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INFLUENCE OF THE ZINC SUBLAYER METHOD PRODUCTION AND HEAT TREATMENT ON THE MICROHARDNESS OF THE COMPOSITE Ni-Al_2O_3 COATING DEPOSITED ON THE 5754 ALUMINIUM ALLOY

WPŁYW SPOSOBU WYTWARZANIA PODWARSTWY CYNKU ORAZ OBRÓBKI CIEPLNEJ NA MIKROTWARDOŚĆ KOMPOZYTOWEJ POWŁOKI Ni-Al_2O_3 NA POWIERZCHNI STOPU EN AW 5754

In this study, the effect of zinc interlayer on the adhesion of nickel coatings reinforced with micrometric Al_2O_3 particles was examined. Nickel coating was applied by electroplating on EN AW – 5754 aluminium alloy using Watts bath at a concentration of 150 g/l of nickel sulphate with the addition of 50 g/l of Al_2O_3. The influence of zinc intermediate coating deposited in single, double and triple layers on the adhesion of nickel coating to aluminium substrate was also studied. The adhesion was measured by the thermal shock technique in accordance with PN-EN ISO 2819. The microhardness of nickel coating before and after heat treatment was additionally tested.

It was observed that the number of zinc interlayers applied does not significantly affect the adhesion of nickel which is determined by thermal shock. No defect that occurs after the test, such as delamination, blistering or peeling of the coating was registered. Microhardness of the nickel coatings depends on the heat treatment and the amount of zinc in the interlayer. For both single and double zinc interlayer, the microhardness of the nickel coating containing Al_2O_3 particles increased after heat treatment, but decreased when a triple zinc interlayer was applied.

Keywords: nickel coatings, zinc interlayer, Al_2O_3 particles, thermal shock

W pracy badano wpływ międzywarstwy cynku na przyczepność powłok niklowych zbrojonych mikrometrycznymi cząstkami Al_2O_3. Powłokę niklową wytworzono galwanicznie wykorzystując kąpiel Wattsa o stężeniu siarczanu niklu 150 g/l z dodatkiem 50 g/l Al_2O_3 na stopie aluminium EN AW – 5754. Badano również oddziaływanie międzywarstwy cynku osadzanej pojedynczo, podwójnie i potrójnie na przyczepność powłok niklowych do aluminiowego podłoża. Przyczepność określono metodą udaru cieplnego wg normy PN-EN ISO 2819. Dodatkowo określono mikrotwardość powłoki przed i po obróbce cieplnej.

Zaobserwowano, że ilość wytworzonych międzywarstw cynkowych nie wpływa znacząco na przyczepność powłok niklowych która została określona metodą udaru cieplnego. Nie zarejestrowano wad powstałych po badaniu takich jak: odwarstwienia, pęcherze czy łuszczenia się powłoki. Mikrotwardość powłok niklowych jest uzależniona od obróbki cieplnej oraz od ilości międzywarstw cynku. Dla pojedynczej i podwójnej podwarstwy cynku mikrotwardość po obróbce cieplnej zwiększa się a dla potrójnej podwarstwy cynku spada.

1. Introduction

When exposed to air, the unprotected aluminium surface tends to form a tight and transparent oxide coating that strongly adheres to the substrate. This coating protects aluminium and its alloys from the adverse effect of atmospheric corrosion and mildly aggressive environments but has to be removed before the galvanic treatment starts. To reduce the re-oxidation of the material surface, different kinds of protective coatings are applied, e.g. zinc coatings [1]. The intermediate zinc layers have another important role to play, namely that of improving the adhesive behaviour of nickel composite coatings [2]. The main chemical compounds included in the composition of the galvanising solutions are sodium hydroxide and zinc oxide added in proper proportions [3]. To a mixture of these two compounds, some other substances are also introduced to improve the adhesion of metal coating to aluminium and its alloys. These are compounds such as e.g. iron chloride and potassium-sodium tartrate [4]; small amounts of $FeCl_3$ in combination with the tartrate ions significantly improve the adhesive power of the coating, especially as regards aluminium alloys containing magnesium [5]. Adhesion of zinc layer to the aluminium surface is strongly influenced, besides the zinc oxide-to-sodium hydroxide ratio, also by the process duration and the temperature of the bath. These researchers also defined the quantitative relationship between dissolved aluminium and deposited zinc, which changes in the following way: dissolved aluminium 0.017 mg/cm^2 – deposited zinc 0.062 mg/cm^2. Comparing the lattice constants of aluminium (4.04 Å) and zinc (2.66 Å), the authors have found that during the exchange of two aluminium atoms for three zinc atoms, zinc forms a crystallographic plane of (110) orienta-

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tion which is a new layer of atoms with small distortion. This layer does not cover the entire surface. Initially it forms an epitaxial semi-continuous layer on all the major aluminium lattice planes, to grow in the next stage as separate crystals, observing the epitaxial continuity with the primary particles of zinc deposited earlier from the substrate [5]. The main aim of this study is presents a method use to produce single-, double- and triple-layer zinc interlayer on the EN AW-5754 aluminium alloy. The effect of the manufacturing process and heat treatment on the microhardness and adhesion of nickel coatings reinforced with micrometric 50 g/l Al_2O_3 particles was discussed, too. The adhesion was measured by the thermal shock technique in accordance with PN-EN ISO 2819.

