

EVALUATION OF CORROSION AND TRIBOLOGICAL BEHAVIOR OF ELECTRODEPOSITED TUNGSTEN ALLOYS

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Abstract: Tungsten alloy coatings with iron group metals (Ni, Fe, Co) are considered as advanced materials for various surface engineering applications. Such coatings should be resistant to mechanical and corrosive damage, and to have improved functionality and durability. Accordingly, the objectives of this review consist in a comparative study of available literature on corrosive and wear behavior of electrodeposited tungsten alloys with iron group metals, including our recent results on evaluation of electrodeposited Co-W coatings. The wear and corrosion resistance of Ni-W, Fe-W and Co-W strongly depends on the chosen deposition conditions and subsequently on tungsten content and structure of obtained protective coatings.

Key words: electrodeposition, Fe-W, Ni-W, Co-W, wear rate, corrosion resistance.

INTRODUCTION

It is a great interest to fabricate iron-group based alloy coatings possessing functional properties for various applications in industry. Currently, the hard chromium coatings are used most extensively due to high hardness, excellent wear resistance, low coefficient of friction and excellent protection against corrosion [1–3]. However, because of the environmental and health risks associated with usage of toxic and carcinogenic hexavalent chromium baths during the electroplating, there is an urgent demand in a potential replacement for this coating. Tungsten based alloy coatings have been found to be very promising candidates for such purpose as they provided to have competitive physical and mechanical characteristics, combined with improved ductility, high thermal stability, satisfactory barrier layer capability in microelectronic devices and increased deposition rates compared to those determined for electrodeposited hard chromium [4]. Tungsten can be easily co-deposited from aqueous solutions with an iron group (Fe, Co, Ni) metals forming the corresponding alloys [5]. Thus, comprehensive studies were conducted by a number of researchers, during which different models were proposed to explain the co-deposition mechanism depending on the chosen iron group metal and plating bath composition [4].

Tungsten alloy coatings having various compositions and tailored microstructures can be obtained by varying the plating solution chemistry and deposition parameters. Amorphous and crystalline Fe-W, Ni-W and Co-W electrodeposits have been reported in the literature [6–8]. XRD analysis results indicated that as-deposited Ni-W alloys having tungsten content in their composition higher than 19–23 at.% forms nanocrystalline (“amorphous-like”) structure [9–12]. Meanwhile for electrodeposited Co-W and Fe-W alloy coatings the crystallographic structure is changing from polycrystalline to nanocrystalline at tungsten content above 20 at.% [4, 11]. During the structural transformations the crystallite sizes are reduced from 60 nm to 7 nm for Co-W, from 41 nm to 3–4 nm for Fe-W and Ni-W alloys [13]. From practical point of view, alloys having nanocrystalline or amorphous structures have gained more interest since they usually possess better corrosion resistance and tribological properties (e. g. wear resistance). The later can be related to an increase in tungsten

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content in the alloy which results in the grain size refinement and consequently in strengthening effect [14, 15].

Evaluation of different tungsten alloy coatings and their properties can be ambiguous, because it is depending on the given iron group metal, elemental composition, structure, grain size, etc. Accordingly, in this paper an attempt has been made to estimate wear and corrosion behavior of tungsten alloy coatings with iron group metals published elsewhere and to compare these results with our study on Co-W and Fe-W alloys.

