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FORMATION OF OUTBURST STRUCTURE IN HOT DIP GALVANNEALED COATINGS ON IF STEELS

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Outburst structure in two industrially produced hot dip galvanized interstitial free steel sheets for automotive industry after additional annealing has been examined. Ti IF steel was found to form weak outburst structure in the early stage of annealing, followed by frontal growth of Fe-Zn phases during further heating. The high reactivity of this steel was confirmed by rapid Γ-phase formation. Under the same conditions, Ti-Nb-P IF steel exhibited frontal growth of Fe-Zn compounds without Γ-phase formation due to relatively high phosphorous content, which is known as inhibitor of Fe-Zn reaction, but simultaneously significant occurrence of undesired outburst structures was recorded. It was assumed that the phosphorous content was insufficient and/or ferrite grain was very fine.

Key words: *galvanizing, galvannealing, Fe-Zn intermetallic compounds, outburst structure*

Stvaranje ljuskave strukture u zaštitnim prevlakama toplo cinčanih IF čelika. Ljuskave strukture na dva toplo pocinčana IF čelična lima za automobilsku industriju ispitana su nakon dodatnog žarenja. Ustanovljeno je da IF Ti-čelik obrazuje slabo ljuštena strukture u samoj fazi žarenja nakon koje slijedi čelni rast faza Fe-Zn tijekom zagrijavanja. Visoka neaktivnost tog čelika potvrđena je brzim obrazovanjem Γ faze. Pod istim takvim uvjetima čelik Ti-Nb-P pokazao je površinski rast spojeva Fe-Zn bez obrazovanja Γ faze zbog relativno visokog sadržaja fosfora koji je poznat kao inhibitor reakcije Fe-Zn, ali je simultano uočena i značajna pojava neželjenih naljuštenih struktura. Motri se, da je sadržaj fosfora bio nedovoljan i/ili je zrno ferita bilo vrlo sitno.

Ključne riječi: *galvaniziranje, galvano žarenje, Fe-Zn međukovinski spojevi, ljuskava struktura*

INTRODUCTION

Rapid development of automotive industry brings also increased requirements for sheets properties, involving relatively high strength and good formability together with excellent corrosion resistance. Increasing requests for corrosion resistance lead to the production of coated car parts, protected mainly by zinc coatings. Whereas, majority of European producers of passenger cars use preferentially pure zinc for coatings [1], Japan and American automobile factories are oriented in the first place on Zn-Ni, Zn-Fe or Zn-Al alloyed coatings. Fe-Zn coatings obtained by heat treatment of galvanized steel sheets, containing 8 - 12 % Fe found practical application in production of steel sheets for autobodies. By means of diffusion between zinc and steel substrate initiated by annealing, nearly pure zinc η phase in the coating is transformed into Fe-Zn alloyed coating, containing various Fe-Zn intermetallic compounds. Individual phases, present in the galvannealed coating can be seen in the right bottom corner of Fe-Zn binary diagram, Figure 1.

To improve the properties of hot dip coatings, aluminum is added to the zinc bath. One of the most important roles of Al, whose content ranges from 0,1 - 0,2 wt. %, in the zinc bath is to form thin Fe-Al interfacial layer immediately after dipping the steel sheet in the zinc bath. This inhibition layer acts as a diffusion barrier during the initial stages of galvannealing, preventing the interactions between Fe and molten zinc and inhibiting the formation of Fe-Zn compounds. Inhibition layer breaks down and Fe-Zn compounds form during galvannealing. The final microstructure of the coating forms as a result of solid-state interdiffusion process of Fe and Zn during the isothermal holding time in the galvannealed furnace [2 - 4].

