal time period (8-10 min) in the zinc bath. When the total time for the steel in the bath is longer, the coating thickness can reach over 1500 micrometers. The resulting coatings are formed of non-oriented monoclinic crystals of the zeta (ζ) phase ($FeZn_{13}$). Due to the dominance of this phase, the coatings are very fragile and susceptible to mechanical damage [3].

When dipping steel parts with a silicon content in the "Sandelin range" a thin layer of group phase delta ($\delta_{ik} + \delta_{ip}$) is formed on the surface which is covered with a layer of phase zeta (ζ). Continued immersion time in the galvanizing bath results in a discontinuous layer of group phase delta ($\delta_{ik} + \delta_{ip}$) on the steel's surface. This layer is unable to limit the diffusion of iron towards the phase zeta (ζ), because the external phase (bordering with molten zinc L (Zn)) grow uncontrollably in thickness. Virtually unlimited access to zinc atoms and a high rate of formation of intermetallic $FeZn_{13}$ is the explanation for the formation of very disordered crystals of monoclinic phase zeta (ζ). The slurry of fine crystals encloses the pure, unreacted zinc atoms. The surface of such coatings further often contains defects caused by intense diffusion of iron from galvanized steel (e.g.shrinkage porosity, etc.). For steels with this silicon content, an outer layer formed of substitutional solid solution of iron in zinc (i.e. η phase) does not form [1 - 3].

A suitable compromise for achieving zinc coating on silicon killed substrate is to use steel with a silicon content in the "Sebisty range" (~ 0,15 to 0,25 wt. %). These coatings are typically thicker and more brittle than those arising from silicon - killed steels, but thinner and with better pronounced structure than those formed on steels with silicon content in the "Sandelin range" (0,03 to 0,12 wt. %). However, the thinner coating consists of a

compact group of delta phase ($\delta_{ik} + \delta_{ip}$) and often the grouping phase gamma1 (Γ_1) and gamma (Γ). The mechanical resistance of the coatings formed on these steels is sufficient [2].

Conversely, steels with silicon content above 0,28 wt. % are not recommended for hot dip galvanizing. The coating again consists of disordered crystal phase group zeta (ζ) which block unreacted zinc atoms [3].

Figure 1 summarizes the effect of silicon content in the galvanized steel on the coating thickness formed on a profile with a wall thickness of approximately 5 mm.

Effect of Phosphorus

In unalloyed steels, a small amount of phosphorus appear as a ballast material from the steel production process itself [1].

In the case of batch galvanizing, it is generally accepted that phosphorus, like silicon, increases the dissolution rate of iron in the zinc melt and thereby promotes formation of a thicker coating with phase zeta (ζ) dominating the structure. This problem was observed primarily in rolled sheets destined for the automotive industry, where the coating was created by continuous hot-dip galvanizing with the addition of aluminium in the working bath. It has, however, been accepted that the negative effect on the zinc coating of the silicon content of the steel outweighs the negative effect of the phosphorus ballast [3, 4]. Therefore, empirical relationships were established summarizing the negative influence on coating formation of both elements within continuous hot dip galvanizing. Equation {1} presents the relationship limiting the maximum levels of both ballast elements for cold rolled steel to achieve high-quality coating. Equation {2} presents the same for hot-rolled sheets (unit representation of individual elements in the steels is given in wt. %) [1,3].

$$Si < 0,03 \text{ and } Si + 2,5 P < 0,04 \quad \{1\}$$

$$Si < 0,02 \text{ and } Si + 2,5 P < 0,09 \quad \{2\}$$

The effect of phosphorus content in the steel on the development and thickness of the zinc coating resulting

