

TRIBOCORROSION PROPERTIES OF NANOCRYSTALLINE W-rich Co–W, Ni–W AND Fe–W COATINGS

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Abstract: Electrodeposited binary tungsten-rich alloys with iron-group metals, namely Co, Ni and Fe, reveal great potential that makes them suitable as surface coatings for engineering materials. In this context, tribocorrosion plays an important role in the lifetime of such engineering materials e.g. metallic machinery components. In the present paper, the corrosion behaviour of electrodeposited ultra-nanocrystalline Co–32W, Ni–29W and Fe–31W (in at.%) was investigated by monitoring the open circuit potential (OCP) before and after the sliding against an alumina ball in 0.5 M Na₃PO₄ solution. The W-rich alloy coatings were compared in terms of friction coefficient during sliding; and wear track evaluation. Under the experimental conditions of the present study, the results showed that all investigated alloys are in active state and the corrosion resistance under sliding occurs through the dissolution of W and iron group metals along with the formation of oxides – wear debris on the contact surface.

Keywords: electrodeposition, tungsten alloys, wear, tribocorrosion.

1. INTRODUCTION

The need to design new surfaces for future machinery equipment as well as minimize its operating costs and extend the lifetime has led to demands for a much better understanding of surface degradation phenomenon particularly when tribological components are operating in corrosive environments. However, the rate of material degradation cannot be predicted simply by adding the wear rate in absence of corrosion to the corrosion rate in absence of wear due to the synergistic effects that usually result in accelerated material degradation (tribocorrosion). Tribocorrosion phenomena is encountered in many technological areas where they cause damage to installations, machines and devices. Often tribocorrosion damage is a problem for safety or for human health.

The metallic surface is considered to be in an active state if corrosion products are composed of the simple or complex ions that are soluble in corrosion media. While some metals/alloys in some specific media during interaction between metallic surface and corrosive environment form the insoluble corrosion products with low porosity and with good adhesion to metal surface. Such samples with natural passivation ability are stable in corrosion media. In other words, the existence or rebuilding rate of the passivation layer after its damage determine the corrosion resistant of the metallic surface during tribocorrosion processes [1].

Nanocrystalline W-rich alloys with iron group metals (Co, Ni, Fe) are of special interest in the materials science due to their enhanced strength, superior hardness [2, 3] and corrosion resistance [4]. Furthermore, such alloys have become an important component in catalytic hydrogen evolution reaction [5], microelectromechanical systems (MEMS), for wear protection of cutting tools and for the reduction of friction in sliding parts [6].

However, in some cases these alloys are subjected to simultaneous wear and corrosion, which leads to accelerated degradation of their components, such as in off-shore, power generation and/or food processing applications. Thus, there is an urgency to investigate their tribocorrosion behaviour in order to meet the needs of the industry.

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Accordingly, the aim of this study was to investigate the corrosion behaviour of electrodeposited ultra-nanocrystalline Co–W, Ni–W and Fe–W alloys having ~ 30 at.% W in the presence of sliding and to determine the formation of a passive film on top of these alloys.

2. EXPERIMENTAL

W-rich Co–W, Ni–W and Fe–W alloy coatings were electrodeposited from electrolytes containing 0.2 M (CoSO₄ or NiSO₄ or FeSO₄) + 0.5 M Na₂HCitr + 0.4 M Na₂WO₄ at pH 8. All solutions were prepared from chemicals of analytical grade purity dissolved in distilled water. The pH was adjusted by adding concentrated solution of NaOH. The volume of electrodeposition bath was 250 ml. The deposits in all cases were obtained at the current density of 10 mA/cm² and temperature of 60°C. Electrodeposition was carried out on stainless steel substrate foils (2 cm²) with the chemical composition (in wt.%) of Fe–70, Cr–19, Ni–8, Mn–2, Si, Al, P–1. The substrate was chemically degreased and cleaned in an ultrasonic bath with acetone, ethanol and rinsed with distilled water. In order to improve the adhesion of the alloys to the substrates, a thin nickel seed layer (~ 30 nm) was electrodeposited from an electrolyte containing 1 M NiCl and 2.2 M HCl, at a cathodic current density of 10 mA/cm² for 1 min.

A platinized titanium mesh (~ 20 cm²) has been used as a counter electrode (CE). Ag/AgCl/KCl_{sat} electrode has been used as a reference electrode (RE) and all potentials presented in this study are referred to this electrode. The electrodeposition time for W-based alloys and iron group metals was controlled in a way until the desired coating thickness of around 15 µm was achieved. The given thickness allows to avoid any interference from the stainless steel substrate.