Reaction between Fe and Zn on the ferrite grain boundaries depends on the ability of alloying elements to segregate. These elements can be divided into two groups. The first group consists of elements segregating at grain boundaries (e.g. C, P) and the second group consists from

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compounds forming elements (e.g. Ti, Nb), segregating inside the grains and leaving purified grain boundaries. Such grain boundaries are thermodynamically more active than ferrite grains themselves. Therefore accelerated reaction between Fe and Al is induced, resulting in a drop of Al content in the galvanizing bath near the grain boundaries of the steel surface, consequently nucleating Fe-Zn intermetallic compounds formation. Local growth of Fe-Zn intermetallic compounds is possible on the surface of steel material, phenomenon is called outburst [5] and is characterized by following manner. During galvanizing or galvannealing, liquid zinc penetrates through inhibition Fe-Al layer and diffuses into the pure boundaries of ferrite grains. Formation of Fe-Zn compound in the grain boundary causes volume expansion simultaneously with microcracks formation in the thin Fe-Al layer. Outburst is interpreted like a direct reaction between Fe and liquid zinc. The occurrence of outburst structure is directly connected with presence of Fe-Al layer [6, 7]. This occurrence is undesirable, because it has a negative influence on the surface finish of the zinc coating [8]. It has been proved, that larger ferrite grain size increases stability of Fe-Al inhibition layer and incubation time of Fe-Zn phases formation [6].

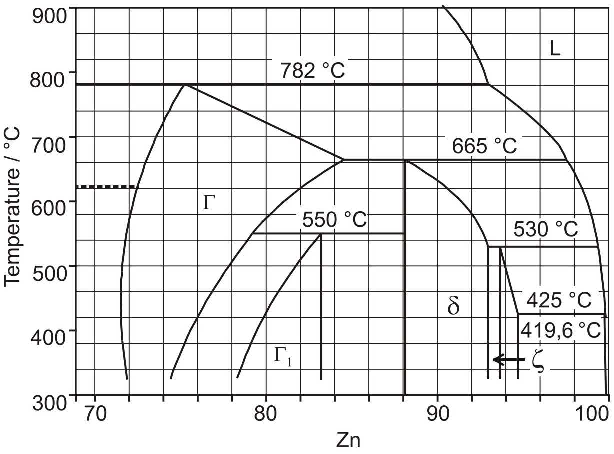

Figure 1. **Part of binary Fe-Zn diagram in wt. / %**
Slika 1. **Dio binarnog dijagrama Fe-Zn, težinski / %**

Demand for steels with excellent drawability in the last years forced the increase in IF steel production [9]. As grain boundaries of these steels do not contain interstitial elements, they are very sensitive to the diffusion processes [6] and so they have more reactive behavior in comparison with other drawing grade steels during zinc coating processing. Consequently, reactive behavior of IF steel is connected with danger of over alloying during post-dip alloying, resulted in poor formability of the coatings during press-forming operations [6, 10].

Mechanisms of formation and growth of Fe-Zn compounds in Ti IF and Ti-Nb-P IF zinc coatings after additional annealing of hot dip galvanized steel sheets with emphasis on the formation of outburst structure are described in the paper.

EXPERIMENTAL WORK

Two different types of IF steel sheets with various titanium, niobium and phosphorous contents, zinc coated on industrial galvanized line were used as starting materials, marked as Ti IF and Ti-Nb-P IF. The chemical composition of used steels is given in the Table 1.

Table 1. **Chemical composition of steel substrates, wt. / %**
Tablica 1. **Kemijski sastav substrata čelika, težina / %**

	C	Mn	Si	P	S	Al	N_2	Cu
Ti IF	0,0040	0,146	0,011	0,006	0,004	0,060	0,0061	0,021
Ti-Nb-P IF	0,0045	0,303	0,006	0,048	0,007	0,040	0,0065	0,052
	Ni	Cr	As	Ti	V	Nb	Mo	
Ti IF	0,011	0,012	0,008	0,082	0,004	0,002	0,003	
Ti-Nb-P IF	0,018	0,014	0,008	0,027	0,001	0,045	0,004	

Samples of 120 × 20 mm size were cut from galvanized sheets and additionally heat treated in Nabertherm laboratory furnace with protective nitrogen atmosphere at 450, 500, 550 °C for 10 and 60 s holding times. The temperature of samples was verified by a contacted thermocouple, after annealing samples were air-cooled.

