EFFECT OF CURRENT DENSITY ON MICROSTRUCTURE AND CORROSION BEHAVIOR OF PURE COBALT COATINGS OBTAINED BY ELECTRODEPOSITION

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Abstract: Pure cobalt coatings were electrodeposited on copper substrate by means of direct electric current in a chloride solution at different current densities in the range of 10-70 mA cm^{-2}. The surface morphology and microstructure were investigated via X-ray diffraction analysis and scanning electron microscopy. Corrosion behavior of cobalt coatings was also studied in a 3.5 wt% NaCl solution using potentiodynamic polarization and impedance spectroscopy techniques. The results showed that corrosion resistance of deposits was strongly influenced by the coating's morphology. Co deposit obtained in lower current densities exhibited the highest corrosion resistance, due to their lower grain boundaries and so the least density of active sites for preferential corrosion attacks.

1. INTRODUCTION

Surface coatings are used to increase the lifetime of components, exposed to corrosive condition, in many engineering applications. The electrodeposition has been recently recognized as a technologically and economically superior technique for surface coatings production. This technique is easier to handle and much cheaper in comparison with other modern methods, which are extensively used in diverse commercial, industrial, medical, and military applications. As the morphology and microstructure of the deposits strongly dependent on process parameters (temperature, applied potential, current density, pH solution, etc.), their control is an important task, which should be considered in the electrodeposition of metals with high mechanical, corrosion and magnetic properties [1-5].

Electrodeposited Co and Co alloys are strategic materials for technological applications in magnetic/electrical industry (i.e. magnetic recording, transformer core materials, thin film inductors, and giant magneto-impedance sensors) and defense with excellent properties such as thermal stability, hardness and corrosion resistance [5-7]. Recently, the electrodeposited nanocrystalline Co and Co-based alloys have been identified as a candidate material for replacing hexavalent Cr deposits that is used extensively in decorative and functional applications including aircraft manufacturing industry and military maintenance depots for applying wear and/or corrosion resistant coatings [8]. Both acidic and alkaline baths have been used for the plating of Co deposits [9-11]. The advantages of using chloride electrolytes compared with sulphate can be summarized as: higher electrical conductivity in the electrolyte, lower overpotential for deposition of cobalt and lower anodic overpotentials and higher catholic current efficiency [11].

Despite the numerous reports on the corrosion behavior of nickel and iron groups, there have been very few reports on the corrosion properties of cobalt coatings in the literature. Therefore, in this study, cobalt coatings were deposited in an acid chloride solution to investigate the effect of current density on morphology, microstructure and corrosion behavior.

2. EXPERIMENTAL PROCEDURES

2. 1. Deposition of Electroplating Co Coatings

Copper plate (with a dimension of 1cm×1cm)

and pure cobalt plates were used as cathode and anodes, respectively. Before electroplating process, the copper substrates were polished and thoroughly degreased for 2 min in an alkaline solution (containing 10 gL^{-1} NaOH and 40 gL^{-1} Na$_2$CO$_3$) at 70 °C. After cleaning in distilled water, they were activated in 5% HCl for 30 s and then were immediately put in the plating electrolyte to avoid contamination of their surfaces.

The chloride solution (Merck analytical grade) used for direct current (DC) electrodeposition contained cobalt chloride (210 gL^{-1}), boric acid to avoid the pH variation and formation of hydroxide species near the electrode (20 gL^{-1}), and saccharine (0.25 gL^{-1}). The pH of electrolyte was adjusted to 3 by adding HCl and deposition was carried out at 55°C. In this electroplating, the direct current density was altered form 10 to 70 mA cm^{-2}.

2. 2. Morphology and Microstructure of Co Coatings

The surface morphologies of the coatings were investigated by using MV-2300 scanning electron microscopy (SEM). The microstructure was also determined via X-ray diffraction (XRD) analysis by using a diffractometer (model Philips X'Pret Pro) with Cu–K$_\alpha$ radiation (λ= 1.54056 Å) operated at 30 kV and 20 mA in the 2θ range of 30–100° at a scan rate of 0.8° s^{-1}.

