On the influence of some factors on the functional properties of electrogalvanic coatings promising for medical applications

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This work investigates some functional properties of galvanic chromium coatings deposited from a non-standard chloride electrolyte of *Chromispel type*, modified with combined, complexly acting additive containing $CoCl_2.6H_2O$. The influence of various technological factors such as current density, $CoCl_2.6H_2O$ content and stirring, on the properties of the electrolyte and the coatings was studied. The experimental results obtained showed that stirring and higher current density (15-50 $A.dm^{-2}$) make coating smoother, brighter and increase the deposition rate and cathode current efficiency. It was experimentally established that increase in concentration of $CoCl_2.6H_2O$ in the range 1-5 $g.L^{-1}$ results in reduction of reflectance and thickness of layers. For the determination of the surface morphology of the investigated coatings an atomic force microscope was used. Root mean square roughness of the deposited coatings was measured and the average size of grains observed was determined.

Key words: Cr-Co alloy, functional properties, Chromispel electrolyte

INTRODUCTION

Medical implants are products that must meet functionality requirements in human body conditions as a working environment. Ideally, they must have biomechanical properties comparable to those of autogenous tissue, must have no adverse effects and must ensure safe and efficient operation.

There is a huge variety of materials and alloys used for the production of implants. After stainless steel, various binary and ternary cobalt alloys are most widely used. They are characterized as non-magnetic and resistant to corrosion, high temperature and mechanical stress [1]. Their properties are closely related to the crystallographic structure and the ability to form hard carbides, which give strength to implants.

Because of their excellent resistance to degradation in the oral cavity, the main medical applications of Cr-Co alloys are for dental implants.

Various in vivo and in vitro tests give evidence that cobalt alloys have good biocompatibility. That is why they are used for the manufacture of surgical instruments, orthopaedic prostheses, fixtures, knee, hip and shoulder replacement prostheses [2–4].

Cr-Co alloys are also applications for the production of cardiac stents [5].

Sometimes, implants are produced from a combination of various types of materials, e. g. femoral heads manufactured from highly cross-linked polyethylene in combination with ceramic materials or Cr-Co alloy [6].

The difficulties in working with metallurgical Cr-Co alloys are associated with the fact that they are more difficult to process. This problem can be solved by a continuous development of technology and establishment of new, modern methods for specialized casting [7] and selective laser sintering.

The purpose of this study is to develop a technology for electrochemical deposition of cobalt alloys which helps avoiding difficulties in machine processing after metallurgical casting.

In this new technology, a non-standard electrolyte for chromium plating of *Chromispel* type is used. What is typical of it is that it operates at room temperature and has current efficiency several times higher than that of the conventional sulphate electrolyte.

EXPERIMENTAL CONDITIONS

Standard concentrated (250 $g.L^{-1}$ CrO_3) chloride electrolyte of *Chromispel* type modified with combined complexly acting additive was used for deposition of coatings. The basic composition is registered with a copyright license [8].

In the experiments performed the current density varied in the range 15–50 $A.dm^{-2}$. Cathodes were

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copper plates which surface was 0.02 dm^2. Deposition time was 5 minutes. Some of the coatings were obtained in stationary conditions, others - by stirring the electrolyte at a speed of 600-1000 rpm/min.

Cobalt was imported into the galvanic bath by $CoCl_2.6H_2O$ and its concentration in different compositions was within the range from 1 g.L^{-1} to 5 g.L^{-1}.

Faraday's laws were used for determining the cathode current efficiency (K_{Cr}).

An important characteristic of each electrolyte is the deposition rate (U_e). It is calculated using the Eq. (1):

$$U_e = 0.047 i_k K_{Cr} \qquad (1)$$

Coatings were deposited at operating temperature of $(20\pm2)^oC$, and their thickness (d) was determined by a fluorescence analysis.

The reflectance was measured using a gloss meter of Lange type.

The surface morphology of all samples was investigated by means of Atomic force microscope (NANOSURF Flex AFM). The samples were scanned with a standard silicon cantilever (type Tap 190Al-G) and the measurements were performed in ambient atmosphere, and dynamic operating mode. The applied force was always minimized, not to deform the samples. The surface topographic images of the samples were taken and the diameter of the obtained grains in the plane of the picture was calculated.

