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ISSN 0543-5846
METABK 55(1) 111-114 (2016)
UDC – UDK 669.14.5:621.795:536.425:531.3 = 111

REACTION KINETICS OF THE FORMATION OF INTERMETALLIC Fe – Zn DURING HOT - DIP GALVANIZING OF STEEL

Received – Primljeno: 2015-01-06
Accepted – Prihvaćeno: 2015-07-10
Review Paper – Pregledni rad

This review article mainly describes the composition of intermetallic Fe - Zn, i.e. zeta (ζ), delta ($\delta_{1k} + \delta_{1p}$), gamma$_1$ (Γ_1) and gamma (Γ) on galvanized steel during low temperature galvanization (t ~ 450 °C). It gives detailed the formation, growth of individual phases during galvanization and their interaction. In terms of the kinetics, the formation of the coating is defined by a parabolic kinetic equation of the growth of different intermetallic phases under ideal conditions. From the available literature the rate constants of the formation of individual intermetallic phases and also for the total coating are cited. The composition of the intermetallic phases, iron content, crystal structure, and group symmetry in which the surface of galvanized steel forms.

Key words: hot-dip galvanized steel, surface treatment, intermetallic Fe - Zn, reaction kinetics, temperature

INTRODUCTION

During hot-dip galvanizing of steel, a coating of different intermetallic phases Fe - Zn gradually forms on the sample. These phases are formed by a complex diffusion processes between the iron atoms of the surface layer of the steel and zinc atoms from the melt (t ~ 450 °C). These are arranged on the steel structure in layers with gradually descending iron content. The intermetallic compounds vary not only in composition and morphology of the crystals, but also significantly in hardness and resistance to compressive load. The closest to the steel surface, the gamma phase (Γ) crystalizes, having an iron content of 23,5 - 28 wt. %. The morphology of the crystals of this phase is planar. Recent research has shown that phase gamma$_1$ (Γ_1) differs from phase gamma (Γ) not only in terms of composition and crystal structure, but that this phase's iron content is 17 – 19,5 wt. %. The morphology of the crystals of this phase is again planar. Columnar structure has a delta (δ) phase, the iron content is 7 – 11,5 wt. %. This phase exists in two variations, i.e. δ_{1k} (closer to the steel surface), and δ_{1p}. The variations have slightly different sized crystal lattice and composition. At this stage, an intermetallic containing iron 5 – 6,2 wt. %, referred to as phase zeta (ζ), is built. This phase also has columnar morphology. Above this phase can be observed various strong phases of pure zinc, or substitutional solid solution of iron in the zinc. This is not an intermetallic phase, but is called eta (η). The composition of various intermetallic phases, iron content and their structure is summarized in Table 1. Their arrangement on the surface of galvanized steel is schematically illustrated in Figure 1. The results summarized in Figure 1 and in Table 1 correspond to the results of modern research work [1].

Table 1 **Summary of the structure of individual intermetallic phases [2]**

phase	formula	wt. % (Fe)	structure	space group
eta (η)	Zn	0,03	hcp	$P6_3mc$
zeta (ζ)	$FeZn_{13}$	6,17	monocl.	C2/m
delta$_{1p}$ (δ_{1p})	$FeZn_{10}$ / $Fe_{13}Zn_{126}$	7,87 / 8,09	hcp	$P6_3mc$
delta$_{1k}$ (δ_{1k})	$FeZn_7$	10,87	hcp	$P6_3mc$
gamma$_1$ (Γ_1)	Fe_5Zn_{21}	16,90	fcc	F43m
	$FeZn_4$	17,60	fcc	F43m
	$Fe_{11}Zn_{40}$	19,02	fcc	F43m
gamma (Γ)	Fe_3Zn_{10}	20,40	bcc	I43m
	$FeZn_3$	22,16	bcc	I43m
	Fe_4Zn_9	27,52	bcc	I43m

CREATING INDIVIDUAL INTERMETALLIC PHASES DURING HOT DIP GALVANIZING

The presence of various intermetallic Fe - Zn phases is influenced by complex factors. First and foremost, is the content of impurities in galvanized steel - especially

