

General Hot-Dip Galvanizing

Materials – Technologies – Layer Formation – Properties – Defects

Wolf-Dieter Schulz, Marc Thiele

1st English Edition containing
95 Illustrations and 19 Tables



Specialist publishing house for

- Surface Technology - Plating
- Printed Circuit Boards

and Electronic Assembly Industries

Preface

Hot-dip galvanizing according to EN ISO 1461 is the most effective corrosion protection method for atmospherically stressed components both with regard to the protection period and to the costs. In this regard, no other method gets close to it or even outperforms it.

In this book, the process of hot-dip galvanizing, its technology and here, in particular, layer formation are comprehensively explained, theoretically as well as with the help of practice examples. This enables the reader to recognize causes of faults in hot-dip galvanizing and to eliminate them in the galvanizing practice or to avoid them right from the beginning. In addition, the corrosion behaviour of zinc coatings is being described. A final chapter contains questions and answers, where the reader has the possibility to consolidate his knowledge.

The examples from science and practice given here are the results of almost 40 years of professional experience gained at the Institute for Corrosion Protection Dresden (IKS), from 1990 as managing director and as a nationally accredited reviewer.

I wish to thank the Industrial Association for Hot-Dip Galvanizing in Düsseldorf as well as many peer colleagues, in particular, Mr. *Marberg*, Dr. *Katzung* and Mr. *Huckshold*. My thanks also go to my successor in the management of the Institute for Corrosion Protection Dresden, Dr. *Schütz*, who has always been of support throughout the years of my activity. I am also very indebted to my co-author, Dr. *Thiele*, for the good cooperation and the provision of most of the pictures, which are all obtained from research works and industrial damages.

Wolf-Dieter Schulz
Dresden, Spring 2012

1 Introduction

Hot-dip batch galvanizing acc. to DIN EN ISO 1461 is a highly effective corrosion protection method in particular for atmospherically stressed steel components, but also for tubes, barn equipment, harbour facilities, car and lorry parts and much more, if certain requirements are given or can be met.

In many applications, protection term and useful life of the zinc coating coincide to a large extent, so the specific corrosion protection costs – i.e. the costs per useful life – which include also maintenance and care are low and cannot not be undercut by other corrosion protection methods. In this respect, hot-dip galvanizing is the most efficient corrosion protection measure for atmospherically stressed steel components. Compared to other corrosion protection methods, the requirements concerning corrosion-protective material, design and manufacturing as well as the actual corrosion protection process are partly significantly higher and require the respective company responsible for corrosion protection to have expert knowledge, for example in the technology and, in particular, in layer formation. Here it is important to know the properties of the basic materials, steel and zinc, very well and to be able to assess the layer growth in dependence on the applied steel material, on the zinc melt and on the temperature and to draw the respective conclusions on the quality of the coatings and on changes in the galvanizing technology, which are probably required.

It is only with this knowledge that failures in the galvanizing process can be corrected. It is understood that technological know-how and know-how regarding the corrosion behaviour of zinc coatings, but also general knowledge, are extremely useful.

The consistent approach to the hot-dip galvanizing process made in the following chapters shall provide the reader with information on the aforementioned issue. Here, statements on the galvanizing technology as well as on the individual processes involved in layer formation are made and discussed on the basis of detailed research results. These results have mainly been worked out with the support of the Joint Committee of *Galvanizing e. V.* at the *Institute for Corrosion Protection Dresden* and at the *Institute for Steel Construction, Leipzig*. *Chapter 7* is the heart of the book. It contains a holistic representation of layer growth in dependence on steel composition and galvanizing temperature in connection with the resulting layer structure. Other chapters describe common melts in practical application as well as the corrosion behaviour of zinc coatings and give examples which support the offered topics and theories. Typical defects as well as selected questions and answers to the topics discussed will round out the book.

2 The Materials Steel and Zinc, Flux

The material steel, the zinc melt and the intermetallic phases of both metals formed during batch galvanizing are responsible for the concrete process of the iron/zinc reaction. This reaction determines the properties of the zinc coatings formed with regard to their adhesive strength and layer thickness and also with regard to their appearance and corrosion resistance. A certain, but by no means minor role in layer formation is played by the flux. The following explanations include the facts which are important and necessary for the general understanding and in particular for the hot-dip galvanizer.