2. Test materials and methods

Nickel coating was deposited on EN AW – 5754 aluminium alloy samples of 30×100×2.0 mm dimensions. The chemical composition was determined by optical emission spectrometry using an ARL 4460 spectrometer.

TABLE 1
Chemical composition of EN AW – 5754 aluminium alloy expressed in [%]

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
0.218	0.306	0.04	0.415	2.79	0.04	0.02	0.01	rest

Sample preparation before the trial consisted in grinding the edges with 120 grit sandpaper and degreasing with acetone. The next step included etching the samples in NaOH (100g/l) and brightening in HNO_3 (200g/l). Onto thus prepared samples, electroless zinc coating was applied in a solution containing ZnO (50g/l), NaOH (215 g/l), $FeCl_3 \cdot 6H_2O$ (2g/l) and sodium-potassium tartrate (20 g/l). The zinc coating was applied in single, double and triple layers. To obtain a fine-grained and compact zinc layer, a concentrated solution was used [6]. Before each next layer of zinc was applied, the previous layer had to be removed in a solution of 5% HNO_3 operating for 10 seconds [5]. Detailed step-by-step flow diagram of the production of successive zinc layers is shown below.

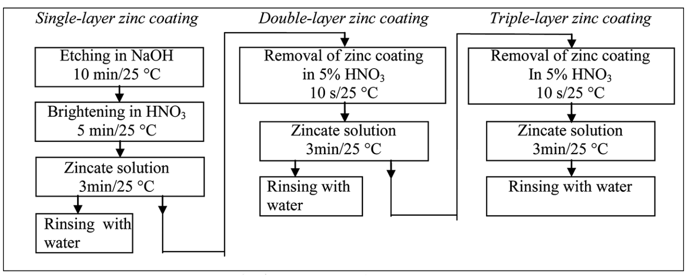

Fig. 1. A method for the preparation of individual zinc coating layers

To produce a zinc coating, the sample should be etched, brightened, dipped in the zincate solution, and then carefully rinsed with water. The application of each subsequent zinc layer is similar except that the pre-existing layer of Zn is removed in 5% nitric acid solution to create it once again.

The structure of a single layer of the zinc coating and its adhesion to the substrate depend on the chemical composition of the substrate. The effect of substrate on the zinc coating layer can be reduced by removing the layer of zinc in a 5% HNO_3 and creating another layer of zinc, which will have a different structure since zinc existing on the surface of the sample will influence the morphology of zinc produced in the next step [7, 8].

On thus prepared samples, a nickel coating was produced in a Watts type bath prepared in two variants:

– containing dispersed particles of Al_2O_3 of the >1 μm size, and
– free from the Al_2O_3 particles

The composition of the bath and the coating production parameters are listed below:

Chemical composition of bath:		Parameters of nickel coating production:	
$NiSO_4 \cdot 7H_2O$	150 g/l	Current	4 A/dm^2
$NiCl_2 \cdot 6H_2O$	30 g/l	Temperature	60°C
H_3BO_3	30 g/l	Time	1800 s
$C_7H_5NO_3S$	2 g/l	pH	3.5-4.5
Al_2O_3	50 g/l		

With so selected parameters, a coherent nickel coating was obtained. It was characterised by good adhesion to the substrate, a thickness of about 20 μm and Al_2O_3 particles uniformly distributed within the entire coating volume.

Microhardness was performed on the device MICROMET Buehler 5103. It allows measurement of the hardness of the intermetallic phase, the matrix, as well as films and coatings Vickers or Knoop method, under loads of from 0.01 to 1 kG. The work load was applied HV0.5.

3. Heat Treatment

Heat treatment consisted in annealing the samples at 130°C according to PN-EN ISO 4526 [9] and cooling with furnace (Fig. 2).

