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ORIGINAL PAPER

Pulse nickel electrolytic colouring process of anodised aluminium

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Abstract The influence of frequencies of periodic reverse current on the morphology of nickel-pigmented aluminium finishes has been studied. The pigmentation of the anodised aluminium was realised by electrolytic colouring in electrolytes with additives and in additives-free electrolytes. Additives-free electrolytes generally provide advantageous quality of pigmentation with regular and homogenous nickel morphology on the aluminium substrate at all applied frequencies. The presence of 5-sulphophtalic acid additive strongly influences the deposit quality. The deposits obtained from nickel sulphate electrolytes at all used frequencies with the use of periodic reverse current with citrate acid and sulphosuccinic acid additives provide the similar poor quality of colouring under studied plating conditions.

Keywords Aluminium anodic oxidation · Pigmentation · Periodic reverse current · Frequency · Morphology

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1 Introduction

Nickel pigmentation has been extensively studied among metal salt solutions for electrolytic colouring of anodised aluminium for its appreciable optical properties in anodic alumina conversion layer for solar collectors [1–4]. Electrolytic colouring (EC) mostly uses AC current to deposit metal in the pores of anodic aluminium oxide. Nowadays, periodic reverse current (PRC) is in the centre of study to influence morphology of the deposited coatings. In the beginning, the pulse current (PC) was studied also as a substitute of additives for electrolytes determined for metal deposition [5–8]. At present, PC serves namely to control morphology and composition of electrodeposits in nanocrystalline scale and especially to alter the prevailing mass transport conditions as well as to control the composition of electrodeposited alloys by varying the process parameters [9–11]. Generally, pulse current is characterized by the current-on time, current-off time and peak current. In our study, rectangular shape of the current wave was applied to keep anodic and cathodic cycle of the wave constant with constant value of cathodic and anodic current-on time. It follows that the whole charge running the process equals zero.

Additives in electrolytic solution play an important role to control the local growth and overpotential of the electrode in electrodeposition. The surface morphology of electroplated metal films strongly depends upon the composition and the concentration of additives. Various kinds of additives such as levellers, brighteners, accelerators, etc., have been developed in electroplating engineering. Additives in the electrolytes improve the deposit properties and influence deposit morphology by adsorbing on the cathode and inhibiting various processes during electrodeposition [12]. 5-Sulphophtalic acid, citrate acid, and sulphosuccinic acid are applied in the industrial production to assure the quality of pigmentation serving as complexing agents. The complex is supposed to act as a reservoir of simple ions and to dissociate rapidly enough to keep the cathode reaction operative [13]. The aim of our work was to study influence of the additives and frequency on the quality of pigmentation by electrolytical colouring of anodised aluminium finishes.

2 Samples preparation and experimental method

The aluminium sheets with purity of 99.5% and with dimensions of 30 mm × 80 mm × 0.5 mm were first chemically pre-treated. Each operation, degreasing in a 20 g dm^{-3} commercial solution Aktigal 12 (MAG, Slovakia), chemical etching in a 50 g dm^{-3} sodium hydroxide bath (Mikrochem, Slovakia), and brightening in a 400 g dm^{-3} bath of nitric acid (Mikrochem, Slovakia) was carried out at 70 °C for 3 min. After each step, the samples were rinsed under running water. Anodic oxidation was done in 180 g dm^{-3} sulphuric acid solution with a constant current density of 1.5 A dm^{-2} at (18–22) °C for 40 min. The thickness of the formed anodic aluminium oxide (alumina) was 18 ± 1 μm. The samples were rinsed for 30 min and dried in hot air for 10 min afterwards. The power supply (pe86c plating electronic Germany) was used for PRC current control. Peak current density of the anodic and cathodic half cycles was equal at the each applied frequency. It was 0.95 A dm^{-2} for the additives-free electrolytes and 1.43 A dm^{-2} for the electrolytes without additives. Duration of the anodic, cathodic half cycles and off-time during the cycle was at each applied frequency equal, e.g. 11–11–11 ms at frequency of 30 Hz. The time of electrolytical colouring was 7 min. The additives-free electrolytes and electrolytes with additives were applied. Between additive-free electrolytes were tested typical Watts bath and basic S bath containing $NiSO_4$ (105 g dm^{-3}) and H_3BO_3 (30 g dm^{-3}) components. Citrate electrolyte with citric acid (C), SJ electrolyte with sulphosuccinic acid and SIF electrolyte with 5-sulphoisophthalic acid were used as electrolytes containing additives. All chemicals used have been of analytical grade. Value of pH for all used bathes was about 4. The sample weight and film thickness was measured after electrolytic colouring by analytical balance and by MINITEST 500 system based on the eddy currents as well. After colouring, the weight and the thickness of the non-conductive anodic alumina layer were measured. Also, after stripping of the anodic alumina in the determined time interval, the rest of anodic alumina layer was measured. Film thickness was checked with a MINITEST 500 (Fischer Permascope, Germany). The error of thickness measurement was less than 3% of the reading value, a negligible error in our case.

