

Corrosion Behavior of Electrodeposited Cobalt-Tungsten Alloy Coatings in NaCl Aqueous Solution

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Alternative process to hexavalent chromium, substitute materials and new designs are urgently needed owing to the requirement of “clean” manufacture. Corrosion behavior of the coatings deposited on copper substrates was studied at room temperature in 3.5 wt.% NaCl aqueous solution by using open-circuit potential, electrochemical impedance spectroscopy and polarization techniques. The physicochemical characterization of the alloy coatings was carried out by scanning electron microscopy and energy dispersive X-ray analysis techniques. The Co-W alloys exhibited a high as-deposited hardness. The study revealed that the extent of shift in corrosion potential towards the noble direction, decrease in corrosion current density, increase in charge transfer resistance and decrease in double layer capacitance values for Co-W coatings. The corrosion resistance of Co-W alloys increased with tungsten content up to 21.5 wt.% and then decreased. Among the various Co-W coatings studied here, the Co_{78.5}W_{21.5} layer presented the best corrosion behavior and superior corrosion potential compared to pure cobalt coating.

Keywords: Co-W; Electrodeposition; Corrosion resistance; Microhardness; Electrochemical impedance spectroscopy

1. INTRODUCTION

Chromium electrodeposition is a well-established technique for the production of decorative and functional coatings which possess attractive properties such as high hardness, excellent wear resistance and low coefficient of friction. Chromium coatings can also provide excellent protection against corrosion. As a consequence, chromium electrodeposits have found extensive use, particularly for their resistance to wear, in a wide range of engineering industries. However, replacement of hard chromium electrodeposits is being actively pursued on environmental grounds. The primary concern with the processing of such materials is that normally a hexavalent chromium solution is employed in

the electrodeposition bath, which produces large volumes of chrome contaminated toxic waste requiring special disposal methods [1]. Expensive breathing apparatus and exhaust systems must also be employed to deal with emissions during plating. Hexavalent chromium in solution is also a recognized carcinogen and causes other health problems such as skin and lung irritation [2]. A further technical concern is associated with the fact that chromium-plating baths are generally only ~15% efficient and that operator often have difficulty maintaining uniformity of coating thickness [3]. As a result, the plating industry has been forced to consider alternative materials and/or processes that do not involve hexavalent chromium [4-6].

The co-deposition of alloys of tungsten with one or more of the iron group metals provides a number of electrodeposited systems that may be considered as possible replacements for conventional hard chromium electrodeposits. It is well known that alloys such as Co-W/B and Ni-W/B are characterized by high surface hardness; Vickers hardness values between 450 and 650 kgf/mm² have been reported for these coatings in the as-deposited condition [6-8].

Tungsten-containing alloy coatings can be produced with widely different compositions and microstructures depending on the composition of the plating bath and the deposition parameters. Amorphous, crystalline and nanocrystalline forms of Co-W and Ni-W electrodeposits have all been reported in the literature [9-14].

The development of Co-W and Ni-W alloys with amorphous or nanocrystalline structures is expected to be of particular future interest since materials with such microstructures often possess better corrosion resistance and tribological properties when compared to their crystalline counterparts. Generally, Co-W alloys are known to exhibit higher hardness, higher heat resistance and also a better corrosion behavior compared to elemental cobalt. During the corrosion process tungsten preferentially migrated toward the surface and formed oxides.

The aim of this work is to study the electrodeposition of Co-W alloys coatings from environmentally friendly citrate-ammonia solutions containing high amounts of ammonia. Also, in this work, a comparative study is made of the corrosion and microhardness properties of electrodeposited Co and Co-W coatings.

2. EXPERIMENTAL DETAILS

2.1. Electrodeposition

Solutions were prepared from analytical grade chemicals, dissolved in water purified by a Millipore Milli-Q system. Cobalt and Co-W coatings were electrodeposited on copper sheets embedded in epoxy resin, with a geometric area of approximately 1 cm² of exposure.

The electrodeposition were performed in a single-compartment Pyrex glass cell, with a Teflon cover containing holes to fix the Cu cathode and the platinum mesh anode.