EXPERIMENTAL RESULTS AND DISCUSSION

Current efficiency

Deposition of chromium coatings from aqueous solutions of chromic anhydride is not possible without the presence of external anions acting as catalysts for the primary reaction - chromium deposition. In chloride *Chromispel* electrolytes these are Cl$^-$. Their concentration is determined by the ratio CrO_3:Cl$^-$ = 20:1 and for standard concentration compositions it is approximately 12.5 g.L^{-1}.

According to the theory of the chromium plating, at least three partial reactions take place simultaneously on the cathode during electrolysis:

$$Cr^{6+} \rightarrow Cr^0$$
$$2H^+ \rightarrow H_2$$
$$Cr^{6+} \rightarrow Cr^{3+}$$
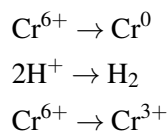
An important characteristic of each electrolyte is cathode current efficiency (K_{Cr}) i.e. that part of the to-

tal amount of electricity which is only consumed for the useful reaction of chromium deposition.

Standard sulphate electrolytes have maximum current yield 10-12%.

Pure chloride electrolytes, i.e. without additive, with concentrations from 500 g.L^{-1} CrO_3 to 750 g.L^{-1} CrO_3, can reach 60%, and modified standard concentration (250 g.L^{-1} CrO_3) chloride *Chromispel* about 40% [9, 10]. According to the obtained experimental results, the higher the operating current density, the better its cathode efficiency - Fig. 1. The same relationship was also observed when stirring the electrolyte. For example, at a density of 25 A.dm^{-2}, if the liquid were not mixed, the determined value of $K_{Cr} = 24\%$. After stirring, the yield increased to value of $K_{Cr} = 34.2\%$.

Coatings deposited with operating current densities above 50 A.dm^{-2} are characterized with high internal stresses and are not recommended for practical applications.
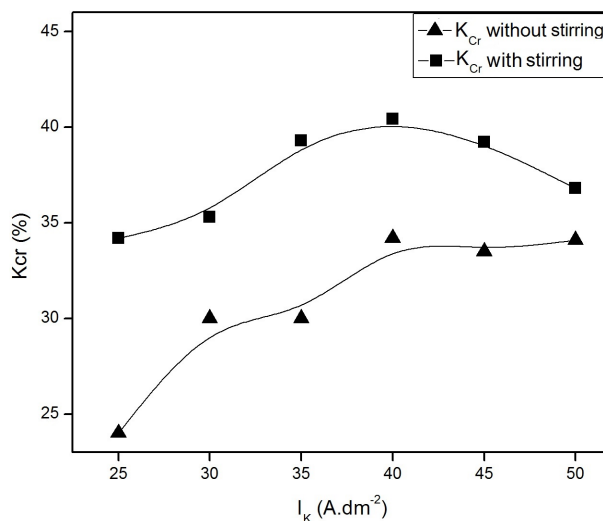

Fig. 1. Dependence of K_{Cr} on both cathode current density and stirring for electrolyte containing 1 g.L^{-1} $CoCl_2.6H_2O$.

Deposition rate and thickness of the coatings

Both of these parameters are a function of the current density and are important for the practical properties of the coatings. Galvanic rate is a particularly important feature when thick coatings need to be deposited. At small rates chromium plating may take several days. In the literature, standard sulphate electrolytes at temperature 50°C, current density 48 A.dm^{-2} and cathode efficiency 18.8% have deposition rate of 42.3 μm.h^{-1} [11]. The dependence of U_e and
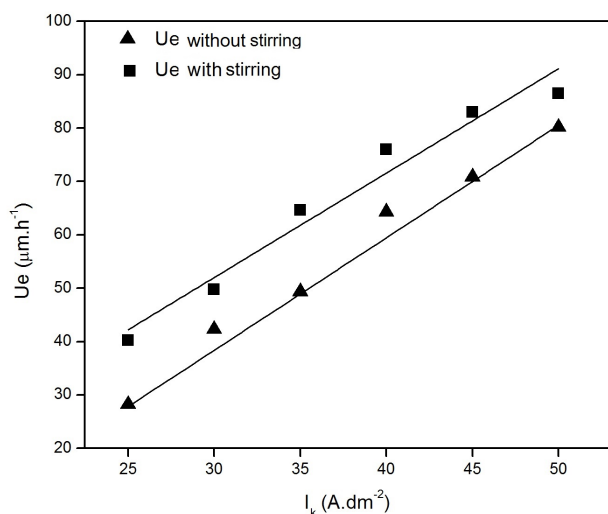
Fig. 2. Influence of cathode density and stirring on deposition rate for electrolyte containing 1 g.L^{-1} CoCl$_2$.6H$_2$O.

d on the current density is proportional and is illustrated in Fig. 2 and Fig. 3.