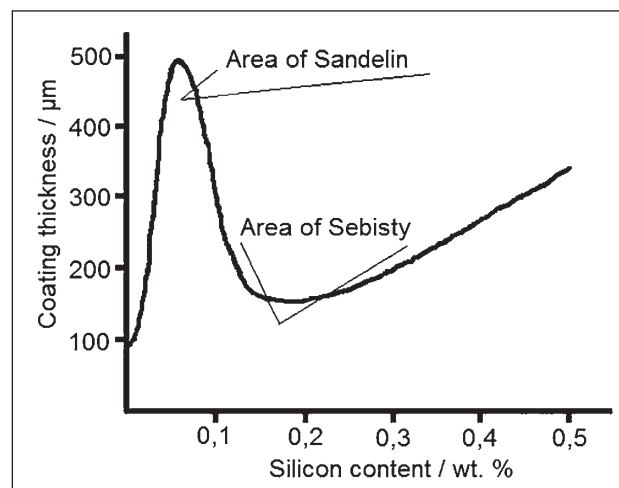


Figure 1 Effect of silicon in the steel on the total thickness of the resulting zinc coating

from batch, low - temperature hot-dip galvanizing is discussed only marginally. The findings summarized above are based on practical experience rather than substantiated research work. The reason is probably that for steels intended for batch zinc galvanizing, the composition and the coating thickness is primarily affected by the silicon content of the steel and possibly other parameters (thickness of galvanized parts). The effect of phosphorus on development, composition and total thickness of the coating is then distorted [1,2].

The influence of the phosphorus content on the composition and the thickness of the zinc coating is closely discussed in professional circles with regard to continuous galvanizing ($t \sim 450^\circ\text{C}$) of plates. Sheets are made of ferritic steel and, therefore, contain a low carbon content for improved malleability. The steel is further alloyed with low contents of Ti and/or Nb (interstitial - free steels) to further improve the malleability and simultaneously prevent the segregation of carbon in the form of Fe_3C and phosphorus in the form of Fe_3P at the grain boundaries during annealing. In this case, we discuss the influence of these elements on the phase Fe_3P segregation at grain boundaries, since their presence leads to phase segregation of Ti - P and/or Nb - P within the grains. Their influence thus maintains high reactivity of the grain boundaries of ferritic steel. The influence of these factors on the formation, composition and thickness of the zinc coating must be addressed with a further coating in a zinc bath with additional aluminium (usually 0,2 wt. %). Furthermore, the effect of subsequent annealing on the coating process should be considered. Annealing results in diffusion processes forming a continuous layer of intermetallic phases, which ensures the appropriate combination of mechanical and corrosion properties. This grouping ensures high quality coating with a suitable combination of mechanical and corrosion properties and good adhesion to the steel substrate and between phases [4 - 6].

Use of a bath containing aluminium may result in the formation of an undesirable outburst structure, which is an unevenly developed layer of zinc on the steel. This structure is a typical feature of the delta phase ($\delta_{\text{ik}} + \delta_{\text{ip}}$) with strongly scattered grains on the follow-up phase zeta (ζ). The gamma ($\Gamma + \Gamma_1$) phase only occurs marginally in this structure. The formation of this structure is synergistically associated with the aluminium content of the zinc melt and the reactivity of the grain boundaries of steel, while inhibiting the formation of an uneven coating of Fe_2Al_5 . In this regard, we discuss the influence of the phosphorus content on the Fe_3P phase segregation at grain boundaries, which results in reduced activity for the formation of a coating at these locations [6, 7].

In [4] the authors discuss in detail the effect of phosphorus content of steel on the kinetics of formation of intermetallic phases of the zinc coating. The authors conclude that in the case of baths without aluminium content, the phosphorus content does not affect the cre-

ation kinetics and structure of the zinc coating. If the aluminium content of the bath is within the usual amounts (0,2 wt. %), then the kinetics of the formation of the local inhibitory layer of Fe_2Al_5 is not affected by the phosphorus content of the steel. The studied delayed creation of individual intermetallic Fe - Zn is therefore not affected by the content of phosphorus in the steel, but rather by the overall reactivity of the grain boundaries. Jordan and Marder [5 - 7] describe the effect of the content of Ti (Ti + Nb + P) on the kinetics of formation and composition of the zinc in the bath with and without the usual aluminium content at 450°C . In the case of aluminium-free baths, it is obvious that the increased amount of Ti in the steel has no effect on the kinetics of the coating composition; however, an increased amount of phosphorus in steels containing Ti and Nb is likely to slow the growth of phase gamma ($\Gamma + \Gamma_1$). Baths containing aluminium are used to limit the growth phase zeta (ζ). At the same time an increased amount of Ti in the steel accelerates the kinetics of formation of intermetallic phases Fe - Zn. Even in this case, it was verified that an increased amount of phosphorus slows the growth of phase gamma ($\Gamma + \Gamma_1$). Gamma phase grouping ($\Gamma + \Gamma_1$) growth slowdown due to the phosphorus content of the steel is also documented in [7]. According to recently conducted research [8], it has been verified that the addition of phosphorus to steel refines the steel grain, although the Fe_3P phase is segregated at the grain boundaries of the steel. This phase slows the growth of phase gamma ($\Gamma + \Gamma_1$) or even prevents its occurrence. Conversely, with increasing phosphorus content growth phase zeta (ζ) is promoted. It can be summarized that phosphorus has a generally negative effect on hot-dip galvanizing (i.e. even in batch galvanizing processes), probably increases the solubility of iron in the melt, and promotes a negative "Sandelin effect". Additional undesirable effects include constraints on phase gamma ($\Gamma + \Gamma_1$) growth and, simultaneously, increasing the layer thickness of the zeta phase (ζ), which generally impairs the overall mechanical properties of the coating and its adhesion to the substrate.