Metals have been used by man for about 6000 years. The first centres of metal processing and machining were the Middle East and China. Initially, copper materials like bronze were used and later iron, which was smelted from about 800 B.C. Other metals used at an early stage were silver, lead, tin and mercury and, since the late Middle Ages also zinc, which is the oldest of the *modern* metals. It is still disputed who was the first to represent relatively pure zinc metal; several names are under discussion, as for example *Margrave Löhneiß*. It is certain, however, that the mining regions around Goslar and also in Upper Silesia played an important role in this field.

Most other metals widely used today were only discovered in the 19th century and used for the first time only many years after their discovery. An example for this is titanium, which attracted interest only in the Second World War because of its physical and optimal mechanical properties.

The metal consumption increased strongly, in particular in the 20th century. In the course of the 20th century, for example, the global steel consumption increased by a factor of about twenty to twenty-five, from a bit less than 40 million tons in 1900 to almost 900 million tons in the year 2000. For aluminium, the relative increase in consumption is still stronger. The respective figures for the same period are 5000 tons at the beginning of the century and about 20 million tons at the turn of the millennium. Compared to this, there is only a slight increase in consumption of the non-ferrous metals zinc and copper, the annual consumption of which has only increased by the factor 6 in this period. Today, the annual zinc consumption amounts to about 9 million tons, 90 % of it is related to corrosion protection (e.g. galvanizing, pigments in coating materials, brass and other alloys).

The availability of the currently known metal stockpile, which is supposed to be exploitable with modern means and methods, varies. About 400 years are assumed for iron – after all iron is the fourth most common element in the earth's crust – while it is only 50 years for zinc. However, due to intensive research in the earth's surface and earth's crust, new deposits have been continuously discovered which provide yield rates that exceed the consump-

tion rates to a large extent. In addition, improved methods enable the mining and processing of poorer ores, which improves the prospective availability, too. In this context, it should be mentioned that steel in particular has a very high recycling rate. In Germany, it currently amounts to almost 50 % of the consumption with a further increase being expected.

The partly competing metal aluminium, also interesting for galvanizers, accounts for 6 % to 8 % of the earth's crust and is thus sufficiently available. However, at present the extraction of aluminium from its ore is still extremely energy intensive.

Thus, the high price volatility of the aforementioned metals, which is repeatedly noted at the stock exchange, is not caused by an existential shortage of individual metals, but exclusively by temporary supply bottlenecks or by speculative transactions.

2.1 Designation of Metals According to European Standards

2.1.1 Steel

In the following, the extremely differentiated designation of steels is examined in detail, since the steel composition has a great impact on the layer formation in hot-dip galvanizing. The galvanizer should at least have a rough idea of what is behind a steel name.

The designation of steels has been standardized in Europe for quite some time, inter alia, by the standards DIN EN 10020, DIN EN 10025, DIN EN 10027-1, DIN EN 10027-2. This has put an end to the former national diversity of designations; it should be noted, however, that despite these efforts the designation of steels remains a complex topic for the all-round practitioner. For example, there are different names with often identical symbols and, moreover, additional national standards. And in practice, the former designations are also still in use.

The following descriptions of certain standards are made from a galvanizing point of view and do not claim to provide an exhaustive account of the content of the respective standard.

DIN EN 10020 *Definition and Classification of Grades of Steel* subdivides according to the chemical composition (Point 3) and the main quality grades (Point 4). *Table 1* specifies the boundary between unalloyed and alloyed steels with regard to their chemical composition (melt analysis). Particularly interesting for galvanizing is the silicon content which, with a maximum of 0.6 %, can be very high. Statements regarding the equally important phosphorus and sulphur content are not included in the table.

With regard to the quality grade, the Standard differentiates between unalloyed quality steel and unalloyed special steel. Accordingly, unalloyed quality steels are steels for which special requirements are determined, for example, concerning strength, grain size and/or formability. Unalloyed special steels differ from quality steels in that they have higher purity grades concerning the non-metallic inclusions. Usually, their yield strength, toughness and

**Tab. 1: Boundary between unalloyed and alloyed quality steels
(cast analysis)**

<i>Chemical elements</i>		<i>Limiting value in mass%</i>
Al	(Aluminium)	0,30
B	(Boron)	0,008
Bi	(Bismuth)	0,10
Co	(Cobalt)	0,30
Cr	(Chromium)	0,30
Cu	(Copper)	0,40
Mn	(Manganese)	1,65
Mo	(Molybdenum)	0,08
Ni	(Nickel)	0,30
Pb	(Lead)	0,40
Si	(Silicon)	0,60
Ti	(Titanium)	0,05
V	(Vanadium)	0,10
W	(Tungsten)	0,30
Zr	(Zirconium)	0,05
Others (except C, P, S and N)		0,10

impact strength are closely limited and they are often particularly suitable for cold-forming and welding. The maximum content of phosphorus and sulphur is 0.020 % (cast analysis).

