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RESEARCHES REGARDING STRUCTURAL CHANGES DUE TO NICKEL MICROLALLOYING OF HOT GALVANIZING BATHS

Radu BOICIUC[1], Adriana PREDA[1], Simona BOICIUC[2]

[1] S.C. Uzinsider Engineering S.A. Galați,
[2]"Dunărea de Jos" Galați University
e-mail: boiciuc.simona@ugal.ro

ABSTRACT

This work offers a synthesis of researches performed in laboratory and regards the nickel microalloying of hot galvanizing baths. Experiments followed the structural changes of both hot galvanizing bath and deposed layer with effect on layer properties.

Characterization of deposed layer and nickel microalloying of galvanizing bath performed by spectral chemical analysis, optical microscopy and X ray diffraction emphasized the structural constituents nature as well as changes shown up depending on nickel concentration of galvanizing bath. Correlation diagrams between deposed layer thickness and structural constituents were also made.

Experimental results emphasized a close interdependence between nickel concentration and microstructure. This allowed to settle the optimal nickel concentration required by galvanizing bath microalloying with maximum effect upon hot galvanizing coating properties.

1. Generals

Experiments performed on a pilot plant used A5K steel strip (as per STAS 10.318) or A35 – 401 type (according to ZE French standard) and included coating by hot galvanizing of several samples (P_1-P_7 code) suitable for the following nickel concentrations in galvanizing bath: 0%; 0,02%; 0,06%; 0,09%; 0,11%; 0,16% and 0,20%.

Galvanizing technology used is the classical one. Samples were degreased, pickled, preheated for 30 seconds, immersed in galvanizing bath for 60 seconds and then freely cooled in air.

2. Spectral chemical composition of deposed layer

Spectral chemical analysis on coating layer performed by Baird DV 6 optical emission spectrometer got the results included in table no.1.

Table no.1 *– Spectral chemical composition (%) of samples galvanized and microalloyed by nickel*

Sample code	Ni	Fe	Cu	Pb	Sn	Cd
P_1	0	**4.651**	0.000	0.001	0.004	0
P_2	0.02	**1.599**	0.001	0.001	0.008	0.001
P_3	0.06	**0.412**	0.001	0.001	0.005	0.001
P_4	0.09	**0.264**	0.001	0.001	0.005	0.001
P_5	0.11	**0.177**	0.001	0.001	0.003	0.001
P_6	0.16	**0.168**	0.001	0.001	0.002	0.001
P_7	0.20	**0.163**	0.001	0.001	0.002	0.001

It may be seen an important decrease of Fe content in the coating layer in the same time with increasing the degree of bath microalloying up to 11% nickel content.

Over this value the Fe content will stay approximate constantly.

3. Structural methallographic determinations

Methallographic analysis performed by Olympus microscope, endowed by data acquisition automatic system, on specimens sampled from galvanized steel sheets and galvanizing bath.

Measurements results are given in table no.2.

Table no. 2. *Thickness of zinc layer and intermetallic layers*

Sample code	Zn layer thickness (eta) [µm]						Intermetalllic composes layer thickness [µm]					
	g_1	g_2	g_3	g_4	g_5	$G_{m\,Zn}$	g_6	g_7	g_8	g_9	g_{10}	$g_{m\,Cmet}$
P_1	31.64	32.52	30.77	29.10	29.84	30.77	48.35	49.77	48.52	50.25	50.11	49.40
P_2	46.61	42.19	48.41	48.34	46.59	43.43	37.55	34.89	37.07	35.16	36.93	36.32
P_3	58.89	57.16	56.87	58.02	58.89	57.96	15.85	15.82	15.81	15.26	15.82	15.71
P_4	61.73	60.68	60.65	60.65	61.54	61.05	14.85	15.59	15.49	15.94	15.77	15.53
P_5	71.19	71.24	71.22	71.19	70.95	71.16	15.70	15.33	15.78	15.43	15.20	15.48
P_6	69.25	69.34	70.11	70.08	69.53	69.66	15.82	15.27	15.84	15.83	15.83	15.72
P_7	70.34	70.86	70.64	71.48	71.20	70.84	20.21	19.13	20.23	20.21	20.19	19.99

Note: g_m – the average value of deposed layer

Analyzing the results it may be remarked that changes of deposed layers thickness took place depending on Ni percentage added in the bath.

Up to 11% Ni content inside bath the Zn layer thickness increase and intermetallic compounds layer thickness decrease are recorded. Over this value the deposed layers thickness is kept approximately steady and it is a relevant aspect on diagrams in figures no.1 and 2.