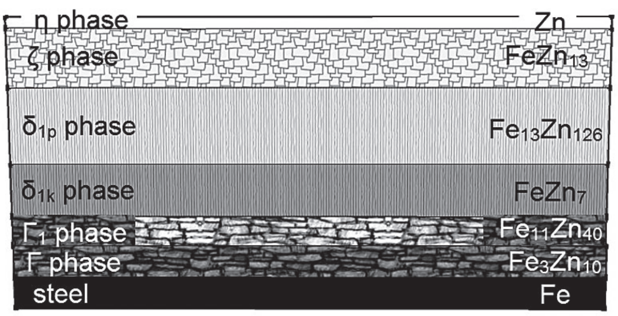

Figure 1 Ideal arrangement of individual phases on the surface of galvanized steel [1]

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the content of Si (silicon-killed steels) and P. Bath temperature and time in the bath also have major impacts. First, coating thickness affects the alloy contained in the melt of zinc (Al, Sn, Pb, Bi). Among other factors affecting the presence and thickness of the intermetallic layers include the method of mechanical surface treatment of galvanized steel (turning has a crucial influence), heat treatment and the wall thickness of the steel. Finally, are factors such as the nature and duration of cooling of the galvanized product [1].

In the case of galvanizing low-silicon steel (silicon content < 0,03 wt.%), with ferritic structure and a very low content of phosphorus, with a perfectly clean surface without mechanical and thermal treatment in a bath at 450 °C containing pure zinc free from alloying elements, all of the phases described above in the coating (Figure 1) may be expected. In order to separate phase Γ_1 from and phase Γ and phase δ_{1k} and phase δ_{1p}, delay time must be longer than the galvanized steel standard (8 - 10 min), and gradual cooling of the galvanized steel must be selected.

Under these ideal conditions, it is possible to create the described individual intermetallic phases sequentially, as incurred. Shortly after immersion of the galvanized steel in the prepared zinc bath, separated crystals of zeta (ζ) phase (Figure 2) begin to form on the surface. At a later stage this leads to formation of a thin compact zeta phase (ζ) on the galvanized steel. After a short delay from the formation of primary crystal zeta (ζ) phase, there is a thin layer of compact delta (δ) phase (Figure 3). The thickness of the delta phase gradually grows and forms an effective barrier against the diffusion of iron atoms from the surface and prevents the formation of thicker zeta (ζ) phase layers. The time lapse between the initial formation of crystals and a compact layer of both mentioned phases is no longer than 5 s. Delta (δ) phase in the period of layer creation already incorporates both phase δ_{1k} and phase δ_{1p} wherein phase δ_{1p} achieves a greater thickness than phase δ_{1k} [1,2].

A significantly longer incubation time is needed for the formation of the gamma phase (Γ). This phase is formed in the interval 30 to 45 seconds after immersion of the galvanized steel in a bath of molten zinc (Figure 4). From its inception, the gamma (Γ) phase integrates the gamma_1 (Γ_1) phase.

The thickness of this phase is considerably lower than the other. The usual thickness is not more than 1 to 2 microns. Long time intervals for the galvanized steel in the zinc bath provide for the formation of clearly visible (metallographic cross section) intermetallic phases. For optimal visibility, gradual but prolonged cooling of the galvanized steel is important. Usually separation of the gamma_1 (Γ_1) phase from the gamma phase (Γ) occurs in the cooling phase.

The separation of the delta into phase δ_{1k} and phase δ_{1p} is not visible. Precision analytical methods should be used for their determination. Finally, the zeta phase can be visually separated into the primary stage zeta_1 (ζ_1) and the columnar secondary stage zeta_2 (ζ_2). Among branches of the zeta_2 phase and above this phase is the eta (η) phase.

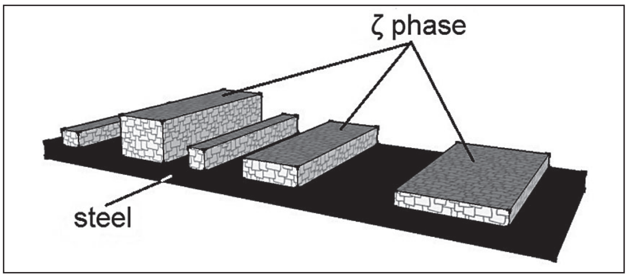

Figure 2 The initial phase of the coating is linked to the exclusion of separate crystal phase zeta (ζ) and their groupings [1]