According to the data illustrated in Fig. 2 for current densities 45-50 A.dm^{-2} the deposition rate is 70-80 μmh^{-1}, i.e. almost twice as high as that of standard sulphate electrolytes. This fact makes the chloride *Chromispel* electrolytes some of the most highly efficient electrolytes for deposition of chromium coatings.

The stirring influences favourably the coating thickness (Fig. 3). For example, when cathode current density is 40 A.dm^{-2} and the content in the galvanic bath is 1 g.L^{-1} CoCl$_2$.6H$_2$O, if the electrolyte is not mixed, $d = 2.6$ μm, and if mixed, $d = 3.3$ μm.
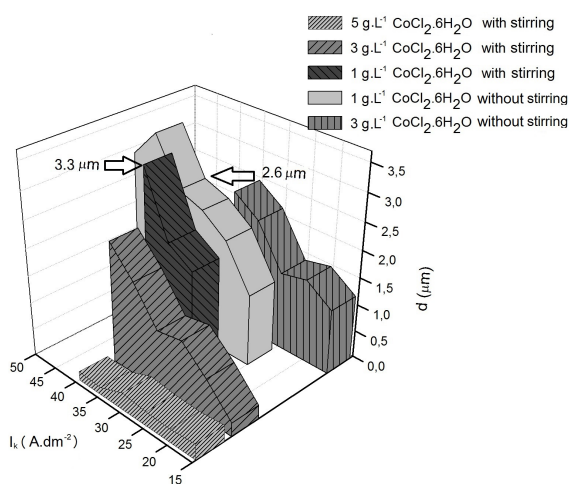

Fig. 3. Thickness of coatings deposited with and without stirring of the electrolyte at different current densities for a period of 5 minutes.

The higher concentration of CoCl$_2$.6H$_2$O slows down the electrocrystallization, and under the same conditions of chromium plating, e.g. 40 A.dm^{-2} and stirring of the electrolyte, if the amount of CoCl$_2$.6H$_2$O of 1 g.L^{-1} is increased to 5 g.L^{-1} the thickness decreases from 3.3 μm to 0.17 μm, i.e. about 20 times. To make an unbiased interpretation of this fact, it is necessary to examine the kinetics of cathode process in order to determine how the ratio between the rates of the partial cathode reactions.

Surface morphology and reflectance

These properties determine the decorative qualities and the beautiful appearance of chromium coatings.

Today most of the electroplated coatings are deposited glossy directly from the electrogalvanic baths. Thus, the need for additional mechanical polishing of the layers is eliminated.

According to [12], the reflectance does not depend on their texture, so it is not subject to examination in this study.

Surface morphology of the samples investigated by AFM was judged by their root mean square roughness S_q. Figs. 4 and 5 show surface topographic images of the samples.

Line graphs and 3-D images on Fig. 4 and Fig. 5 show that, in general, when increasing the concentration of CoCl$_2$.6H$_2$O, the crystals of coatings become larger in size. For example, with 1 g.L^{-1} CoCl$_2$.6H$_2$O the value of the root mean square roughness is $S_q = 5.84$ nm, and with 5 g.L^{-1} CoCl$_2$.6H$_2$O, it is $S_q = 10.88$ nm. Such roughening of the layers was also found in case of stirring the electrolyte – Fig. 5. Regardless of whether the electroplating is carried out with or without stirring, the highest root mean square roughness is of coatings obtained from compositions containing 5 g.L^{-1} CoCl$_2$.6H$_2$O.

