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DESCRIPTION OF STRUCTURE OF Fe-Zn INTERMETALIC COMPOUNDS PRESENT IN HOT-DIP GALVANIZED COATINGS ON STEEL

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The article is describing formation, composition, morphology and crystallographic characteristics of intermetalic compounds Fe - Zn present in the coating formed during the process of low-temperature hot-dip galvanizing of carbon steels. In mutual confrontation we introduce older bibliography and results of latest modern researches based on combination of most precise analytical methods.

Key words: hot – dip galvanized steel, intermetalics Fe – Zn, binary phase diagrams, group of symmetry

INTRODUCTION

During hot-dip galvanizing in the zinc melt (450 - 470 °C), a Fe - Zn coating grows on galvanized parts as a result of rather complicated process of atomic diffusion of both metals with formation of elementary intermetallic bonds and subsequent phase transformations. These processes are running in the surface layer of galvanized metal, then on the interface of the surface of metal and melt of the zinc and finally in the actual melt close to the galvanized part. Depending on composition of the steel, temperature and composition of the electrolytic bath, thickness of the galvanized part, duration of the stay in the bath, surface condition and method and speed of cooling a coat is formed consisting of various intermetallic compounds of Fe - Zn.

Layers consisting of these compounds have different composition and thickness. They are usually marked with Greek alphabet letters, i.e. gamma (Γ), gamma$_1$ (Γ_1), delta (δ), zeta (ζ), sometimes eta (η). Individual phases differ significantly not only by composition and morphology of the grain but also by mechanical characteristics. Formation of individual phases in the coating is ruled by the binary phase diagram Fe - Zn. The binary phase diagram Fe - Zn is shown on the Figure 1. Detail of the diagram marking the existence of individual intermetallic compound is shown on the Figure 2. Formation of individual phases is based only on diffusion processes and sometimes the individual phases are visible only after thermal processing of already hot-dip galvanized steel [1,2].

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DESCRIPTION OF INIDIVIDUAL INTERMETALLIC PHASES

Iron content in the alloy coating is declining towards the outer surface. Indeed, definition of composition, structures of individual intermetallic phases and their morphology in the hot-dip galvanized coating on the steel had become more precise in the course of time. We introduce complete summary assessing individual phases based on an older literature but also results of most modern researches [1].

Eta (η) phase

The upper layer of so called η-phase is consisting practically of the pure zinc and is formed by simple solidification of the zinc melt. From the metallurgic aspect, however, this phase is defined as a solid substitutional solution of iron in the zinc (content of the iron is about 0,03 wt. %). Zinc crystallizes in the hexagonal system (hcp) and is characterized in relatively high toughness under common temperatures and low hardness [2].

Zeta (ζ) phase

Intermetallic phase zeta (ζ) can be stoichiometrically generally defined as $FeZn_{13}$. Content of the iron in this phase is about 5 – 6,2 wt. %. It crystallizes in the coating in base centered monoclinic system with the C2/m group of symmetry [3]. Brown [4] assumed that the oblique angle between cubic body centered vectors ***a*** and ***b*** is β = 127,30 ° (cubic body parameters *a* = 1,3424 nm, *b* = 0,7608 nm, *c* = 0,5061 nm). On the contrary, Gellings [5] attached the cubic body a lower angle β = 100,53 ° and the cubic body parameter *a* = 1,0862 nm. Belin [6] specified the projection from [4] by placing the centring Fe atom in the centric position of the cubic body parameter *c* (position 2*c*). The only iron atom is surrounded with 12 atoms of zinc located in an-

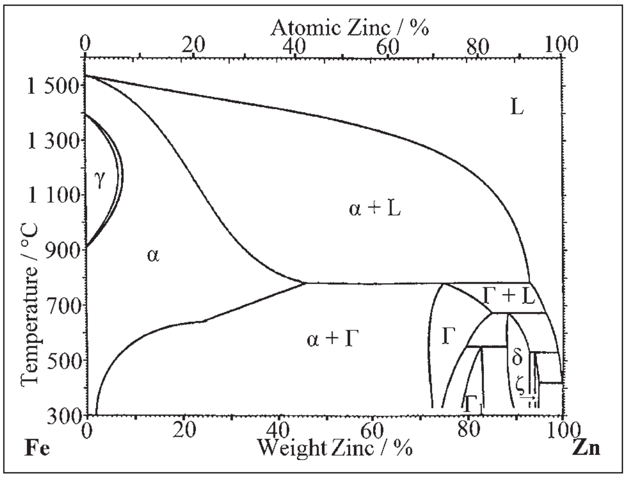

Figure 1 Phase diagram Fe - Zn [3]