DIN EN 10027-1 *Designation Systems for Steel; Abbreviations, Main Symbols* includes the rules for the designation of steels using letter symbols and figures. The letter symbols and figures are selected in a way that they provide information on essential characteristics, for example on the main field of application, on mechanical and physical properties or on the chemical composition. The symbols of the steels are as follows:

- Category 1: Symbols containing indications regarding use and mechanical or physical properties of the steels
- Category 2: Symbols containing indications regarding the chemical composition of the steels

The main symbols given below are compiled in a well-organized sequence and serve to form the abbreviations of a steel grade according to category 1. It is allowed to add further symbols.

The main symbols consist of prefixed capital letters indicating the steel classes – for example S for construction steels or G for cast steel – with the minimum yield strength in N/mm² for the smallest product thickness (further examples are given in *Table 2*). The additional symbols – subdivided into group 1 and 2 – may contain information or indications regarding weldability and notched bar impact work according to the following *Table 3* or regarding certain properties and applications according to *Table 4*. In older standards, even symbols for the type of deoxidation (DIN EN 10025; 1993) could be appended.

Note: In the last named standard, which is no longer applicable today, the following symbols were used:

- G1 = FU rimmed steel
- G2 = FN rimmed steel not permitted
- G3 = FF fully-killed steel (with > 0.02 % Al or Si)
- G4 = FF fully-killed steel (with > 0.02 % Al and Si).

The additional symbols of special importance in connection with hot-dip galvanizing are summarized in *Table 4*.

Tab. 2: Selected main symbols for groups of steel grades

<i>Letter symbol</i>	<i>Group of steel grades</i>
S	Steels for general steel construction
E	Engineering steels
P	Steels for pressure vessel construction
L	Steels for pipeline construction
B	Concrete reinforcement steels
Y	Pre-stressing steels
H	Cold-rolled flat products of higher-strength steels for cold forming
D	Flat products for cold forming
G	Cast steel

Tab. 3: Additional symbols of group 1 (category 1)

<i>Notched bar impact work</i>			<i>Test temperature</i>
<i>27J</i>	<i>40J</i>	<i>60J</i>	
JR	KR	LR	+20
J0	K0	LO	0
J2	K2	L2	-20
J3	K3	L3	-30
J4	K4	L4	-40
J5	K5	L5	-50
J6	K6	L6	-60

Tab. 4: Important additional symbols of group 2 (category 1)

<i>Additional symbol</i>	<i>Meaning</i>
C	with particular cold formability
D	for hot-dip coatings
E	for enamelling
F	for forging
H	hollow sections
L	for low temperatures
M	thermomechanically rolled
N	normally annealed
P	for sheet piles
Q	hardened and tempered
S	for shipbuilding
T	for tubes
W	weather-proof
an	chemical symbols for additional (other) elements

For a complete steel designation, it is necessary to put the material and the number of the European Standard in front of it. An example of a complete designation of medium tensile construction steel according to category 1 is:

Steel EN 10025 – S420J2C+D

Steel according to DIN EN 10025 for general steel construction, minimum yield strength 420 N/mm², notched bar impact work 27 J at -20 °C, with particular cold formability and – linked with a plus sign – suitable for hot-dip galvanizing.

Note: The abbreviations of steels of group 1, common before the EN-standardization, were often differently composed and partly the code letters had different meanings. In Germany, the code letters St for steel or GS for cast steel were followed, for example, by the minimum tensile strength in kp/mm² or in case of the code letters StE by the minimum yield strength in N/mm².

Since a Europe-wide standardization of all technically and nationally important designations was not possible, national standards continue to apply, which contain further possibilities for designations – in Germany, for example, the DIN V 17006-100: 1999 *Designation Systems for Steels; Additional Symbols*.

The abbreviations according to category 2 consist of main symbols and additional symbols. The steels commonly used for galvanizing usually begin with a C for Carbon and are followed by a number which corresponds to one hundred times the average carbon content in mass percent. Subsequent additional symbols indicate the main purpose of use (*Tab. 5*) and/or provide information on additional elements, possibly followed by a number which indicates the concentration of the alloy element multiplied by 10.