Prior to the alloy plating, the Cu surfaces were polished with 600, 2000 and 3000 SiC emery paper, degreased in a hot NaOH solution, rinsed in distilled water, etched in 10% H₂SO₄ solution, and

finally rinsed again with distilled water. Table 1 gives the composition of the Co-W plating solution and the operational parameters used to electrodeposit the Co-W coatings.

Table 1. Composition and operating conditions of the bath used for electrodeposition Co-W alloy coating

Chemical reagents	Concentration
CoSO ₄ ·7H ₂ O	0.071 mol L ⁻¹
Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	0.412 mol L ⁻¹
Na ₂ WO ₄ ·2H ₂ O	Variable (0-0.196 mol L ⁻¹)
(NH ₄) ₂ SO ₄	0.066 mol L ⁻¹
CH ₃ (CH ₂) ₁₀ CH ₂ OSO ₃ Na	0.00001 mol L ⁻¹
Operational deposition parameters	
Current density = 30 mA cm ⁻²	
Plating temperature = 60 °C	
pH = 9.2 (adjusted with ammonia)	

2.2. Characterization

The surface morphology of the Co-W electrodeposits was analyzed using a Philips XL30 scanning electron microscope (SEM).

The coating compositions were analyzed by an energy dispersive X-ray (EDX) apparatus attached to the SEM. The thickness of the deposits was large enough (average thickness of 19 μm) so that no signal from the underlying gold substrate was observed. Each sample was measured at different locations to confirm uniformity.

Microhardness of the deposits was determined by using a Vickers diamond pyramid model BUEHLER with a load of 10 g and loading time of 15 second. An average of 10 readings was taken to obtain the microhardness values of the coatings.

2.3. Electrochemical measurements

All the electrochemical corrosion tests involved at least triplicate samples and were conducted at room temperature in an aerated 3.5 wt.% NaCl aqueous solution, using a conventional three-electrode cell. A platinum sheet of the geometric area of about 20 cm² was used as counter electrode, while all potentials were measured with respect to a commercial saturated calomel electrode (SCE). The electrochemical methods used were: open-circuit potential (E_{OCP}), linear Tafel polarization and electrochemical impedance spectroscopy (EIS). Electrochemical experiments were carried out using a Princeton Applied Research, EG&G PARSTAT 2263 Advanced Electrochemical system run by PowerSuite software. The r.m.s amplitude of the modulation potential for the EIS measurements was 10 mV, and the frequency range was 100 kHz-10 mHz).

3. RESULTS AND DISCUSSION

3.1. Microhardness of the deposits

Figure 1 illustrates the relationships between microhardness and tungsten content of Co-W deposits with sodium tungstate concentration in the electrolyte. As sodium tungstate concentration was increased, the tungsten content increased so that the deposit hardness increased from $Hv450$ to approximately $Hv680$. The as-electrodeposited Co-W coatings have a slightly higher microhardness value than the pure cobalt coating. According to He et al. [15], this behavior is associated with the enlargement of crystal lattice aberrations caused by tungsten, which leads to a lower likelihood of dislocation. Microhardness may increase due to solid solution hardening and/or reduction of grain size [16]. Also, the variation of microhardness can be attributed to tungsten content as solid solution in the hcp cobalt structure. Capel et al. [17] reported that the microhardness value of Co-30%W is 450 VHN. In contrary to Co-W alloy coatings, it has been reported that in Ni-W coatings, the role of solid solution hardening is negligible compared with the effect of grain size [16]. The maximum hardness was achieved for the Co-35.5 wt.% W alloy, which was about 680 HV, as shown in Figure 1. This value (680 HV) is higher than Co-W coatings deposited by others [18, 19].

