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Preliminary studies on electrodeposition of Zn-Fe-W alloy coatings from citrate-sulphate baths

Badania wstępne nad elektroosadzaniem powłok stopowych Zn-Fe-W z kąpeli cytrynianowo-siarczanowych

Exploratory studies of the electrodeposition process of zinc coatings containing iron and tungsten were carried out using SEM/EDS and XRD techniques. It was shown that from a citrate-sulphate plating bath composed of (mol dm⁻³): ZnSO₄ – 0.2, FeSO₄ – 0.2, Na₃Cit (tri-sodium citrate salt) – 0.4, (NH₄)₂SO₄ – 0.1 and Na₂WO₄ – 0.01 Zn-Fe-W alloys can be obtained on a rotating disc electrode. It was noted that the induced co-deposition of tungsten with iron only occurred at pH > 6.0. Below this value, a Zn-Fe alloy coating was obtained. In the pH range from 5.0 to 9.0, the maximum contents of tungsten (15.96 wt. %) and iron (29.36 wt. %) were shown by the coatings deposited at pH 7.0. The increase in the bath pH from 5.0 to 9.0 resulted in clear changes in the phase composition of the deposited coatings. According to the results of XRD analyzes, the following can be indicated as probable: Fe₂₂Zn₇₈ and Fe₇W₆. However, the recorded diffractograms are difficult to interpret and it was very difficult to clearly define the type of phases present in the coating without additional tests.

Keywords: electrodeposition, protective coatings, zinc coatings, alloy coatings, surface morphology, XRD, SEM

1. Introduction

Electrodeposition of zinc and zinc alloy is extensively used in many industries and has distinctive advantages on other finishing

Stosując techniki SEM/EDS i XRD, przeprowadzono rozpoznawcze badania procesu elektroosadzania powłok cynkowych zawierających żelazo i wolfram. Wykazano, że z cytrynianowo-siarczanowej kąpeli galwanicznej o składzie (mol dm⁻³): ZnSO₄ – 0,2, FeSO₄ – 0,2, Na₃Cit (cytrynian tri-sodu) – 0,4, (NH₄)₂SO₄ – 0,1 i Na₂WO₄ – 0,01 można otrzymać na wirującej elektrodzie dyskowej powłoki stopowe Zn-Fe-W. Zauważono, że indukowane współosadzanie wolframu z żelazem zachodziło dopiero przy pH > 6,0. Poniżej tej wartości otrzymywano się powłokę stopową Zn-Fe. W zakresie pH od 5,0 do 9,0 maksymalną zawartość wolframu (15,96% mas.) i żelaza (29,36% mas.) wykazały powłoki osadzone przy pH 7,0. Wzrost pH kąpeli od 4,5 do 9,0 powodował wyraźne zmiany w składzie fazowym osadzanych powłok. Zgodnie z wynikami analiz XRD można wskazać jako prawdopodobne występowanie: Fe₂₂Zn₇₈ oraz Fe₇W₆. Zarejestrowane dyfraktogramy są jednak trudne w interpretacji i jednoznaczne określenie rodzaju faz obecnych w powłoce bez wykonania dodatkowych badań było mocno utrudnione.

Słowa kluczowe: elektroosadzanie, powłoki ochronne, powłoki cynkowe, powłoki stopowe, morfologia powierzchni, XRD, SEM

processes. In practice, Zn-Ni and Zn-Co coatings are required harmful metal salts with Ni(II) and Co(II) ions as compared to Zn-Fe coating with iron (II) sulphate salt which is less harmful. Many extensive research works have been reported on the deposition mechanism