2. 3. Electrochemical Measurements

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques were used to study the corrosion behavior of Co coatings in a 3.5 wt. % NaCl solution. The tests were carried out in a three-electrode cell using an EG & G Potentiostat/Galvanostat, model 273A at room temperature. Platinum plate and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Potentiodynamic polarization tests were carried out by sweeping the potential at a scan rate of 1 mVs^{-1} in the range of −400 to 400 mV (vs. SCE). The EIS measurements were undertaken using a Solartron Model SI 1255 HF Frequency Response Analyzer (FRA) coupled to a Princeton

Applied Research (PAR) Model 273A Potentiostat/Galvanostat. The EIS measurements were obtained at the open circuit potential (OCP) in a frequency range from 0.01 Hz to 100 kHz with an applied AC signal of 5 mV (rms) using EIS software model 398. The equivalent circuit simulation program (ZView2) was used for data analysis, synthesis of the equivalent circuit and fitting of the experimental data.

3. Results and discussion

3. 1. Microstructure and Morphological Analysis of the Coatings

Fig.1 shows the surface morphology of Co coatings obtained at different current densities. All coatings are crack-free and uniform. As it is seen, the current density plays an important role on the morphology and grain size of electrodeposited cobalt coatings. The SEM micrographs reveal that the coatings created under low current density formed spherical grains, while those prepared under high current density formed acicular structure. Further increasing of the current density will result in a less uniform coating together with much larger acicular crystallites (with an average length size of 2-5 μm). Some researchers have reported these changes of morphology to a decrease in surface energy, due to the adsorption of species such as halide ions and intermediates. Furthermore, from the SEM images, it can be seen that the grain size of deposits decreases with increasing the current density from 10 to 30 mA.cm^{-2}. Generally, the grain size of electrodeposited layers is a competition between the nucleation rate and crystal growth. With an increase in the current density, the free energy of new nuclei formation rises (due to an increase in the overpotential), which results in a higher nucleation rate and smaller grain size [12-13]. However, by further increase in the current density from 30 to 70 mA.cm^{-2}, the grain size of deposits increases and acicular crystals appear. This phenomenon for nickel deposits has been reported by several researchers. They attributed the increase in the grain size by increasing of current density to a decrease in the concentration

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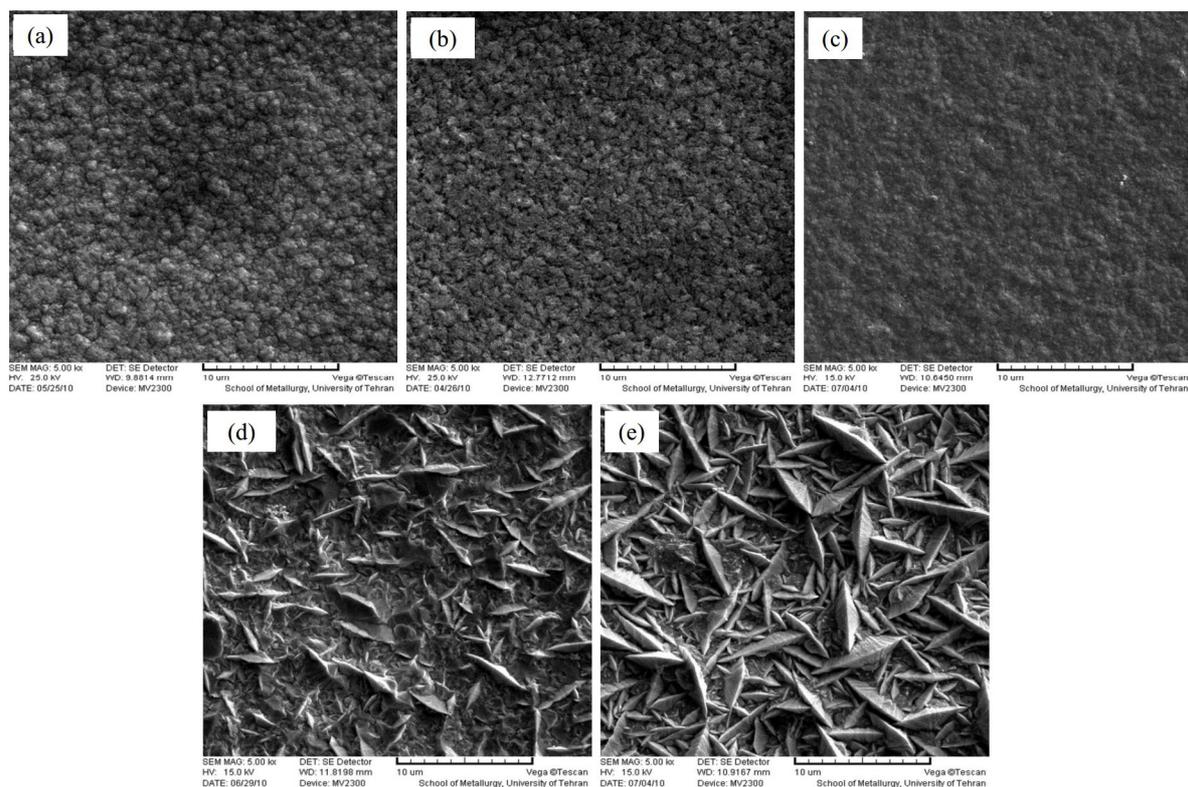
Fig. 1. Surface morphology of Co coatings deposited at (a) 10 mA.cm⁻, (b) 20 mA.cm⁻², (c) 30 mA.cm⁻², (d) 50 mA.cm⁻² and (e) 70 mA.cm⁻².