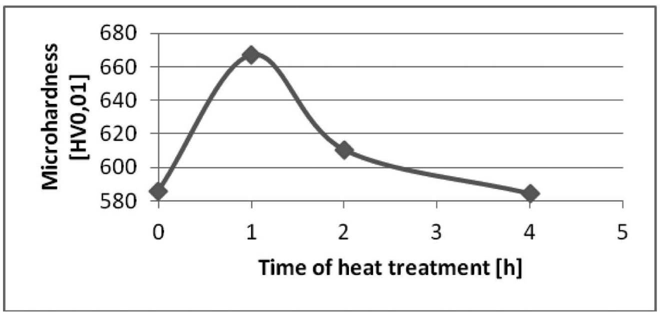

Fig. 2. Effect of heat treatment time on the microhardness of nickel composite coating. Double-layer coating

The heat treatment was carried out for 1 h, 2 h and 4 h, with maximum microhardness of nickel coating obtained after 1 hour of the treatment. The value amounted to about 667 HV0.01, and so it was decided to carry out the treatment for 1h.

4. Thermal shock

Nickel coating adhesion to the substrate was determined by the thermal shock method. According to PN-EN ISO 2819 [10], samples were heated in furnace to a temperature of 220°C, and then cooled in water at 25°C. The result is considered positive when the surface of the sample is free from the signs of the coating detachment from the substrate, such as blistering, peeling or delamination.

5. Test results

An analysis of the percent content of elements in the surface layer of zinc coating has showed that with increasing number of the deposited zinc layers, the content of zinc increases, too. For a single-layer coating it amounted to 6.7%, to assume the value of 8.2% for the double-layer coating and as much as 12.1% for the triple-layer coating. Other chemical elements present on the zinc coating surface are presented in Table 2.

TABLE 2
Chemical composition of surface with zinc coating: single layer, double layer, triple layer in [%]

	single layer	*double layer*	*triple layer*
Element	mass [%]	mass [%]	mass [%]
O	1.92	1.72	2.34
Mg	2.02	3.2	2.65
Al	88.23	85.73	81.49
Fe	1.09	1.13	1.36
Zn	6.73	8.21	12.15

Figure 3 shows images of the sample surface with zinc coating produced in single-, double- and triple-layer version.

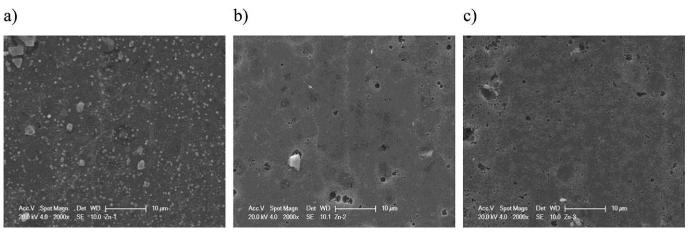

Fig. 3. Images of the sample surface with zinc coating: a) single layer, b) double layer, c) triple layer

First image show (Figure 3a) the separation of larger and smaller zinc distributed unevenly on the surface of the sample. The percentage of zinc, for this case is the smallest. In Figure 3b, it can be seen much less clear zinc precipitates, but the percentage content of Zn is more than a single layer of zinc. Small dark spots in Figure 3b indicate the pits on the aluminium substrate, these are defects of the double zinc interlayer (in figure 3a they are not presented). On the last picture (Fig. 3c), it can be seen that the zinc coating is more uniform. The content of chemical elements ie.: zinc, oxygen, iron is the largest.

Figure 4 shows nickel-coated samples after thermal shock, comparing also the sample appearance before and after heat treatment.

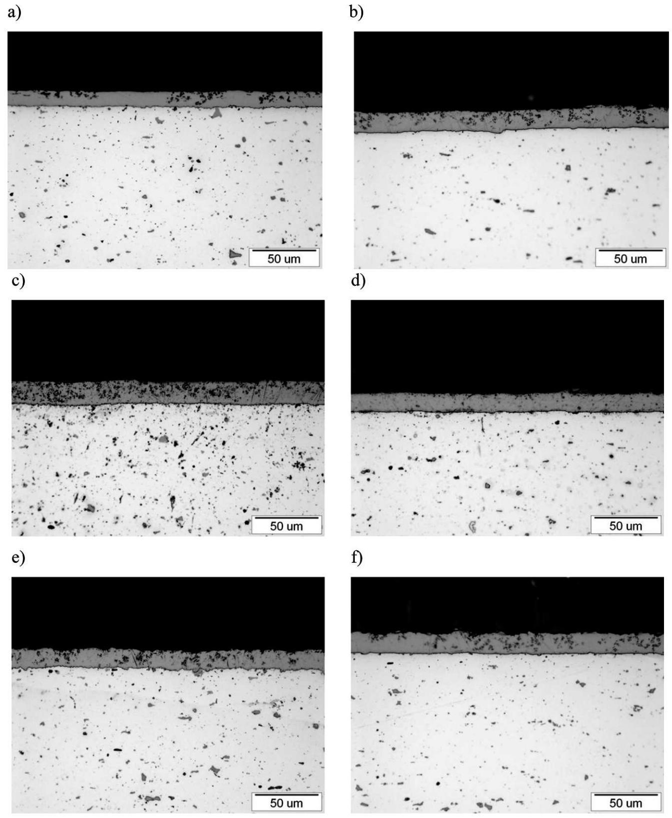

Fig. 4. Microstructure of nickel coatings deposited on: a) single-layer zinc coating before heat treatment, b) single-layer zinc coating after heat treatment, c) double-layer zinc coating before heat treatment, d) double-layer zinc coating after heat treatment, e) triple-layer zinc coating before heat treatment, f) triple-layer zinc coating after heat treatment. All microstructure are after thermal shock