EXPERIMENTAL

Co-W and Fe-W alloy coatings were obtained by electrodeposition under galvanostatic mode from a citrate electrolyte, which was described in our previous publications [16–19]. The pH was adjusted to 5.0, 6.7 or 8.0 by the addition of concentrated H₂SO₄ or NaOH. The plating temperature for Co-W alloys was kept at 20 and 60 °C to observe the influence of temperature on the properties of coatings. Fe-W electrodeposits were prepared at room temperature. The corrosion behavior of Co-W coatings was studied in 0.01 M H₂SO₄ solution by using electrochemical impedance spectroscopy (EIS) and linear voltammetry methods. Electrochemical corrosion measurements of obtained Fe-W coatings were performed in the mixture of 0.012 M Na₂SO₄ and 0.027 M NaCl (pH 5) at 90 °C. In both cases thicker coatings of ~10 µm have been deposited in order to avoid substrate influence on measurements. During the corrosion studies the registration of EIS and voltammetric data has been started after stabilization of the OCP within 15 min in the tested media. The amplitude of the sinusoidal voltage was 5 mV and the spectrum was obtained in the frequency range: 10 kHz–0.01 Hz. The charge transfer values for tested alloys were extracted from Nyquist's plots since the diameter of medium-frequency capacitive loops is considered as corrosion resistance (R_{corr}). The electrodeposition and corrosion tests were performed in a three-electrode cell with a platinized mesh as a counter electrode and saturated Ag/AgCl electrode as a reference electrode. All potential values are expressed vs. this reference electrode. The surface morphology of the coatings and content of alloys was investigated by scanning electron microscopy (Hitachi TM-3000 equipped with EDS analyser and software Swift ED-3000). Hardness of Fe-W and Co-W coatings was determined from nanoindentation tests (Nano-Hardness Tester, CSM) carried out at normal loads varying from 2 up to 200 mN. Linear loading and unloading speeds between 4 and 400 mN min⁻¹ were used. A Berkovich indenter was used and 5 indentations were performed at each normal load, and analyzed statistically.

RESULTS AND DISCUSSION

Tribological properties

Nanocrystalline materials with the grain sizes less than 100 nm, are typically very hard and are commonly produced as protective coatings which can assist in decreasing the wear. The Hall-Petch mechanism predicts that as the grain size decreases the hardness values increases, but it was demonstrated, that this mechanism is not applicable for very small grain sizes [20]. In our previous studies we have shown that the hardness of Co-W alloys increases up to ~917 HV₂₀ at increase in the tungsten content from 8 to 25 at.% which is linked to a decrease in the grain size till the critical value. After this critical value of 5 nm the inverse Hall-Petch relation is observed for Co-W alloys [17]. Meanwhile for Fe-W alloy the critical grain size of about 4 nm was determined, while the hardness reaches the maximum value of 1020 HV₉₈₀ when tungsten content in Fe-W deposit increases up to 26 at.% [21]. Overall, Fe-W alloy coatings are characterized by higher hardness than that of Co-W deposits in the range of normal loads of 2–100 mN [18]. The maximum hardness values for Ni-W deposits usually are lower (in the range of 734±70 HV₁₀) than for Co-W and Fe-W alloys [12, 14, 22, 23]. At higher applied loads the hardness of Fe-W and Co-W alloys can decrease, e. g. for Fe–24 at.% W deposits decreases up to 500 HV₉₈₀ [19], and for Co–13 at.% W – up to 600 HV₉₈₀ [24]. Overall, it should be noted that the electrodeposited binary tungsten alloy coatings are harder than those prepared from pure iron group metals [14, 25].

The hardness of tungsten alloy coatings with iron group metals can be improved by applying heat treatment due to partial crystallization, which causes the strengthening effect of the iron metal matrix containing the dissolved tungsten. Annealing also yields reduced internal stresses of the deposit that were related to the hydrogen evolution reaction occurring simultaneously during tungsten alloy co-deposition with iron group metals. For example, the hardness of Co-27 at.% thin film increases up to 1200 HV₂₅₀ after the heat treatment at 600 °C for 2 hours in Ar atmosphere [26]; for Ni-25 at.% the hardness reaches maximum of 1450 HV₂₀₀ at annealing temperature of 600 °C for 24 h in vacuum [12]. Other authors have also reported the maximum hardness for Ni-W alloys with different compositions after annealing at ≤700 °C [27–29]. The hardness of as-deposited Co-12 at.% W sample increased from 450 HV₉₈₀ (as-deposited) to ~700 HV₉₈₀ following heat treatment for 1 h at 600 °C in the air [30]. At the higher temperatures, the hardness decreases due to the increased grain size [12].