The pH of the electrolytes before and after electrodeposition process was monitored with a ProLine pH meter B210. Notable, in all cases the pH value changed by no more than 0.1 and such variation did not influence the results of the experiments. More accurate explanation related to solution pH influence on W-based alloys composition is given in our previous work [7].

The phase composition and microstructure of the deposited alloys were identified by X-ray diffractometer (XRD, Rigaku MiniFlex II) and scanning electron microscope (SEM, Hitachi TM3000), supplied with an Oxford EDS analyzer.

The electrodeposited alloys were transferred to tribometer following common treatment (decreasing, rinsing). The tests were performed using a Ducom Tribometer and a Bio-Logic SP200 potentiostat. The sample holder was made of polymeric material and designed in order to avoid any electrical contact with the metallic parts of the tribometer. The exposed surface of the alloy samples to the electrolyte was 2.83 cm². 150 ml of fresh 0.5 M Na₃PO₄ solution has been used for each test. The tribocorrosion properties of W-rich alloys have been studied under the following conditions: normal force 10 N; the displacement amplitude 5 mm; a corundum (Al₂O₃) ball of 3 mm diameter was used as the counter body.

3. RESULTS AND DISCUSSION

Composition, structure and morphology of W-rich alloys. In this study the designed electrodeposition conditions allowed to prepare iron group metal based alloys containing the tungsten content close to 30 at.%, namely Co–32W, Ni–29W and Fe–31W (in at.%). The presence of amount of oxygen, hydrogen and carbon was detected by EDS analysis. Though, the previous studies revealed that these elements are presented only on the top surface layer and only their traces are observed in the bulk coatings [8].

The structure and crystallite size of the electrodeposited W-rich alloy coatings with Co, Ni and Fe was evaluated earlier by XRD analysis [5]. The broad peaks at $2\theta \sim 43\text{--}44^\circ$ which are characteristic to an “amorphous-like” structure were observed for Co–32W, Ni–29W and Fe–31W (in at.%) alloys.

It is well known, that the broadening of the XRD peak is related to the refinement of the crystallite size that typically occurs with increasing the W content in the deposit. Indeed, the TEM analysis supported [5] that W-rich alloys have ultra-nanocrystalline structure composed of the grains with the

size around 2–5 nm which is consistent with the grain size estimated from XRD results.

The mapping of elements, both iron group metal (Co, Ni, Fe) and W, indicated that metals are distributed almost evenly onto entire surface even at nanometric scale [5]. However, there are some regularly located spots with higher W amount. Probably, it is due to mixed structure resulted from the electrodeposition: tungsten solution in cobalt, nickel or iron and corresponding intermetallic compounds, i.e. Co_3W , Ni_4W , Fe_2W .

Notable, that high amount of tungsten in the alloys with iron group metals leads to refining the structure and the formation of nodular morphology composed of larger globules (Fig. 1). It was found that the electrodeposited alloys are well adhered to the substrate. The morphology of Ni–29 at.% W alloy deposits was found to be particularly sensitive to the co-evolution of hydrogen during the electrodeposition, and some of the Ni–W coatings display a net of cracks (can be seen from SEM images made at lower magnification, Fig. 1). The further analysis showed that the cracks form only on the top of the surface and are not deep enough to reach the stainless steel substrate.

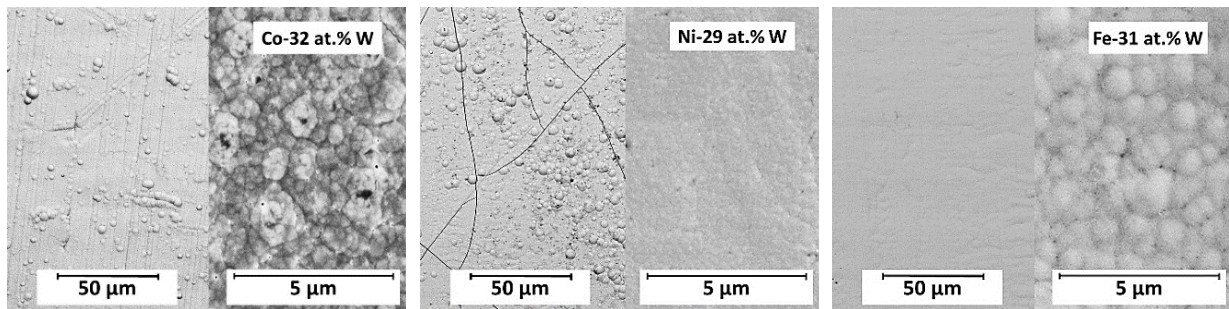


Figure 1. SEM images of as-deposited W-rich alloys.