The images above show the structure free from delaminations, peeling of the coating, or blisters on nickel-plated samples with and without the heat treatment. So, it can be concluded that the nickel coating adhesion is good, and the number of produced zinc sublayers has no major effect on this adhesion.

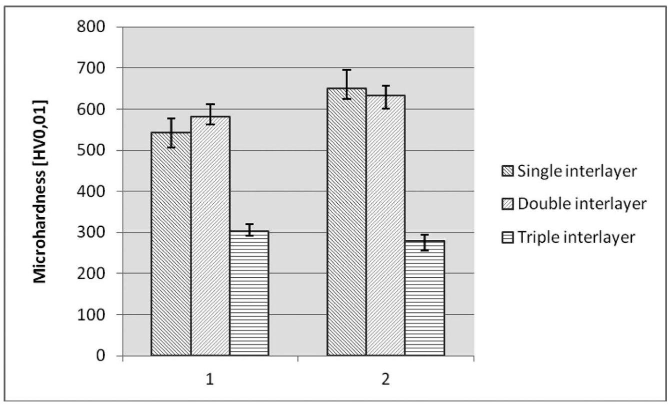

Fig. 5. Microhardness of nickel composite coatings with single, double and triple intermediate zinc layer: 1- before heat treatment,
2 – after heat treatment

Analysing the heat treatment effect on nickel coating microhardness it can be stated that in the case of single and double zinc sublayers, the microhardness of the composite coating increases after heat treatment, as shown in the respective diagram (Fig. 5). For triple zinc sublayer, however, it decreases after the applied heat treatment.

Another observation regarded the difference in the microhardness of nickel coatings produced in two different variants (with and without Al_2O_3). It has turned out that heating of samples in the furnace increased the microhardness of Al_2O_3 coatings by about 100 HV, while microhardness of nickel coatings without Al_2O_3 practically did not change, and the difference remained within the margin of error (Fig. 6).

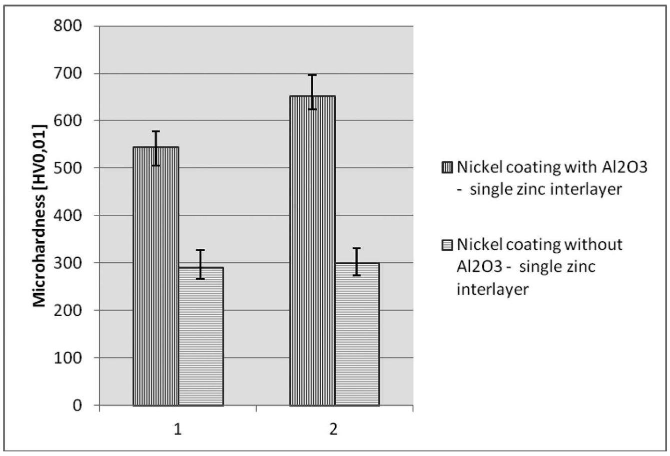

Fig. 6. Microhardness of coatings with and without Al_2O_3:
1 – before heat treatment, 2 – after heat treatment

In the study, two parameters of nickel coatings deposited on aluminium alloys were examined. The first determined parameter was adhesion of the coating to the substrate using a combination of zinc sublayers and heat treatment conducted by the method of thermal shock. The second parameter was the impact of heat treatment and Al_2O_3 particles on microhardness of these coatings.

6. Conclusions

Based on the obtained results the following conclusions can be drawn:

1. The number of produced zinc layers was reported to have no major effect on the adhesion of composite coatings to the aluminium substrate as determined by the method of thermal shock.
2. The thermal shock test carried out in accordance with PN-EN ISO 2819 did not reveal any changes in the nickel coating. There were no traces of delamination, blistering or peeling of the coating on samples regardless of the number of the zinc sublayers or type of the nickel bath (with or without Al_2O_3).
3. The microhardness of nickel composite coatings with the dispersed particles of Al_2O_3 was higher after the heat treatment by about 100 HV. On the other hand, hardness of the coatings without Al_2O_3 particles has remained practically unchanged.
4. For both single and double zinc sublayers, the microhardness of the nickel coating containing Al_2O_3 particles increased after heat treatment, but decreased when a triple zinc sublayer was applied.

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