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THE INFLUENCE OF GLUCONATE BATH PARAMETERS ON THE RATE OF ELECTRODEPOSITION AND MECHANICAL PROPERTIES OF Co–W COATINGS

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Abstract: The given study overview the results obtained for Co–W alloys electrodeposited from gluconate bath. Namely, the influence of different parameters (the concentration of the bath components, pH, temperature, cathodic current density, volume current density, hydrodynamic conditions, insoluble and soluble anodes) on the rate of electrodeposition and microhardness of the coatings has been investigated. The given research determine the conditions ensuring high deposition rate, microhardness and bath efficiency. It was shown, that the deposition rate, tungsten content and microhardness reach the maximum values at pH 6.5, regardless on the concentration of bath components. Also, it was detected the macroscopic size effect of microhardness, which is linked to the fact that for a fixed cathodic current density microhardness depends on volume current density. In addition, different anodes (Pt, graphite, W and Co–W) were investigated to reveal the anode influence on reaching the maximum values of the current efficiency and microhardness.

Keywords: Microhardness, electrodeposition, Co–W coatings, rate of electrodeposition.

1. INTRODUCTION

Electrodeposited Co–W binary alloys have a number of properties that extend the possibilities of their application: high microhardness (up to 1000 HV) and wear resistance, low friction coefficient, ability to control magnetic properties, good corrosion resistance and catalytic properties [1–9]. That is why some researchers recommend such coatings as an alternative to electrolytic chromium coatings [1, 4, 9]. A high number of papers are devoted to the deposition of such coatings, but there is still not determined concept of the deposition mechanism, which is affecting the advanced properties of these alloys [10–12]. Nanocrystalline Co–W coatings with advanced properties can be obtained by co-deposition from different electrolytes, including from boron–gluconate bath [1–6].

It has been shown [13–15], that for Co–W alloys electrodeposited from the gluconate and citrate baths, microhardness could also depends on the plated area or volume of electrolyte, while keeping other parameters (electrolyte composition, temperature, current density, hydrodynamic conditions) constant. In other words, the properties of Co–W coatings are influenced by the volume current density (VCD). VCD takes in consideration current density applied on the specific surface area at the given bath volume. The dependence of microhardness on the VCD could be defined as macroscopic size effect of microhardness and it will be further referred as microhardness size effect.

One of the important parameter to be considered for long–duration operation of the electrolytic bath is the concentration of the precursors of co–depositing metals. Thus, the precursor concentration can deplete very fast, leading to a decrease of mechanical performance and current efficiency of obtained

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alloys [15, 16]. In order to increase long–duration operation of the electrolytic bath for Co–W alloys deposition the concentration of precursors can be increased and soluble anodes can be used [2, 16].

The given study provides an overview of the influence of the electrolytic bath parameters (concentration of alloying components, pH, cathodic current density, volume current density, the anodes (insoluble (Pt, graphite), and soluble (Co–W)) on the electrodeposition rate and mechanical properties of Co–W coatings. The main aim of this research was to determine the optimum parameters of the bath providing the maximum deposition rate and microhardness of the coating.

2. EXPERIMENTAL

The electrodeposition was performed from a bath with the following composition (mol/L): 0.05 $CoSO_4$, 0.05 Na_2WO_4, 0.55 $C_6H_{11}NaO_7$ (sodium gluconate), 0.65 H_3BO_3 and 0.5 NaCl. Electrodeposition was carried out at the cathodic current density of 2 A dm^{-2} and the bath temperature of 80 °C. In some cases, other current densities were used, the details are given below. Concentrations of alloying components in the electrolytic bath were also varied. Concentrations were increased (up to 0.25 M) in comparison with the concentrations given above.

The need in the given research is based on the fact, that lower–concentration electrolytes during long-term operation undergo the rapid depletion of the electrolyte by alloy–determining components. It was shown by us earlier [14] that if the concentration of the alloy–determining components is increased proportionally to the concentration of the remaining components of the solution, this leads to the negative results. Also, we established [17] that the optimum pH value is 6.5, that provides the maximum deposition rate, the highest content of W, and also improved mechanical properties of the coatings. In this work, these results were verified for other concentrations, in particular, for a high concentrated electrolyte of alloy–determining components. The influence of the electrolytic bath parameters including different anodes used on the deposition rate, the current efficiency (CE) was estimated. It was shown in [13, 15] that the microhardness of coatings (electrodeposited from a low–concentrated gluconate solution) at a fixed cathodic current density also depends on VCD, which can be attributed to a size effect of microhardness. Therefore, one of the objectives of this study was to reveal the effect of VCD on the microhardness of Co–W coatings deposited from electrolyte with high concentration of alloying components. The microhardness was measured with a PMT–3 microhardness tester. The Vickers indenter with a load of 100 g was applied on the surface, the overall time of indentation was 10 s. The CE was measured by weighing samples before and after the deposition. The surface morphology and the elemental composition of the coatings were determined with Hitachi TM3000 scanning electron microscope and EDX analysis.