Effect of Carbon

Most often batch galvanized-steel with a carbon content up to 0,2 wt. % is intended for welded construction. For these steels, it has not been shown that carbon content had a significant effect on the formation, composition and thickness of the zinc layer. Likewise, the different structures due to the resulting steel carbon content are irrelevant, and thus comparable to coatings formed on ferritic and ferritic - pearlitic steels. However, increased carbon content ($> 0,3$ wt. %) can increase the reaction rate of dissolution of iron in the melt and, therefore, disproportionately increase the overall coating thickness of phase zeta (ζ) growth. Such a coating is then very fragile and easily descales from the steel [1 - 3].

Conversely, in professional circles, it has been shown that for steels with a low carbon content the undesirable outburst structure can occur. With increasing carbon content in the tested steels, this phenomenon disappears [9]. However, as shown above, this may be related more to the total area of the grain boundaries, than to the carbon content.

Effect of Aluminium

Because of the risk of formation of unfavorable coatings on silicon-killed steels (“Sandelin effect”) structural steel intended for hot dip galvanizing is often deoxidized by aluminium. Due to its high affinity for nitrogen, it has the added advantage of providing increased resistance to aging. Compared to silicon, aluminium has a higher affinity for iron, and therefore forms intermetallic phases, usually Fe_2Al_3 , FeAl_2 , FeAl_3 . However, the free aluminium may, diffuse to the surface of the steel and create a discontinuous Fe_2Al_3 inhibition layer during hot galvanizing. In parallel, as in baths containing aluminium, the formation of this layer may result in the formation of an undesirable outburst structure. Although there are no specialized studies summarizing the effects of aluminium content on the kinetics of formation, composition and thickness of the zinc coating, it is believed that a comparable aluminium content in the steel, compared to silicon content, does not cause the undesirable “Sandelin effect” [1,3, 6, 10].

Effect of Manganese

Because of its position in the periodic table and comparable size with iron atoms, manganese is commonly contained in construction steel as a ballast material [1]. Unlike other elements, its effect on the kinetics of formation, the thickness and composition of the zinc layer is entirely negligible. Conversely, it was shown that an increased amount of manganese (> 1,25 wt. %) in silicon-killed steel positively influences the mechanical properties of the coating. This is most likely due to the closer arrangement of the resulting zeta (ζ) phase [1,3,11].

Effect of Sulfur

The increased sulfur content in steel due to deliberate alloying, e.g. cutting steel (manufacture of fasteners), ensures its easy machinability [1]. In operation, galvanizing showed that sulfur contents greater than 0,15 wt.% again increase the solubility of iron in molten zinc, and lead to the formation of thick coatings with insufficient mechanical properties. Changing the overall geometry of the threaded surfaces leads to malfunction [3,11].

CONCLUSION

The operating parameters of hot dip galvanizing have a major impact on the structure and thickness of the zinc coating. Influences arising directly from the steel itself cannot be disregarded, e.g. wall thickness of the profile, quality of the surface before galvanizing and the content of ballast elements in the steel.

The content of silicon, phosphorus, aluminium and sulfur in the steel has a substantial adverse effect on the thickness and composition of the coating in batch hot-dip galvanizing. Via various mechanisms, an inappropriate amount of these elements in the steel increases the risk of poor coatings from the viewpoint of mechanical properties and final appearance.

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