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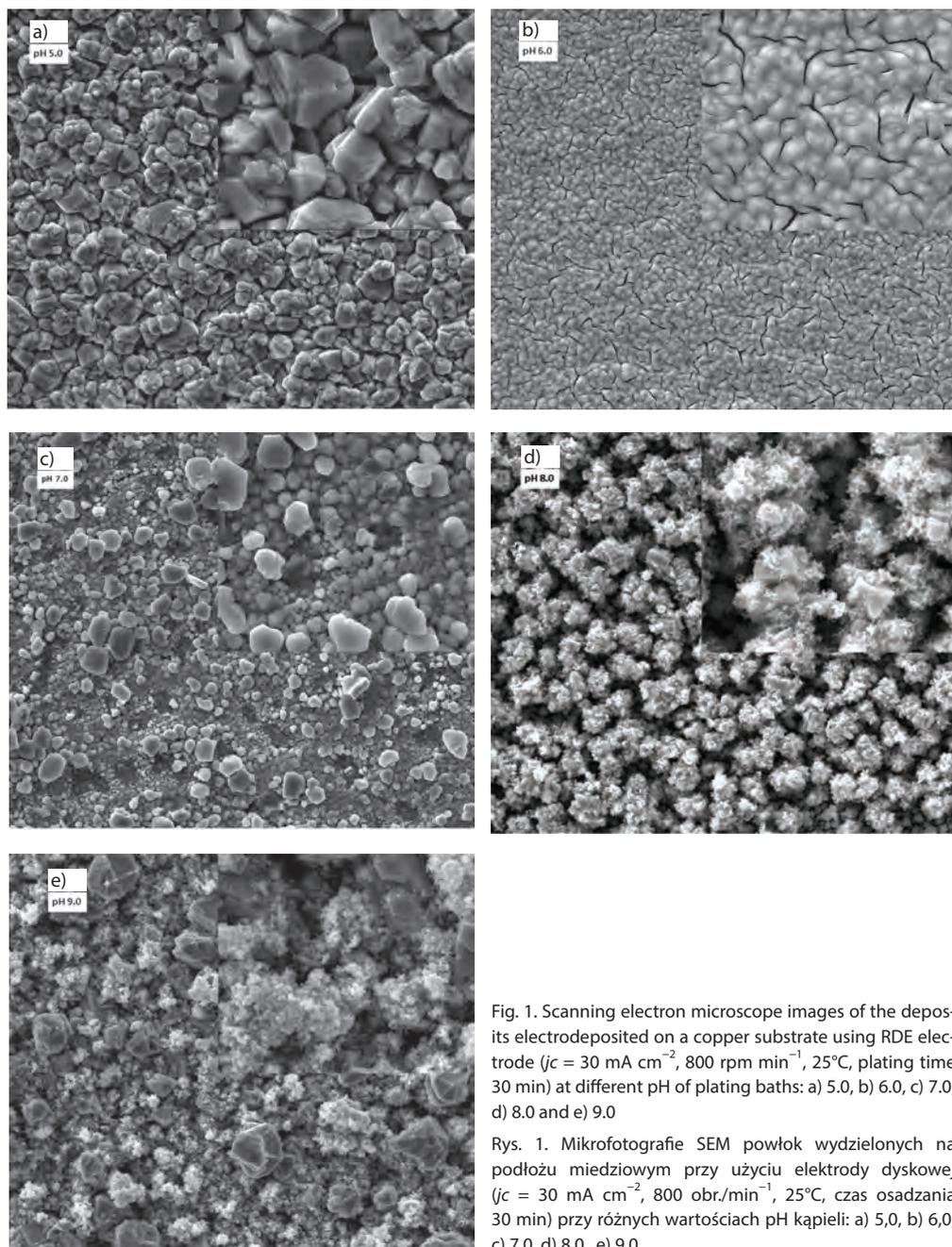


Fig. 1. Scanning electron microscope images of the deposits electrodeposited on a copper substrate using RDE electrode ($j_c = 30 \text{ mA cm}^{-2}$, 800 rpm min^{-1} , 25°C , plating time 30 min) at different pH of plating baths: a) 5.0, b) 6.0, c) 7.0, d) 8.0 and e) 9.0

