Short Communication

Microstructure and Properties of Electroplated Ni-Co Alloy Coatings

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Ni-Co alloy coatings were deposited to copper substrate electrochemically from a sulphate bath. An increase of cobalt sulphate concentration in the electrolyte from 20 g.l^{-1} to 45 g.l^{-1} resulted in a gradual increase in the content of cobalt in the alloy coating from 31.8 wt% Co up to 49.2 wt% Co [1,2]. Ni-Co alloy coatings were deposited at various current densities, namely, 1, 2, 4 and 6 A.dm^{-2}. The values of the current efficiency were achieved in the range of 90 – 98.5 %, when increase of current density led to decrease in current efficiency of process [3,4]. Morphology and grain size of alloy coatings are greatly affected by Co content and current density of process. By increasing Co content, surface morphology of alloy coatings had a finer grain structure. The relationship between concentration of Co in the coating and in the sulphate bath, and the HV0.1 hardness of the deposited coating was shown that the highest value of hardness, 556.3 HV0.1 was measured for coating with 42.6 % Co and concentration of 30 g.l^{-1} CoSO$_4$ in sulphate bath.

Keywords: Ni-Co, coatings, morphology, hardness, current density

1. INTRODUCTION

The development in the field of surface treatment of metallic materials leads to an increase of their wear and corrosion resistance. The operating conditions and increases of process efficiency require an improvement of tools and equipment quality [3,5,6]. The increase of the surface quality is necessary for decorative as well as functional coatings. Surface treatments, which meet these requirements, include electrodeposition of alloy coatings.

Authors [1,7,8] observed that nickel-based coatings are used in a broad range of practical applications due to their good properties, such as magnetic and thermal conductivity, mechanical properties and resistance to abrasion and corrosion. Increased hardness and strength can be achieved

by alloy coatings. Nickel and cobalt build solid solutions in the whole range of concentrations. The ability of nickel and cobalt to produce alloys at all ratios allows one to utilize their magnetic properties under various conditions [9,10]. In the work [2] have described an increasing interest in electrodeposition of alloy coatings, particularly due to their application in the area of surface treatment.

Production of coatings of required adhesiveness is conditional on adequate preparation of material surface. Microstructure and properties of electrodeposited simple and alloy coatings depend on chemical composition, pH and temperature of the bath, intensity of its mixing and physical parameters of the process, particularly current density [4]. In the work [11] has been found that changes in deposition conditions can result in coatings of different chemical composition, structure or phase composition. Important aspects of deposition of alloy coatings, according to [9] include concentration and stability of the other component (cobalt) in an electrolyte.

Authors in the work [12,3] in their work noticed that current density is one of the essential factors affecting structure and morphology of electrodeposited coatings. Current density affects not only the deposition rate and intensity of coating growth but also the size and distribution of individual crystallites.

The present work deals with the effect of current density on the microstructure, morphology, chemical composition and mechanical properties of Ni – Co alloy coating. The increase of current density showed a decrease of the current efficiency of electrodeposition process and the content Co in alloy coating, too.

2. MATERIAL AND EXPERIMENTAL METHODS

Ni-Co alloy coating was electrodeposited from a sulphate bath, which contained 640 $g.l^{-1}$ nickel sulphate, 20 – 45 $g.l^{-1}$ cobalt sulphate; 10 – 20 $g.l^{-1}$ nickel chloride and 30 $g.l^{-1}$ boric acid. Ni-Co alloy coating was deposited to a copper substrate at current densities of 1, 2, 4 and 6 $A.dm^{-2}$, and bath temperature of 55 °C [13,14]. The pH of the bath was maintained at 4.0 owing to the presence of boric acid. Before coating, the copper substrate was prepared by a procedure used under real operational conditions, namely by steel grit blasting and mechanical grinding to a mean roughness of about 3.8 μm. The following steps involved degreasing by agents based on sodium hydroxide and rinsing with demineralised water. The surface was then activated by a mixture of sodium hydrogen sulphate and sodium fluoride and by an activating salt consisting of sodium hydrogen sulphate and sodium hydrogen fluoride [15,16]. Demineralised water was used for final rinsing. The Ni-Co coating of thickness of approximately 30 μm was then deposited onto the prepared surface. The content of cobalt sulphate, the major component of the sulphate bath, was determined by atomic absorption spectrometry [7]. Morphology of electrodeposited coatings was examined and photographed by an electron microscope JEOL JSM 7000F. Chemical composition of the Ni-Co coat was determined by a microanalyser INCA xSight (Oxford Instruments), which was a part of the electron microscope. Hardness of the Ni-Co coat was measured by a Vickers using 100 g loading [3,6].

