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EFFECT OF Al_2O_3 CERAMIC PARTICLES ON CORROSION BEHAVIOUR AND TRIBOLOGICAL PROPERTIES OF NICKEL COMPOSITE COATINGS

The paper presents a study on corrosion behaviour and tribological properties of nickel composite coatings deposited by electrochemical method on aluminium alloy from 2xxx series (AlCu4MgSi). The nickel composite coatings were produced in a Watts bath of the following chemical composition: $NiSO_4 \cdot 7H_2O$ 150 g/l, $NiCl_2 \cdot 6H_2O$ 30 g/l, H_3BO_3 30 g/l with the addition of saccharin in an amount of 2 g/l. As hard ceramic dispersed particles embedded in the coating, alumina (Al_2O_3) was used in an amount of 12,5; 25; 50 and 75 g/l. Coatings were produced using cathodic current density of 6 A/dm^2, bath temperature of 60°C, pH 4, and the time 60 minutes. The electroplating bath was stirred with a mechanical stirrer (350 rpm).

The results obtained were compared with a nickel coating deposited without the ceramic particles. It was found that the presence of Al_2O_3 increases the wear resistance of composite coatings, but does not significantly improve the corrosion properties.

Keywords: Composite coating; Al_2O_3; Corrosion resistance; Tribological properties

1. Introduction

Nickel composite coatings reinforced with hard particles are used as anti-abrasive protection on parts of machinery and equipment made from aluminium alloys and exposed to abrasion during regular operation, such as toothed gears and belt transmissions for packaging machines, and also cylinder blocks in internal combustion engines. As regards some aluminium alloys, these coatings are competitive with hard anodic oxide coatings which, applied on these alloys, offer lower hardness HV and abrasion resistance. This is due to the fact that anodic coatings belong to the group of conversion coatings, which means that their properties depend on the type of aluminium alloy substrate. In contrast to anodic coatings which have thermal insulating properties, nickel-based coatings are characterised by good thermal conductivity. Therefore they can be used on aluminium products in all those cases when it is necessary to provide an efficient heat transfer, to mention as an example cylinders and pistons in internal combustion engines. Currently, on the elements made of aluminium, electrolytic nickel coatings with dispersed hard ceramic particles of micrometric dimensions (1-10 μm) are applied. Anti-abrasion properties of these coatings depend, among others, on the content of hard particles, and on their type, size and shape [1,2]. This study discusses the influence of the content of alumina as a dispersed phase on the corrosion behaviour and tribological properties of composite coatings.

2. Experimental

This study describes the corrosion and tribological tests carried out on nickel composite coatings deposited by electrochemical method on an aluminium alloy from 2xxx series (AlCu4MgSi). The coatings were produced in a Watts bath of the following chemical composition: $NiSO_4 \cdot 7H_2O$ 150 g/l, $NiCl_2 \cdot 6H_2O$ 30 g/l, H_3BO_3 30 g/l with the addition of saccharin in an amount of 2 g/l. Single layer zinc coating was also applied according [3]. As a reinforcing phase, alumina of submicrometic size was used in amounts of 12.5, 25, 50 and 75 g/l. Prior to the deposition of coatings, the bath was stirred with a mechanical agitator in the presence of ultrasounds to ensure a homogeneous distribution of ceramic particles in the entire bath volume. Coatings were produced at a cathodic current density of 6 A/dm^2, bath temperature of 60°C, pH 4 and the time of 60 minutes. The electroplating bath was stirred during the production of coating with a mechanical stirrer (350 rev/min.).

The microstructure of the composite coatings was examined by scanning electron microscopy (SEM) using a Philips XL30 microscope and by transmission electron microscopy (TEM) using a TECNAI G2 microscope with an attachment for EDX and STEM studies and with a HAADF detector.

Coating thickness was determined by coulometric method using a CULOSCOPE CMS STEP Fischer device (F6 electrolyte, dissolution rate of 20 μm/min.) The structural analysis of alumina and measurement of the nickel crystallite size were carried out by X-ray diffractometry on a BRUKER D8 ADVANCE apparatus. The content of the composite particles in the coating was determined by gravimetric method, dissolving the coating in HNO_3 solution. The results obtained were compared with the deposited nickel coating free from any ceramic particles. Abrasion tests were performed after 24 h sample acclimatisation under the following environmental

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conditions: temperature of 23 ± 2°C, relative humidity 50 ± 5%, using a Taber Abraser model 5155 apparatus and CS-17 abrasive wheels, a load of 1000 g and 1000 abrasive cycles.