Further additional symbols, for example regarding existing coatings, may be added to the above designations by a plus sign (+). Important selected symbols are given in *Table 6*.

An example for a complete designation of steel according to category 2 is:

Steel EN 10083-1 – C35R+Z

Steel according to DIN EN 10083-1 with carbon content (cast analysis) of 0.35 mass percent and a specified range of sulphur content, hot-dip galvanized.

DIN EN 10027-2 *Designation System for Steels; Numbering System* indicates the steel grades according to a numbering system. It comprises all steels included in European Standards and supplements the abbreviations according to DIN EN 10027-1. About 2000

Tab. 5: Selected additional symbols of group 1 (category 2)

<i>Additional Symbol</i>	<i>Meaning</i>
C	for cold forming
D	for wire drawing
E	specified maximum sulphur content
R	specified range of sulphur content
S	for springs
U	for tools
W	for welding wire
G	other features

3 The Technology of Hot-Dip Galvanizing

In the following chapter, layer formation in hot-dip galvanizing will be described from the technological point of view, since apart from the chemical composition of the steel to be galvanized, the zinc melt, and the galvanizing temperature, the quality of the zinc coatings achieved also depends on the hot-dip galvanizing technology. Although this book deals exclusively with hot-dip batch galvanizing acc. to DIN EN ISO 1461, a short overview of other common hot-dip coating methods is given first for the sake of completeness and comparability.

3.1 Process Variants

A distinction is made between

- continuous methods (for steel strips and wire)
- discontinuous methods
(for profiles cut to length, construction parts and small parts)

All cases require the iron or steel substrate to be free from similar substances (rust, scales) and dissimilar substances (oils, fats, coating residues, welding residues, molding sand residues on cast parts, residues of drawing aids and the like), i.e. hot-dip galvanizing generally requires surface preparation just like any other surface coating method.

The kind of surface preparation depends on both process and product. It may be an annealing treatment (common for continuous methods), cleaning by means of aqueous solutions (common for discontinuous methods), mechanical cleaning (e.g. blast-cleaning) or a combined aqueous/mechanical cleaning.

3.1.1 Continuous Hot-Dip Galvanizing of Steel Strips and Steel Wire

In modern continuously working steel strip galvanizing plants, the strip runs from the coil through an annealing furnace with combustion zone, oxidation zone and reduction zone. Afterwards, it is fed into the zinc melt bath under protective atmosphere. Having left the zinc melt, the steel strip passes stripper rollers or nozzles, which smooth out the zinc coating. Before the steel strip is recoiled, it passes the cooling section. To ensure the continuous passage through the annealing furnace and the zinc melt, loop pits are arranged in front of

and behind the zinc bath, in which the required strip reserve has its place. This enables the beginning of the strip to be welded to the end of the previous coil at the beginning of the line and then to be separated at the end of the line (Fig. 15). Throughput speeds of up to 200 m/min and more are possible according to the thickness of the strip and the desired thickness of the coating.

The strip width is usually up to 1650 mm and the sheet thickness up to 3 mm. The thickness of the zinc coating is variable in a wide range (approx. 5 to 40 μm), the thickness is mostly indicated in g/m^2 on both sides, i.e. in case of a coating with the same thickness on both sides 10 μm correspond to a zinc layer of about 140 g/m^2 . Process variants also allow one-sided galvanizing or galvanizing with different coating thicknesses on both sides of the steel strip. It is also possible to specifically influence spangle formation on the solidified coating. Figure 16 shows a microscopic section through a continuously hot-dip galvanized coating.

In consequence of the high throughput rate of the strip, the reaction period between steel and zinc melt is very short, which results in the formation of extraordinarily thin iron-zinc-

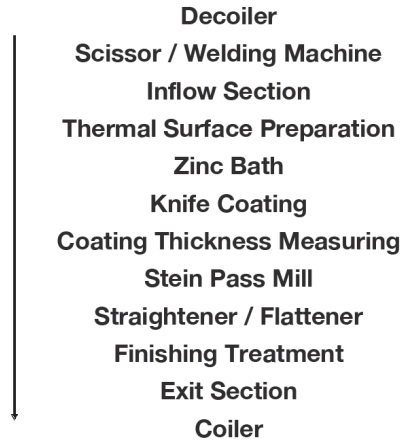


Fig. 15: Cycles and machine equipment (selection) for the application of hot-dip coatings on steel strips in continuous flow, schematically