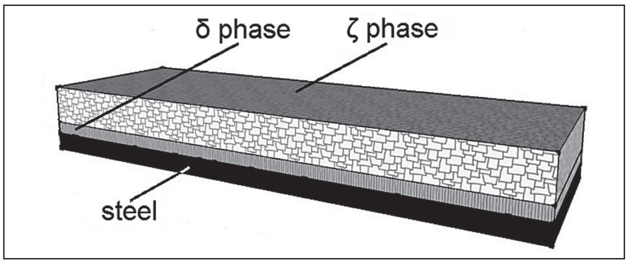

Figure 3 After a very short incubation period, the delta (δ) phases are created between the steel surface and the zeta (ζ) phase [1]

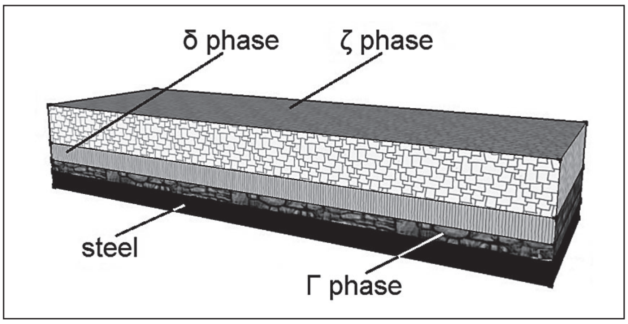

Figure 4 After approximately 30 s, both intermetallic gamma (Γ) phases separate from the substrate [1]

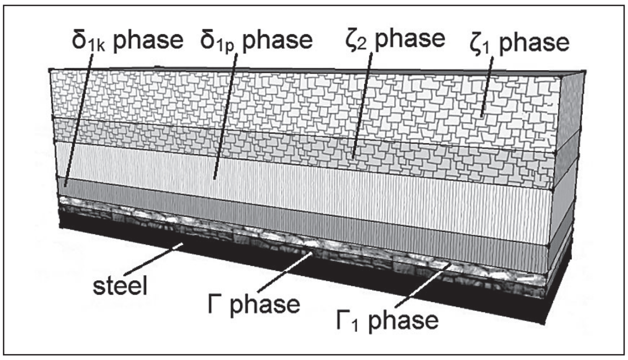

Figure 5 Arrangement of intermetallic phases on the surface of galvanized steel is ideal during hot-dip galvanizing and subsequent cooling [1]

Figure 5 shows the final representation of intermetallic phases in the coating formed under ideal conditions [1,2].

DESCRIPTION OF THE REACTION KINETICS OF THE FORMATION OF INTERMETALLIC PHASES

The emergence and growth of the intermetallic phases on the surface of galvanized steel is managed in a completely different reaction mechanism. The total coating thickness is affected only by growth of intermetallic phases determined by the growth of phase delta (δ) and phase zeta (ζ), or the substitution solution of iron in the zinc solution - phase eta (η). Growth of phase gamma (Γ) or the phase gamma + gamma$_1$ ($\Gamma + \Gamma_1$) group is very limited and the total thickness of the coating is not affected. The kinetics of formation of various intermetallics similarly as in the study of other processes is significantly influenced by temperature. It is necessary to study the kinetics of formation and growth of individual intermetallics outside the temperature range 480 – 530 °C, because in this temperature range there is rapid growth in the rate of dissolution of iron in molten zinc. This leads to a large increase in coating thickness and misshaping impairment geometry of the galvanized parts and additionally to degradation of the zinc bath, in which the crystals of phase zeta (ζ) $FeZn_{13}$ are formed. In this temperature range galvanizing is not carried out, and therefore description of the kinetics of individual intermetallic phases is unknown.