Cross sectional samples were prepared via classical metallographic method, polished with diamond paste and etched by a mixture of 1 % picric acid in amyl alcohol and 1 % HNO_3 in amyl alcohol. Specimens were cleaned in methanol using ultrasound method for coatings observations by scanning electron microscope (SEM) TESLA BS 340 with LINK ISIS 300 analyzer. Energy dispersive X-ray microanalysis (EDX) was conducted across the coating (from coating/steel substrate interface) at 20 kV accelerating voltage to determine the composition of individual compounds.

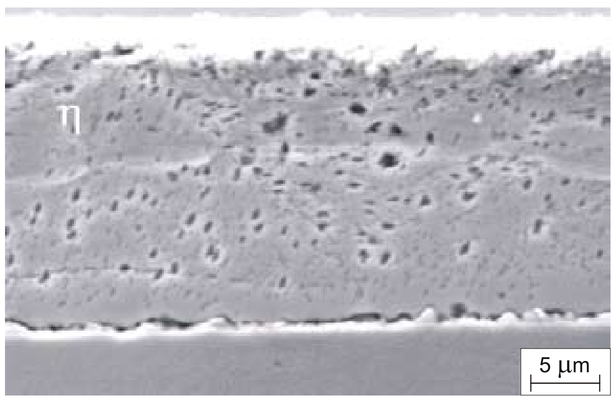

Figure 2. **Zinc coating after industrial galvanizing typical for both steels**
Slika 2. **Prevlaka cinka nakon galvaniziranja tipična za oba čelika**

RESULTS AND DISCUSSION

Both, Ti IF and Ti-Nb-P IF used galvanized steel materials were free of any intermetallic compounds before additional laboratory annealing, Figure 2. Gradual diffusion between Fe and Zn started by annealing at controlled temperature and time.

The process of structure formation in annealed galvanized coatings, containing inhibiting Fe-Al interfacial layer can be generally interpreted by two Fe-Zn reaction types [2]. The first reaction is typical by gradual formation and growth of ζ and δ crystals above the surface of ferrite grains. At the beginning of this reaction, crystals of ζ phase nucleate on the compact surface of Fe-Al layer. During the growth of ζ crystals, Fe-Al layer loses its inhibiting ability and the layer dissolves. This process results to the gradual nucleation and frontal growth of δ and Γ phases, in expense of original pure zinc η phase. Low reaction rate is typical for this process. The second possible reaction in galvannealed coatings is the outburst reaction, resulted into so-called outburst structure, which is composed by ζ and δ phases, possibly also by Γ phases. The rate of this reaction is higher in comparison to the first alloying reaction.

Interstitial free (IF) steels can contain addition of titanium and/or niobium at extremely low contents of interstitial elements. Formation of carbide, nitride, sulfide and phosphide precipitates prevents the segregation to the grain boundaries in these steels. To estimate the resistance of these steels to the outburst formation, the concept of excess titanium, Ti**, has been introduced [11]:

$$Ti^{**} = \text{Total Ti} - 3{,}99C - 1{,}49S - 3{,}42N - 1{,}55P$$

A positive Ti** value indicates excess titanium and therefore a clean, reactive grain boundary. A negative value of Ti** would indicate that not all of solute interstitial elements (mainly carbon) are tied up and zinc diffusion along the boundaries would be blocked.

Ti IF steel

For Ti IF steel it was found, that there is an excess of titanium anf therefore grain boundaries would be reactive ($Ti^{**}_{\text{Ti IF}}$ = 0,0299). Overview of galvannealing results can be seen in Figure 3. Ten seconds of Ti IF steel annealing at 450 °C, resulted in formation of zinc coating with relatively thick δ phase, crystals of ζ phase, appearing of thin Γ phase, while remaining of zinc η phase was detected too. It can be seen, that high reactivity of the steel substrate at the shortest