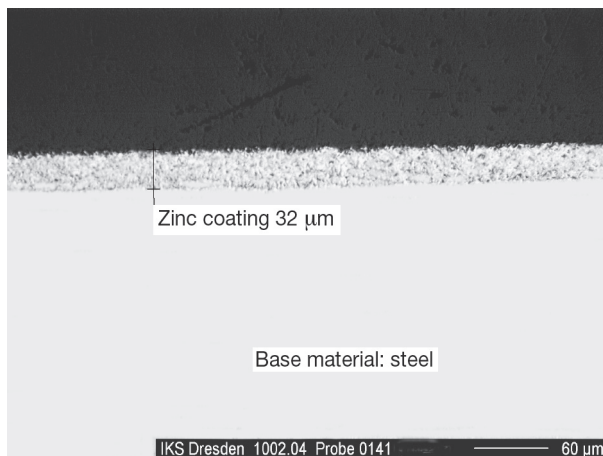


Fig. 16: Microsection through a zinc coating on continuously galvanized thin sheet, coating thickness approx. 30 μm

alloying phases, which are usually not identifiable in the microsection. The predominant part of the coating consists of zinc according to the composition of the zinc melt. This bears the advantage of good cold formability of the hot-dip galvanized strip, which depends exclusively on the steel grade. According to the requirements, the strip is temper-rolled, straightened, chemically passivated and/or oiled.

A special variant of continuous galvanizing is the galvannealing (a combination of the words galvanizing and annealing), where the continuously galvanized sheet steel is tempered in the coil or in continuous passage (e.g. still in the galvanizing line). During this homogenization process, the whole zinc coating is transformed specifically into iron-zinc-alloy phases, whereby the surface has a mat grey appearance. This product is particularly suitable for applications that require good weldability, varnishing, and adhesive properties.

DIN EN 10346 informs about the availability (rolls, foils, split strip, rods, steel types), the coating types (zinc, zinc-iron-alloys), the zinc coatings, the coating finish (usual spangle, small spangle, zinc-iron-alloy), the kind of surface (usual surface, improved surface, best surface), the surface treatment (chemically passivated, oiled, chemically passivated and oiled, untreated) and the processing. For some decades, also alloys of approx. 55 % aluminum by weight, 43.4 % zinc by weight and 1.6 % silicon by weight have been used as coating metals, which came on the market as *Galvalume* (AZ), but which, depending on the license holder, is also known under numerous other names. Another development is the application of alloy composed of approx. 95 % zinc by weight, 5 % aluminum by weight and traces of the composition metals Cer and Lanthanum, known as *Galfan* (ZA). Furthermore, there is the zinc alloy AS with a silicon content of about 10 %, for example suitable for higher thermal stress. The application process of these Al-Zn or Zn-Al coatings basically corresponds to *Figure 16*, however the galvanizing temperature is partly considerably increased (AZ at 565 °C) due to the proportion of aluminum and the formation of eutectic mixtures, but partly also reduced (ZA at 385 °C).

Advantages of these alloy coatings of zinc and aluminum are the partly improved deformation behavior and higher corrosion resistance in case of thermal stress and atmospheric corrosion load.

The fields of application of the strip-galvanized or alloy-galvanized thin sheets, often with additional strip coating (DIN EN 10169-1; -2 as well as DIN 55634), are primarily found in the construction industry, in car manufacturing and the domestic appliance industry as well as in engineering.

Wire galvanization (DIN EN 10264-1 to -3) takes also place in continuously operating lines, where the process flow is usually a mixture of the process flows shown in *Figure 15* and *17*.

3.1.2 Hot-Dip Galvanizing

Common batch galvanizing occurs discontinuously and follows the principle process flow shown in *Figure 17*, which nowadays usually means *dry galvanizing process*. Only in exceptional cases the original *wet galvanizing method* is applied. The high-temperature galvanizing at 530 °C to 600 °C, mainly used for thinner and mating coatings on small parts, is mainly carried out by means of dry galvanizing.