of nickel ions and the hydrogen codeposition at the cathode/electrolyte interface. Totally, it can be deduced that the shape and grain size of the electrodeposited cobalt coatings were significantly altered due to a change in deposition parameters such as current density.

The deposition was also supported by XRD results. Fig. 2 displays the XRD patterns of as-deposited Co coatings as a function of current density. The diffraction peaks indicate a crystal structure of the coatings. The electrodeposited Co coatings have face centered cubic (fcc) structure at lower current densities, and favors hexagonal close packed (hcp) structure at higher current densities. According to this figure, the coatings show main peaks corresponding to (002), (100) and (110) crystallographic planes. At the current density of 10 mA cm⁻², the coatings are preferentially orientated in the (0 0 2) plate directions, and with an increase in current density, the intensity of (0 0 2) peaks decreases

and the reflection of (1 0 0) peak becomes more pronounced. Moreover, some diffraction lines correspond to copper substrate is also present in the XRD patterns (due to the low thickness of coatings). Different findings have been reported by researchers. According to Paranthaman and et.al [14], cobalt coatings have hcp structure in lower current densities and in higher ones they have fcc structure and mixed phases of them in between. Wang and et.al [1] reported that Co coatings shows a hcp lattice, and mainly showed hcp (100)+(110) orientation. According to the literature, the surface morphology of cobalt deposits is mainly affected by phase structure and preferential orientation. When the preferential orientation is (1 0 0) and (1 1 0) planes, acicular-like morphology can be generally observed. Accordingly, in this study, the acicular-like morphology of Co may be corresponded to its hcp (100)+(110) preferential orientation. The crystallite sizes of Co deposits were also
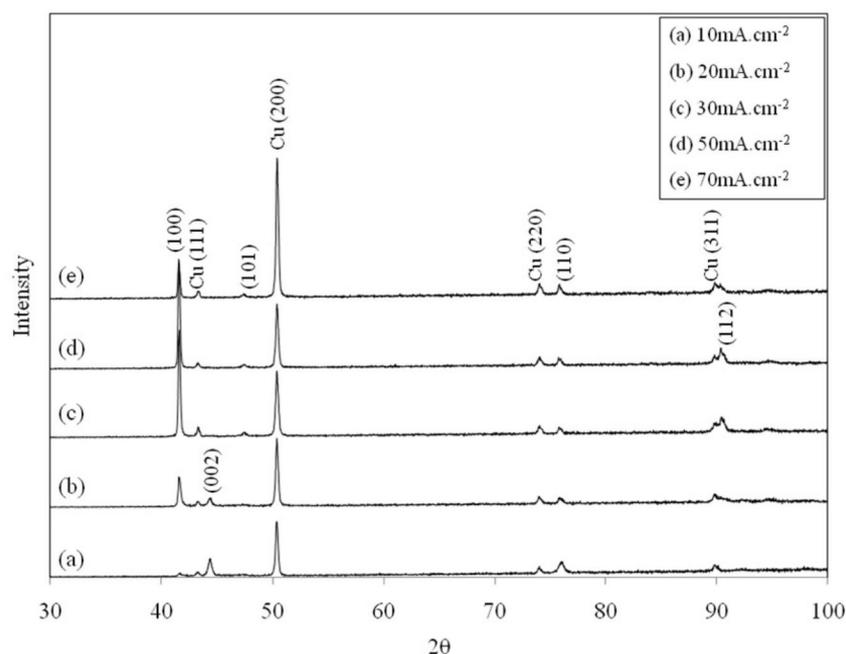
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Fig. 2. XRD patterns of Co coatings deposited on Cu substrate at different current densities.