3. RESULTS AND DISCUSSION

It has been shown in our previous research [14, 17], that the use of concentrated electrolyte on alloy–determining components allows not only to increase its long operation, but also to substantially increase the current efficiency from cca 60% to cca 90% for freshly prepared bath [14]. For comparison, we also evaluated current efficiency depending on the quantity of charge passed through electrolyte (Q). It was depicted, that the use of the electrolyte, having high concentration of alloying components, leads to a significantly smaller influence of Q on CE.

Another parameter, which influence CE, is pH. We have shown that pH influences on the current efficiency (CE), the tungsten content and microhardness; achieving the maximum values for all mentioned properties at pH 6.5 (Table 1). Thus, all further experiments were done namely at this pH. However, we found that microhardness can be strongly influenced by volume current density (VCD) (Table 1). This means that working area or volume of the electrolyte will play essential role if we consider to use such electrolytic bath for up-scaling tests.

Table. 1. Influence of pH on the CE, microhardness and tungsten content, at 2 A dm^{-2}.

pH	CE, %	C_W, at.%	HV, kg mm^{-2}	pH	VCD, mA L^{-1}	HV, kg mm^{-2}
3.5	75	6.4	597±7	6.5	4	832±4
6.5	94	13.7	774±13		160	774±13
9	72	10.5	653±10		400	641±5

The significant influence of VCD on microhardness is a consequence of the change in the structure of the coatings [14, 15], which is reflected in the morphology changes when the VCD is increased. Moreover, the coatings are transformed from nanocrystalline to amorphous only by increasing VCD and Q [14], which is also influences on the tungsten content, that is growing from 15 at.% till 29 at% only with long duration operation of the bath. All the mentioned above, have been done using graphite electrode.

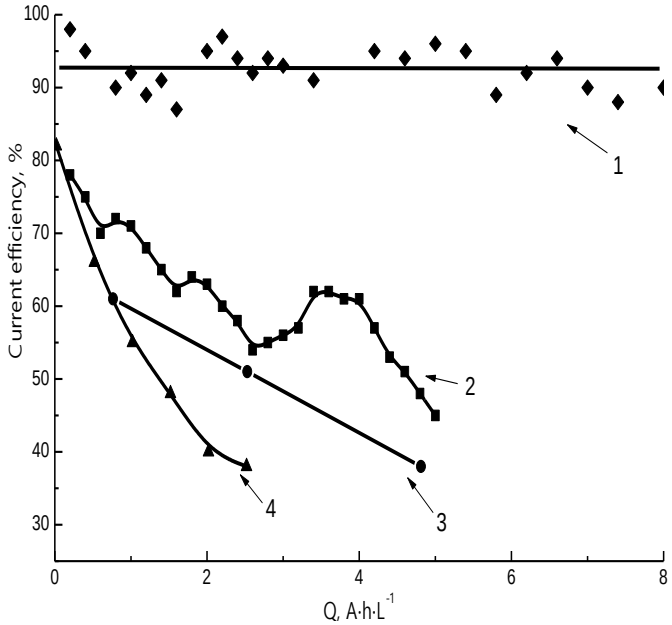

Figure 1. Influence of the quantity of charge passed (Q) on the current efficiency for different anodes used: soluble Co–W (1), W (2) [16], graphite (3), Pt (4).

The current efficiency and the microhardness of Co–W coatings is significantly influenced by the anode used for co-deposition (Figures 1 and 2). If soluble anodes are used the current efficiency increases (Figure 1) (see also [12]). This is the most evident for a soluble Co–W anode, which ensures the constant concentrations of alloying components during the entire period of electrolysis (Figure 1). In contrast, the use of insoluble anodes leads to: a) lower values of CE, b) a significant influence of Q on CE (Figure 1). In addition, it can be seen, that the use of the Pt anode results in a more evident reduction of CE compared to the graphite anode with the increase of the quantity of charge passed, which can be link to the different hydrogen evolution on these electrodes.