3. RESULTS AND DISCUSSION

As it was previously mentioned, cobalt sulphate was component of the sulphate bath during electrodeposition of the Ni-Co alloy coating. In order to determine the influence of this component on composition of the coating, the concentration of $CoSO_4$ added to the bath varied between 20 – 45 g.l^{-1}. The effects of the respective changes were investigated by spectrometric analysis of the electrolyte and EDX analysis of the deposited coatings and the results are presented graphically in Fig. 1. An increase in concentration of cobalt sulphate in the electrolyte from 20 g.l^{-1} to 45 g.l^{-1}, according to [1,2,4] resulted in a gradual increase in the content of cobalt in the alloy coating from 31.8 wt% Co up to 49.2 wt% Co. This allowed us to state that increasing concentration of cobalt sulphate caused the increased of Co ions activity as was reported also in the study. Authors of this study also mentioned that concentration of cobalt sulphate ranging between 20 and 50 g.l^{-1} resulted in production of a glossy coat with low surface roughness and high toughness.
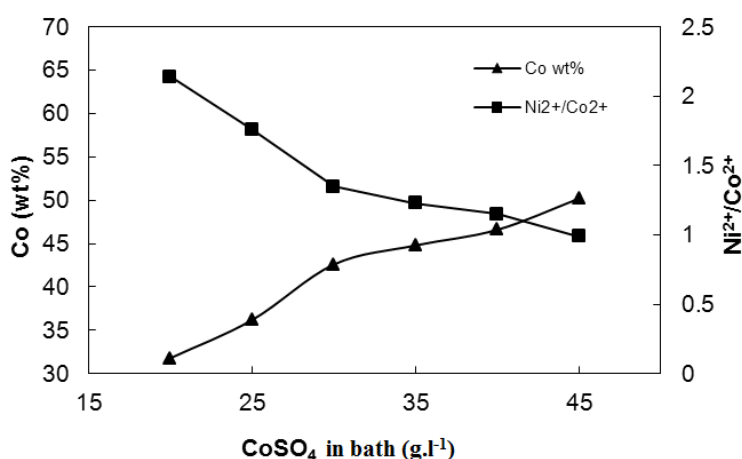

Figure 1. The influence of cobalt sulphate added to electrolyte bath on composition of Ni-Co coating
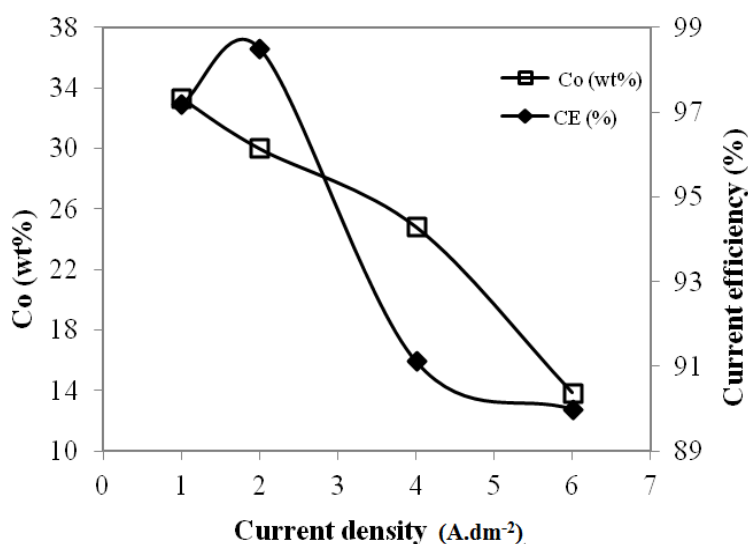

Figure 2. The influence of current density on current efficiency of electrodeposition process

The authors [4,6] in their work confirmed that current efficiency decreases with current density which indicated an increase in the rate of hydrogen discharge. In our case, we also observed a decrease of current efficiency of the electrodeposited process. The influence of current density was observed in the content of Co in the deposited coating [17]. It was observed (see Fig. 2) that the proportion of Co in the coating decreased with increasing current density. The authors [11,18] who measured the level of strain in the Ni-Co coating, deposited from a sulphate bath, observed that the alloy coating produced at current density of 2 A.dm^{-2} exhibited the lowest values of tensile strain. This was also reflected in good mechanical properties of the respective coating [19]. Increasing current density resulted in increasing deposition rate and, on the other hand, in declining content of Co in the deposit. When determining optimum current density, one should consider not only adequate deposition rates of the alloy coating abut also its required chemical composition. According to [4], increasing current density may result in decreasing current efficiency, which is indicated by development of hydrogen at hydrogen cathode reduction.