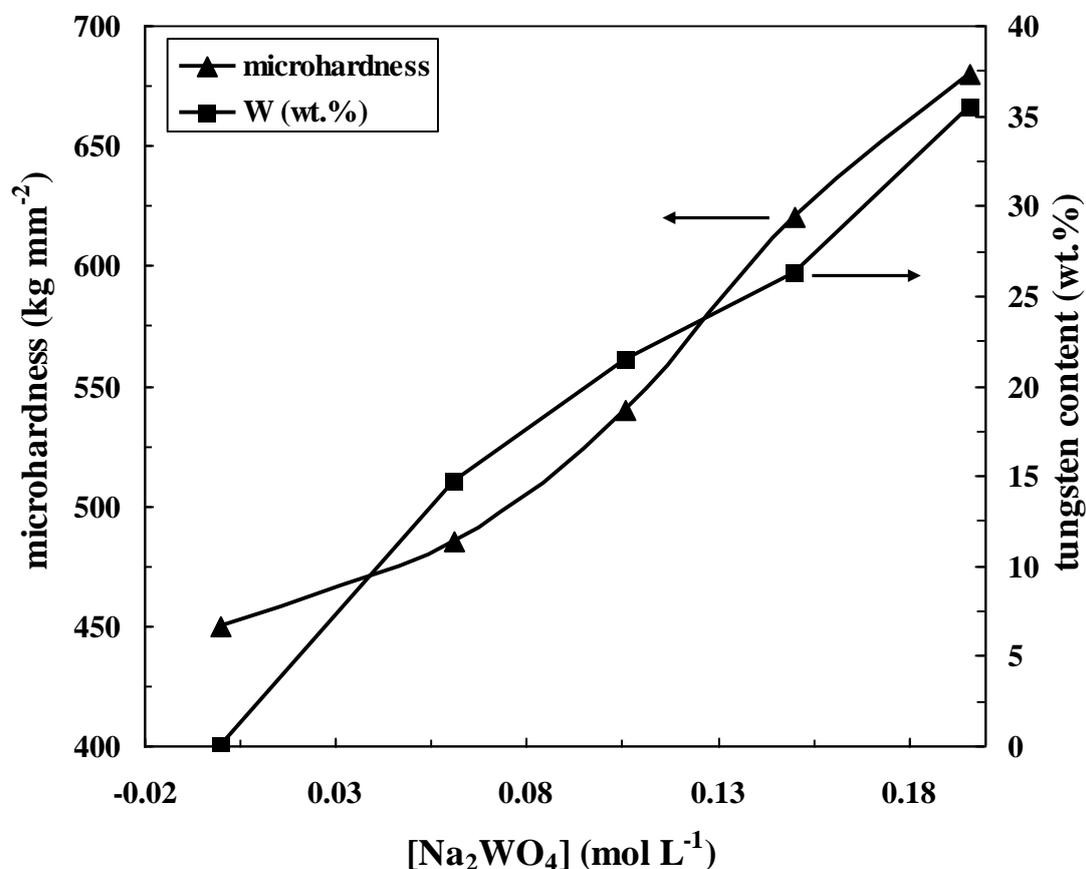


Figure 1. Effect of sodium tungstate concentration in the electrolyte on the tungsten content and deposit microhardness.