Parameters *L*a*b* in the colour space were measured with commercially available spectrocolorimeter Spectrodense A 504009 Premium (Techkon, Germany): the calibration was done against the white standard. Nickel content in the pigmented samples was determined by energy dispersive X-ray analysis (EDX) and atomic absorption spectroscopy (AAS) measurements. EDX was realised after stripping of anodic alumina coatings by JEOL JXA-840 A (Japan) and AAS by dissolving the pigmented layer in the nitric acid solution and determining the content of nickel in the solution with use of equipment Perkin Elmer 1100 (USA).

The stripping [2] was done in a solution of 35 cm^3 of phosphoric acid (p.a. Metrochem, Slovakia), with density $\rho = 1710$ g dm^{-3} and of chromium oxide (VI) (purum, Lachema Brno, Czech Republic) with $\rho = 20$ g dm^{-3} at 80 °C. The samples were rinsed and dried afterwards for 1 min and then stored in desiccator for 30 min. The dissolving was carried out in a solution of 400 g dm^{-3} of nitric acid at 80 °C for 15 min.

Randomly selected stripped samples from the series of the prepared ones were cut in the middle to get squares with dimensions of 1 cm × 1 cm. Such processed samples were further investigated by Scanning Electron Microscope (SEM). SEM was realized by BALZERS SCD 050 Czech Republic, CARL ZEIS EVO 40 Germany (to reach higher magnification). Acceleration voltage of the equipments was 20 kV. Study of the stripped surface of the aluminium was done by atomic force microscopy (AFM) measurements as well by Veeco diCP-II (USA) in non-contact mode by a tapping regime.

3 Results and discussion

Colour quantification of the pigmented coatings was done through the CIE (Commision Internationale de l'Eclairage) *L*a*b* system. This system characterizes any colour by a luminance parameter *L* and two colour coordinates *a* and *b* which specify the point on the chromaticity diagram [14]. These parameters for an ideal black body are 0*0*0. CIE *L* parameters for prepared samples are summarized in Table 1 where parameter *L* of the finishes pigmented in additives-free electrolytes reaches acceptable values especially at the frequencies of 30 Hz. Colouring with S electrolyte provides sufficient results at all used frequencies of 30, 50, 70 Hz and samples pigmented by W electrolyte provide at frequency of 50 Hz satisfactory results as well. The studied frequencies less than 100 Hz were chosen on the Sato and Sakai results [15]. They found out the frequency below 100 Hz assures the shade of obtained colour constant even if these measurements were done with the use of AC. As to the electrolytes with additives, just SIF electrolyte gives comparable *L* values of the pigmented samples except the frequency of 30 Hz. Electrolytic colouring done by C electrolyte at the studied range of cathodic/anodic current-on time provide unsatisfactory quality of pigmentation confirmed by *L* values of the tested finishes. *L* values reached by the colouring with SJ electrolytes are the best ones at frequency of 50 Hz; however, the quality of pigmentation for all tested frequencies is not sufficient enough. It follows the best results were reached with additives-free electrolytes and comparable results were obtained with the use of SIF electrolyte by PRC.

Investigation of the morphology of the prepared finishes at different frequencies is connected with knowledge about the arrangement of the nickel fibres in the pores of anodic alumina. Stripping is used to remove the layer of anodic aluminium oxide and to see the arrangement of the particles (Fig. 1). The loss of anodic alumina weight and mass during stripping in dependence on time of stripping was measured. Figure 2 shows the dependence of mass loss to thickness loss of anodic alumina. One can see that the dependence is after certain time a straight line with an unsteady tendency. In spite of the fact that 10 min-stripping time was chosen to study the morphology of the analysed finishes. The time was chosen because of the fact that the change of mass loss and thickness is not fundamental.

