

# OBTAINING AND CHARACTERIZING TIN-LEAD COATINGS ON STEEL BAND

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## ABSTRACT

The experimental research was at the basis of the hot immersion coating technology with Sn-Pb alloy of the steel bands presented in the study. The characterization of these layers was achieved through microscopic analyses and the analysis of resistance to corrosion. Coatings with four tin-lead alloys were carried out. The micro-structural aspect of the tin-lead alloys, the aspect of the covered band surface, the micro-structure of the layers, the layer thickness variation according to the duration of the immersion and the chemical composition of the layers are presented. The resistance to corrosion was assessed through the gravimetric index. The samples were exposed in sea water for five weeks. The corrosion speed was determined for every type of coating, according to the period of exposure to the corrosive environment and the kinetic process for the time intervals studied.

KEYWORD: tin lead coatings, structure, corrosion

## **1. Introduction**

The tin alloys are important in the production of coatings through hot immersion. The most important of these are the tin-zinc, tin-nickel, tin-cobalt, tipcopper and tin-lead alloys. The tin-lead coatings are mainly used for protection against corrosion and for preparing the surfaces for soldering. The protective layer made of Pb-Sn alloys gives the steel plate a good resistance to corrosion, a very good capacity for welding and soldering, and improves deformability.

The coating presents a high resistance to corrosion in the atmosphere which contains sulphur agents, in environments with oil products, in sulphuric and phosphoric acids. In the case of corrosion resistance of the plate covered in Pb-Sn alloys, a very important role is played by the Fe-Sn transition layer, formed at the separation limit of the steel-coating. According to the iron-tin equilibrium diagram, the inter-metallic compound FeSn<sub>2</sub> is formed with 80.95% tin, stable up to 496°C. Like tin, this material presents a crystalline tetragonal structure. The FeSn<sub>2</sub> layer gives a good coating adherence to the steel support but, because of its fragility, it is not recommended to go beyond a certain thickness.

The reduction of the tin content during the coating, through its replacement with lead, influences

the  $FeSn_2$  layer by reducing it and worsens its adherence properties. In order to compensate this shortcoming, modifications were made in the fabrication technology of the lead plate with a low content of tin, respectively applying a more intense capping process, using new fluxing etc., to activate the surface.

## 2. Experimental research

For obtaining Sn-Pb alloy coatings, the following technological steps were followed:

-preparing the surfaces of the steel bands;

-development of tin alloys with different lead concentrations;

-achievement of deposits through immersion in melt;

-cooling of the samples.

Preparing the steel surface in view of coating is a very important stage, because the perfect cleaning of the surface determines the obtaining of an adherent layer, uniform and without flows.

The surface of the samples was chemically degreased and then degreased in organic solvents (acetone), etched in hydrochloric acid (17% concentration) and covered in zinc chloride flux and ammonium chloride dried at 150 °C.



The sample steel bands on which the deposit was achieved were 0.18mm thickness; their chemical

composition is shown in Table 1.

Table 1.	Chemical con	nposition oj	f the support s	steel bands, in %
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С	Si	Mn	Р	S	Al	As	Ti	V	Cu	Ni	Cr	Мо
0.025	0.015	0.210	0.013	0.010	0.046	0.004	0.002	0.001	0.005	0.008	0.025	0.001

Alloy code	Comp [9	osition, %]	Alloy melting temperature		
	Sn	Pb	[°C]		
1	80	20	180		
2	70	30	185		
3	50	50	220		
4	32	68	260		

Table 2. Elaborated Sn-Pb alloy chemical composition

The immersion temperature was 30-50°C above that of the alloy melting temperature, and the immersion duration varied between 3 and 12 seconds.

A first observation is that a growth in the alloy lead concentration influences the aspect of the surface. The aspect of the surface varies from silver in the case of coating with an alloy with a high content of tin (80%Sn-20%Pb), to opaque dark grey in the case of the layers obtained in alloy code 4 (32%Sn68%Pb). The surface analysis through optical microscopy shows a difference in the solidification process, respectively a structure with fine dendrites for alloy code 1 compared to the other alloys, as can be observed in the micrographs in Figure 1.

The increase of the dendrite dimension is influenced by the increasing of the solidification interval [1] of the alloy codes 2 and 3, as compared to 1 and 4.

be observed is an increase in the eutectic quantity,

with the solid solution  $\alpha$  in the case of hypoeutectic

alloys [3, 4] codes 2 and 3 and with the solid solution



a) 80%Sn-20%Pb

b) 70%Sn-30%Pb

c) 50%Sn-50%Pb

 $\beta$  in alloy code 4.

d) 32%Sn-68%Pb



Figure 2 presents the micro structural aspect of the lead-tin alloys, elaborated in view of coating the steel bands. According to the phase equilibrium diagram [2], depending on the lead content, what may



b) 50%Sn-50%Pb



c) 32%Sn-68%Pb

Fig. 2. Microstructural aspect of the tin-lead alloy, X100



During the research carried out, the determination of the alloy layer thickness deposited on the steel bands was achieved metallographic ally as the average of three measurements in different areas. As can be observed from the data presented in Figure 3, the layer thickness depends on the immersion duration, as well as on the chemical composition of the alloy deposited.

The increasing of the lead concentration and immersion period over 6 seconds determined increasing of thickness for the alloy coating codes 3 and 4. In the case of alloys with a low content of lead (20-30% Pb), the immersion duration does not influence the layer thickness significantly. This can be explained due to the much better flow of the alloys which are rich in tin [5, 6].