3.2. Morphology and composition of coatings

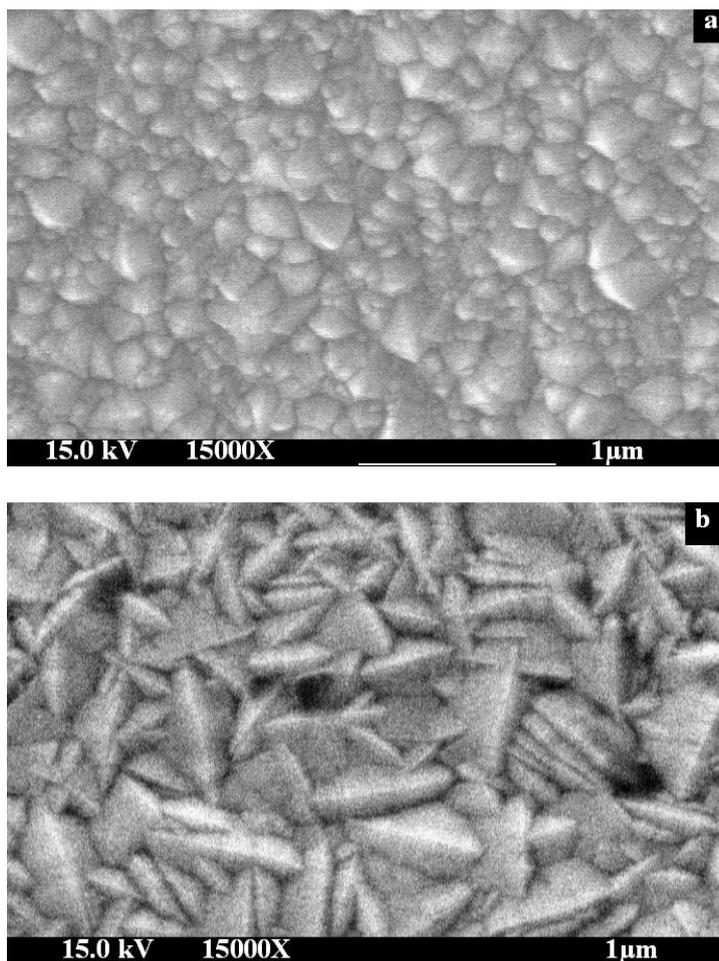


Figure 2. SEM surface morphology of pure cobalt electroplating and Co-21.5 wt.% W alloy coating deposited from plating baths containing various concentrations of Na₂WO₄: (a) 0 mol L⁻¹ and (b) 0.106 mol L⁻¹

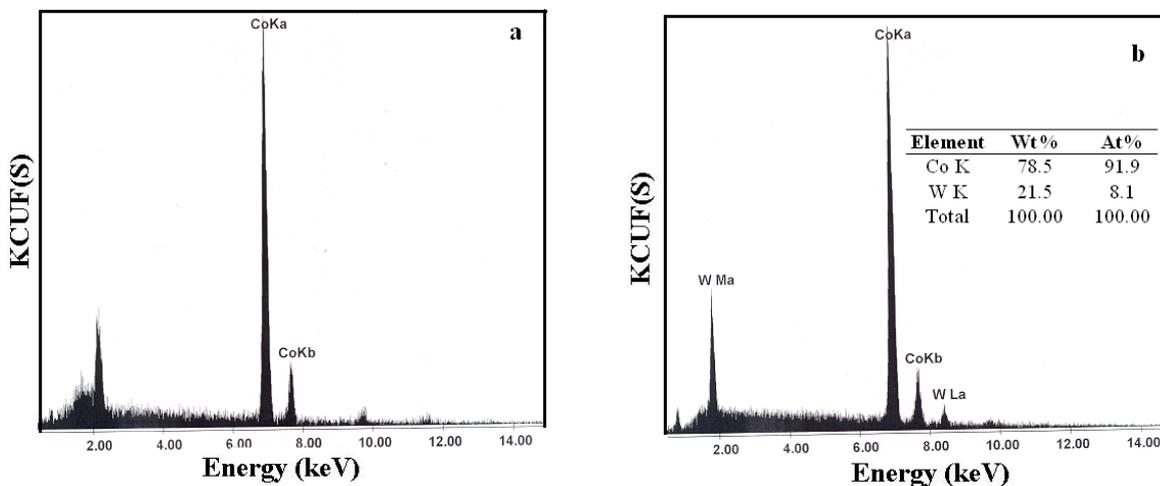


Figure 3. (A and B) EDX spectra of pure cobalt and Co-21.5 wt.% W alloy coatings

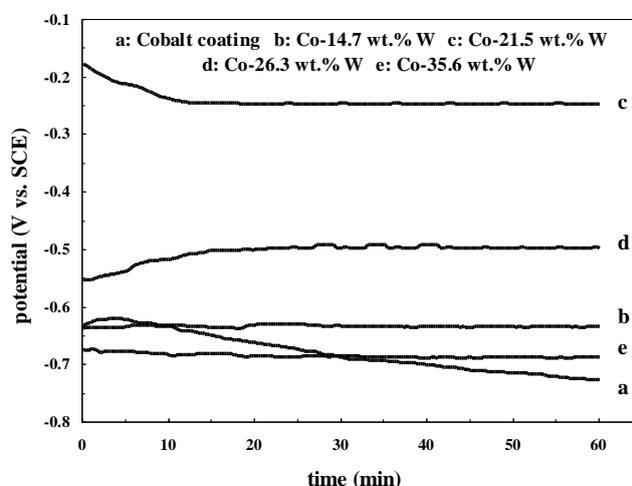
Table 2. Proportion of components Co and W for various the Co-W baths