calculated by measuring the peak's width in the XRD patterns and using the Scherer's Eq. (1):

$$\tag{1}$$

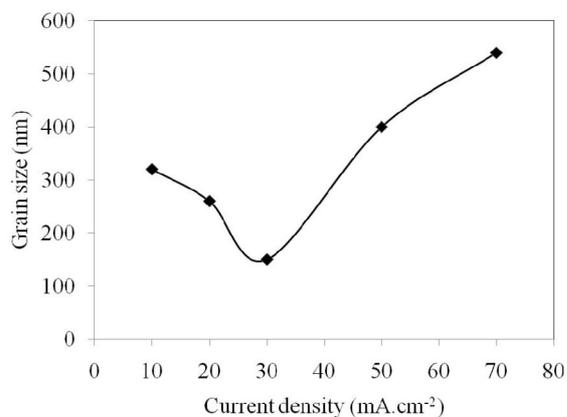Where β is the full width at half maximum (FWHM) height of the diffraction peak, λ is the wavelength of the incidental X-ray, D is the grain size and θ is the diffraction angle of corresponding peak [13]. Based on this equation, the average crystallite size was calculated and has been presented versus current density in Fig. 3. With increasing the current density from 10 to 30 mA.cm^{-2}, the grain size decreases from 320 to 150 nm. However, further increasing of current density to 70 m.Acm^{-2} leads to the crystal size increasing from 150 to 540 nm, that confirms the SEM results.

3. 3. Electrochemical Results

3. 3. 1. Potentiodynamic Polarization Tests

Fig. 4 shows the polarization curves (E vs. I plots) for electrodeposited Co coatings in 3.5wt % NaCl solutions. Upon increasing the anodic polarization, all coatings displayed active behavior without any distinctive transition to passive up to 0.5 VSCE. The non-passivating behavior of Co coatings observed in the present study is in agreement with a previous study for pure Co [15]. It was reported that pure Co deposits (99.9%) do not show any passivation in
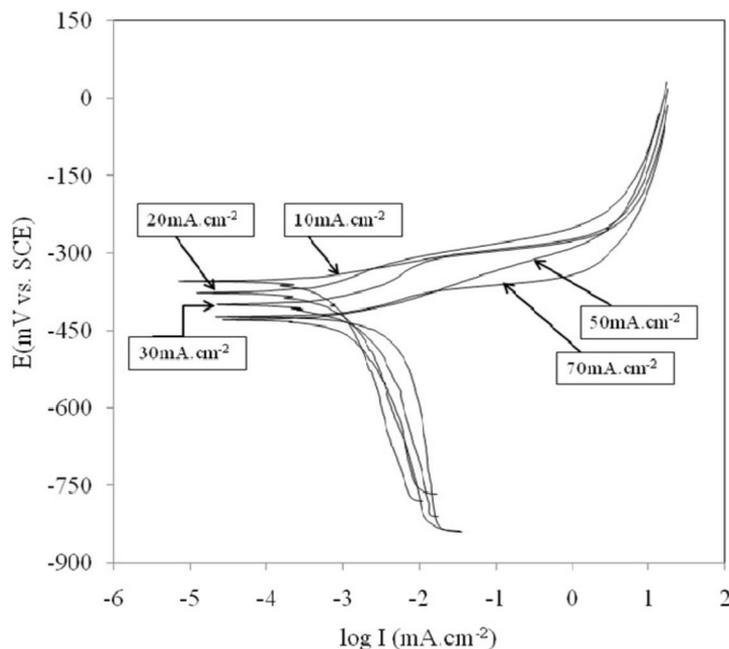

Fig. 3. The effect of current densities on grain size values of Co coatings.

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Fig. 4. Polarization curves of Co coatings obtained in 3.5wt.% NaCl solution.