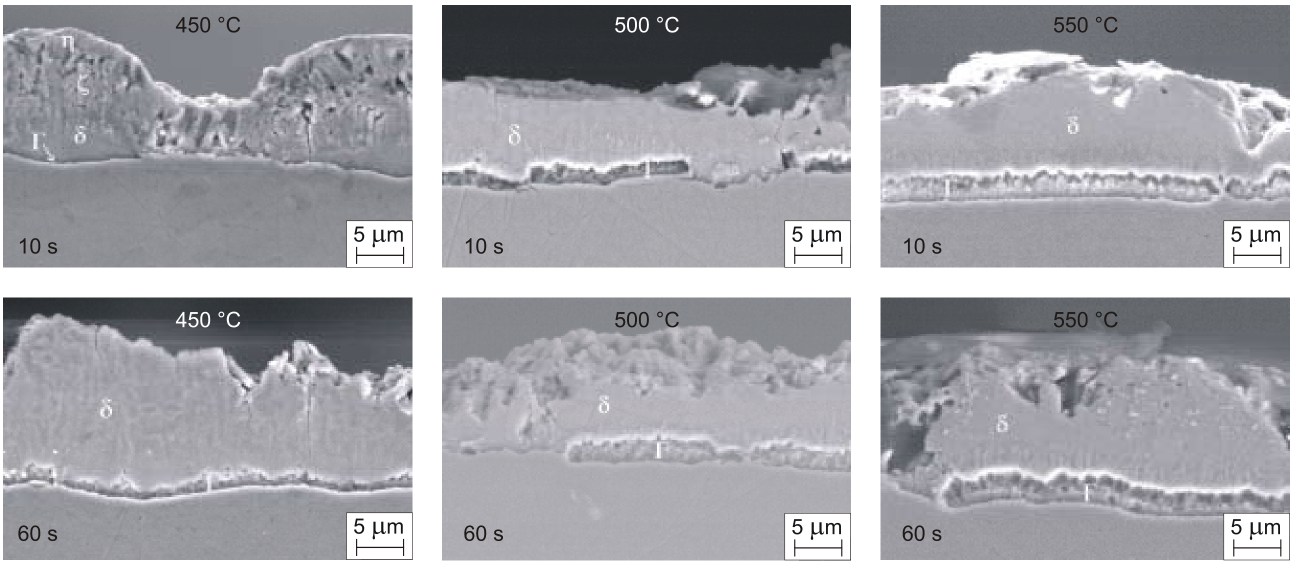

Figure 3. **Results of annealing, Ti IF steel**
Slika 3. **Rezultati žarenja Ti IF čelika**

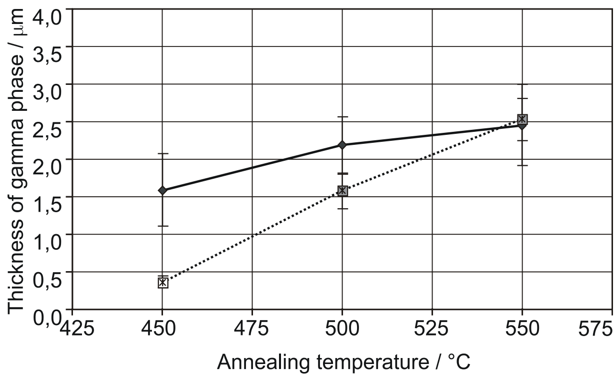

Figure 4. **Average thickness of Γ phase in dependence on the annealing temperature, for Ti IF steel (- 10 s, - 60 s)**
Slika 4. **Prosječna debljina Γ faze u ovisnosti o temperaturi žarenja za Ti IF čelik**