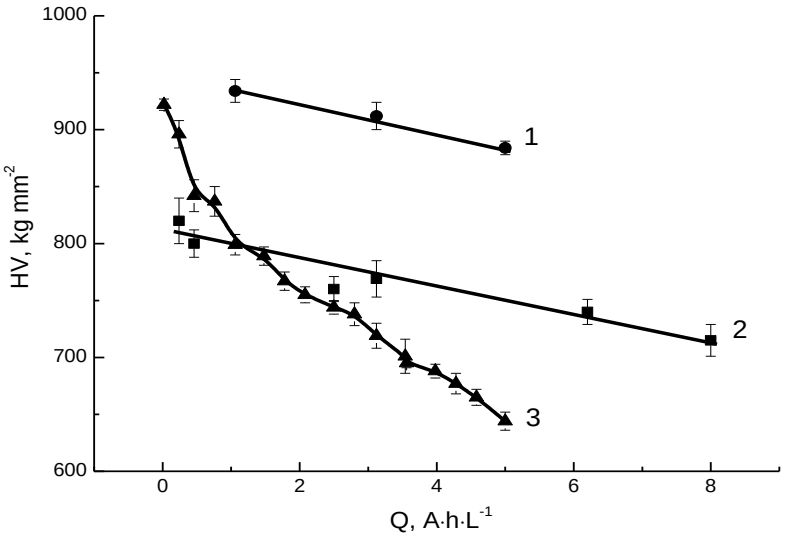

Figure 2. Effect of the quantity of charge passed (Q) on Co–W coatings microhardness, electrodeposited using various anodes: graphite (1), Co–W (2), Pt (3) at VCD 20 mA L^{-1} (1, 3) and 200 mA L^{-1} (2).

The influence of the anode on the microhardness of the coatings is presented in Figure 2. Some analogous trend with Figure 1 can be noticed; the only difference is link to the use of soluble Co–W anode. The use of Co–W anode leads to practically constant dependence of CE on Q, while in the case of the microhardness we observe an evidential decrease.

The obtained results can be to some extreme explained based on the mechanism of induced co-deposition, based on the hypothesis presented in [12]. The basis of this hypothesis is grounded on an assumption that the first stage in the process of obtaining the alloy is the electroreduction of the metal precursor (in our case, the cobalt complex) to the intermediate ($Co(OH)_{ads}$) (Figure 3). The concentration of the metal precursor is changing with different rate, which is also determined by VCD (smaller or bigger working area). This will results in a mechanism which is determined by the reactions (2 and 3), (Figure 3) in order to obtain the alloy, or the co-deposition will take place in accordance with reaction (4) – formation of hydroxides, accompanied by a decrease in microhardness (high values of VCD).

The influence of the anode on co-deposition could be explained if we assume that along with the reduction process, the metallic compounds participates also in the oxidation process (reaction (5)). The different rate of oxidation at different anodes leads to the influence of the anode on the deposition rate and microhardness of the coatings.

The mechanism of induced codeposition, presented in Figure 3, do not takes into account the role of the different complexes formation during codeposition of Co–W coatings. The different behaviour of soluble Co–W anode on the current efficiency and the microhardness of the obtained coatings can be explained taking into consideration, that the structure of the corresponding complexes in the solution is formed in time.

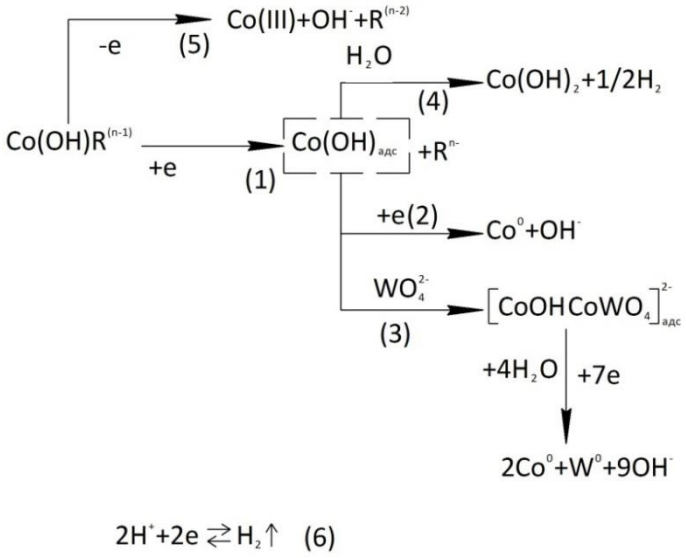

Figure 3. Scheme of electrochemical processes at electrodeposition of Co–W coatings.

4. CONCLUSIONS

1. It has been demonstrated, that the microhardness of Co–W coatings obtained from a concentrated electrolyte decreases with increasing of volume current density at a constant current density.

2. The influence of the anode material during electrodeposition on the current efficiency is shown.

3. The use of a soluble Co–W anode during long–term operation of the electrolyte allows to obtain higher values of the microhardness for investigated coatings.

4. The mechanism of electrodeposition proposed by Krasikov, offer an explanation of the anode material influence on coatings and their characteristics.

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