	Co (wt.%)	W (wt.%)
Na ₂ WO ₄ (0 mol L ⁻¹)	100	0
Na ₂ WO ₄ (0.061 mol L ⁻¹)	85.3	14.7
Na ₂ WO ₄ (0.106 mol L ⁻¹)	78.5	21.5
Na ₂ WO ₄ (0.15 mol L ⁻¹)	73.7	26.3
Na ₂ WO ₄ (0.196 mol L ⁻¹)	64.4	35.6

Figure 2 compares the surface structure of pure cobalt coating and electrodeposited Co-21.5 wt.% W alloy coating under a scanning microscope. The surface of cobalt coating is made up of regular pyramidal crystals with a uniform grain size (Figure 2a). Tungsten codeposition with cobalt radically change the structure of the coating: disorder the regular crystal structure and the structure of the cobalt matrix becomes finely crystalline (Figure 2b). Generally, the morphology of the Co-21.5 wt.% W alloy coating is needle-plate structure while cobalt coating shows fine-grained structure. In this study, the coatings without visible defects and cracks are formed in compare to Co-W alloy coatings in literature [18]. Figure 3 shows the results of EDX component analysis of the coatings. The weight percentages of Co and W are listed in Table 2. They support the idea induced effect of cobalt in tungsten codeposition successfully.

3.3. Corrosion behavior

The corrosion processes of these coatings were evaluated over the course of 60 minutes in the 3.5% NaCl electrolyte.

**Figure 4.** Open-circuit potential vs. time curves in 3.5% NaCl solution for pure cobalt and Co-W alloy coatings.

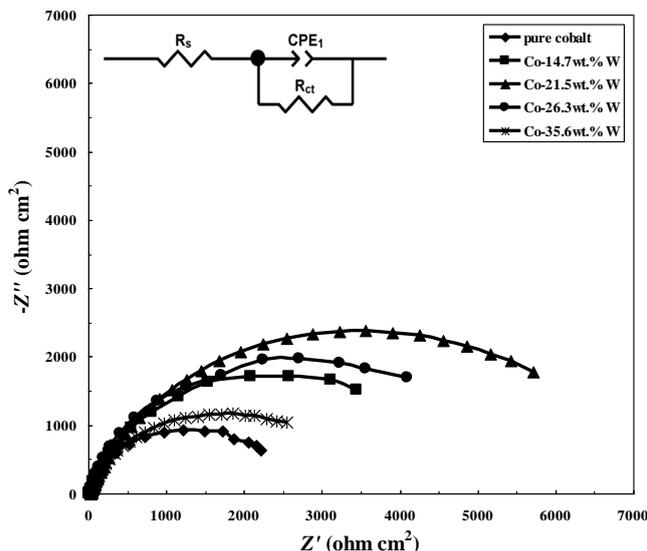


Figure 5. Equivalent circuit and Nyquist plots for pure cobalt and Co-W alloy coatings in 3.5 wt.% NaCl solution; the dots indicated measured data while lines represent best-fit data based on electric circuit shown in Figure 5.

The evolution of the open circuit potentials (E_{OCP}) for Co-W and Co coatings as a function of immersion time in 3.5% NaCl solution are shown in Figure 4. It can be seen that the E_{OCP} of the Co-W alloy coatings became more positive than pure Co coating, whereas the E_{OCP} value for the Co-21.5 wt.% W coating is the noblest and remains approximately constant during the whole immersion test.

The equivalent circuit and Nyquist plots obtained for pure cobalt and Co-W alloy coatings, in 3.5% sodium chloride solution, at their respective open circuit potentials, are shown in Figure 5. The Nyquist plots of all coatings studied exhibit a single semicircle in the frequency range studied. However, the curves differ considerably in their size. This indicates that the same fundamental process is occurring on all the types of studied coatings, but over a different effective area in each case. The occurrence of a single semicircle in the Nyquist plots indicates that the corrosion process of Co-W alloy coatings involves a single time constant.