Nickel content of the pigmented samples was determined by EDX and AAS methods as it is seen in Fig. 3a, b, respectively. The nickel content of the samples pigmented with the use of PRC was analysed by EDX on the samples after 10 min stripping for all the studied electrolytes and frequencies. The results shown in Fig. 3a confirm the conclusion from spectrocolorimetry measurements. It was found out that the highest content of nickel was analysed by applying S electrolyte, the highest content of nickel was analysed at frequency of 30 Hz. The Watts electrolyte contains a high amount of nickel for frequencies of 30 and 50 Hz. Concerning the electrolytes-containing additives, the highest amount of nickel was analysed for all these electrolytes at a frequency of 50 Hz. These amounts are comparable with additives-free electrolytes namely for SIF electrolyte. The samples coloured at a frequency of 70 Hz for C electrolyte and 30 Hz for SIF electrolyte could not be determined. Figure 3b shows the dependence of nickel content determined by AAS on the frequency at PRC electrolytic colouring. The highest content of nickel in the

Table 1 Values of *L* parameter in dependence of applied frequencies of periodic reverse current for samples pigmented in the colouring electrolytes

f/Hz	Δ*L*—C	Δ*L*—SIF	Δ*L*—SJ	Δ*L*—S	Δ*L*—W
30	68.61	70.24	67.26	28.57	26.51
50	71.51	25.39	47.81	38.94	29.59
70	78.27	31.17	57.55	36.03	46.79

C citrate, *SIF* sulphoisophtalic, *SJ* sulphosuccinic, *S* nickel sulphate and boric acid, *W* Watts

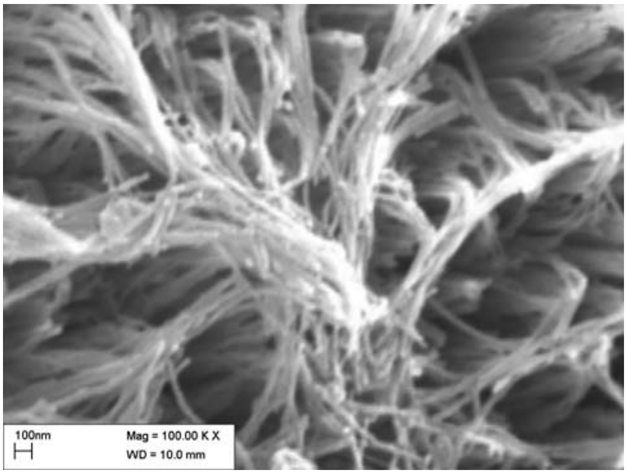


Fig. 1 SEM micrograph of nickel fibres after 10 min stripping of anodic alumina for samples coloured in Watts electrolyte at frequency of 50 Hz by PRC

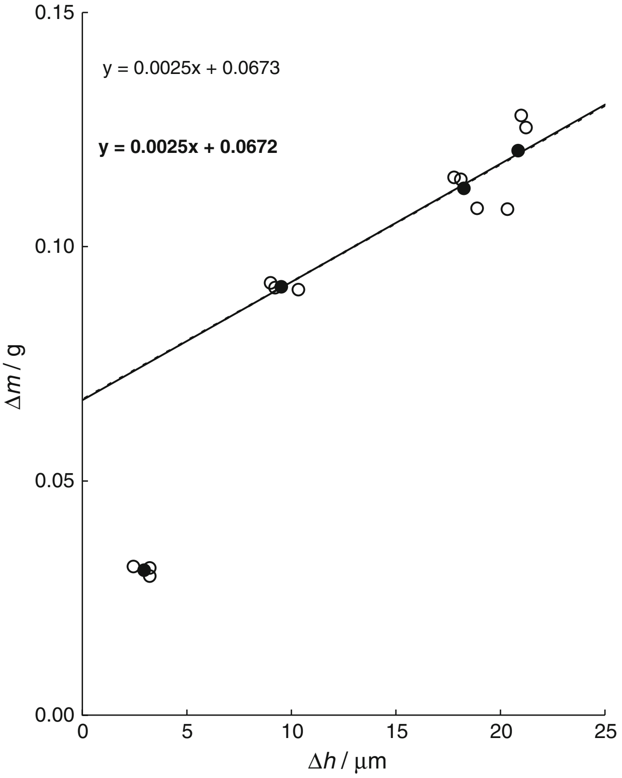


Fig. 2 Dependence of mass change on thickness change of the stripped, pigmented and anodised samples. *Empty marks* denote measured values. *Full marks* denote average values

pores of anodic alumina was found for the coatings pigmented in Watts and SIF electrolytes. All electrolytes on the nickel basis containing additives (C, SIF, SJ) reach the highest content of nickel in the coating at a frequency of 50 Hz. Watts and S2 electrolytes provide the maximum of nickel content at a frequency of 30 Hz.