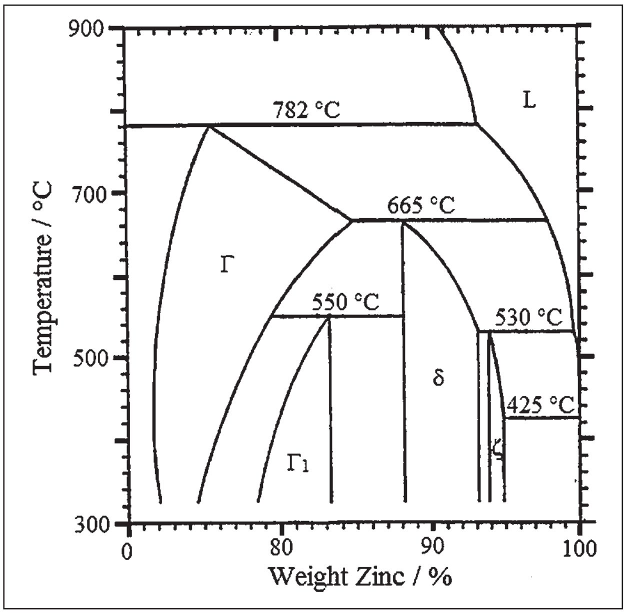

Figure 2 Section of phase diagram of Fe - Zn alloys with high ratio of zinc [3]

gular points of slightly deformed icosahedron. These icosahedrons are grouping in full hexagonal arrangement. Okamoto [7] further specified connection of icosahedrons of the phase ζ – $FeZn_{13}$ sharing of zinc atoms in positions 2*a* along the axis *c*.

This phase is formed by peritectic reaction {1} between delta phase (δ) and zinc melt (L) under the temperature 530 ± 10 °C. It was proved that it is formed between the phase eta (η – solid Fe solution in the zinc) and delta phase (δ) [3].

$$\delta + L \rightarrow \zeta \qquad (1)$$

This phase has typical prismatic morphology in the coating of hot-dip galvanizing. Sometimes from this continuous prismatic structure a separately formed fine crystals unreel from this zeta phase ($FeZn_{13}$) growing perpendicularly from the surface of coated steel. Formation of fine crystals is subject to sufficient saturation of the zinc melt with iron atoms otherwise the continuous prismatic structure of this phase is formed as superior one [1,3].

Delta (δ) phase

In case of delta (δ) phase the existence of two different crystallic structures marked as δ_{1k} (or δ) and δ_{1p} (or δ_1) is discussed. Equivalent crystall structures to these phases are $FeZn_7$ (δ_{1k}) or $FeZn_{10}$ (or also $Fe_{13}Zn_{126}$). The latest works support the existence of both different delta phases [7-9]. On the contrary, Bastin [10] with help of XRD described the only delta phase stable up to the temperature of about 670 °C. The content of iron in delta phase is 7 – 11,5 wt.%. Latest scientific works clearly confirm the existence of two different phases [9, 11]. Both above mentioned intermetallic compounds form the hexagonal crystal structure with the group symmetry $P6_3$/mmc or close to it. Among two delta phases are singularities from the view of crystallography. Belin [12] described structure of the phase marked δ_{1p} with detailed XRD analysis on the monocrystal of this phase. Vast hexagonal crystallic cubic body is formed in total by four polyhedrons and isolated zinc atoms. Polyhedrons consist mainly of regular icosahedrons centered by zinc atoms, other majority crystal structure is the capped pentagonal prism coordinated by zinc atoms. From minority structures it is the irregular icosahedron coordinated by zinc atoms but in angular points filled with iron atoms and finally by the icosioctahedron filled with and coordinated by zinc atoms. Irregular polyhedron is isolated in the structure whilst other formations share zinc atoms on angular points or through sides. Belin attributed the intermetallic a summary formula $FeZn_{10}$. Okamoto [11] specified this already complicated structure with combined analysis XRD with transmission electron microscopy and stated that the phase consist of isolated zinc atoms and polyhedrons. Regular icosahedrons are present and filled with zinc atoms but coordinated by iron atoms and also these regular formations coordinated and filled with zinc atoms. Particularized structure is also described by irregular icosahedron centered by iron atoms with angular point filled with zinc and finally the icosioctahedron coordinated and filled with zinc atoms. Irregular icosahedrons are isolated in the structure whilst other polyhedrons share zinc atoms in angular points or in side positions. Okamoto assigned the intermetallic a summary formulation $Fe_{13}Zn_{126}$ instead of the older expression $FeZn_{10}$. Cubic crystal lattice of the phasee δ_{1p} can be assigned following lattice parameters *a* ~ *b* ~ 1,28 nm; *c* ~ 5,73 nm.