Morphology and surface structure of Ni-Co alloy coatings with different content of Co, deposited at various current densities, were observed by SEM [20]. Results are presented in Fig. 3 and 4. The morphology shows uniform spherical fine-grain nodules which are characteristic of cobalt alloy deposits. It can be seen that the crystal size of the deposit with higher Co content is much smaller. Thus the higher content of Co in the coating resulted in its finer structure. On the other hand, one should also consider the influence of current density [6].
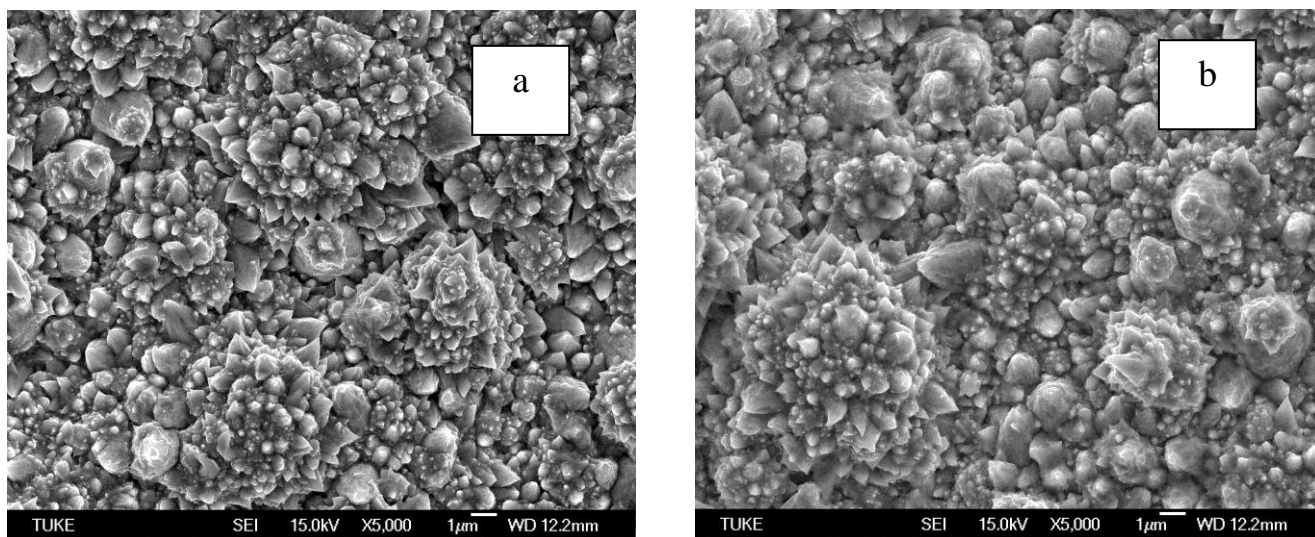

Figure 3. Morphology of Ni-Co alloy with: a) 33.32 wt% Co, deposited at 1 A.dm^{-2}, b) 31.8 wt% Co deposited at 2 A.dm^{-2}

In our study, we observed a more pronounced growth of crystallite size at 6 A.dm^{-2}, as shown in Fig. 4d. According to [1,13], morphology of the coating surface is determined by the character and ratio of electrochemically active ions or complexes and kinetics of the electrodeposition process.

In comparison with simple Ni coatings, the Ni-Co alloy coatings exhibit higher hardness and strength. However, for maintenance reasons, it is necessary to keep adequate level of cobalt ions in the bath [21]. The relationship between concentration of Co in the coating and in the sulphate bath, and the HV0.1 hardness of the deposited coating, is illustrated in Fig. 5. The broken curve shows the coating hardness versus cobalt content in the bath and the coating, deposited at current density of 2 A.dm^{-2}. Maximum hardness, namely about 556 HV0.1, was reached at the level of 30 g.l^{-1} CoSO$_4$ and was exhibited by a coating containing 42.6 % Co. In work [21] was the hardness of electrodeposited Ni-Co coatings in the range 482 – 610 HV depending on the current density of process. The study [17] reported that such levels of hardness are associated with exceedingly high level of tensile strain preventing galvanoplastic applications.
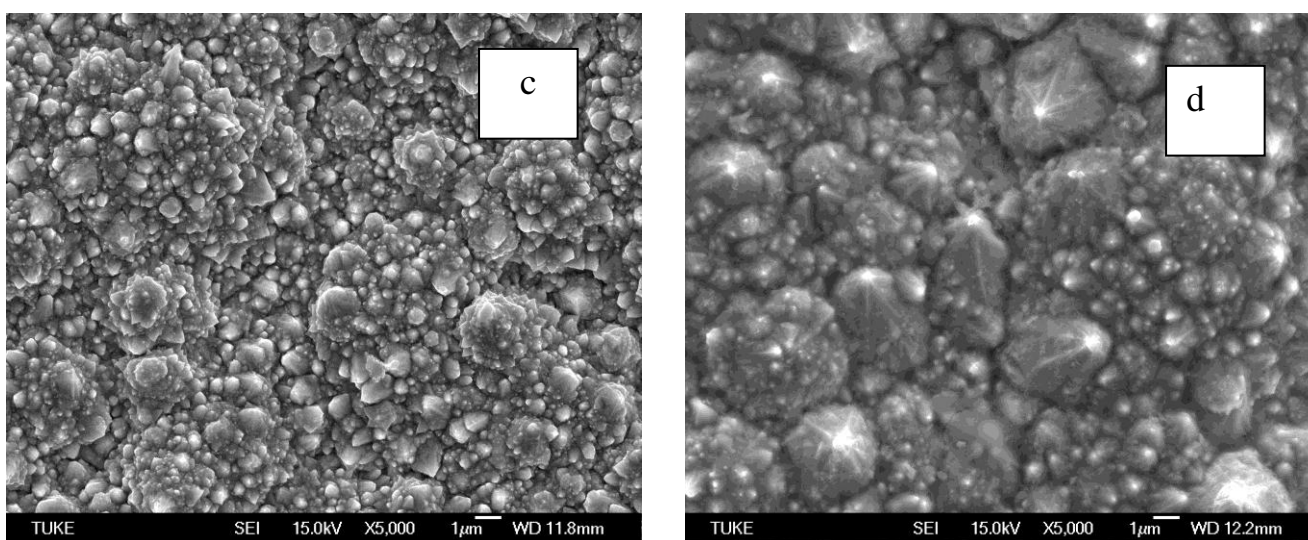