Rys. 1. Mikrofotografie SEM powłok wydzielonych na podłożu miedzianym przy użyciu elektrody dyskowej ($j_c = 30 \text{ mA cm}^{-2}$, $800 \text{ obr./min}^{-1}$, 25°C , czas osadzania 30 min) przy różnych wartościach pH kąpeli: a) 5,0, b) 6,0, c) 7,0, d) 8,0, e) 9,0

of Zn-Fe group metal alloys. It has been concluded that deposition of zinc with iron metal (Zn-Fe) alloy coating shows good resistance to corrosion as compared to single metal deposition [1, 2]. Another possibility to enhance the corrosion resistance and better mechanical properties is to introduce a third alloying component in binary zinc alloy coatings. Many studies have been found about the ternary alloy coating. Due to its high melting point, high wear resistance, high hardness, and good anti-friction properties tungsten W attracted the attention of many researchers [3]. It has been proved that the addition of the W element in the ternary alloy Ni-Fe-W refined the grains, improved uniformity, and enhanced the surface hardness of the composite coating [3]. Therefore, it is more convenient to use zinc and iron (Zn-Fe) alloy coating in addition to tungsten (W) or (Zn-Fe-W) ternary alloy coating. Much basic research has been found investigating the electrochemical deposition process of zinc, iron, and tungsten (Zn-Fe-W) alloy coating [4].

However, the influence of different parameters on the deposition process of alloy coatings has already been discussed. It has been seen that electrodeposition of metal tungsten from aqueous solution is difficult because tungstate ion predominantly exists as oxyanions such as paratungstates $[\text{HW}_6\text{O}_{21}]^{5-}$, metatungstates $[\text{H}_2\text{W}_{21}\text{O}_{40}]^{6-}$, and tungstate $[\text{WO}_4]^{2-}$ ion, meanwhile presence of iron-group elements enable tungsten W to be co-deposited as alloys based on the principle of induced co-deposition [5]. Anomalous co-deposition has been observed mostly at high current density, whereas at low values of current density the co-deposition is normal [6, 7]. The deposition rate increases and the content of both Fe and W increases with the pH value [3].

Variations in deposition parameters in different studies in which bath chemical compositions and pH were various offered distinct results. In this recent work, it has been discussed how pH of the citrate sulphate plating bath affects the microstructure and chemical composition of Zn-Fe-W alloy coatings through SEM/EDXS and XRD analysis.

2. Experimental

2.1. Sample preparation and research techniques

Alloy coatings were deposited using RDE-2 (Metrohm) rotating disk electrode on the tips made of pure copper with 1 cm^2 surface area. The electrode were refined with successive grades of abrasive paper up to 1200 grit before use. The disks were then

cleaned ultrasonically, degreased in acetone, and activated for 10 seconds in a solution of 10 wt. % H_2SO_4 at room temperature. Each step had been preceded by thoroughly rinsing with distilled water. Afterwards, Zn-Fe-W alloy coatings were deposited from a citrate-sulphate bath with the following composition (mol dm^{-3}): $\text{ZnSO}_4 - 0.2$, $\text{FeSO}_4 - 0.2$, $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ (tri-sodium citrate) - 0.4 as a complexing agent, $(\text{NH}_4)_2\text{SO}_4 - 0.1$, and $\text{Na}_2\text{WO}_4 - 0.01$ as the tungsten ion source. Then pH of electrolytes was adjusted to a range of 5–9 with diluted H_2SO_4 or ammonia solution. Electrodeposition was performed in a 200 cm^3 vessel at a temperature of $25 \pm 1^\circ\text{C}$ under galvanostatic conditions (current density $j_c = 30 \text{ mA cm}^{-2}$, rotational speed $\omega = 800 \text{ rpm}$, time $t = 30 \text{ min}$). Platinum plate with a 6 cm^2 surface area served as the anode. The surface morphology and structure of the deposited coatings were examined using Quanta250 (FEI) scanning electron microscope (SEM) equipped with an X-ray microanalyzer. The concentration