The kinetics at zinc bath temperature favourable to the formation of high quality coatings containing all of the above intermetallic phases is well described. Studies involving shorter periods of time for galvanized steel in a bath (300 s; 450 °C) show that from the start of coating, only the phase zeta (ζ) grows rapidly. According to the observed kinetic regulation, thickness in this phase increases rapidly, but eventually stops growing. Conversely, the delta (δ) phase grows slowly, but the increase of thickness under favourable conditions gradually accelerates. The gamma phase ($\Gamma + \Gamma_1$) grouping occurs slowly and does not practically contribute to the total coating thickness. The growth of the gamma phase grouping is rather linear with an incubation period of 30 - 45 s, after 300 s the thickness increase of this phase group is negligible. The revised graph in Figure 6 shows the thickness of the individual phases in the case of short immersion time in the zinc bath. In the case study, underscoring coating in an unnaturally long time interval (6 h, 457 °C), results are shown in the revised chart in Figure 7. Kinetics of formation of the phase gamma ($\Gamma + \Gamma_1$) grouping in this case has a slightly parabolic character but again it is evident that their thickness even after prolonged galvanizing remains practically unchanged. Growth direction of the phase gamma ($\Gamma + \Gamma_1$) grouping is towards the galvanized steel. The phase growth is controlled by the rate of diffusion of Fe into the near-surface layer. Figure 7 presents a gradual decrease in the intensity of growth in the thickness of phase zeta (ζ). The parabolic character signals that the phase growth process is diffusion controlled. A significant slowdown in the growth of phase zeta (ζ) is due to the rapid increase in the thickness of phase delta, especially δ_{1p}. Diffusion of iron atoms in this phase is significantly hindered, the reason is the crystal structure of the phase - hcp structure similar to the crystal structure of zinc substituted with a tight arrangement polyhedron. Another reason is of course the fact that the rate of reaction of the δ_{1p} phase formation is clearly high (linear dependency of the growth of coating thickness versus time for a longer immersion time of galvanized steel in the zinc bath, see Figure 7). Therefore, most of the iron atoms, which diffuse through phase gamma ($\Gamma + \Gamma_1$) and δ_{1k} phase are consumed for the production of the δ_{1p} phase. Conversely, as seen in Figure 7, there is easy diffusion of zinc atoms in the zeta (ζ) phase. Growth of phase zeta (ζ) is directed toward the molten zinc, and the growth phase of delta (δ) is in both directions with a slight predominance toward the molten zinc [1 - 3].

The mathematical description of the kinetics of the individual phases can be expressed by the equation {1}:

$$Y(t) = Kt^n \qquad \{1\}$$

Where *Y* (nm) symbolizes growth thickness of specific intermetallic layer of Fe - Zn, *K* is the specific constant (pre-exponential factor), *n* the time constant, and *t* (s) symbolizes the reaction time. The exact kinetic sequence depending directly on the time constant value of *n*. In the case that $n = 1$, then the graph is a straight line (linear equation), while in the case of $n = 0,5$ the graph is an ideal parabola. The time constants *n* for each intermetallic phase Fe - Zn were determined experimentally and differ depending on the type of experiment (choice of shorter exposure time of the galvanized steel in the zinc bath versus a longer time). Crucial to the process of creating a layer of zinc on the steel, is the total reaction constant n_c. Tables 2, 3 summarizes the results obtained by different authors in the case of galvanized steel over longer time periods (h).

According to the presented studies, it can be stated that the rate constant *n* for the phase gamma ($\Gamma + \Gamma_1$) grouping is close to 0,25, the delta phase ($\delta_{1k} + \delta_{1p}$) is always higher, about 0,55, finally for phase zeta (ζ) it is about 0,30. The results obtained for n_c cannot be generalized independently of the time duration in the zinc bath. Rate constants for the individual *n* intermetallic phases Fe - Zn are independent of the length of immersion of the galvanized steel in a bath of molten zinc. In the initial stages of the process, the phase interface between the steel substrate and the molten zinc is soon saturated by iron atoms. Iron content at interfaces between the emerging zeta (ζ) and delta ($\delta_{1k} + \delta_{1p}$) phases and also in these phases directly exceeds the equilibrium composition. Except $c^{\zeta L}$ concentration where there are substantially stable concentrations of Fe throughout immersion of the galvanized steel in the zinc bath. This can be easily proved by the permeability of the iron atoms in phase zeta (ζ) [3]. Parabolic diffusion mechanism is the control factor for the flow of zinc and iron atoms in phase zeta (ζ), and the emerging phase gamma ($\Gamma + \Gamma_1$) grouping. Conversely, it is obvious that the formation of the δ_{1p} phase is controlled by the rate of a chemical reaction forming the complex intermetallic $Fe_{13}Zn_{126}$ [4]. The calculated values of diffusion coefficients of Fe in phase gamma ($\Gamma + \Gamma_1$) and Zn atoms in

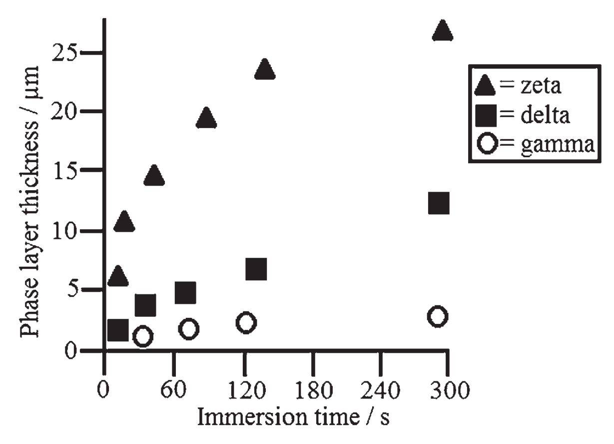

Figure 6 Dependence of the thicknesses of the individual intermetallic phases on short (s) immersion time [5]