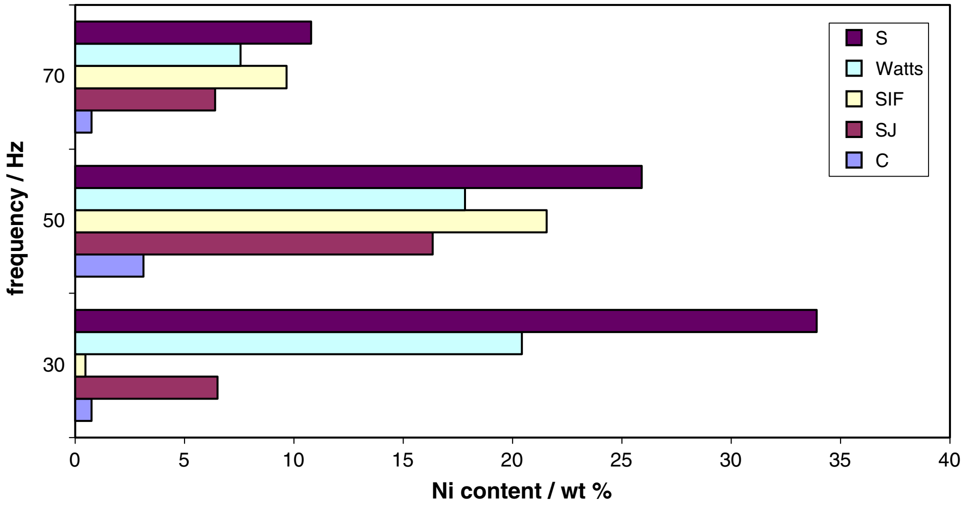
Figure 4 shows the nickel arrangement after removing of anodic alumina for the samples coloured in S and SIF electrolytes at the studied frequencies. It is clearly seen the regular and homogenous nickel arrangement on the aluminium surface. Influence of the additive is shown on the different nickel fibres arrangement. These results are in good agreement with results presented in Table 1. Better distinguishing of the nickel arrangement on the aluminium is recorded with the use of AFM (Fig. 5, 6). Especially 2D AFM records show high density of nickel fibres after stripping of anodic alumina (except of 30 Hz frequency colouring for samples coloured by SIF electrolyte).

Concerning pigmentation quality on the nickel content of the sample, it is evident that there is dependence between the amounts of nickel fibres on the quality of pigmentation characterized by parameter *L* of the colour space. The high density of nickel fibres on the stripped sample confirmed by the used analytical methods (EDX, AAS) provides the high quality of pigmentation and low value of the parameter *L*. Even though both methods do not offer the identical results for nickel fibres amount for all tested samples and frequencies a tendency of the results is evident to conclude above presented statement. The obtained results are similar to those one found out by Kallithrakas-Kontos et al. [16]. They derived an exponential relation between the optical properties (absorbance) as a function of the surface density of the deposited metal.

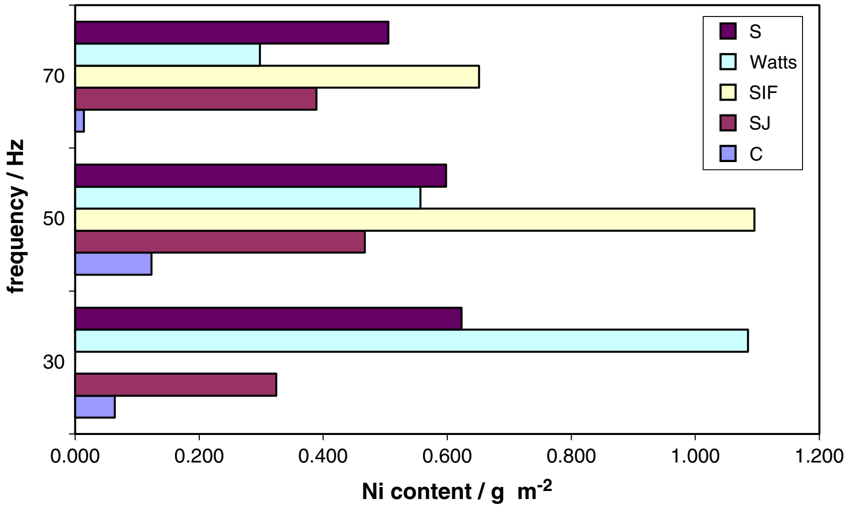
Role of the addition agents in aqueous electroplating baths is an important parameter owing mainly to the

Fig. 3 Nickel content of the samples coloured in the studied electrolytes with applied AC determined by **a** EDX, **b** AAS

