

Zn-Ni alloy coating made of chloride electrolyte

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Abstract: Electrodeposition coating based on Zn-Ni alloys was made of chloride electrolyte which contains 142.56 g/dm³ NiCl₂·6H₂O; 109.03 g/dm³ ZnCl₂; 30.9 g/dm³ H₃BO₃; 223.65 g/dm³ KCl; 40.99 g/dm³ CH₃COONa. As the result coatings of different sizes and different amount of Ni in each coating were prepared. The samples were tested in salt spray chambers according to BS EN ISO 10289:2001 standard. The best results showed coatings which were over 10 μm thick and which contained up to 15% of Nickel. There were no signs of corrosion even after 2160 hours of being in salt spray chambers.

INTRODUCTION

Resistance of zinc coatings towards the corrosion processes is well known so these coatings were the first choice of protection for a long time during the production of the steel constructions. As technology developed and demands for thinner coatings but with much higher corrosion stability increased, zinc coatings were not satisfactory enough anymore. Research showed that alloy coatings based on zinc and other elements of iron triads can satisfy these conditions very well. There are many factors influencing features of deposited coatings based on double and in recent time even triple alloys based on zinc. Those factors are mostly concentration of metal ions, chemical composition of electrolytes that caused deposition and current density. [Esih 2010; Gamburg 2011; Vujičić 2002]

In this paper, coatings based on Zn-Ni alloys made of chloride electrolytes were tested. Depending on conditions (current density and deposition time), coatings of different sizes and with different amount of Ni in each coating were made. [Kanani 2005; Ramesh Bhat 2011; Eliaz 2014; Gou 2008] So far research showed that it is possible to get coatings based on Zn-Ni alloys which have corrosion characteristics, out of chloride electrolytes. [Jović 2009; Bajat 2009; Roventi 2000]

Depending on the amount of Ni in alloy and the thickness, coatings were exposed to test in salt spray chambers and characterized according to standard BS

EN ISO 10289:2001. [Stupnišek-Lisac 2007; BS EN ISO 10289:2001; EN ISO 9227].

EXPERIMENTAL

For electrochemical deposition of Zn-Ni based coatings chloride electrolyte was used. In table 1. The composition of chloride electrolyte is showed in Table 1.

Table 1. Chemical composition of electrolytes for deposition of coating Zn-Ni alloys

	NiCl ₂ ·6H ₂ O	ZnCl ₂	H ₃ BO ₃	KCl	CH ₃ COONa
mol/dm ³	0.6	0.8	0.5	3	0.5

Electrolyte used is prepared using chemicals of p.a. purity. Tiles from plane construction steel were used as working electrodes for deposition of Zn-Ni based coatings. Electrode of high cleanliness Nickel (99.9%) was used as an auxiliary electrode during deposition of alloys. Relation between the surface of working and auxiliary electrode was 1: 2. Before the deposition, working electrodes were processed with abrasive paper, granulation 800 and 1200, degreased in NaOH solution then in ethanol and etched in 10% HCl solution. Between every phase of preparation, electrodes were washed with distilled water. Electrochemical cell for

deposition was laboratory glass of 500 cm³ of volume. Current density which is used for deposition was 1; 2 and 3 A/dm², the temperature of solution was 35°C and pH was 4.5. Time of deposition was 10, 15, 20 and 35 minutes to get the coatings of different sizes and with different amounts of Ni. Chemical composition thickness of Zn-Ni alloys were done in SurTec Eurosjaj d.o.o. Konjic, na Fischerscope® XRAY XDL-B laboratory. The results are showed in table 2.

Table 2. The thickness of Zn-Ni alloy and the amount of Ni in coating

Sample label	Sample label in salt chamber	Working conditions	Thickness of coating, μm	Amount of Ni in coating, %
1R	49	$i=2\text{A/dm}^2$ $\tau=20$ min	5.805	10.79
4R	50	$i=1\text{A/dm}^2$ $\tau=20$ min	9.326	11.93
2P	47	$i=2\text{A/dm}^2$ $\tau=20$ min	8.126	12.13
1K	43	$i=1\text{A/dm}^2$ $\tau=20$ min	5.273	13.60
2K	45	$i=2\text{A/dm}^2$ $\tau=20$ min	10.180	14.34
3K	46	$i=3\text{A/dm}^2$ $\tau=20$ min	12.62	17.89
1KT	40	$i=2\text{A/dm}^2$ $\tau=10$ min	5.036	11.27
2KT	41	$i=2\text{A/dm}^2$ $\tau=15$ min	7.111	11.49
6KT	42	$i=2\text{A/dm}^2$ $\tau=35$ min	14.97	14.86

Testing in salt spray chamber was done in SurTec-Eurosjaj d.o.o. Konjic. Chamber is JW-150-NS Salt Spray Chamber type. Testing lasted for 2160 hours. Conditions of testing in chambers were following : test space temperature was 35 °C; moisturizer of compressed air temperature was 45-50°C; compressed air pressure was 7-1,4 bars; solution was 5% NaCl; condensate pH in 25°C was 6,8 while electrical conductivity of distilled water in 25°C was < 20 $\mu\text{S/cm}$.