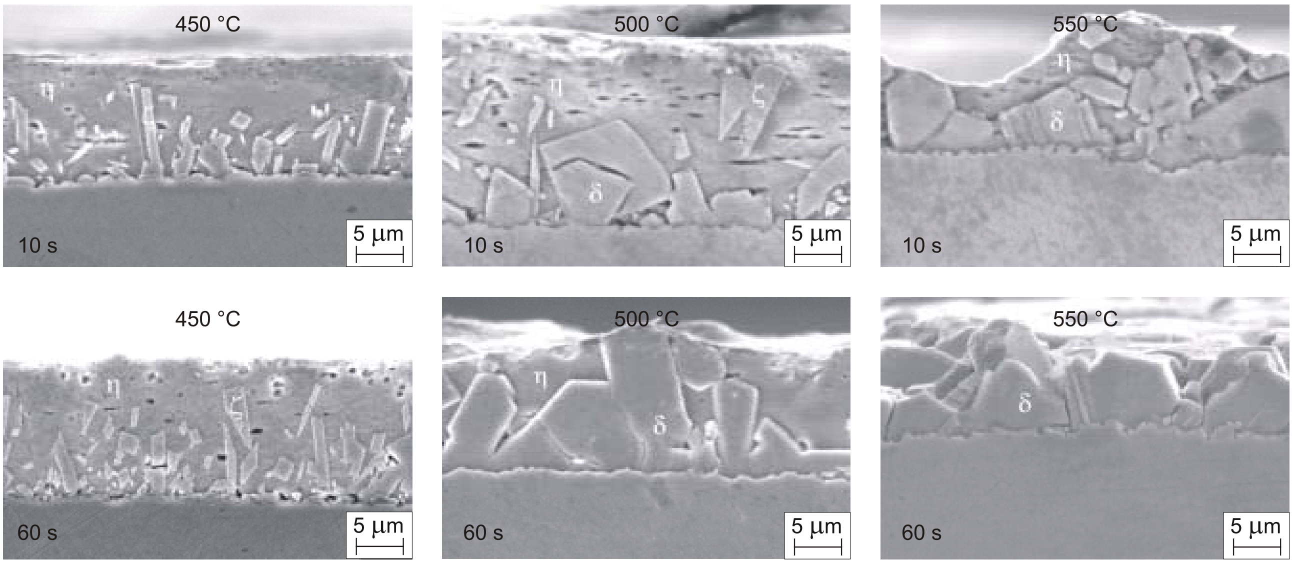

Figure 5. **Results of annealing, Ti-Nb-P IF steel**
Slika 5. **Rezultati žarenja Ti-Nb-P IF čelika**

time and the highest temperature of the annealing resulted in overall slight outburst reaction. Longer times and higher temperatures of annealing initiated the frontal diffusion of Fe into zinc, resulting in transformation of η and ζ phases and formation of coating, consisting of thicker Γ phase and compact δ phase. High growth rate of Γ phase confirmed increased reactivity of this steel, Figure 4. The surface of this steel was without undesirable effects.

Generally, for good formability of zinc coated steel, fully alloyed zinc coating is required, containing compact δ phase and interfacial layer of Γ phase with thickness of up to 1 μm [12]. Nearest structure was obtained by annealing at 450 °C for 60 seconds. Annealing at temperatures 500 °C and 550 °C resulted in thick, but discontinuous Γ phase and compact δ phase, which somewhere bordered directly on steel substrate. This phenomenon could be called like bridges of δ phase and it is supposed that such growth of Γ phase is connected with gradual dissolution of Fe-Al layer. Authors [7] found undisturbed regions of Fe-Al layer till 300 seconds of annealing. This rugged interface is supposed to increase the adhesion force of the coating [13].

Ti-Nb-P IF steel

In case of Ti-Nb-P IF steel, it is necessary to include also Nb content into the equation for titanium excess calculation, because Nb plays similar role as Ti and combines remaining

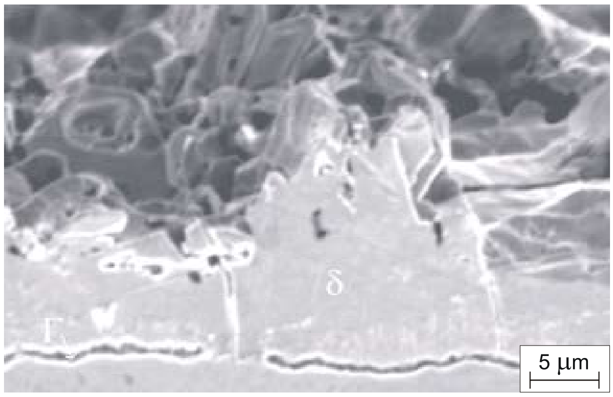

Figure 6. **Annealing for 360s, Ti-Nb-P IF steel**
Slika 6. **Žarenje tijekom 360 s, Ti-Nb-P IF čelik**