(a) EDX



(b) AAS



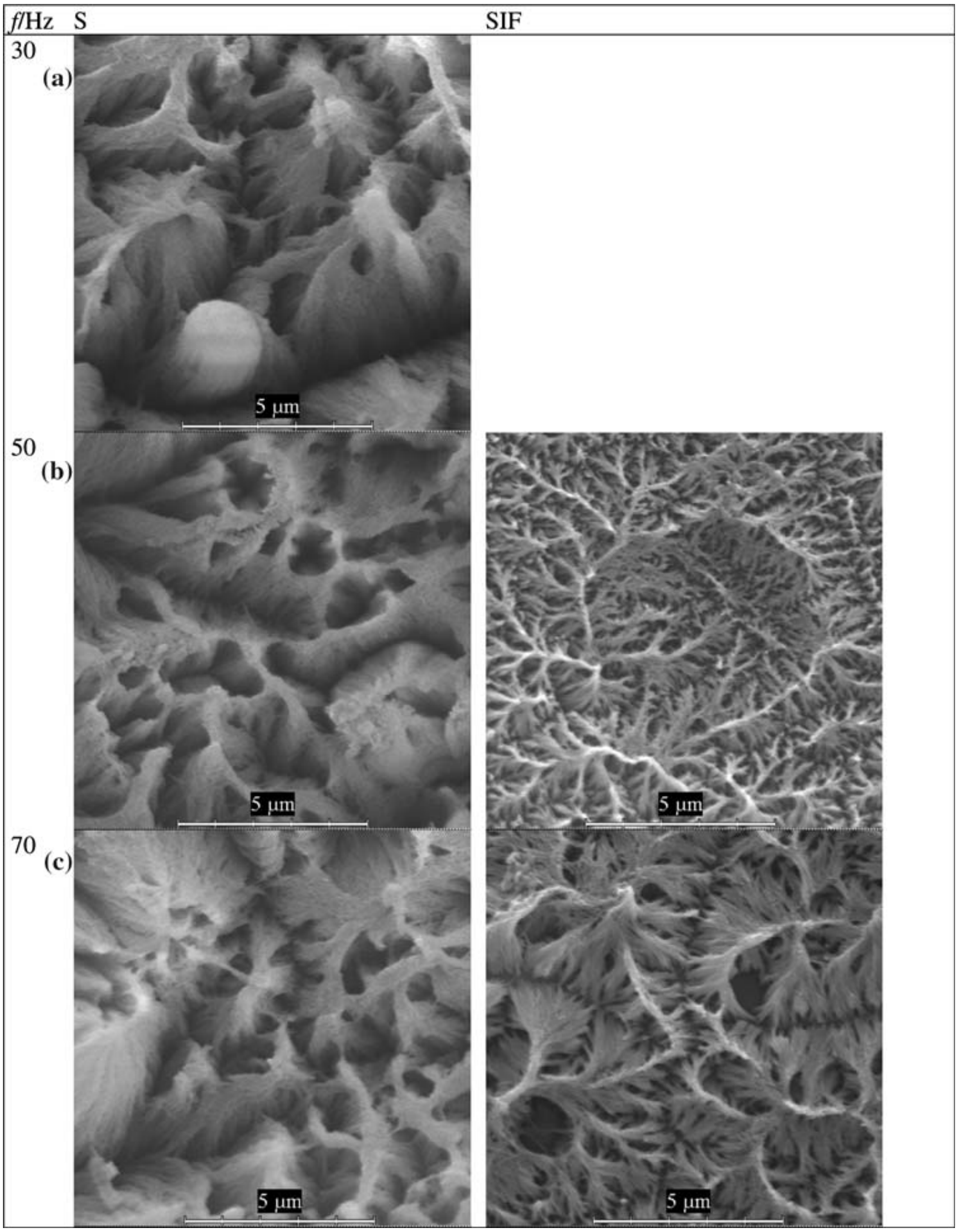


Fig. 4 SEM morphology study after 10 min stripping time with applied PRC at frequencies of **a** 30 Hz, **b** 50 Hz, **c** 70 Hz, with use of S and SIF pigmentation electrolytes

interesting and important effects produced on the growth, structure and glossiness (brightness) of deposits. Applied additives act as complexing agents. The slow dissociation of the complex ion is supposed to be one of the causes of higher polarization that usually attends the deposition of metals from solutions of complex ions. The concentration polarization due to the discharge of a complex ion increases with current density [13]. In general, the additives increase the throwing power of electrolyte and help the deposition of the metal on the cathode surface [17, 18]. These effects were proven for electrodeposition of e.g. zinc [19, 20], copper [12]. To my best knowledge, the influence of the analysed organic-types additives influencing the quality of colouring was not studied. The additives produce significant changes in the morphology of an electrolytically growing crystal as one can see in Fig. 7. Shaffei et al. [4] were studying the use of chloride and magnesium additives on the quality of colouring using AC. In this study, just chloride anions were influencing the quality of colouring (measured by absorbance). Regarding our measurements, additives in the colouring electrolytes increased the polarization of the process having effect on morphology of nickel fibres. Influence of citric acid on quality of colouring during PRC electrodeposition is without pigmentation effect on the other hand usage of sulphosuccinic acid influences in the equal degree the amount of nickel in the alumina coating. Especially sulphoisophtalic acid at frequency of 50 and 70 Hz allows increasing of nickel fibres