To account for the corrosion behavior of Co-W alloy coatings, at their respective open circuit potentials, an equivalent electrical circuit model (Figure 5) consists of solution resistance (R_s), a constant phase element (CPE) and charge transfer resistance (R_{ct}), in which the CPE and R_{ct} are parallel to each other, has been utilized to simulate the metal/solution interface. In this model, constant phase element may have some combination of capacitive, resistive and inductive character [20]. The CPE is defined by two parameters, T and P, in the equation for impedance [21].

$$Z = \frac{1}{T(j\omega)^p} \tag{1}$$

The value of the exponent P may vary from 0 to 1. If P equals 0, then the CPE is a resistor. A CPE is often used in an equivalent circuit model in place of a capacitor to compensate for inhomogeneity in the system.

Table 3. Fitting results of the impedance spectra of pure cobalt and Co-W alloy coatings in 3.5 wt.% NaCl solution

Element	cobalt	Co-14.7 wt.%W	Co-21.5 wt.%W	Co-26.3 wt.%W	Co-35.6 wt.%W
R_s (ohm cm^2)	6.01	6.18	6.69	7.05	6.46
CPE_1-T (F cm^{-2})	0.0008927	0.0002049	0.0001012	0.000162	0.000285
CPE_1-P	0.811	0.823	0.817	0.819	0.838
R_{ct} (ohm cm^2)	2572	4576	7117	5362	3047
Error (%)	5.15	3.4	2.69	5.7	5.07

The charge transfer resistance (R_{ct}) and constant phase element (CPE) values, derived after fitting the data (Nyquist plot) using ZSim software, for Co-W alloy coatings are compiled in Table 3. The data in this table indicate that the mean error of modulus is smaller than 6%, indicating a good fitting of the experimental data. In Table 3, the charge transfer resistance (R_{ct}) and CPE-P values of Co-W alloy coatings are larger than those of the pure cobalt coating, indicating the smooth nature of these deposits.

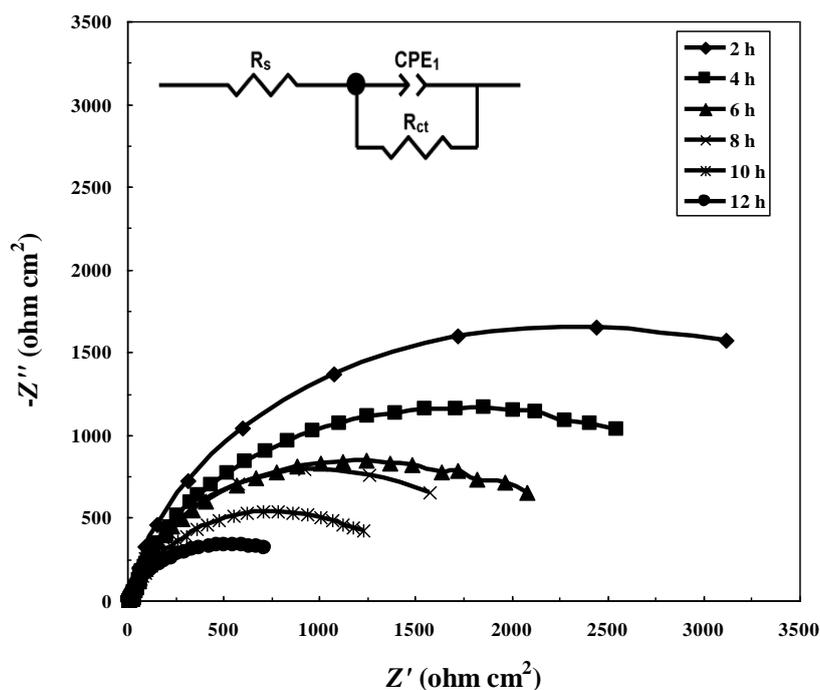


Figure 6. Equivalent circuit and Nyquist plots for Co-21.5 wt.% W alloy coating in 3.5 wt.% NaCl solution after different immersion times; the dots indicated measured data while lines represent best-fit data based on electric circuit shown in Figure 6.

It has been established that high values of R_{ct} and low values of CPE-T imply a better corrosion protective ability of coatings [22]. The highest value of charge transfer resistance (7117 ohm cm^2) was obtained for Co-W alloy coating deposited from solution with concentration of 0.106 mol L^{-1} sodium tungstate (Co-21.5 wt.% W alloy coating). The superior corrosion resistance of Co-W alloy films was maybe due to preferential dissolution of cobalt and formation of tungsten rich film or $\text{Co}(\text{OH})_2$ passive films on the surface.