Corrosion tests were carried out with an AUTOLAB PGSTAT model 302 device. The working electrode was nickel- coated sample with the surface area of 1.8 cm^2, the reference electrode was Ag/AgCl/3M KCl electrode and the auxiliary electrode was made of platinum. Polarisation measurements were performed in a glass cell at 25°C using 1M NaCl as a corrosive solution. The scane rate of polarisation was 5 mV/s.

3. Results and discussion

Figures 1-2 show the microstructure of selected coatings examined by SEM on polished cross-sections. SEM observations revealed differences in the distribution of Al_2O_3, depending on the amount of alumina powder. The particles are well surrounded by the metallic nickel matrix, and their distribution throughout the volume of the composite coating is satisfactory. However, microscopic observations showed the particle agglomeration effect.

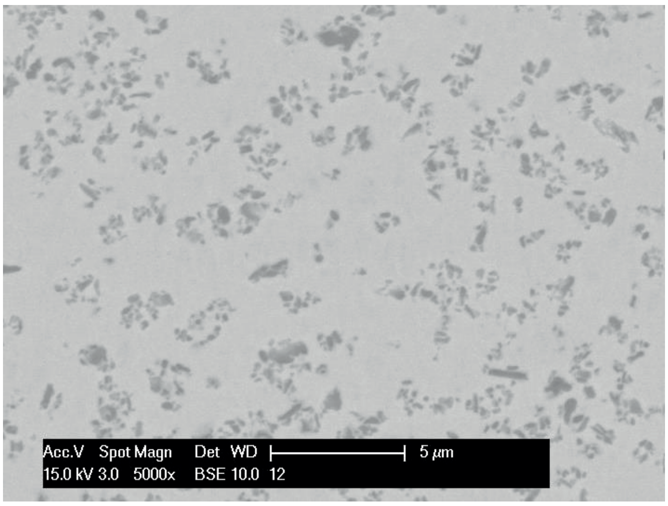

Fig. 1. The structure of composite coating containing 25g/l Al_2O_3

The TEM structure of Ni coating shows very fine grains (Fig. 3a) and occasionally high-density dislocations within the grain boundaries (Fig. 3b). The nanometric structure of grains has been proved not only by the measurement of the grain size but also by the angle of disorientation. From point diffraction of the examined area it follows that individual reinforcements are arranged in the form of rings, which may indicate a large diversity of orientations in the examined area. Chemical analysis in microregions has revealed that in thicker layers of the thin film in a coating, some areas have the embedded particles of Al_2O_3 while matrix is mainly composed of Ni (Fig. 4).