Fig. 6 shows the dependence of reflectance on cathode current density and stirring. By increasing the cathode density (due to high plating rate) more small crystal and smooth coatings are deposited, and the reflectance increases. After density of 35 A.dm^{-2}, in case of no stirring, gloss decreases, which can be associated with some concentration restrictions changing the deposition mechanism and properties of coatings, or by impurities in their composition.
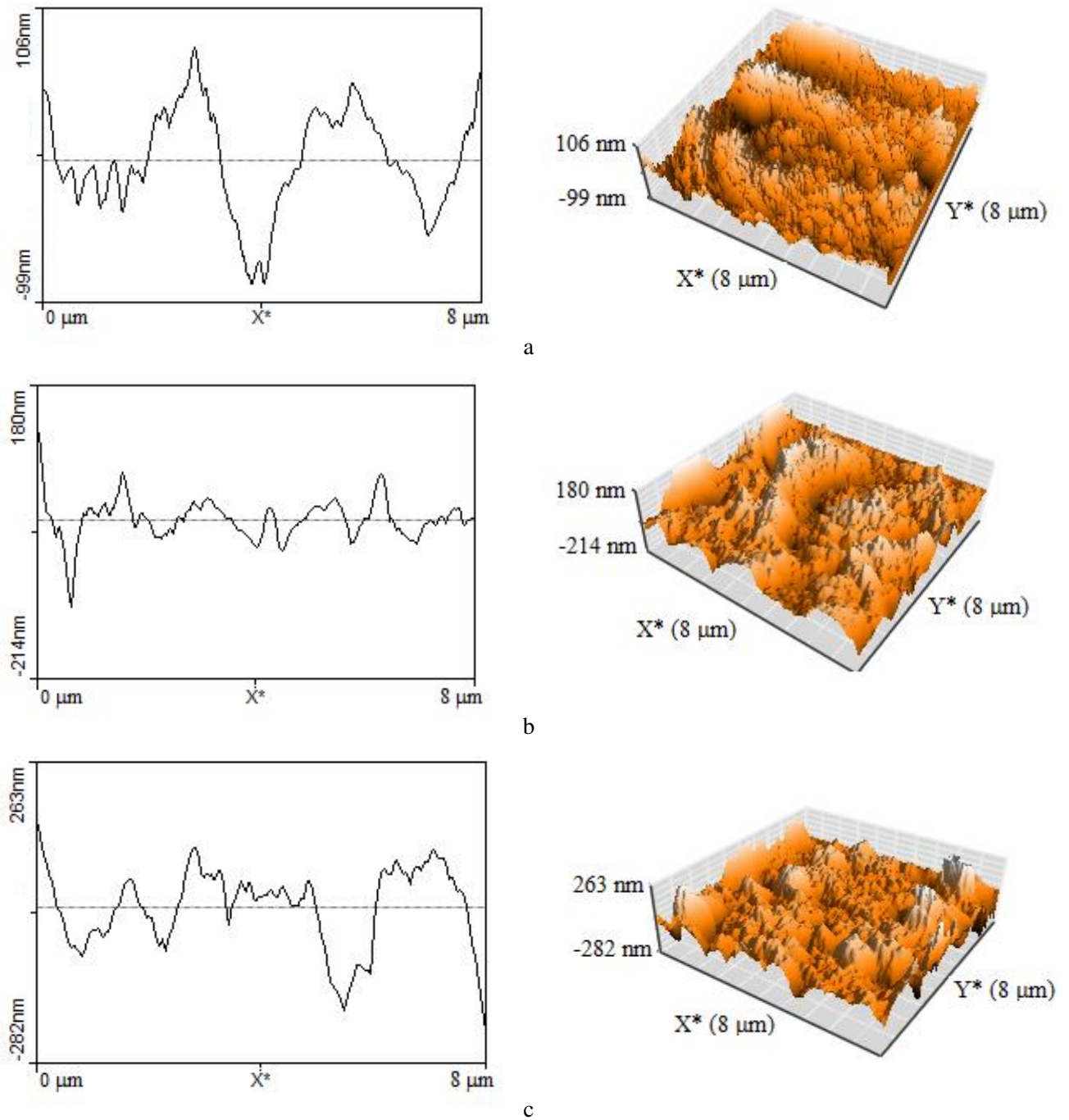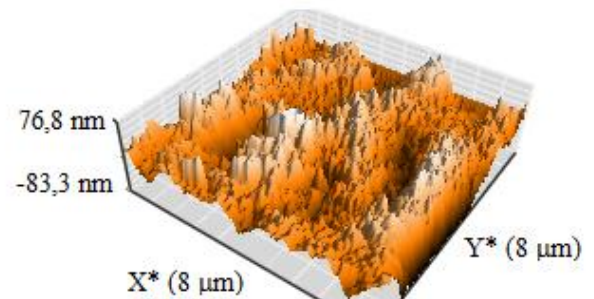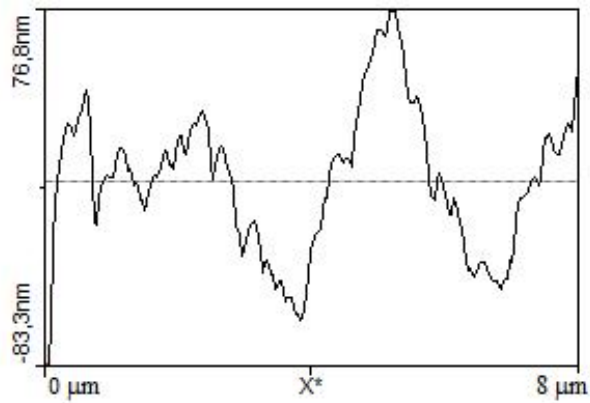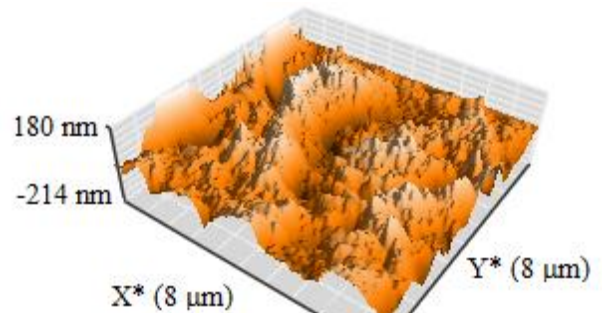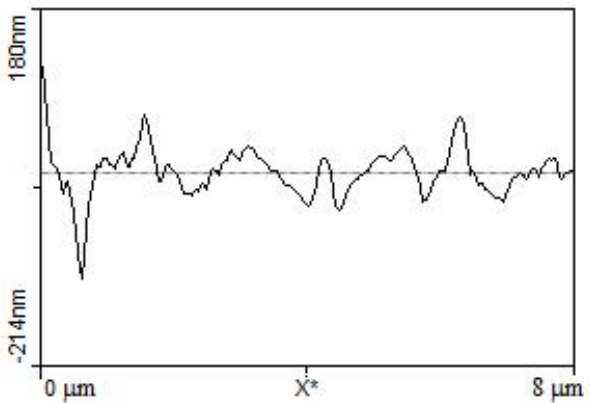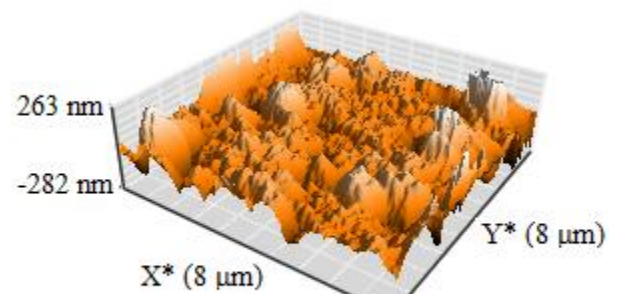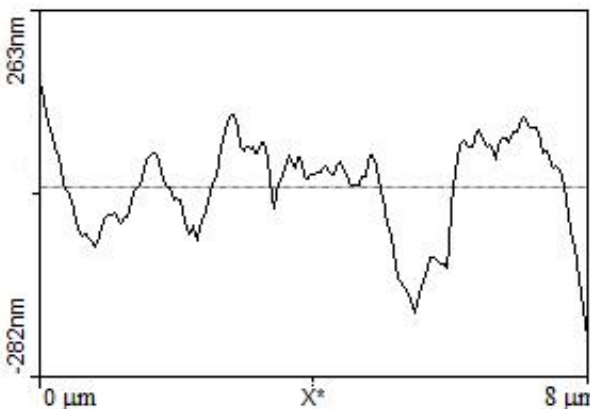
Fig. 4. Values of S_q for coatings deposited at $i_k = 35$ A.dm^{-2} from electrolytes without stirring containing different amounts of CoCl$_2$.6H$_2$O: a) 1 g.L^{-1} CoCl$_2$.6H$_2$O; $S_q = 5.84$; b) 3 g.L^{-1} CoCl$_2$.6H$_2$O; $S_q = 6.80$; c) 5 g.L^{-1} CoCl$_2$.6H$_2$O; $S_q = 10.88$.