Table 4. Corrosion data obtained from EIS spectra of Co-21.5 wt.% W alloy coating in 3.5 wt.% NaCl solution after different immersion time calculated with equivalent circuit from figure 6.

Immersion time (h)	R_s (ohm cm^2)	T_1 (F cm^{-2})	R_{ct} (ohm cm^2)	CPE_1 -P	Error (%)
2 h	6.9	0.0002988	4579	0.853	4.68
4 h	6.46	0.000272	3100	0.829	4.12
6 h	6.22	0.0006778	2175	0.867	4.8
8 h	6.83	0.000351	2070	0.841	5.35
10 h	6.05	0.0003112	1462	0.802	4.92
12 h	6.76	0.0002864	970.8	0.773	2.62

The equivalent circuits and Nyquist plots for Co-21.5 wt.% W alloy coating at different immersion times in 3.5 wt.% NaCl solution are shown in Figure 6. With increasing of immersion times, the diameter of capacitance loop decreased, which indicated that the corrosion resistance of Co-21.5 wt.% W alloy coating became worse.

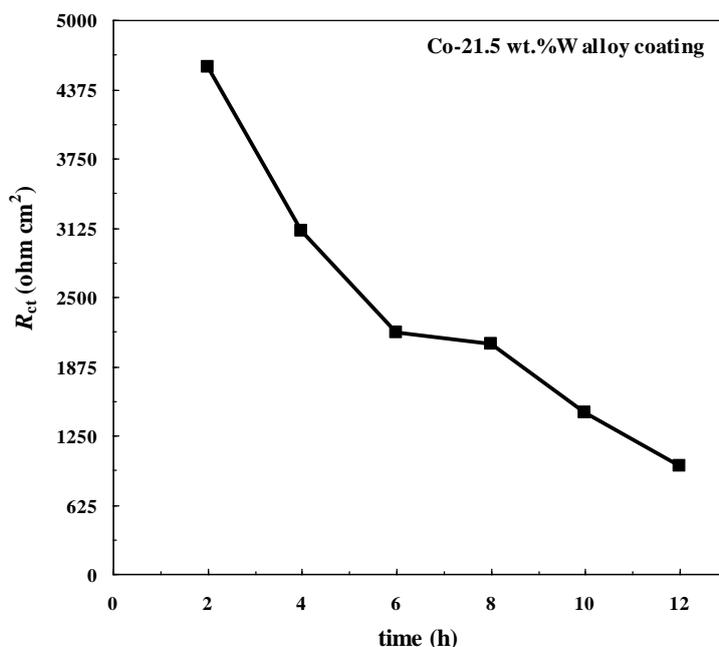


Figure 7. Changes of charge transfer resistance of Co-21.5 wt.% W alloy coating with immersion time in 3.5 wt.% NaCl solution.

It can be seen that the immersion time has a same effect on the corrosion behaviour of Co-21.5 wt.% W in 3.5% NaCl solution. Nyquist diagram after different immersion times in NaCl comprised only one capacitance loop for all of the scan frequency regions. This implies that there existed one time constant for Co-21.5 wt.% W coating in NaCl solution. It is necessary to claim that the corrosive electrolyte has not penetrated through the Co-21.5 wt.% W alloy coating. The dependence of R_{ct} on immersion time is clearly indicated in Table 4 and Figure 7. With increasing of immersion time, the R_{ct} values reduced gradually.