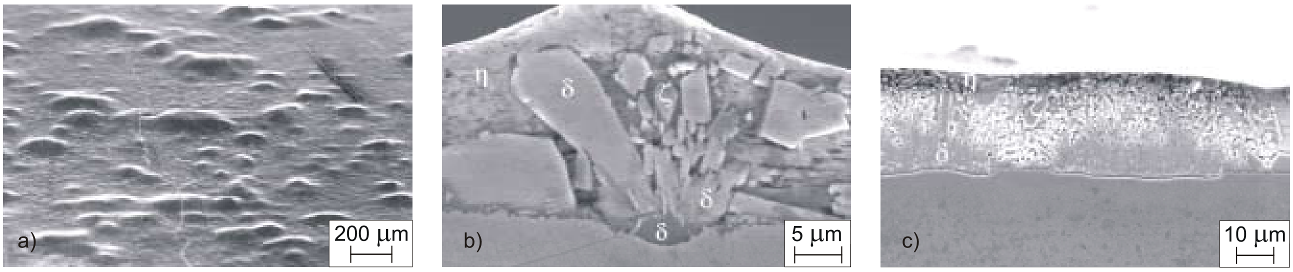

Figure 7. **Example of outburst, Ti-Nb-P IF steel: a) lateral view on the surface, b) transversal section, c) longitudinal section**
Slika 7. **Primjer ljuskanja Ti-Nb-P IF čelika: a) izgled površine, b) poprečni presjek, c) uzdužni presjek**

interstitial elements. For this steel $Ti^{**}_{Ti\text{-}Nb\text{-}P\ IF} = -0{,}0530$. This result would mean retarded Fe-Zn reaction. The shortage of Ti and Nb resulted in the presence of unbounded interstitial elements in the steel. In used Ti-Nb-P-IF steel enriched by P, the most important interstitial element is phosphorous. Phosphorous additions to the IF steel substrate mean, that the growth of Γ phase would be retarded, confirming an idea about segregation of phosphorous on the grain boundaries, preventing Fe-Zn reaction. Phosphorous additions, which suppress activity of the ferrite grain boundary, would result in the decreased growth rate of Γ phase without influence on the growth rate of ζ and δ phases [7]. Changes in the microstructure of the coating during annealing, which have been observed, confirmed this concept, Figure 5. From this figure can be seen, that in this steel Fe diffusion into zinc coating was retarded, resulting in restricted formation of Γ phase, but continuous formation of ζ and δ phases and simultaneous presence of remaining pure zinc η phase. Even annealing at the highest temperature 550°C for longest time of 60 seconds did not initiate the formation of Γ phase. This interfacial layer formed only when the time of annealing was several times extended. The example of structure after 360 s annealing is documented in the Figure 6. In this figure also bridge morphology of δ phase can been seen, which was typical for Ti IF steel, but was found in the earlier stages of heating. Observations supported the theory, that growth of Γ phase is restricted by phosphorous content. On the other side, P increasing content in the steel substrate resulted in the outburst phenomenon formation - the mixture of δ and ζ phases. Strong outburst structure formed at all experimental temperatures and times of annealing for this steel. Firstly it occurred at annealing conditions 450 °C / 10 s and with increasing the time and temperature, the frequency of its occurrence also increased.

Lateral view on the steel surface with outburst is documented in the Figure 7.a. In the Figure 7.b and Figure 7.c views on the grain boundary with outburst through the coating are shown in transversal and longitudinal sections. In the last figure combination of two outburst structures can be also seen. This combination can be supported by annealing of the coating resulted in formation of continuous δ phase. Outburst formation in this steel can be also the consequence of the finer ferrite grain (approx.15 μm) in comparison to grain size of Ti IF steel (approx. 25 μm). The size of the outburst structure is comparable with the grain size of the steel.

For better visualization of outburst structure appearance its schematic representation is in Figure 8. In Figure 8.a top view on steel substrate is shown with grain boundary where outburst was formed. Cross sections in transversal and longitudinal directions on grain boundary are given in Figure 8.b and Figure 8.c. The formation of outburst structure is described in the relation to the ferrite grain boundaries and represents schematically structures from Figure 7.b and 7.c, respectively. Formation of ζ phase is tightly connected with the temperature of annealing and its existence can be explained by peritectic temperature 530 °C, see Figure 1. In our conditions, its occurrence was possible and was confirmed only for temperatures 450 and 500 °C.