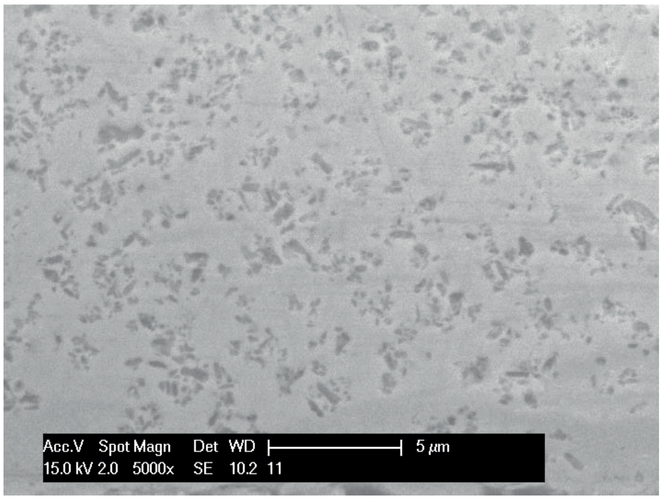

Fig. 2. The structure of composite coating containing 50g/l Al_2O_3

For the analysis of crystallite size, natural surfaces of the nickel coating samples were adopted. The examinations were carried out on the first five diffraction reflections of nickel. The diffraction patterns were measured with a D8 Advance diffractometer in Bragg-Brentano system with characteristic X-ray radiation of tubes with copper anode. Calculations were based on the Williamson-Hall method which is an improved Scherrer technique to measure the crystallite size [4-6]. The results of the analysis are compared in Table 1. They allow the conclusion that there is no significant difference in the size of the forming crystallites no matter if the alumina content is 25 or 50 g/l. More than double size of the crystallites was found in the coating with Al_2O_3 content amounting to 75 g/l. The D8 Advance diffractometer was also used for the characterisation of alumina powder embedded in the composite coating. The X-ray analysis showed that it is composed of crystallographically pure corundum powder.

TABLE 1

A comparison of the results of measurements of the crystallite size

Al_2O_3 content [g/l]	0	12,5	25	50	75
Crystallite size [nm]	35	39	46	45	115

Electrochemical corrosion tests (Table 2) conducted with a kit from AUTOLAB showed that the highest corrosion resistance was offered by a composite coating produced with an alumina content of 12.5 g/l. This coating shows the lowest corrosion current density (6.20 A/cm^2) and the highest polarisation resistance (1915 Ω). The composite coating has, however, a more anodic character than the coating which does not contain alumina in its composition (Fig. 5). Other composite coatings produced with an alumina content of 25-75 g/l are also of an anodic nature, compared to the nickel coating which is free from the dispersed particles of alumina.

TABLE 2

The results of electrochemical studies

Sample designation	I_{corr} [A/cm^2]	R_p [Ω]	E_{corr} [mV]
0 g/l Al_2O_3	14.07	1589	-584
12.5 g/l Al_2O_3	6.20	1915	-664
25 g/l Al_2O_3	45.20	42.77	-884
50 g/l Al_2O_3	89.47	224.2	-875
75 g/l Al_2O_3	22.38	684.9	-843