Tribological investigation includes the processes of interaction at the interface between two bodies forming a tribo-system and during the evaluation of tribological behavior of materials both surfaces, their properties and testing conditions (load, time, speed, displacement, relative humidity, temperature, etc.) must be taken into consideration. Accordingly, it is difficult to compare the wear rates for tests performed for Ni-W, Co-W and Fe-W systems in different laboratories and under different conditions (Table 1). Nevertheless, Co-W alloy electrodeposits in some works has been characterized by the lower rate of wear due to their relatively high hardness combined with the formation of the stable hexagonal close-packed (hcp) structure that is resistant to the high loads [30]. Meanwhile the fretting of Fe-W alloys at dry friction is accompanied by tribooxidation during which iron oxides are accumulated leading to increased wear loss [13].

Table 1. Wear resistance under dry conditions of the different tungsten alloys coatings.

Alloy, reference	Counter body	Load	Wear loss
Fe-W [18]	Corundum	10 N	Wear track depth ~6 μm
Co-W [26]	Martensitic stainless steel	61 N	Wear track depth 20.9 μm
Ni-W [27]	St52 steel, Ni-W	20 N	7.14×10 ⁻⁶ mm ³ /mN
Co-W [25]	Martensitic stainless steel	15, 30, 61 N	3×10 ⁻¹⁵ m ³ /Nm
Ni-W [31]	GCr15 stainless steel	5 N	3.49×10 ⁻⁵ mm ³ /mN
Ni-W [32]	Tungsten carbide	5 N	2.77×10 ⁻⁶ μm ³
Ni-W [33]	Tungsten carbide	3 N	9.8×10 ⁻⁶ mm ³ /Nm
Ni-W [34]	Untreated ductile iron	1, 3, 5 N	5×10 ⁻⁵ mm ³ /m
Co-W [35]	Stainless steel	15 N	0.095 mg/h
Ni-W [36]	Hardened steel	1 N	1.14×10 ⁻⁵ mm ³ /Nm

Corrosion resistance

The investigation of the corrosion properties of functional materials is an integral part of modern materials science and crucial in terms of their potential technological applications. However, till now we can only speculate on a systematic investigation of corrosive properties of tungsten with iron group metal alloys. The composition of coatings, their microstructure and morphology strongly depend on alloys' preparation methods and parameters of ones. Thus, the wide variation of corrosion parameters can be observed even for the alloys with similar composition and the overall picture of corrosion behavior of Ni-W, Fe-W and Co-W alloys remains inconclusive.

In our study we presented the mapping of corrosion behavior of various compositions of Co-W alloy deposits (2.4–30 at.% of W) since previous papers reported that Co-W is characterized by the corrosion resistance that is similar to that of the hard-chromium plate [30]. Usually the corrosion behavior of the prepared metal alloy coatings is investigated mainly by means of electrochemical technique, such as open circuit potential (OCP), linear voltammetry and electrochemical impedance spectroscopy (EIS). However, there are some limitations for the correct estimation of corrosion parameters (e. g., charge transfer resistance, corrosion potential, corrosion current density) by using mentioned above electrochemical techniques. The porosity, cracks, smoothness and thickness of the deposits should be evaluated impartially to ensure that the obtained data corresponds particularly to the tested alloys and the substrate below has no influence on the results. But in some papers related to

tungsten alloys electrodeposition the discussion about the coating morphology or structure is suppressed and we can only guess about the accuracy of the summarized anti-corrosive characteristics, which sometimes are presented as more attractive than those determined for electrolytic chromium or metallurgical steel. For example in [37] it was concluded that the anticorrosive protection ability of Co-7 at.% W alloy coating can be 6–14 times better than mild steel and that corrosion resistance varies in the range of 170–375 kOhm cm⁻² depending on to the tested acid (1 M HCl > 1 M H₂SO₄ > 1.0 M HClO₄). Interestingly, our results show that comparable charge transfer resistance values in acidic environment (0.1 M H₂SO₄) can be found only for stainless steel substrate ($R_{corr} = 123.7$ kOhm cm⁻²) (Fig. 1).