a

b

c

Fig. 5. Values of S_q for coatings deposited at $i_k = 35$ A.dm^{-2} and stirring of electrolytes containing different amounts of CoCl$_2$.6H$_2$O: a) 1 g.L^{-1} CoCl$_2$.6H$_2$O; $S_q = 6.11$; a) 3 g.L^{-1} CoCl$_2$.6H$_2$O; $S_q = 11.35$; c) 5 g.L^{-1} CoCl$_2$.6H$_2$O; $S_q = 14.61$.
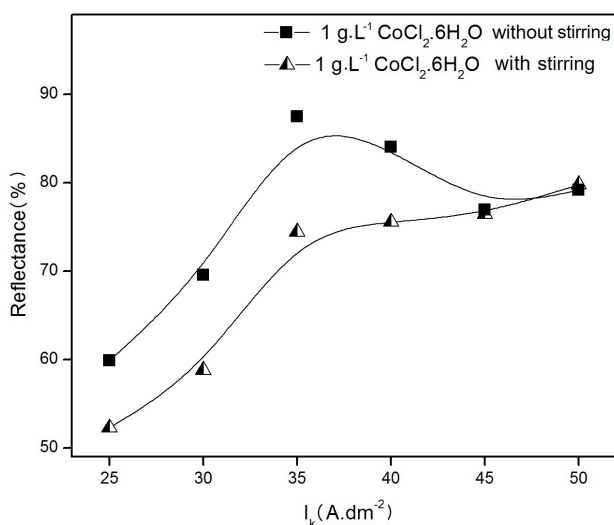
Fig. 6. Dependence of reflectance on cathode current density and electrolyte stirring.

The data presented in Table 1 indicates that higher concentration of $CoCl_2.6H_2O$ and stirring of the electrolyte increase root mean square roughness and reduce reflectance of coatings.

Table 1. Class of roughness and reflectance of coatings deposited for a period of 5 minutes at i_k = 35 A.dm^{-2} and different concentrations of $CoCl_2.6H_2O$

No	$CoCl_2.6H_2O$ g.L^{-1}	S_q nm	Grain size nm	δ %	Note
1	1	5.84	458.60	87.5	without
2	3	6.80	1122.0	76.04	stirring
3	5	10.88	1280.00	25.56	
4	1	6.11	658.20	77.92	with
5	3	11.35	674.60	64.24	stirring
6	5	14.61	1140.00	20.28	

CONCLUSION

Some functional properties of electroplated chromium coatings deposited from non-standard, modified electrolyte of *Cromispel* type were studied. The influence of different technological factors - current density, $CoCl_2.6H_2O$ content and stirring – on the most important characteristics of the electrolyte and the coatings was studied.

It was found that higher cathode current density and stirring may increase current yield to 35%, i.e. almost twice as high as that of conventional sulphate electrolytes. Deposition rate, coating thickness and root mean square roughness were also increased.

It was demonstrated that increasing the content of $CoCl_2.6H_2O$ in the investigated range of 1-5 g.L^{-1} makes the coating rougher and less glossy.

To highlight particular areas of the application of these chromium coatings, it is advisable to determine the content of cobalt in them and to study their biocompatibility.

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ЗА ВЛИЯНИЕТО НА НЯКОИ ФАКТОРИ ВЪРХУ ФУНКЦИОНАЛНИТЕ СВОЙСТВА НА ГАЛВАНИЧНО ОТЛОЖЕНИ ПОКРИТИЯ, ПЕРСПЕКТИВНИ ЗА МЕДИЦИНСКО ПРИЛОЖЕНИЕ

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(Резюме)

В настоящата работа са изследвани някои функционални свойства на галванични хромови покрития, отложени от нестандартен хлориден електролит тип "Cromispel", модифициран с комбинирана, комплексно действаща добавка $CoCl_2.6H_2O$.

Изследвано е влиянието на различни технологични фактори като плътност на тока, съдържание на $CoCl_2.6H_2O$ и разбъркване върху свойствата на електролита и покритията. Получените експериментални резултати показват, че прилагането на разбъркване и нарастването на плътността на тока от 15 $A.dm^{-2}$ до 50 $A.dm^{-2}$ правят покритията по-гладки, по-блестящи и повишават скоростта на отлагане и използваемостта на катодния ток. Експериментално е установено, че по-високата концентрация на $CoCl_2.6H_2O$ води до намаляване на отражателната способност и дебелината на слоевете.

За определяне на повърхностната морфология на изследваните покрития е използван атомен силов микроскоп. Измерена е средната квадратична грапавост на изследваните покрития и е определен средният размер на наблюдаваните зърна.