Tribocorrosion properties. Since the effects of tribocorrosion are most pronounced on passive metals which demonstrate increased corrosion resistance due to the protective oxide film, in this work the tribocorrosion tests have been performed in 0.5 M Na_3PO_4 solution because in this media W-rich alloys with iron group metals showed passivation (Fig. 2).

The open circuit potential (OCP) monitoring is the simplest electrochemical method for corrosion evaluation. Thus, to study the effect of wear, OCP was monitored before and after reciprocating sliding tests (Table 1). It can be seen, that the OCP values did not change significantly, therefore can be assumed that the potential reaches again the same initial value due to build-up of the oxide film on the alloys surface occurred due to immersion in phosphate electrolyte. However, seems that the re-passivation (oxide film formation) was not fast enough during the sliding test in corrosion media and the further analysis showed that active dissolution of W-rich alloys occurred.

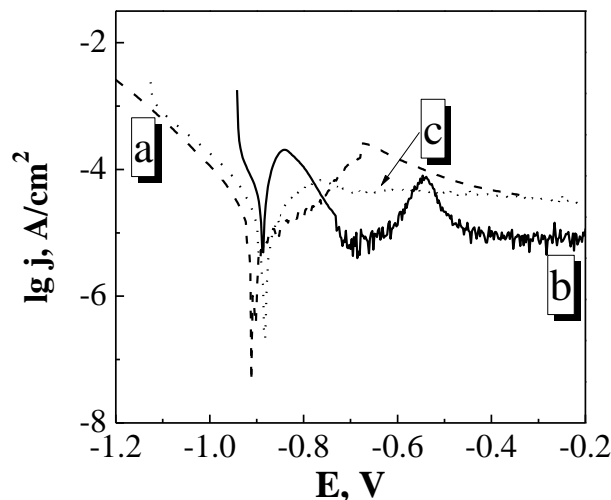


Figure 2. Polarization curves for Co–31W (a), Fe–32W (b) and Ni–30W (c) alloy coatings in 0.5 M Na_3PO_4 .

Table 1. OCP values of W-rich alloys recorded before and after tribocorrosion test in 0.5 M Na₃PO₄.

Sample	OCP before tribocorrosion test	OCP after tribocorrosion test
Co-32 at.% W	-401 mV	-401 mV
Ni-29 at.% W	-539 mV	-540 mV
Fe-31 at.% W	-768 mV	-767 mV

The evolution of the coefficient of friction during the sliding for Co-32 W, Ni-29 W and Fe-31 W (in at.%) is plotted in Fig. 3. The coefficient of friction under sliding conditions in 0.5 M Na₃PO₄ at 10 N load decreases in a sequence: NiW > FeW > CoW. It can be seen, that the effect of the initial cracks formation on Ni-W alloy coating is evident and for this coating the highest coefficient of friction was determined.

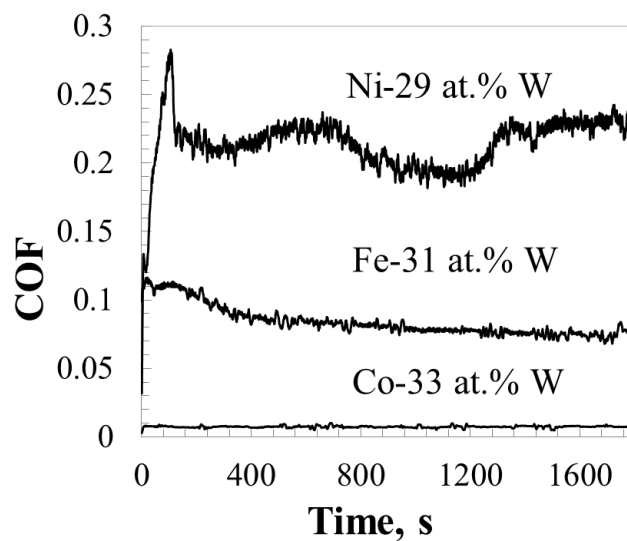
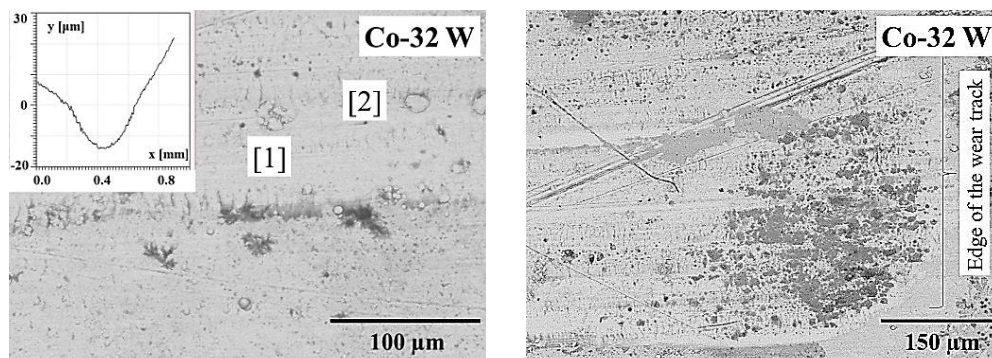