Structure of the phase δ_{1k} is similar to the phase $\delta_{1p,}$ but even more large-sized. It is again a hexagonal crystal structure with triplex periodic of crystallic formations along the axis comprising of one-dimensional irregular arrangement of structural units (called order-disorder (OD) packets) along the axis c. This complicated phase can be assigned a group symmetry $P6_3$/mcm [9].

Generally both phases are formed by peritectic reaction {2} between gamma phase (Γ) and zinc melt (L) under the temperature of about 665 °C [3].

$$\Gamma + L \rightarrow \delta_{1k} / \delta_{1p} \quad (2)$$

In the hot-dip galvanized zinc coating, the δ_{1p} phase has rather palisade character and usually has higher thickness than the phase δ_{1k}, which is on the contrary rather compact. Sometimes it is assumed that texture of the phase δ_{1p} does not have to be necessarily basaltic, or crystals might grow longitudinally with the surface of coated metal [13]. Both phases are after the actual zinc dipping usually mutually unidentifiable, resolution can be more often found after a specific annealing. [9].

Gamma$_1$ (Γ_1) phase

It is the top phase from the gamma group. It can be stoichiometrically expressed as Fe_5Zn_{21} [3] (or rather $FeZn_4$ [14], however most recently as $Fe_{11}Zn_{40}$ [8]). It crystallizes in the face centered cubic system (fcc) with iron content 17-19,5 wt. %. Unlike to previous phases it is formed by mutual reaction between two intermetallic phases, i.e. gamma (Γ) and delta (δ) under the temperature 550 ± 10 °C (peritectic reaction). Course of reaction is expressed by the equation {3} [3].

$$\Gamma + \delta \rightarrow \Gamma_1 \quad (3)$$

This phase is forming a continuous transition between phase δ and gamma phases (Γ) with higher iron content. It is easily observable on zinc dipping samples subjected to annealing under lower temperatures for longer time periods [1]. It was proved that it is really a stable regular phase, from the aspect of crystal structure different from the group of phases Γ. It was also proved that the lattice parameter of Γ_1 phase is about double (a ~ 1,798 nm) compared to parameter of the phase Γ (a ~ 0,895 nm). Unlike phases η, ζ, δ_{1k} a δ_{1p} this phase and also the phase Γ are close with its composition to the α(Fe). However during formation of the coating on the steel substrate the cubic lattice is transformed from bcc to fcc thus enlarging the basic parameter (transition from Γ to Γ_1) [15,16].

Gamma (Γ) phase

This phase is usually assigned the intermetallics with sumary formulat Fe_3Zn_{10} but also the existence of intermetallics was proved with even higher ratio of iron atoms in the structure (Fe_4Zn_9 [14], or $FeZn_3$ [17]), which is also part of the coating. Both mentioned phases are crystallizing in the body centered system (bcc), with total content of iron atoms 23,5 – 28 wt.%. The Γ phase is formed by peritectic reation between α-ferite and zinc melt under the temperature of 782 °C (see {4}) [3].

$$\alpha(\mathrm{Fe}) + \mathrm{L} \rightarrow \Gamma \quad (4)$$

In the basic crystal lattice the Γ phase is very similar to the structure α(Fe) (both crystallizing in bcc). It was discovered that the basic lattice parameter a in the cubic body of intermetallic phase Γ is about three times bigger (a ~ 0,895 nm) than in the cubic body α(Fe) (a ~ 0,287 nm) [15].