0.5 M Na_2SO_4 at different pH of 3, 7 and 10.

Corrosion parameters such as the OCP as well as corrosion potential (Ecorr) and corrosion current density (Icorr), which are used to characterize the active dissolution ability of materials and were extracted from the intersection of the cathodic and anodic curves (using Tafel extrapolation method) are shown in table 1 [1]. As the results of polarization tests show, increasing the current density causes an increase in the corrosion current density (Icorr) and potential towards more negative values, indicating a better corrosion behavior of deposition at lower current densities. The lowest current density (0.1778×10^{-6} A cm^{-2}), the highest potential (-357.86 mV) and so, the best corrosion resistance was obtained from the Co coating electrodeposited at the current density of 10 mA cm^{-2}. Therefore, it can be deduced that the corrosion behavior of Co coatings was not greatly affected by reducing the average grain size, which is in agreement with Kim et.al results [15].

3. 3. 2. Electrochemical impedance spectroscopy studies

Electrochemical impedance spectroscopy (EIS) measurements were performed for better understanding of the anticorrosive ability of the

Table 1. Corrosion current density (icorr), and corrosion potential (Ecorr) measured in 3.5wt.% NaCl solutions.

Current density of electrodeposition (mA.cm^{-2})	i$_{corr}$ (µA.cm^{-2})	E$_{corr}$(mV vs. SCE)	OCP (mV)
10	0.1778	-357.86	-342.65
20	0.1995	-379.78	-367.83
30	0.2511	-403.27	-412.32
50	0.3548	-431.22	-446.79
70	0.7079	-427.35	-441.52
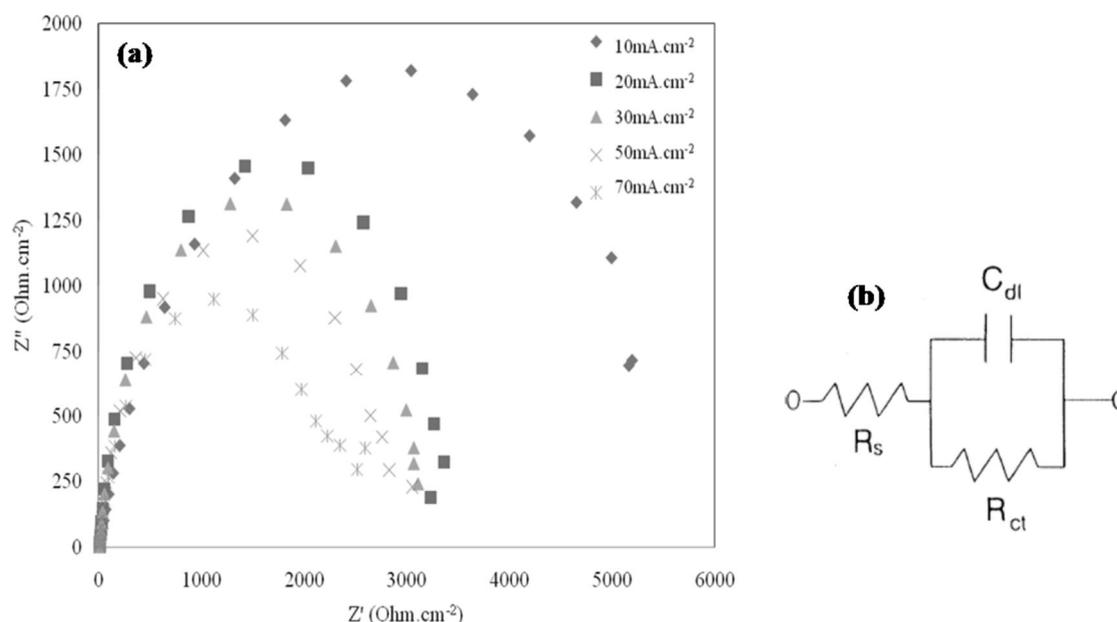
Fig. 5. (a) Nyquist plots of Co coatings and (b) Equivalent electrical circuit model used to analyze the EIS data of the Co coatings obtained in 3.5wt.% NaCl solution.