After testing, the samples were taken out of salt chamber and visually evaluated according to BS EN ISO 10289:2001 standard. Samples 42 and 45 obtained after the testing in salt spray chambers are showed in P1 and the results are showed in Table 4.



Figure 1. Samples without appearance of corrosion after 2160 hours in salt spray chamber

RESULTS AND DISCUSSION

As it is seen in picture 1. and table 4., samples 40, 41, 48, 49 and 50. (40/1KT, 41/2KT, 48/3P 49/1R and 50/4R) did not satisfy the salt spray chamber test. The red corrosion appeared much earlier than the expected for this type of coating after 720 hours of testing. Although the Ni part in Zn-Ni alloy coating is satisfying and that is 8-15%, the coating thickness is small which is the cause of appearance of red corrosion much earlier than expected.

The rest of the samples satisfied the salt spray chamber test according to norms of DIN EN ISO 9227 NSS standard. For example, the sample (45/2K) which has 14,34% Ni and the coating thickness was 10,180 μm , did not show the appearance of red corrosion even after 2160 hours, so, according to BS EN ISO 10289:2001 standard, it has the assessment of protection and look (Rp/RA) 10/8sC.

According to standard, the rest of the samples that satisfied the salt spray chamber test are also described.

Sample 42 shows the appearance of white corrosion after 720 hours of testing but on the surface area smaller than 0,25%. There were no visible defects. It is mostly caused by corrosion products made of anodic coating. The appearance of red corrosion is not noted even after 2160 hours of being in salt spray chamber. According to the assessment of protection and look Rp/ RA was 10/8sC. Sample 46 shows the appearance of white corrosion after 720 hours and on the surface area smaller than 1%. There are no visible defects. The amount of corrosion products was moderate. It is mostly about corrosion product made of anodic coating. The appearance of red corrosion is not noted even after 2160 hours of being in salt spray chamber. According to the assessment of protection and look Rp/RA was 10/6mE.

Sample 43 shows the appearance of white corrosion after 480 hours and in that time it does not show any visible defects on coating. After 846 hours it shows visible defect and the appearance of red corrosion in the area of small drilled hole on the top of the electrode. The amount of corrosion products is moderate. Corrosion products reach the base that started to peel. According to the assessment of protection and look Rp/RA was 3/2mF.

Sample 47 shows the appearance of white corrosion after 720 hours and in that time it did not show any visible defects on coating. After 1176 hours it showed visible defect and the appearance of red corrosion in the area of small drilled hole on the top of the electrode and edges of the tested sample. The amount of corrosion products was moderate. Corrosion products reached the base but they were only on the top of the metal. There was no

peeling. According to the assessment and look Rp/RA equaled 6/5mE

Table 4. The test results from salt spray chamber

Sample	Thickness of coating, μm	Amount of Ni in coating, %	Start of the test	End of the test	White corrosion (hours)	Red corrosion (hours)	Assessment of protection and look
40/1KT	5,036	11,27	28.09.2015	05.10.2015	168	192	-
41/2KT	7,111	11,49	28.09.2015	06.10.2015	96	192	-
42/6KT	14,97	14,86	28.09.2015	28.12.2015	720	2160 (no corrosion)	10/8sC
43/1K	9,273	13,60	28.09.2015	03.11.2015	480	864	3/2mF
45/2K	10,180	14,34	28.09.2015	28.12.2015	720	2160 (no corrosion)	10/8sC
46/3K	12,62	17,89	28.09.2015	28.12.2015	720	2160 (no corrosion)	10/6mE
47/2P	8,126	12,13	28.09.2015	16.11.2015	720	1176	6/5mE
48/3P	5,951	13,71	28.09.2015	08.10.2015	120	240	-
49/1R	2,805	10,79	28.09.2015	02.10.2015	48	96	-
50/4R	9,326	11,93	28.09.2015	06.10.2015	96	192	-

CONCLUSION

Samples with Ni part of 8-15%, which had the red corrosion appear earlier than the expected for this type of coating, after 720 hours of testing did not passed the testing despite the the thickness of the coating As resault red corrosion appeared much earlier than expected. The rest of the samples that had the thickness of Zn-Ni alloy coating higher than 10 μm and the needed part of Ni 15%, fully satisfied the salt spray chamber test. That means they did not show any signs of red corrosion appearance in the testing time of 2160 hours.

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Summary/Sažetak

Izvedena je elektrodepozicija prevlaka na bazi legura Zn-Ni iz hloridnog elektrolita sastava $142,56 \text{ g/dm}^3 \text{ NiCl}_2 \cdot 6\text{H}_2\text{O}$; $109,03 \text{ g/dm}^3 \text{ ZnCl}_2$; $30,9 \text{ g/dm}^3 \text{ H}_3\text{BO}_3$; $223,65 \text{ g/dm}^3 \text{ KCl}$; $40,99 \text{ g/dm}^3 \text{ CH}_3\text{COONa}$. Dobivene su prevlake različite debljine i sadržaja Ni u prevlaci. Uzorci su ispitivani u slanoj komori prema standardu BS EN ISO 10289:2001. Najbolje rezultate su pokazale prevlake debljine preko $10 \mu\text{m}$ i sadržajem nikla do 15%. Nisu pokazivali pojavu korozije ni nakon 2160 sati provedenih u slanoj komori.