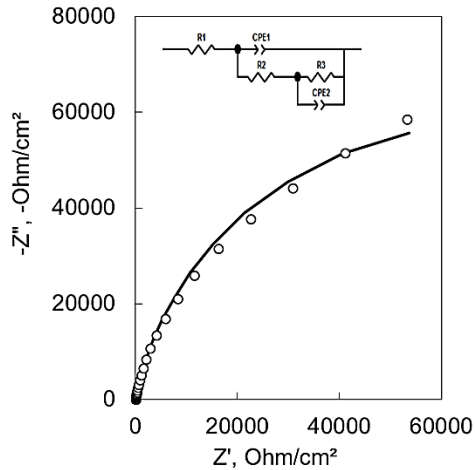


Figure 1. Nyquist plots (dots) for stainless steel substrate (AISI Type 304) and Equivalent circuit used for EIS fitting (continuous line).

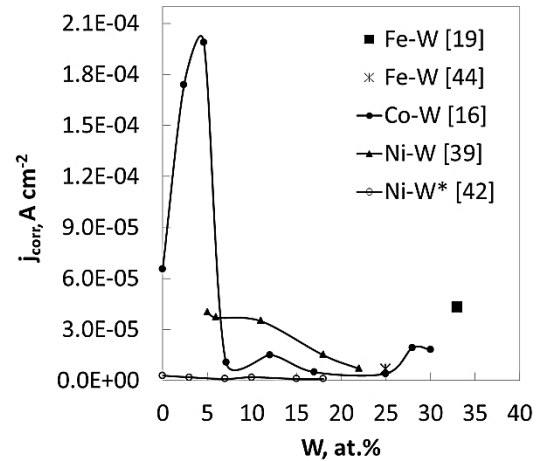


Figure 2. Corrosion current density (j_{corr}) values in acidic media of as-deposited W alloys with iron group metals published in the literature.

Among a number of corrosion parameters, the values of j_{corr} and E_{corr} are often used to compare corrosion behavior of electrodeposited coatings. Notwithstanding the corrosion potential values usually do not show any evident dependence on the composition of alloy thin films and varied independently from the corrosion rate. This is under the assumption that potential values are driven by the rates of cathodic reaction (hydrogen evolution) and anodic reaction (electrolytic dissolution or passivity of the metal) of corresponding system and are strongly affected by the corrosive media, chemical composition of material and its surface state. Thus, the further investigation of the corrosion behavior of tungsten alloy with iron group metal coatings is mainly based on the j_{corr} determined from linear voltammetry analysis results. Noticeably, here can be also found some disagreements between different studies. Hence, for Co-W alloys containing >7 at.% of tungsten the obtained voltammograms are asymmetrical and j_{corr} cannot be determined by applying the regular routine, i.e Tafel extrapolation method. In such case all curves should be transformed into Allen-Hickling coordinates that enable to estimate the corrosion rate using a narrow range of potentials [38].

It is noted that the lowest corrosion currents were obtained for Co-W alloys electrodeposited at 60°C, because those electrodeposited at room temperature were full of cracks and could be easily peeled off mechanically from the stainless steel substrate and exhibited high corrosion rate ($j_{corr} = 2.4 \times 10^{-4}$ A cm⁻²) [16]. In mostly works the co-deposition of tungsten with iron group metals is performed at the higher temperature (60–75 °C) which enables not only to improve the quality of the thin film, but also allows increasing the tungsten content in the alloy which leads to ameliorate the corrosion resistance. Thus, our study depicted that by increasing the tungsten content in Co-W thin coatings from 5 at.% up to 25 at.%, crystallite size reduces from ~60 nm to 3–6 nm and the corrosion current density in acidic media decreases from 2×10^{-4} A cm⁻² up to 4.2×10^{-6} A cm⁻², respectively (Fig. 2) [16]. The highest determined corrosion resistance value at 25 at.%W is most likely related to the formation of thermodynamically stable intermetallic compound Co₃W. Similar trend by other researchers was also observed for Ni-W alloy coatings which showed that the corrosion rate of Ni-W samples in acidic environment decreases with grain size reduction from 63 nm to 5 nm, i. e. when the