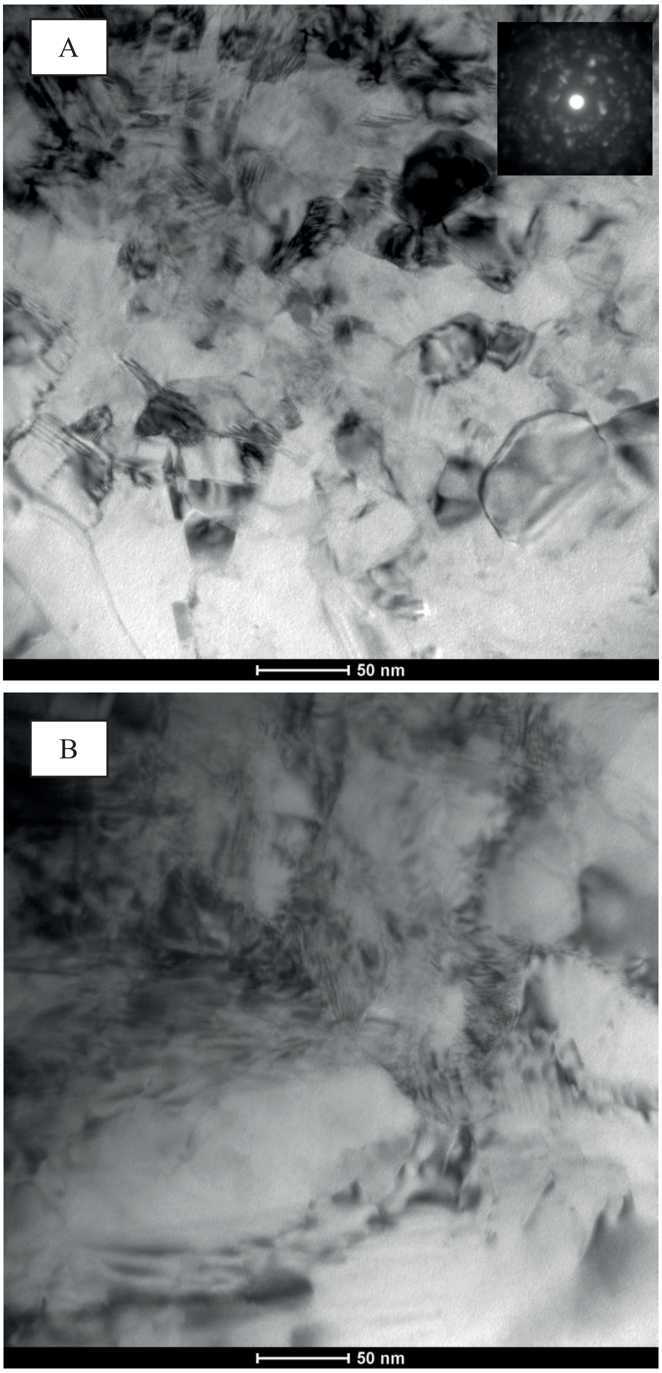

Fig. 3. TEM microstructure of Ni coating (a) grains of nanometric size (b) occasional spots surrounded by high-density dislocations

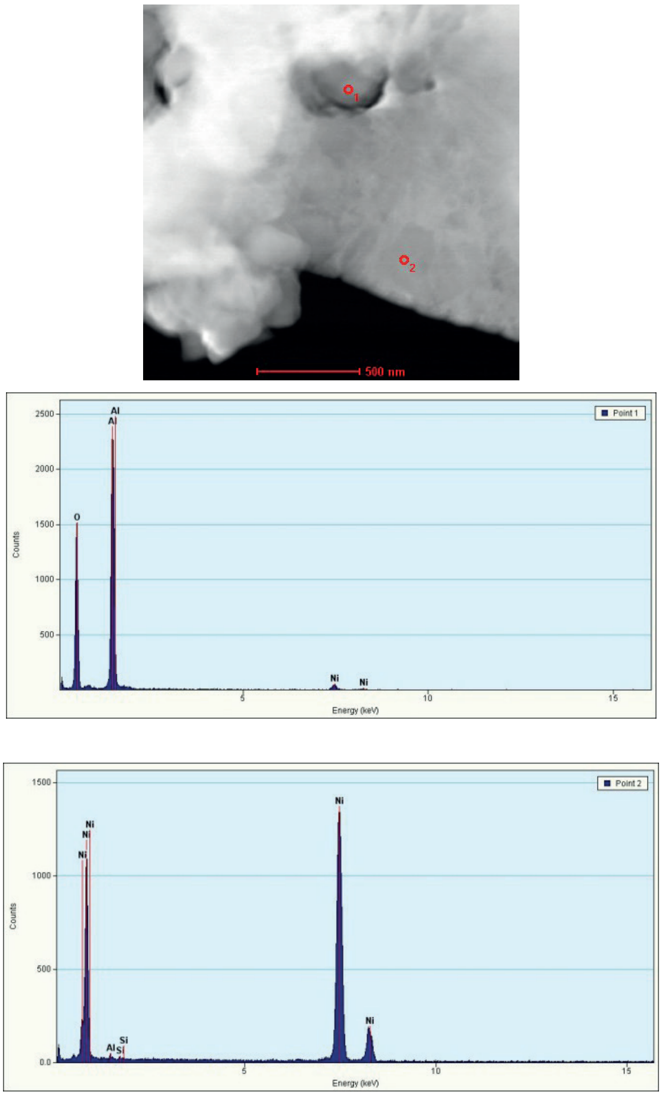

Fig. 4. Chemical analysis in microregions of the composition of coating. STEM image from HAADF

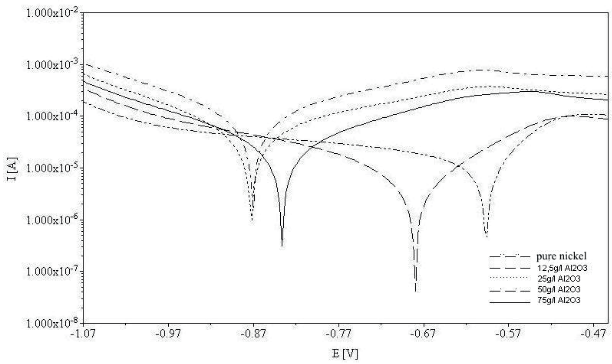

Fig. 5. Polarisation curves of nickel coatings reinforced with Al_2O_3 with different content of particles in the bath and coatings free from the ceramic particles

The results of coating thickness measurements are shown in Figure 6.