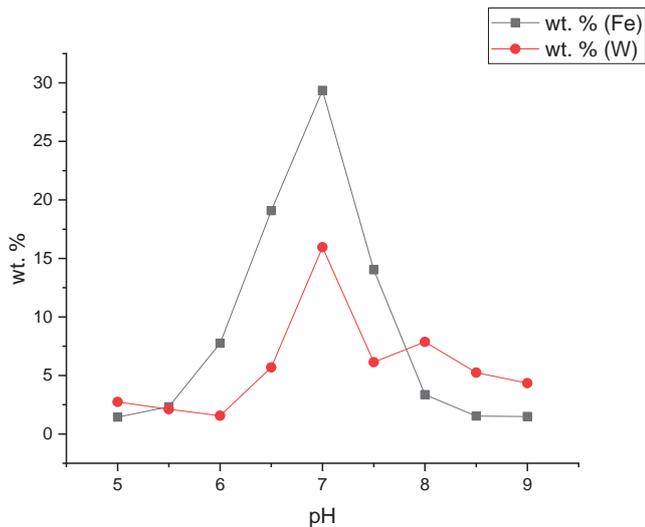


Fig. 2. The effect of electrolyte pH on deposition content (wt. %) of Fe and W plotted at different pH from 5.0 to 9.0

Rys. 2. Wpływ pH kąpeli na zawartość (% mas.) żelaza i wolframu w powłokach wydzielonych przy pH 5,0–9,0

of alloying elements in the deposits was determined by energy dispersive X-ray spectroscopy.

An X-ray diffraction study was conducted on Zn-Fe-W alloys using a D5000 diffractometer (Siemens AG, Munich, Germany) with Cu K α radiation ($\lambda = 0.15406$ nm) at 40 kV and 30 mA, with a scan rate of 0.05° per second to determine phase composition and structure. In order to identify the phases, the experimental patterns were compared to the reference patterns stored in the Powder Diffraction Files database (International Centre for Diffraction Data PDF-2 base, 2022) and with experimental patterns of the copper substrate.

2.2. Results and discussion

SEM images of ternary Zn-Fe-W alloy deposits from the citrate sulphate bath at pH of 5.0–9.0 are shown in Fig. 1. The morphology of the deposits is not homogenous, indicating that there is a clear difference in the substrate coatings at different pH from 5.0–9.0. A non-uniform flaky pyramidal growth structure with different grain sizes was obtained with pH 5.0 (Fig. 1a) and with pH 6.0 shows a significant different smooth structure with cracks (Fig. 1b). A high amount of internal stress may also result in the propagation of cracks in coatings deposited at room temperature due to hydrogen evolution [8]. Granular distribution with crystal grain mounting structure can be observed in Fig. 1c at pH 7.0 due to the high wt. % deposit of Fe. The crystal grain size at pH 7.0 also reduced with the increase of W concentration in the deposited alloy [9]. At pH 8.0 and pH 9.0 cluster formation due to crystal agglomeration can easily be observed (Fig. 1d, 1e).

Fig. 2 presents the effect of plating bath pH on the contents of W and Fe in the alloys. It is evident that deposits obtained at pH 5.0 and 6.0 do not contain a considerable amount of W. When the pH is changed from 6.0 to 7.0, the concentration of W increases significantly from 1.6 to 16 wt. %. It is also worth noting that the tungsten content rises as the iron content rises. The optimal wt. % of W coating was found to maximum at pH 8.0 the composition of the Fe-Ni-W alloy is essentially constant and the concentration of tungsten is highest in the pH range of 7 to 8.5, this pH range was chosen as the ideal and was employed in subsequent depositions [10]. The abrupt shift in Fe concentration from 7.8 wt. % to 29.4 wt. % may also be seen with pH 6.0 to 7.0 changes. These findings are

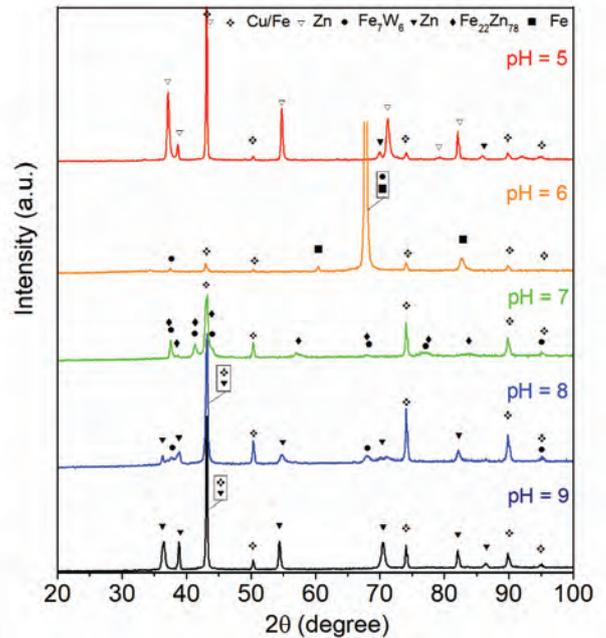


Fig. 3. Diffractograms of the deposits obtained on copper substrate in the plating baths with pH from 5.0 to 9.0