tungsten content arises from 5 to 22 at.% [39]. This correlate with results [40] where it was revealed that at high tungsten content a stable intermetallic compound of Ni_4W is formed. Besides, it is claimed that both Ni and W metals undergo passivation state in electrolytes forming non-porous layer of $Ni(OH)_2$, NiO and WO_3 on the top of Ni-W alloy surface [41]. These oxidation products inhibit the corrosion process and reduce the rate of oxidation reaction. Thus, in [42] where observed that all polarization curves for Ni-W samples show an active/passive transition in H_2SO_4 solution. Notable that in the recent study of Ni-W alloys [42] the corrosion current densities do not show any significant variation versus W content in the deposit and varied in the range between $1 \cdot 10^{-6}$ and $3 \cdot 10^{-6} A cm^{-2}$, however these values were much lower than those measured under similar conditions in other works. This can be influenced by deaerated 1 M H_2SO_4 solution used in this study.

It is claimed that the superior corrosion resistance of Co-W can be related due to the formation of rich film or $Co(OH)_2$ passive films on the surface [43]. In fact, our EDS investigations of Co-W alloys after corrosion test showed significantly increased oxygen content in composition after the corrosion test and this indicates that the electrochemical corrosion process occurs via an intermediate stage of forming oxide-containing compounds on the surface [16]. It is noted that this tendency was less pronounced for alloys containing small amount of tungsten, i. e. which were characterized by higher corrosion rate, and thus it can be summarized that coatings having more than 5 at.% W can protect the substrates from corrosion in acidic media better than the pure Co deposit. However it is hard to distinguish one particular iron group metal which possesses the best anti-corrosive protection in acidic environment after the alloying with tungsten.

For Fe-25 at.% W was found that in 0.5 M H_2SO_4 the surface is covered by iridescent film, which is characteristic for thin oxide films of W and Fe and reveals the passive state of Fe-W, thus the calculated j_{corr} value is comparable to that of Co-W having similar amount of W in composition [44]. Our previous investigation of Fe-W thin coatings revealed an active state and extremely high corrosion rates in acidic environment even when the tungsten content in the alloy reached 33 at.% [19]. Probably this can be explained by different corrosion experiment conditions, since in our case the voltammetry analysis was performed in $Na_2SO_4 + NaCl$ (pH 5) at high temperature of 90 °C. As it can be seen from (Fig. 3), the Ni-W and Co-W alloys in neutral 3.5 wt.% NaCl solutions exhibited a clearly increased corrosion resistance compared to that of the acidic media. Also, in the case of neutral solutions a positive influence of higher tungsten content on corrosion resistance was confirmed [45–47].

According to linear voltammetry results described in different papers, it can be concluded that the tungsten alloy coatings barely have the transition to the passivation state in neutral corrosive solution [11].

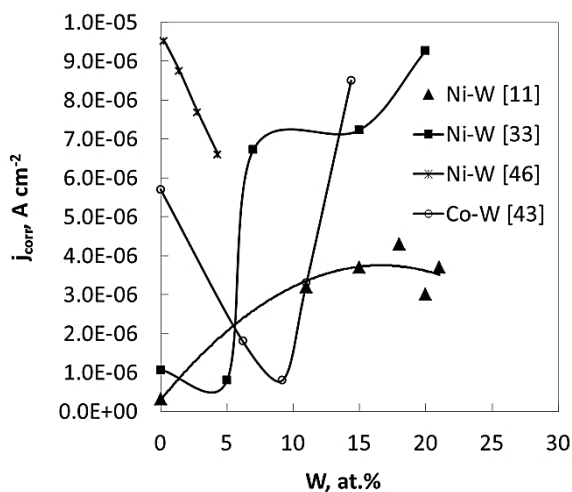


Figure 3. Corrosion current density (j_{corr}) values in neutral NaCl solution of as-deposited W alloys with iron group metals published in literature.