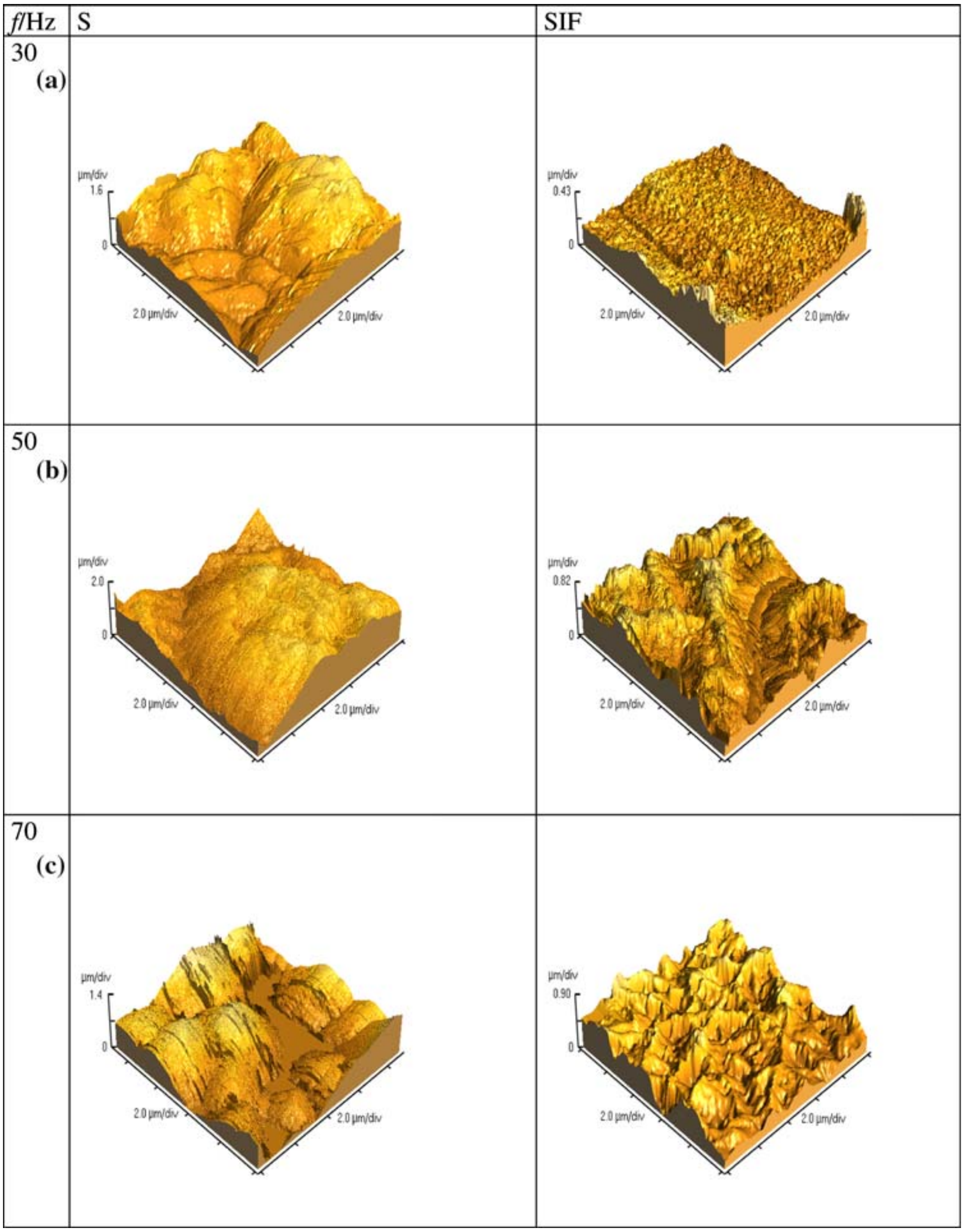


Fig. 5 AFM (3-D) morphology study after 10 min stripping time with applied PRC at frequencies of **a** 30 Hz, **b** 50 Hz and **c** 70 Hz, with use of S and SIF pigmentation electrolytes

amount on the substrate. One can assume the high impact of the additive composition on the quality of the pigmentation. According to Bockris [21], the addition of certain organic substances affects to a very large extent the physical properties and the conditions of formation of electrodeposits. One phenomenological effect produced by additive concerns morphology resulting in the microscopic appearance of the surface as well as in the structural properties of the deposit.