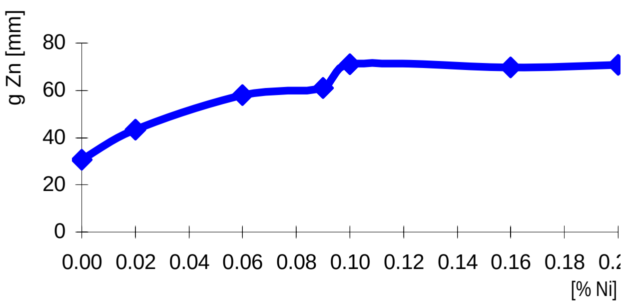

Fig. no.1. *Variation of Zn layer thickness depending on Ni content of metallic bath*

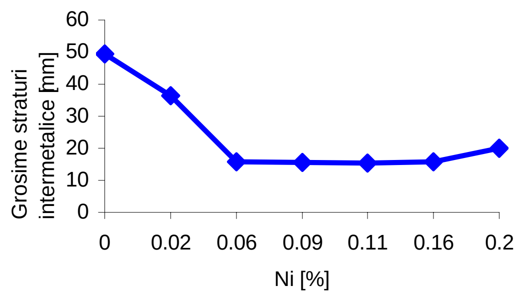

Fig. no.2. *Variation of intermetallic compounds layer thickness depending on Ni content of metallic bath*

Gradually by increasing the nickel microalloying degree of galvanizing bath, metallographic analysis emphasized (figures no. 3÷6) important changes in deposed layer structure:

- Finishing of Zn grains and apparition of Ni-Zn intermetallic compound disperse particles in eta layer;
- Decreasing and finishing the layer in "palisade";
- Coalescence of Ni-Zn intermetallic compound particles precipitated in eta layer.

Metallic bath microalloying by nickel, even in very small concentrations, made essential changes of its microstructure (Fig. no. 7÷12).

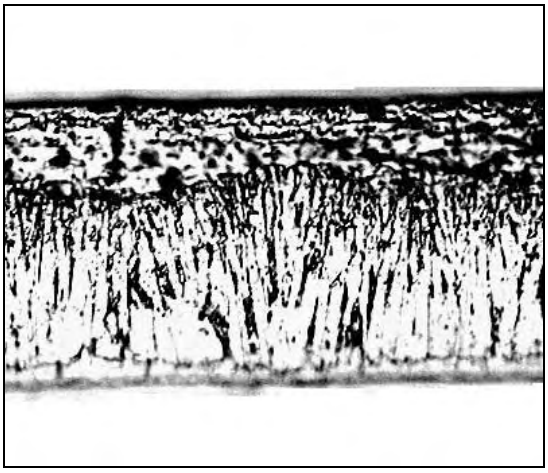

Fig. no. 3 *Microstructure of deposed layer, 0 % Ni. (x 500). 1% nital attach.*

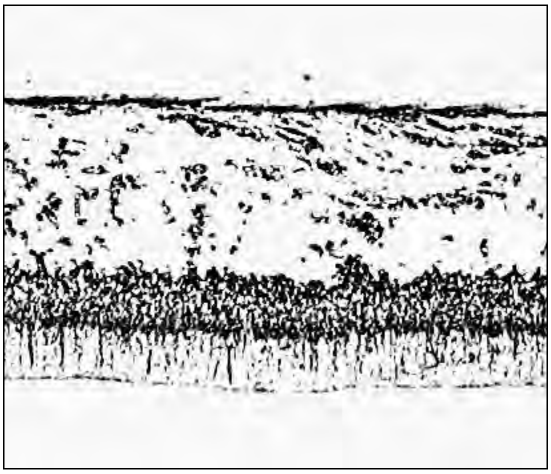

Fig. no. 4 *Microstructure of deposed layer, 0.06 % Ni. (x 500). 1% nital attach.*

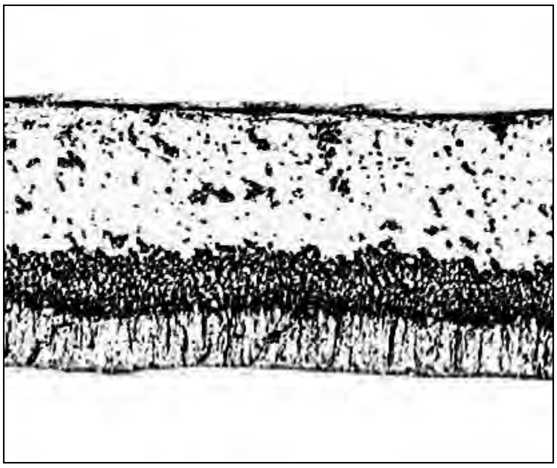

Fig. no. *5 Microstructure of deposed layer, 0.11 % Ni. (x 500). 1% nital attach.*