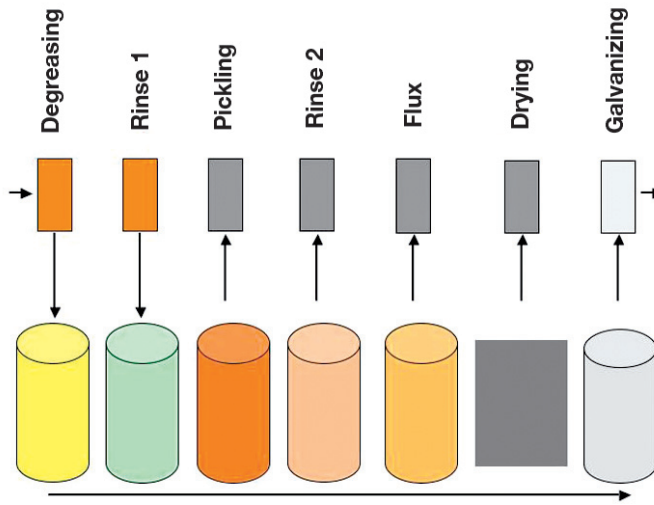


Fig. 17: Schematic process of batch galvanizing according to DIN EN ISO 1461

Dry galvanizing process: In dry galvanizing the items, which are flux-loaded after having been separately dipped in an aqueous flux bath, are dried in a drying furnace at temperatures between 60 °C and 120 °C prior to galvanizing and are then immersed in the zinc melt. The advantage of this method is the technically simple handling of large components and the fact that the galvanized products are relatively free from flux residues.

Wet galvanizing process: In wet galvanizing – partly applied to tubes, containers and hollow bodies – part of the zinc melt surface is covered with flux, e.g. in a profile frame. Thus the component to be galvanized is immersed into the zinc melt in a wet state and, upon completion of the galvanizing process, withdrawn beyond the flux-covered area. The advantage of this method is that the parts do not require drying before they are galvanized, which may be convenient for hollow bodies and tubes. A disadvantage is that the aluminum content of the zinc melt must not exceed 0.002 %, since otherwise defects occur (black spots). In addition, dross formation is higher than in the dry galvanizing process.

3.1.3 Special Processes

Tube galvanizing, standardized in DIN EN 10240, occurs analogous to *Figure 17* in partly automated plants. The process-related difference is the fact that flux tanks and drying furnaces are usually omitted. Therefore, the tubes are not fed into the zinc bath with a dried flux film (dry galvanizing), but arrive from the rinsing bath in wet state and are fed into the zinc melt through a flux cover (zinc chloride-ammonium chloride mixture, foamed with glycerin) floating on the zinc melt (wet galvanizing).

During the withdrawal process (in a flux-free surface area of the zinc melt), the tubes pass through a ring nozzle, in which excessive zinc is blown off from the outer surface of the

4 Layer Growth

4.1 Conventional Zinc Melt

Depending on galvanizing temperature and time as well as on the steel composition, hot-dip galvanizing of common structural steels in conventional zinc melts, mostly alloyed with almost 1 % lead, results in zinc coatings with great differences in layer thickness, growth, crystalline structure and appearance. The differences in reactivity of the individual steels, which are responsible for that, are related to their silicon content and partly to their phosphorus content and they are not without problems for hot-dip galvanizing, since a lot of coating properties are associated with them.

Over the years, a wealth of empiric material has been compiled [2] as well as [35-42] regarding the effect of these influential factors on the formation of hot-dip galvanized coatings, however, holistic systematization principles have been lacking for a long time. Not even the interpretation given by *Horstmann* [43], according to which the formation of the zinc coating derives only from thermodynamic equilibrium states of the reactants can explain a number of phenomena occurring in hot-dip galvanizing.

In [44], first evidence was found that hydrogen dissolved in steel to be galvanized plays a role in the formation of the zinc coating, which was not supposed till then, or can provide an explanation that is worth being discussed. However, this phenomenon is only described for galvanizing in the normal temperature range, i.e. up to about 460 °C. For higher temperature ranges, and in particular for high-temperature galvanizing, there is still no suitable explanation.

In this chapter, works are described and discussed which have been carried out over a number of years with the objective to formulate a comprehensive model concept on layer formation in hot-dip galvanizing under kinetic (growth rate, transport barriers) and thermodynamic (crystalline structure) aspects. As a result of these works, it is possible to explain the differently reactive behavior of structural steels, in particular in conventional zinc melts between 435 °C and 620 °C in a holistic and practically applicable way. The basis for the processes in hot-dip galvanizing is the reaction between zinc and iron or steel. Through reciprocal diffusion, intermetallic Fe-Zn-compounds are formed, which are also called phases. A comprehensive overview is given by [45]. He assumes that the reaction between iron and zinc always proceeds towards the thermodynamic equilibrium given in *Figure 18*, which shows the dependence of the chemical composition on temperature [45].