deposits. Fig. 5 shows the Nyquist plots of EIS obtained for Co coatings in the test media at their respective OCPs. All the Nyquist curves appear to be similar, consisting of a single semi-circle arc and one time constant ($\tau = R_{ct}C_{dl}$) in the high frequency regions, signifying the charge controlled reaction, which has uniformly active and homogeneous surface across the electrode surface. However, it should be noted that although these curves appear to be similar with respect to their shapes, they differ considerably in their size and their diameters decrease by increasing the electroplating current density. This indicates that the charge transfer reaction occurs on all these coatings but over a different effective area in each case. The decreased radius of impedance arc is indicative of the worse anticorrosive property of the deposits at higher current density. Thus, the results of the EIS studies confirm the results obtained from the polarization curves, which showed that the corrosion resistance was increased by decreasing current density. In order to analyze the Nyquist plot, an equivalent electrical circuit model has been utilized to simulate the metal/solution interface via Zview2 software (Fig. 5). This model consists of one time constant, where the solution resistance between the reference

Table 2. Electrochemical parameters (from EIS) of Co coatings in 3.5wt.% NaCl.

Current density of electrodeposition (mA.cm^{-2})	R_{ct} (Ω cm^2)	C_{dl} (μF.cm^{-2})
10	3845	4.21
20	3167	17.821
30	2949	24.708
50	2263	30.599
70	1913	42.135

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electrode and the working electrode (R_s) was in series with a parallel combination of the (R_{ct}) and double layer capacitance (C_{dl}). The R_{ct} and C_{dl} obtained for the Co deposits are compiled in Table 2. As shown in this table, the high values of charge transfer resistance (in the range of 1913-3845 Ω cm^2) imply great corrosion protective ability of Co deposits. The C_{dl} value is related to the coating's porosity. The low capacitance values (in the range of 4-42 µF cm^{-2}) indicate that the present coatings are normally less porous.

By comparing the electrochemical parameters from EIS and the grain size of coatings, it can be seen that the deposit produced at 30 mA cm^{-2} (with the lowest grain size) has more grain boundaries and hence, it is less protective among other coatings deposited at current density of 10 and 20 mA cm^{-2}. With the decrease in grain size, the number of grain boundaries and triple junctions increase, which are the active sites for corrosion attack especially in chloride medium. As a result, the preferential corrosion at grain boundaries accelerates the corrosion rate of the coatings obtained from current density of 30 mA cm^{-2}.

Li [16] reported that the electron work function at the grain boundaries of metallic surfaces decreases, which indicates more electron activities for participating in the electrochemical and passive processes. Since no obviously passive process can be observed, higher grain boundary densities in Co will accelerate corrosion by forming much more micro electrochemical cells between the huge amount of grain boundaries and the matrix and by increasing the electrochemical reactivity during the corrosion process, which is in agreement with the classic corrosion theory. As shown in Fig. 1(d and e), the surface morphologies of Co coatings applied at current densities of 50 and 70 mA.cm^{-2} were acicular-like, which are active sites. These regular shapes of Co crystals are more sensitive and susceptible to corrode seriously in comparison with the coatings obtained in the range of 10-30 mA.cm^{-2} (shown in Figs. a-c), which have more dense structure and smoother surface.

Briefly, in this paper, the corrosion behavior was correlated to grain size and surface morphology. The grain size was decreasing by increasing current density from 10 to 30 mA cm^{-2}, leading to a decrease in corrosion resistance, while, by further increasing of current density from 30 to 70 mA cm^{-2}, in spite of increasing grain size, the corrosion resistance did not increase that can be attributed to the changing of surface morphology from spherical to acicular structure.

4. CONCLUSIONS

Cobalt coatings were electrodeposited from chloride solutions to investigate the effect of current density on the morphology, microstructure and corrosion behavior of the deposits. The results were as follow:

1. According to XRD analysis, Co deposit had fcc structure at low current density and hcp structure at high current density.
2. By increasing the current density, the spherical shape of coatings was converted into a grain structure of "acicular crystals". The grain size reduced with an increase in current density from 10 to 30 mAcm^{-2}. However, further increase in the current density from 30 to 70 mAcm^{-2} had a reverse effect and caused grain coarsening.
3. Among different coatings with fcc structure, which were obtained at lower current densities, the coating with larger grain size exhibited higher corrosion resistance.
4. The lower corrosion resistance of Co coatings belonged ones obtained at the higher current density of 70 mA cm^{-2}.

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