Pulse plating control the microstructure and composition of electrodeposits. The reduction or avoidance of additive usage would be a great simplification for electrodeposition of metal and pulse plating has been considered as an alternative to the additive usage. It is evident that the morphology obtained after usage of additives-free electrolytes with the use of PRC is advantageous one. During periodic reverse plating, we can talk about nickel deposition during cathodic half cycle, anodic oxidation of aluminium during anodic half cycle and relaxation/off time. Relaxation time serves to recover the concentration of metal ions at the pore tips and to improve the homogeneity of the deposition and limits the hydrogen evolution. Reached results confirm that the duration/frequency of the cycle is important for the quality of pigmentation. Additives-free electrolytes reach comparable quality of pigmentation at all studied frequencies; anyhow, the best quality of pigmentation was reached at frequency of 30 Hz with duration of anodic, cathodic half cycles and off time

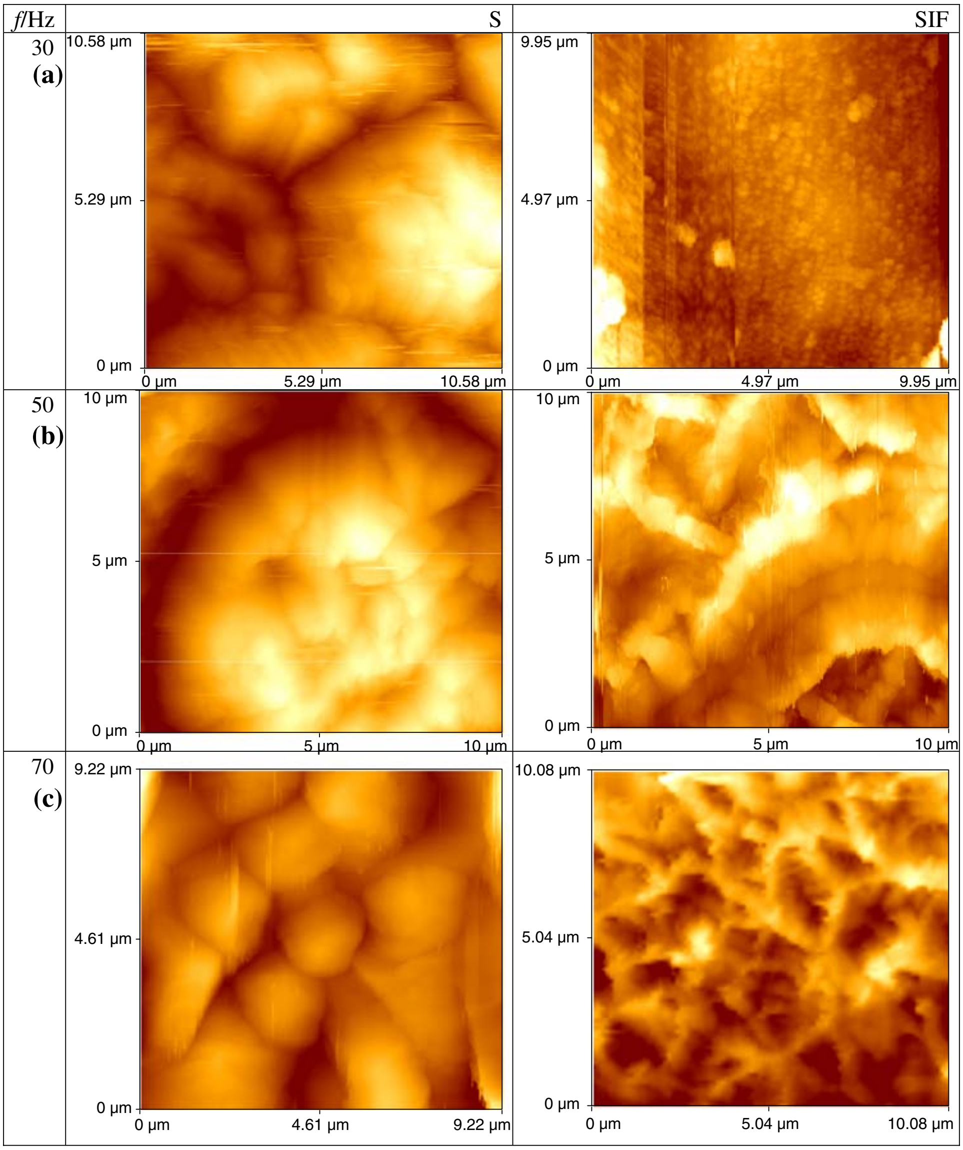


Fig. 6 AFM (2-D) morphology study after 10 min stripping time with applied PRC at frequencies of **a** 30 Hz, **b** 50 Hz and **c** 70 Hz, with use of S and SIF pigmentation electrolytes