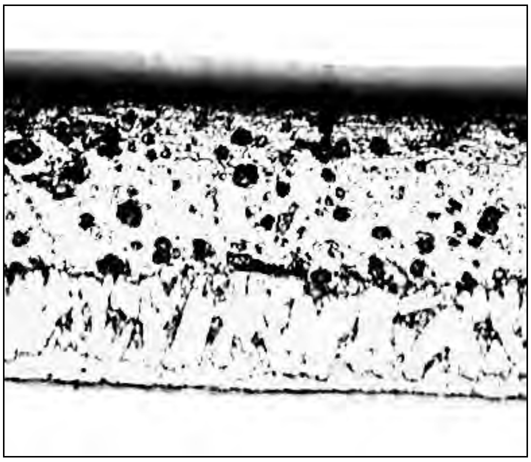

Fig. no. 6 *Microstructure of deposed layer, 0.20 % Ni. (x 500). 1% nital attach.*

Fig. no. 7 *Microstructure of the bath 0 % Ni. (x 100). 1% nital attach. Zn large crystals with macles.*

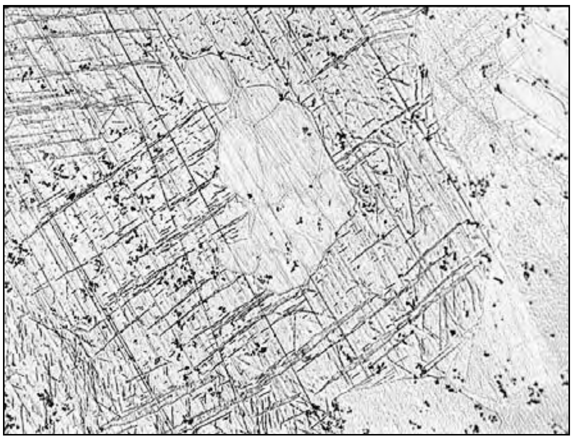

Fig. no. 8 *Microstructure of the bath 0,02 % Ni. (x 100). 1% nital attach. Zn large crystals with tendency to form Zn-Ni eutectic.*

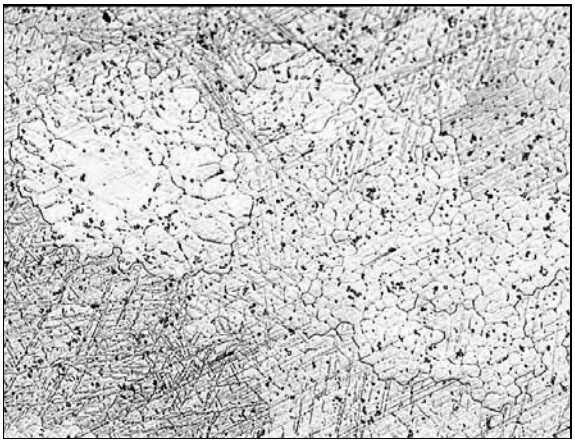

Fig. no. 9. *Microstructure of the bath 0,06 % Ni (x 100). 1% nital attach. Inhomogeneous eutectic structure in which very fine dispersed particles of Ni-Zn intermettalic compound show up.*

Fig. no. 10. *Microstructure of the bath 0,09 % Ni. (x 100). 1% nital attach. Eutectic structure in which fine dispersed particles of Ni-Zn intermettalic compound show up.*

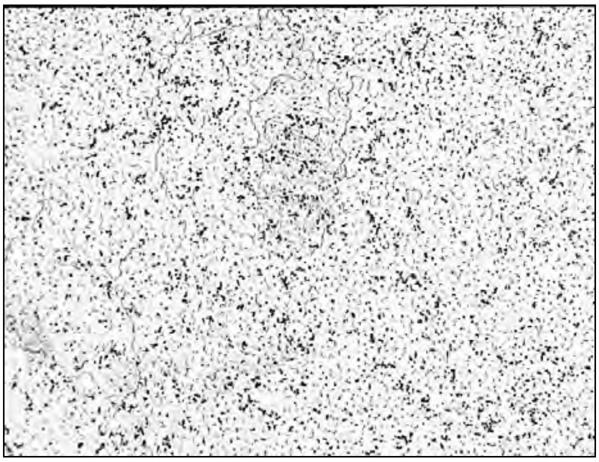

Fig. no. 11. *Microstructure of the bath 0,11 % Ni. (x 100). 1% nital attach. Fine eutectic structure in which fine particle agglomeration of Ni-Zn intermettalic compound show up dispesed.*