Fig. 3. Thickness variation of the Sn-Pb alloy layers according to the immersion duration

The analysis of the microstructures deposited shows that these are uniform and present a structure similar to that of the alloys, thickness varying



Fig. 4. Microstructure of the 70% Sn 30% Pb alloy coating, immersion duration: 6 seconds, temperature 185[°C]

In order to determine the corrosion speed, some samples were extracted from each type of coating resulting from a 6 second immersion, where the layer thickness was approximately equal. according to the immersion duration. Figures 4 and 5 show the microstructural aspects of the coatings, with the layer thickness specified.



Fig. 5. microstructure of the 32%Sn-68% Pb alloy coating immersion duration: 9 seconds, temperature 185[°C]

The corrosive environment used was a 3% NaCl solution. The study was carried out for five weeks. The samples were weighed at 7 days intervals, after they were washed in water and then dried.



In order to determine the corrosion speed, the gravimetric method was used. The corrosion speed was determined using the relation:

$$v_{cor} = \frac{m_{cor}}{S \cdot t} \tag{1}$$

where:  $v_{cor}$  - gravimetric index [g/m<sup>2</sup>·h]; m<sub>cor</sub> - mass loss through corrosion [g]; S - surface area, [m<sup>2</sup>]; t - corrosion duration [h].

Both the corrosion speed at different time intervals and the speed during the intervals were determined; the variation curves were also drawn.

The corrosion speed depends of the chemical composition of the alloy deposited on the steel bands, on the thickness of the deposited layer and of the exposure duration of the samples to the corrosive environment [7, 8, and 9]. Figure 6 shows the behavior to corrosion of the analyzed layers, according to the duration exposure to the corrosive

environment. Analyzing the corrosion test results, we may observe a similar behaviour of the alloy coatings 2 and 3.

This represents a continuous decrease of the corrosion speed after the first three weeks (504 hours). The alloy layers with a lower content of alloying elements (codes 1 and 4) have a lower corrosion speed after 168 hours of exposure, but an increased corrosion speed after two weeks and a decreased one after 504, with larger values however as compared to alloy codes 2 and 3.

The behaviour after 672 hours and after 840 hours respectively becomes the same for all types of alloy, in the sense of a strong increase of the corrosion speed.

The best behaviour is at 32% Sn and 68% Pb. The increase of the lead content in the coating alloy improves the resistance to corrosion in the studied conditions.



Fig. 6. Corrosion behaviour of the analysed layer

Analysing the kinetic corrosion process for each alloy presented in Figure 7, we may also observe the

similar behaviour at corrosion of the alloy layer codes 1 and 4, and of those in code 2 and 3 respectively.



a) 80%Sn-20%Pb







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c) 50%Sn-50%Pb

d) 32%Sn-68%Pb

Fig. 7. Kinetics of the corrosion process for each type of coverage studied

## 3. Conclusions

-The increase in the alloy's lead concentration influences the aspect of the surface, which varies from silver in the case of a coating made from alloys with high tin content (80%Sn-20%Pb) to opaque dark grey in the case of the layers obtained from alloys with 32% Sn and 68% Pb.

-The increase of the immersion duration above 6 seconds leads to a significant increase of the layer thickness, in the case of alloys which are rich in lead.

-The microscopic aspect of the surface also shows a difference in the solidification process of the layer: a structure with fine dendrites in the case of alloy with 80 % Sn - 20 % Pb respectively, as compared to the other alloys (thank to increasing of the alloys solidification interval).

-The tin-lead alloy microstructure shows an increase in the eutectic content, along with the solid solution  $\alpha$  (in the case of hypoeutectic alloys) and along with small quantities of solid solution  $\beta$  in the hypereutectic alloy.

-The analysis of the microstructures of the deposited layers shows that these are uniform and present a similar structure to that of the alloys.

-The corrosion test shows good deposit behaviour at corrosion; analysed, they present values close to

the corrosion speed in time.

-The kinetics of the corrosion process shows a significant increase of the corrosion speed in weeks 4 and 5 for all the studied layers.

-The increase of the lead content in the coating has a positive influence on the resistance to corrosion.

#### References

[1]. Alexandru H.V., Berbecaru C. - *Știința materialelor* - *Creșterea cristalelor*, Ed. Universității din București, (2003).

[2]. Yancy W.Riddle - *Metals Conservation*, Summer Institute, Alloys & Their Phase Diagrams, University of California (2006).

[3]. William D.Callister - Binary Phase Diagrams, 2<sup>nd</sup> ed., Vol. 3.

[4]. Harsh Menon - Lab.Report on Lead-Tin Phase Equilibrium, (2006).

[5]. W. E. Hoare, E. S. Hedges & B. T.K. Barry - The Technology of Tinplate, Ed. Arnold (Publishes) Ltd., London, (2004).

[6]. Silviu Crăciun - Cositorirea la cald a materialelor metalice, 1976.

[7]. Tamara Radu, Stela Constantinescu, Lucica Balint -Materiale metalice rezistente la coroziune. Editura Științifică F.M.R., (2004).

[8]. Opre Flore, Florentina Ionescu, Tamara Radu - Coroziune materialelor metalice, Editura Științifică F.M.R., (2000).

[9]. Stefan Dragomir, Silviu Macuta, Mirela Dobrot -Functional parameters and vibration measurement, performed on a strip tandem mill cold, 28-th Danubia Adria Symposium on Advances in experimental mechanics, Siofok Hungary, 28sep-01oct.2011.