11 ms. The duration time at the other frequencies was 7 and 4.8 ms. It follows that for additives-free electrolytes the longer deposition time supports the instalment of nickel fibres into the pores of anodic alumina with the elimination of undesirable reactions (hydrogen evolution during cathodic half cycle). The conclusion could be supported by results of Nielsch et al. [22]. While metal is deposited at the pore tips, the metal ions are exhausted with decreasing ion concentration. Along each pore, the concentration grows but for the metal ions, it takes time to migrate from the pore opening to the pore ground via thermal diffusion. In the case of electrolytes with additives, sufficient quality of pigmentation is reached just for samples coloured in the electrolyte with additive SIF at frequency of 50 and 70 Hz. One can suppose that longer duration of the cycle, in this case, allows the activity of undesirable reactions and even long relaxation time is not sufficient enough to ensure recovery of the pores to allows the electrocrystallization of nickel into the pores of anodic alumina.

Hence, one can conclude that there is a correlation between nickel content and the pigmentation quality of the tested samples. The higher amount of nickel in the coating supports the lower values of parameter *L*. The lowest nickel content is in the samples of pigmented by C electrolyte that is answering the poor quality of pigmentation confirmed by high values of parameter *L*. The highest nickel content contains samples pigmented in SIF electrolyte at frequency 50 Hz and W electrolyte at frequency 30 Hz. The parameters of *L* answer the fact as well. One can conclude that for electrolytes with additives (except for the C electrolyte at the tested conditions), the high quality of pigmentation was reached for samples at frequency of 50 Hz. The samples coloured in electrolytes without additives reach the best quality of pigmentation with used frequency of 30 Hz. The

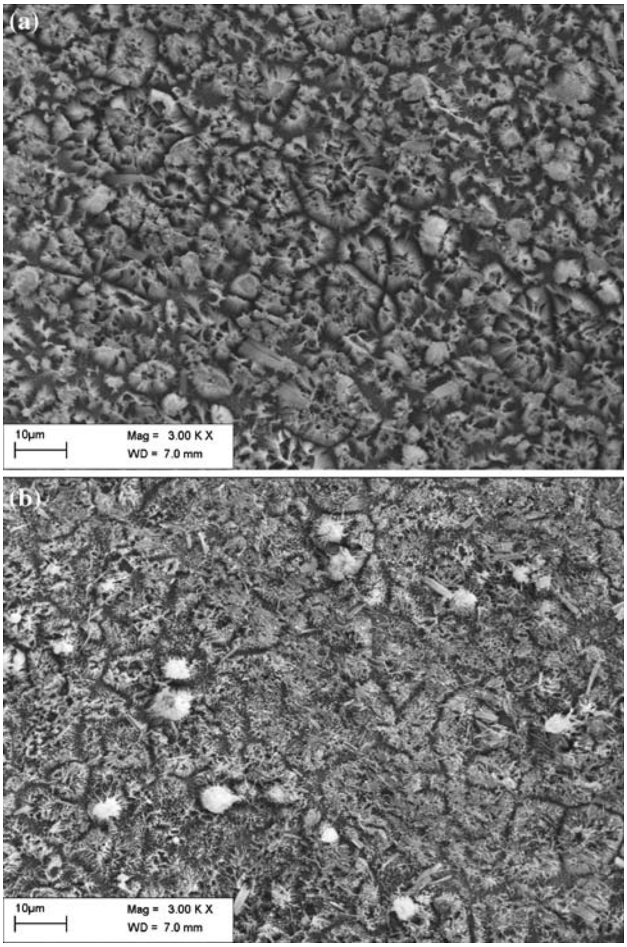


Fig. 7 SEM morphology study after 4 min stripping time with applied PRC at frequencies of 50 Hz with use of **a** W and **b** SIF pigmentation electrolytes

influence of the frequency is for quality of pigmentation the significant one. The influence of additive is with usage of PRC either negligible (C, SJ) or comparable with additives-free electrolytes.

The electrolytic colouring on the aluminium substrate realised by PRC in additives-free electrolytes provide the advantageous coatings with acceptable optical parameters. However, with the use of PRC at the studied conditions the electrolytes with additives provide poor quality of colouring. Just additive 5-SIF gives comparable quality of colouring.

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