Rys. 3. Dyfraktogramy powłok wydzielonych elektrochemicznie na podłożu miedziowym z kąpeli galwanicznych o pH 5,0–9,0

expected to support two ideas on the process of induced codeposition in Fe-W alloys. The first is that metallic W is not electrodeposited by tungstate ions or Cit-W complex ions, but rather by precursor complexes such as $[(Fe)(WO_4)(Cit)(H)]^{2-}$. The second is that the ratio of Fe, Cit, and W ions is critical for the formation of the originator complex, which determines the rate of deposition [4].

The pH of the solutions in which the coatings were prepared has a key influence on the phase composition of the obtained Zn-Fe-W alloy coatings. The diffractograms of the coatings obtained in the range of pH 5.0–9.0 are shown in the Fig. 3. Reflections from the copper substrate (PDF Cart No. 00-004-0836) are visible for all samples. At pH 5.0, the coating consists mainly of zinc (PDF Cart No. 01-078-9362 and PDF Cart No. 01-071-3764). Since the iron-specific peaks occur at the same 2θ angle values as those for metallic copper, they are indistinguishable for XRD analysis. Therefore, the presence of iron in the coating cannot be excluded in this case. The phase composition of the coating deposited at pH 6.0 changes radically. The reflections from the Cu substrate are less intense. There are peaks characteristic for the Fe_7W_6 phase (PDF Cart No. 00-042-1209) and additionally an intense peak at about 68° 2θ angle, which can be attributed to the lattice plane of (2 0 14) and (3 0 0) Fe_7W_6 phase or (2 0 0) Fe phase (PDF Cart No. 04-008-1610). Similar diffraction pattern of the coating is typical when orthogonal/perpendicular orientation of the grains growth with respect to the substrate occurs. This sample also differs in microstructure from the other samples (Fig. 1b). When the pH increasing to the value of 7.0 and 8.0 obtaining a multiphase coating is obtaining. In the diffraction pattern of the sample obtained at pH 7.0, apart from the Fe_7W_6 phase (which was present at pH 6.0), there are reflections characteristic of the zinc-rich phase of the $Fe_{22}Zn_{78}$ (PDF Cart No. 01-071-8477). Again, more intense than the layer obtained at pH 6.0 are the peaks characteristic of iron or copper substrate. The EDS analysis confirms the higher content of Fe and W in the tested coating. At pH 8.0, the intermetallic phase $Fe_{22}Zn_{78}$ disappears, while zinc reflections are again observed (PDF Cart No. 01-071-3764), and

the peaks attributable to iron are more intense. There are still reflections for the Fe₇W₆ phase, which can no longer be identified for the coating deposited at pH 9.0. Peaks from metallic zinc and iron or copper from the substrate are again visible for the coatings prepared at pH 9.0. The change in the phase structure of the coatings is accompanied by changes in the microstructure observed by the SEM microscope (Fig. 1).

3. Conclusions

Zn-Fe-W alloy coatings were obtained through the citrate-sulphate bath with pH 5.0 to 9.0. The pH of the bath from which the coatings are deposited changed the structure and chemical composition of the coatings. The maximum contents of tungsten (15.96 wt. %) and iron (29.36 wt. %) were shown by the coatings deposited at pH 7.0. The effect of pH adjustment from 5.0 to 9.0 also observed in XRD configuration. Based on XRD results, only Fe and Zn are deposited at low and high pH. The Fe₇W₆ and Fe₂₂Zn₇₈ intermetallic phase can be obtained at pH 7.0.

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