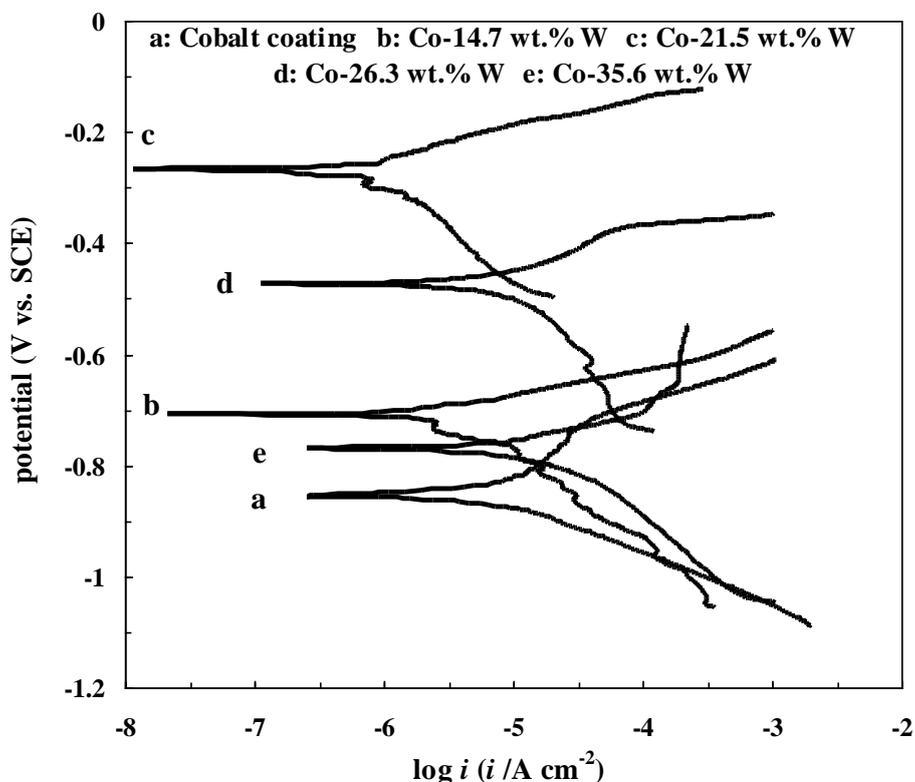


Figure 8. Polarization curves of Co and Co-W alloy coatings in 3.5% NaCl solution at scan rate of 0.2 mV s^{-1} .

The polarization curves measured in 3.5% NaCl solution for Co and Co-W coatings are shown in Figure 8 as curves a-e, respectively.

Table 5 lists the corrosion potential (E_{corr}) together with the corrosion current density (i_{corr}) of these coatings. By combining Figure 8 and Table 5, it is clearly shown that the Co-21.5 wt.% W alloy coating shows nobler E_{corr} , lowest i_{corr} and thus potentially better corrosion resistance in the active region.

The results of polarization studies also indicate a similar trend in the corrosion resistance that is observed by electrochemical impedance studies. Generally, the corrosion resistance of Co-W alloy coatings is higher compare to Co-W coatings deposited by other [18, 23].

Table 5. Corrosion potential and corrosion current of electrodeposited Co and Co-W coatings in 3.5 wt.% NaCl solution

System studied	E_{corr} (mV vs. SCE)	i_{corr} (A cm ⁻²)
cobalt	-855	5.7×10^{-6}
Co-14.7 wt.%W	-708	1.8×10^{-6}
Co-21.5 wt.%W	-267	8×10^{-7}
Co-26.3 wt.%W	-473	3.3×10^{-6}
Co-35.6 wt.%W	-769	8.5×10^{-6}

4. CONCLUSION

Based on the results obtained in the present investigation on electrodeposited Co-W alloy coatings the following conclusions have been drawn. Dense Co-W coatings 19 μm thick and containing ~15 to 36 wt.% tungsten were electrodeposited from a citrate-ammonia solution. The surface morphology of Co-W coatings is different compared with pure cobalt coating: the regular crystal structure characteristic of electroplated cobalt coatings was disturbed. The microhardness of as-plated Co-W coatings reaches 680 *HV*.

The open-circuit potential results exhibited that the incorporation of tungsten in the cobalt matrix results in the shift of E_{corr} towards the noble direction.

The electrochemical impedance spectroscopy results exhibited that the charge transfer resistance values of Co-W alloy coatings were higher compared to pure cobalt coating so that the highest value of charge transfer resistance was obtained for Co-21.5 wt.% W alloy coating deposited from solution with concentration of 0.106 mol L⁻¹ sodium tungstate. Generally, the corrosion resistance of Co-W alloys increased with tungsten content up to 21.5 wt.% and then decreased.

Polarization measurements indicated that present of tungsten in coating led to a decrease in corrosion current density and increase in potential corrosion. These measurements support the results of OCP and EIS studies.

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