Here, reaction-kinetic aspects are not considered.

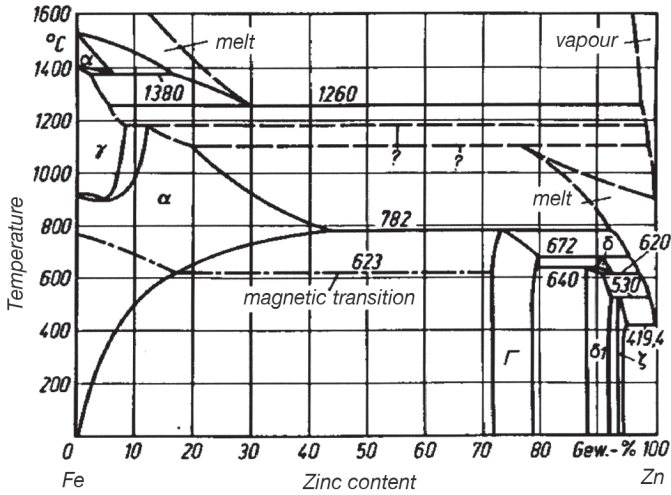


Fig. 18: Iron-zinc phase diagram (simplified) acc. to [45]

Already in 1940, *Bablik* made a significant observation in hot-dip galvanizing [46]. He noticed that between 430 °C and 490 °C, layer growth on rimmed, low-silicon steels followed a parabolic time law, from 490 °C a linear time law and from 530 °C again the parabolic one. When working on the reasons of this strong temperature dependence of layer growth, *Horstmann* [43] realized that during the reaction of pure α -iron with zinc at temperatures of up to 490 °C compact alloy layers form which firmly adhere to the iron, consisting of a very thin Γ -layer, an overlying thicker δ_1 -layer and an adjacent ζ -layer, from which crystals are permanently dissolved out and float off into the melt. Between 490 °C and 530 °C, linear layer growth occurs due to the change of the reaction type, since instead of a compact δ_1 -layer only a δ_1 -layer develops, which is cracked inside, so that the total growth rate of the coating is very high. Over 530 °C, besides the Γ -phase only the δ_1 -phase is resistant, compact and dense, thus the reaction type changes again to parabolic diffusion-controlled growth.

Apart from the immersion time and, of course, from the melting temperature, layer growth is mainly dependent on the chemical composition of the steel. Here, the clearly dominating factor is its silicon-content. Furthermore, a clear effect is at least partially attributed to phosphorus. Recent studies by *Katzung* and *Rittig* [40] show a significant layer-thickness increasing influence of phosphorus – in particular in silicon contents below 0.03 % – i.e. at very low silicon levels. With increasing silicon content, the influence of phosphorus on the layer thickness of zinc coatings decreases. Below 0.02 % phosphorus, its influence can principally be neglected.

The effect of silicon in the steel was first described by *Bablik* [47], *Sandelin* [48] and *Sebisty* [49]. They discovered that silicon triggers layer growth according to the linear time law, except for a parabolic – i.e. inhibited – layer growth in the Sebisty-area at galvanizing tem-

peratures of 450 °C to approx. 470 °C, in literature usually referred to as the Sebisty-effect. *Figure 19* reflects this state of knowledge in the marked areas with linear layer growth in a diagram by *Horstmann* [43].

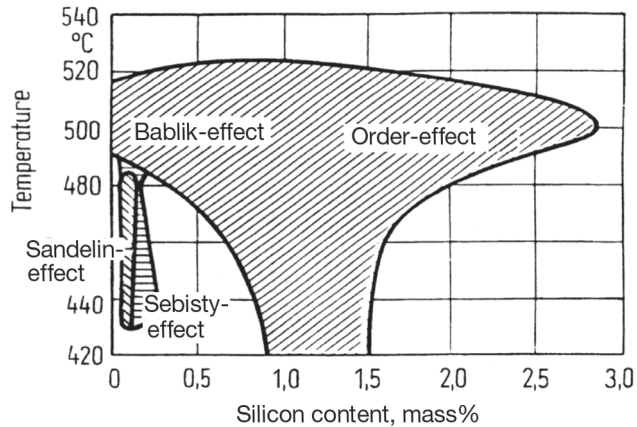


Fig. 19: Areas with linear layer growth [43]