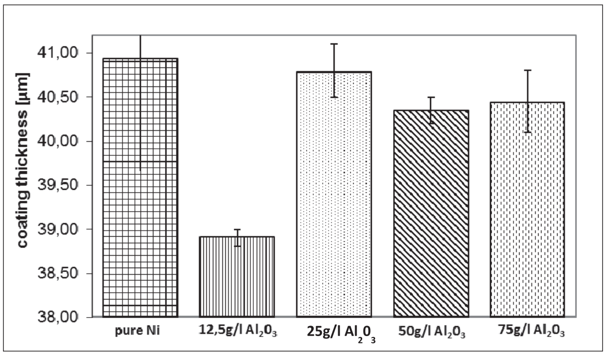

Fig. 6. Thickness of produced nickel coatings

The results of abrasion resistance test showed that the best abrasion resistance has the nickel coating comprising in its composition 25 g/l of the ceramic particles of alumina (8.8 mg weight loss). Coatings containing 12.5, 50 and 75 g/l Al_2O_3 are characterised by similar values of abrasion wear resistance, which amount to 16.9, 18.8 and 15.7 mg, respectively. The highest weight loss among the examined coatings has the coating produced without the addition of ceramic particles (weight loss of 23.2 mg).

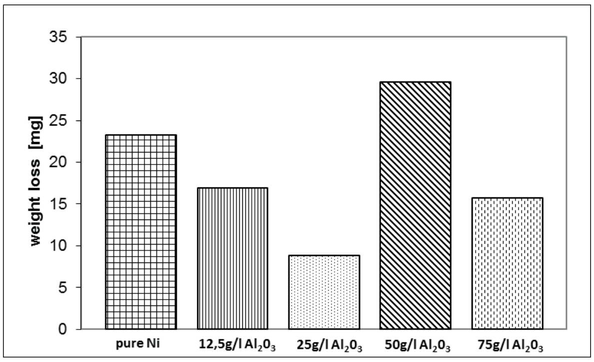

Fig. 7. The abrasion wear resistance of produced nickel coatings determined by TABER method

The results of the measurements of the content of ceramic particles in composite coatings are plotted in the graph below (Fig. 8). They show that the largest amount of ceramic particles is embedded in the composite coating, when the electroplating bath contains in its composition 75 g/l of alumina (21.1%). The content of the ceramic particles produced with 12.5 and 25 g/l does not exceed 2%. However, with the alumina content of 50 g/l of bath, the amount of particles embedded in the coating is approximately 13%.

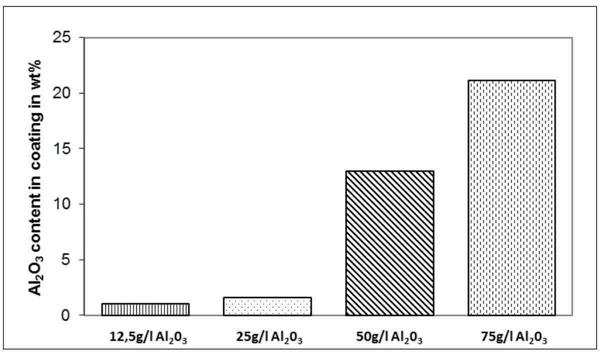

Fig. 8. The content of ceramic particles in coating

4. Conclusions

Based on the studies conducted it was found that the presence of Al_2O_3 ceramic phase increased the abrasion wear resistance of the produced composite coatings. All of the examined composite coatings were characterised by the weight loss lower than the coatings without the addition of ceramic particles. An increase in the percent content of alumina in the electroplating bath from 25 to 50 g/l resulted in an almost eight-fold increase in the content of the ceramic phase in the composite coating, but no beneficial effect of this content on the tribological properties of the coatings was observed. The highest abrasion wear resistance among all the coatings tested had the coating produced with an alumina content of 25 g/l Al_2O_3.

Acknowledgements

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