CONCLUSION

From the aspect of the structure the most complex phase in the hot-dip galvanized zinc coating on the steel is the delta phase (δ), crystallizing in hexagonal crystal system similarly to zinc. From results of latest researches follows that two δ phases exist, i.e. δ_{1k} and δ_{1p}, which must be distinguished. Similar case is the gamma$_1$ (Γ_1) phase differing from gamma (Γ) phase not only by double cubic body parameter but also by transformation of the cubic body from bcc to fcc. Both phases therefore necessarily differ by mechanical properties. Structure of zeta (ζ) phase was only specified by the latest research and it was confirmed that it is only one unique phase crystallizing in monoclinic crystallic system atypical for metals.

Acknowledgments

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REFERENCES

[1] V. Kuklík, J. Kudláček, Žárové zinkování, 1th AČSZ, Praha 2014.

[2] C. E. Housecroft, A. G. Sharpe, Inorganic Chemistry, 4th Pearson Education, Fairford 2012.

[3] A. R. Marder, The metallurgy of zinc – coated steel, Progress in Materials Science 45 (2000), 191-271

[4] P. J. Brown, The structure of the ζ - phase in the transicion metal – zinc alloy systems, Acta Crystallographica 15 (1962), 608.

[5] Gellings P. J., de Bree E.W., Gierman G., Synthesis and Characterization of Homogeneous Intermetallic Fe-Zn Compounds, Part 2., International Journal of Materials Research 70 (1979), 5, 315-317.

[6] Belin R., Tillard M., Monconduit L., Redetermination of the iron-zinc phase $FeZn_{13}$, Acta Crystallographica (Section C) 56 (2000), 267-268.

[7] N. L. Okamoto, M. Inomoto, H. Adachi, H. Takebayashi, H. Inui, Micropillar compression deformation of single crystals of the intermetallic compound ζ – $FeZn_{13}$, Acta Materialia 65 (2014), 229-239.

[8] N. L. Okamoto, D. Kashioka, M. Inomoto, Compression deformability of Γ and ζ Fe – Zn intermetallics to mitigate detachment of brittle intermetallic coating of galvannealed steels, Scripta Materialia 69 (2013), 307-310.

[9] N. L. Okamoto, A. Yasuhara, H. Inui, Order-disorder structure of the δ_{1k} phase in the Fe – Zn system determined by scanning transmission electron microscopy, Acta Materialia 81 (2014), 345-357.

[10] G. F. Bastin, F. J. J. van Loo, G. D. Rieck, On The δ-Phase in The Fe-Zn System, Metallkunde 68 (1977), 359-361.

[11] N.L. Okamoto, K. Tanaka, Structure refinement of the δ_{1p} phase in the Fe-Zn system by single-crystal X-ray diffraction combined with scanning transmission electron microscopy, Acta Crystallographica B70 (2014), 275-282.

[12] C. H. E. Belin, R. C. H. Belin, Synthesis and Crystal Structure Determinations in the Γ and δ Phase Domains of the Iron-Zinc System: Electronic and Bonding Analysis of $Fe_{13}Zn_{39}$ and $FeZn_{10}$, a Subtle Deviation from the Hume-Rothery Standard?, Journal of Solid State Chemistry 151 (2000), 85-95.

[13] V. Rangarajan, C. C. Cheng, L. L. Franks, Texture in the δ-($FeZn_{10}$) phase formed in galvanneal coatings, Surface and Coatings Technology 56 (1993), 209-214.

[14] X. Hu, T. Watanabe, Relationship between the Crystallographic Structure of Electrodeposited Fe-Zn Alloy Film and Its Thermal Equilibrium Diagram, Materials Transactions 42 (2001), 1969-1976.

[15] J. Yu, J. Liu, W. Zhou, J. Zhang, J. Wu, Cross-sectional TEM observation of iron – zinc intermetallic Γ and Γ_1 phases in commercial galvannealed IF steel sheets, Materials & Design 28 (2007), 249-253.

[16] A. S. Koster, J. C. Schoone, Structure of the Cubic Iron-Zinc Phase $Fe_{22}Zn_{78}$, Acta Crystallographica B37 (1981), 1905-1907.

[17] X. Hu, X. Zhou, Effects on Steel Coatings Microstructure on Weldability in Resistance Spot Welding of Galvannealed Steel Sheets, Advanced Materials Research 139 (2010), 610-613.

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