Fe-Zn reaction in Ti-Nb-P IF steel was characterized by the frontal diffusion with gradual nucleation and growth of ζ and δ phases without Γ-phase formation. Retardation

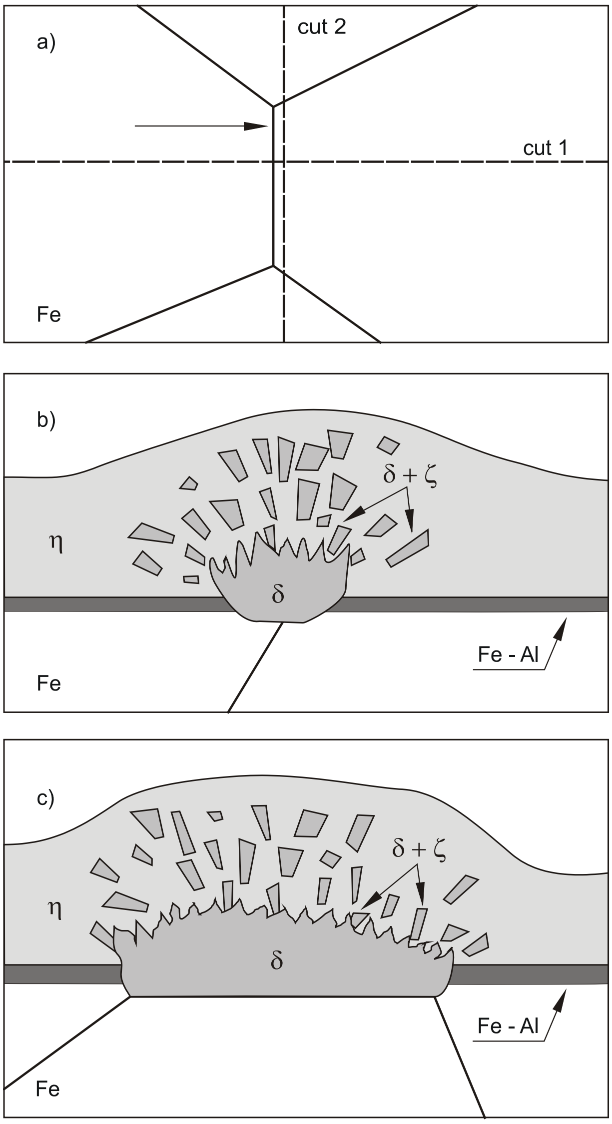

Figure 8. **Schematic representation of outburst structure appearance: a) top view on steel substrate, grain boundary with outburst is noted by arrow, b) cross section of coating in transversal direction on grain boundary (cut 1), c) cross section of coating in longitudinal direction on grain boundary (cut 2)**

Slika 8. **Shematski prikaz ljuskane strukture: a) pogled odozgor na supstrat čelika, granica zrna s ljuskanjem označena je strelicom; b) presjek prevlake u poprečnom pravcu na granicu zrna (rez 1); c) presjek prevlake u uzdužnom pravcu na granicu zrna (rez 2)** of Fe-Zn diffusion was caused by P segregation to the grain boundaries. Simultaneous outburst reactions were probably realized due to presence of ferrite grains, where P was absent. Higher P content and/or larger ferrite grain could probably prevent Ti-Nb-P IF steel substrate from outburst reactions.

CONCLUSIONS

Formation and development of Fe-Zn compounds in coatings of two industrially produced hot dip galvanized steel sheets with various phosphorous content after additional annealing was evaluated.

Higher reactivity of Ti IF steel with low P content was confirmed by rapid G phase reaction as well as slight outburst reaction in the early stages of heating (annealing 450 °C / 10 s). Only frontal diffusion of Fe-Zn compounds was observed for other annealing parameters. Surface of this annealed steel was defect-free.

The reactivity of Ti-Nb-P IF steel was suppressed by higher P content, resulting in the frontal growth of Fe-Zn compounds without Γ phase presence. Simultaneously strong outburst reactions with undesirable appearance of the surface were present for all used annealing parameters. Contrary to high P content in this steel, its content seemed to be relatively low in relation to small ferrite size.

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