With precise scanning electron microscope analyses, *Schubert* and *Schulz* [14] found out that, depending on their silicon contents, steels outgas differently when hot-dip galvanized (*Fig. 20*). For low-phosphorus steels, the authors established the following hypothesis for the processes in hot-dip galvanizing in normal temperature ranges between 440 °C and

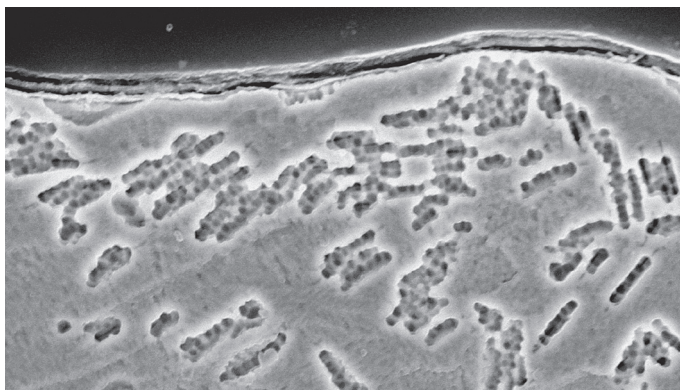


Fig. 20: Scanning electron microscope image showing concatenated pore chains in the zinc coating typical for absorbed molecular hydrogen [14]

460 °C and in conventional iron and lead-saturated zinc melt, which shall be briefly mentioned here for the better understanding of the ensuing explanations:

Low Silicon Range (< 0.03 % Si)

The α -iron surface zone of low-silicon steel, previously mostly called rimmed steel, leads to initially high reactivity between steel and zinc melt and thus to the fast formation of a δ_1 -layer. In the course of the reaction, the material bond between the steel and the δ_1 -layer breaks off leaving a gap between steel and coating. This heavily impedes mass transport and the galvanizing rate decreases to the value typical for such steels. Reason for this behavior is either the inability of the compact δ_1 -phase to follow a changing phase boundary or gases like hydrogen, which diffuse in a decelerated way to the surface into the heated boundary layer (on the solubility of hydrogen in dependence on temperature, see *Chapter 2*) and, due to a pressure build-up (recombination of atomic hydrogen to molecular hydrogen) adversely affect the bond of the rigid and thick δ_1 -layer with the steel base material when effusing. In the further course of the galvanizing process, the gap between steel substrate and zinc coating manifests itself, which causes the transition to the parabolic time law of layer growth.

Sandelin-Range (0.03 % to 0.12 % Si)

Due to the lack of a low-gas boundary layer of α -iron on silicon-killed steel, the formation of compact δ_1 -phase and gap at the beginning of the galvanizing process does not occur. The coating grows evenly and quickly according to a linear time law. At the same time, hydrogen loss sets in immediately after the steel is immersed into the melt. This causes a rapid removal of the Fe/Zn-alloy layers from the reaction zone of steel/coating and a loosening of the developing structure. The zinc melt temperature has great influence on the coating thickness. With decreasing temperature, the Sandelin-peak (Sandelin-effect) disappears due to the reduced hydrogen effusion from the steel and the generally decelerated reaction kinetics. The removal of the alloy particles – thus of the reactants – from the reaction zone is delayed and higher-density alloy layers can be formed, which impede the growth of the coating.

Sebisty-Range (0.12 % to 0.28 % Si)

In the Sebisty-range, the temperature dependence of the layer formation is of utmost importance. It can be seen from *Figure 19*, and even clearer from *Figure 24* that the galvanizing rate surprisingly decreases with increasing melting temperature. At 460 °C, it only amounts to approx. 20 % to 30 % of its value at 440 °C (Sebisty-effect). The effect is explained by the fact that from 450 °C, the δ_1 -phase and a kind of gap become visible in the phase boundary range, which impede material transport between steel and zinc coating, which in turn decelerates layer growth.

High silicon range (> 0.28 % Si)

Due to the increased silicon content of the steel, the propensity to hydrogen effusion of the steel surface has strongly decreased. Thus the structure of the zinc coating in the high-silicon range is no longer influenced by the effusing hydrogen, but only by the chemical