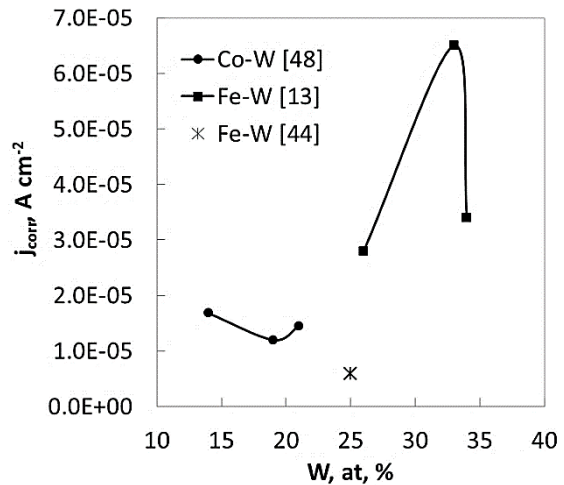


Figure 4. Corrosion current density (j_{corr}) values in neutral Na_2SO_4 or $NaCl + Na_2SO_4$ solution of as-deposited W alloys with iron group metals published in literature.

After adding SO_4^{2-} ions to the neutral corrosive medium containing NaCl, the corrosion resistance of Co-W alloys slightly depends on the coating thickness. Thus, it was depicted that the corrosion current density decreases from $4.6 \cdot 10^{-5}$ (for thin coatings) to $1.4 \cdot 10^{-5}$ A cm^{-2} (for 20 μm), meanwhile the corrosion potential for both samples was similar -0.60 ± 0.05 V [48]. It was not determined a clear correlation between the tungsten content in the deposit and corrosion current density in NaCl + Na_2SO_4 solution neither for Co-W nor Fe-W alloys [13, 48] (Fig. 4). However, for Co-W case the corrosion current density was higher than that in neutral single NaCl solution and this change might be caused by different dissolution mechanism in the presence of Cl^- and SO_4^{2-} ions. An addition of organic additives (saccharin, neonol, OP-10 emulgator, neoinogenic SAS) to the electrolyte prior the electroplating of alloys did not reveal any favourable effect on examined corrosion resistance of Co-W alloys in different neutral solutions, in fact in all cases the prepared coatings demonstrated relatively lower corrosion resistance in neutral NaCl + Na_2SO_4 solution [13, 49]. Significantly poorer anti-corrosive protection was noticed for Co-W alloy coatings in alkaline (6 M KOH) media, when the corrosion current density value increased up to 0.84×10^{-3} A cm^{-2} and corrosion potential decreased up to -1.03 V at 24 at.% of W [49]. However, for nanocrystalline Ni-W alloys having 5–22 at.% of W, j_{corr} values in alkaline solution (pH 10) are lower than those in acidic media (pH 3) [39].

CONCLUSIONS

- The hardness of Ni-W, Fe-W and Co-W alloy coatings increases with increasing W content. The direct Hall-Petch relation is observed up to the minimum values of grain size of 8–15 nm, 4 nm and 5 nm for Ni-W, Fe-W and Co-W deposits, respectively. Among all W alloy coatings, Fe-W deposits possess the highest hardness.
- The evaluation of tribological behavior of the deposits reported in articles is an complex issue due to a large number of variables involved during testing, such as load, speed, time, counterbody material, etc. However wear resistance of Ni-W, Fe-W and Co-W electrodeposits is quite high and comparable to that of electrolytic chromium. Nevertheless, Co-W alloy electrodeposits usually has demonstrated a lower wear rate than in the case of Ni-W and Fe-W.
- The Ni-W and Co-W alloys, in neutral 3.5 wt.% NaCl solutions, exhibited a clearly increased corrosion resistance compared to that of acidic and alkaline media, while this characteristic slightly decreased after SO_4^{2-} ions addition to corrosive solution. The anti-corrosive behaviour of individual Fe-W, Ni-W and Co-W systems depends not only on their elemental composition, but also on deposition conditions and chemistry of electrolyte. Commonly, the corrosion rate decreases with increasing W content in the coating.

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