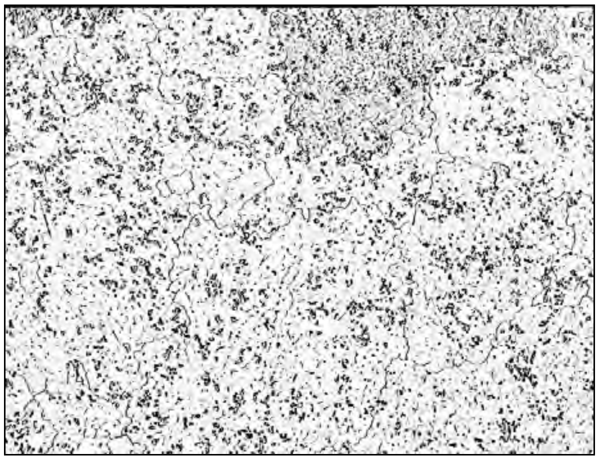

Fig. no. 12. *Microstructure of the bath 0,20 % Ni. (x 100). 1% nital attach. Fine eutectic structure in which globular particle agglomeration of Ni-Zn intermetallic compound show up.*

Large Zn crystals grained in the same time with Ni content increasing up to a very fine eutectic structure where the Ni-Zn intermetallic compound particles precipitated. Coalescence and crowding of these particles made in the same time with alloying percentage increasing.X ray diffractometric analysis confirmed the results got by both spectral chemical and metallographical analysis .

Phases identified in metallic layer were

- (γ) gamma adherence layer : Fe_5Zn_{21};
- (δ) delta frail layer in "palisade" : $FeZn_7$;
- (ξ) zeta intermediary layer - Fe_3Zn_{10};
- (η) eta layer or pure Zn;
- $NiZn_3$ intermetallic compound.

Quantitative ratio of the first four phases varies depending on Ni content up to Fe_3Zn_{10} intermediary phase vanishing.

$NiZn_3$ intermetallic compound apparition was signaled in the same time with feeding the Ni in metallic bath, its quantitative ratio increasing direct proportional by this element content recording a level inside 0.11÷0.16% Ni range (fig. no. 13).

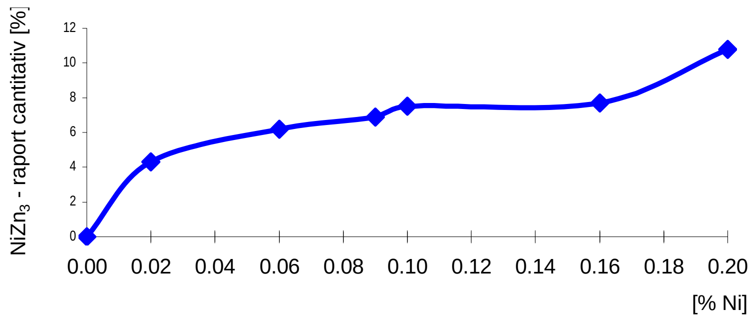

Fig. no. 13. *Variation of $NiZn_3$ phase quantitative ratio depending on Ni content of metalic bath*

Fine structure additionally hardened by $NiZn_3$ intermetallic compound, dispersed in pure zinc in quantitative ratio up to 10.8%, confers special resistance and corrosion properties.

4. Conclusions

Nickel microalloying of hot galvanizing bath determines essential changes of both bath and deposed layer microstructures.

Fe content decreases by Ni content increasing up to 0.11 % as a result of Fe_xZn_y type layers decreasing and apparition of $NiZn_3$ compound.

Eta zinc layer thickness increases by 131% and that one of intermetallic layers decreases by 69% Ni in galvanizing bath. Over this value thickness stays steadily.

Deposed layer structure records the following changes:

- Decreasing and finishing the layer in "palisade";
- Finishing of Zn grains and apparition of disperse particles of Ni-Zn intermetallic compound in eta layer;
- Coalescence of Ni-Zn intermetallic compound particles precipitated in eta layer.

Large Zn crystals grained in the same time with Ni content increasing up to a very fine eutectic.

$NiZn_3$ intermetallic compound presence in deposed layer, in a quantitative ratio of up to 7.5% suitable for 0.11% Ni content determines both structure finishing and additional hardening of coating with maximum effects on coating quality.

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