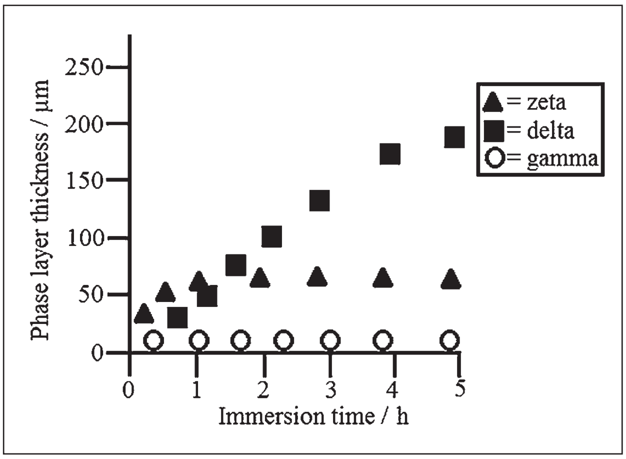

Figure 7 Dependence of the thicknesses of the individual intermetallic phases on longer immersion time (h) [5]

phase zeta (ζ) support this. Data were obtained by calculation from tabulated values of pre-exponential factor D_0 and activation energy values Q_{SP} [5].

Table 2 **Summary of the rate constant *n* and determined overall rate constants n_c for longer exposure times [5]**

source	gamma ($\Gamma + \Gamma_1$)	delta ($\delta_{1k} + \delta_{1p}$)	zeta (ζ)	n_c
Allen	0,25	0,65	0,35	0,55
Rowland	0,13	0,53	0,31	-
Blickwede	0,10	0,60	0,16	-
Horstmann	0,50	0,50	-	-
Sjoukes	0,23	0,58	0,26	-
Onishi	0,23	0,49	0,36	0,43

Table 3 **Summary of the rate constant *n* and determined overall rate constants n_c for longer exposure times [5]**

Fe-Zn alloy layer	n value
gamma ($\Gamma + \Gamma_1$) 0,24 ± 0,06	
delta ($\delta_{1k} + \delta_{1p}$)	0,51 ± 0,11
zeta (ζ)	0,32 ± 0,03
n_c	0,35 ± 0,02

CONCLUSION

The formation and the final thickness of each intermetallic Fe - Zn phase in coating molten zinc on steel is affected by complex factors. Among the most important include the content of impurities in galvanizing steel (especially the content of Si and P), temperature and composition of the zinc bath (especially the influence of alloying elements such as Al and Ni). Of considerable importance is also the thickness of the galvanized profile, the method of its mechanical and thermal treatment and, finally, the method and length of cooling.

Under ideal conditions, phases forming initially on the surface of the galvanized steel in low temperature galvanizing is the zeta (ζ) phase and basically immediately after dipping the steel into the zinc bath also the delta phase ($\delta_{1k} + \delta_{1p}$). Growth of the delta phase makes diffusion of Fe from the steel into molten zinc more difficult, thus slowing growth of phase zeta (ζ). The gamma ($\Gamma + \Gamma_1$) phase grouping occurs with immersion of approximately 30 - 45 s. It is not possible to differentiate the gamma ($\Gamma + \Gamma_1$) phase's effect on total thickness of the coating. The phase grouping reaches a thickness of 1-2 microns. The separation phase Γ_1 from phase Γ usually occurs after suitable cooling of the galvanized steel. There usually is not a sharp border between the two delta (δ) intermetallic phases, i.e. δ_{1k} and δ_{1p}.

In terms of kinetics of the individual phases, it can be collectively observed that the rate constant *n* can now be defined for each intermetallic phase regardless of the period of time of immersion of the galvanized steel in the zinc bath. The highest rate constant *n* is achieved by phase delta ($\delta_{1k} + \delta_{1p}$). The generalization of the overall rate constants (n_c) has not yet occurred. Even under ideal coating conditions, its value depends on the time of immersion of the galvanized steel in the zinc bath.

Acknowledgments

This research has been supported by Czech Science Foundation, project GA ČR No P105/12/G059.

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