Figure 4. Morphology of Ni-Co alloy with: c) 24.82 wt% Co, deposited at 4 A.dm^{-2}, d) 13.83 wt% Co deposited at 6 A.dm^{-2}
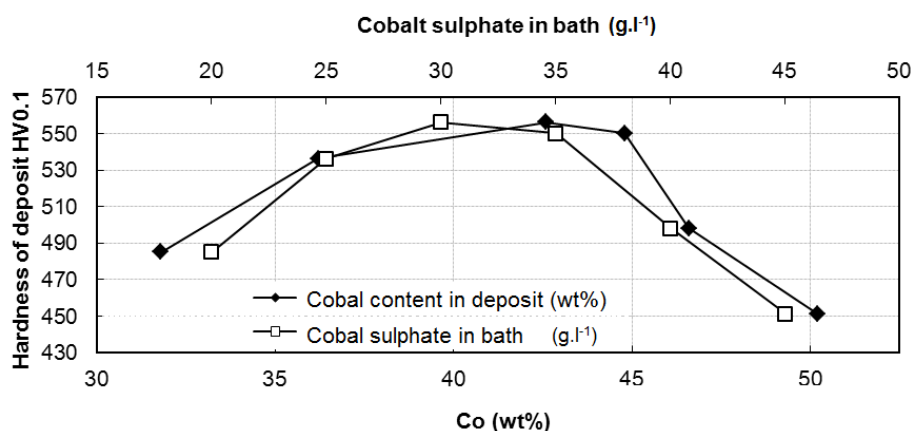

Figure 5. Relationship between hardness of coatings and concentration of cobalt in a sulphate bath

However, such alloys can be used as coatings deposited on a solid substrate. The author of the mentioned study observed that an acceptable threshold level of tensile strain is reached in an alloy

containing about 15 % Co, at hardness levels around 350 to 400 HV. This observation was also confirmed by another study [18].

4. CONCLUSION

The present study examined Ni-Co alloy coatings deposited by electrochemical method from a sulphate bath at various values of current density. Chemical composition of galvanic bath also varied in terms of concentration of its component $CoSO_4$. The experiments and observations allowed us to draw the following conclusions:

- The chemical composition of the bath affected composition and the structure of the deposited coating. The proportion of Co in the coating increased with increasing concentration of $CoSO_4$ in the bath during electrodeposition,

- The increase in current density resulted in a decrease of current efficiency of the process; at the lowest value of 1 $A.dm^{-2}$ was current efficiency 97.19 % and the highest current density 6 $A.dm^{-2}$ was value 89.99 %. According to [3,19] at high current density, the low cathodic efficiency could be due to the predominance of the hydrogen reduction reaction,

- The current density during the process affected both the rate of deposition and proportion of Co in the coating. Optimum level of this parameter should consider not only the rate of the electrochemical process but also ensure the required chemical composition of the alloy coating,

- The content of Co in the coating and the current density affected morphology and structure of the developing coating. Using current density of 6 $A.dm^{-2}$ resulted in the highest growth of crystallites in the Ni-Co coating at the lowest proportion of Co compared to all investigated specimens,

- The proportion of Co in the bath and in the coating was reflected in the measured of hardness values. The hardness achieved a maximum of 556.3 HV0.1 for the alloy coating containing 42.6 % Co, deposited from the bath with concentration of 30 $g.l^{-1}$ $CoSO_4$.

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