Figure 3. Evaluation of coefficient of friction vs. time for W-rich alloys in 0.5 M Na₃PO₄ electrolyte. Test conditions: 10 N, 1 Hz and 5 mm.

Debris of oxide particles are released from the contacting materials during the tribocorrosion tests (the content of oxygen in composition increased in all investigated alloys, see Table 2). For Ni-W coating in the center of the wear track, also small quantities of P (from the electrolyte) and Al (from the corundum ball) were detected. However, in spite of the higher coefficient of friction compared to Co-W and Fe-W, seems that the stainless steel substrate was not reached during the tribocorrosion test of Ni-W alloy coating. On the contrary, the chemical and SEM analysis of the wear track of Fe-W coating indicates that in this case the debris is trapped on the edges of the sliding surfaces and accelerates the wear of Fe-W, i.e. after the tribocorrosion test the elements from stainless steel substrate were found in the composition. These observations also can be proved by the 2D surface profiles that are shown next to the SEM images (Fig. 4).



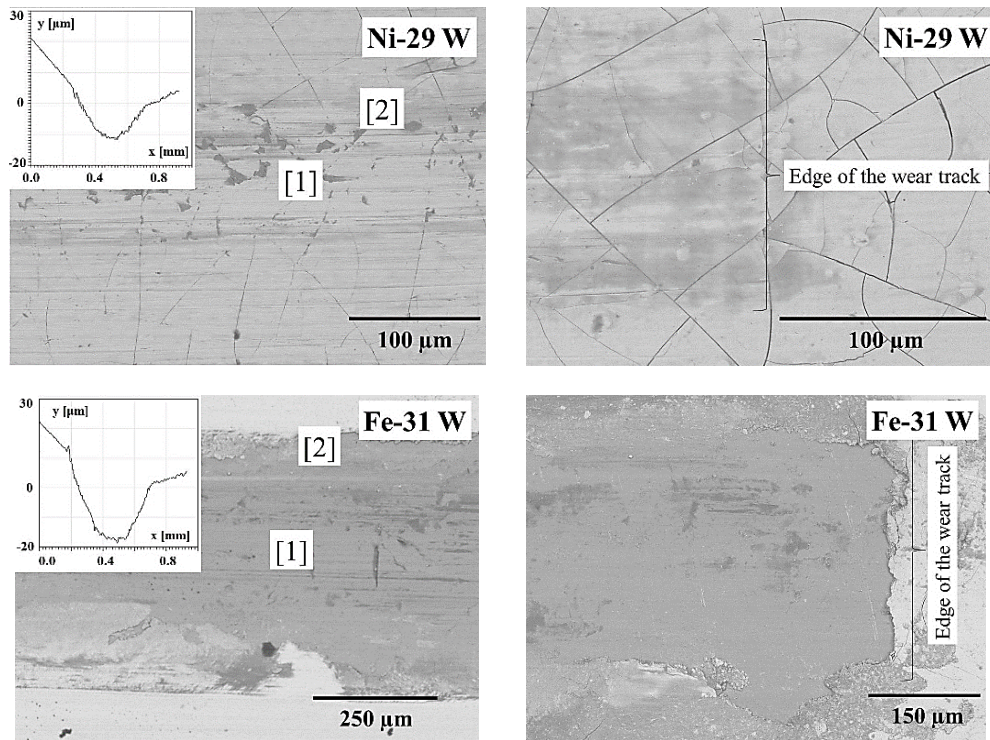


Figure 4. SEM images of W-rich alloy coatings (in at.%) after tribocorrosion tests. Insets represents the 2D surface profiles of wear tracks after tribocorrosion tests: [1] – the center of the wear track; [2] – the edge of the wear track.

Table 2. Chemical composition of W-rich alloys before and after tribocorrosion tests in 0.5 M Na₃PO₄.

Co-33 at.% W			
	As-deposited coating	The center of the wear track	The edge of the wear track
O	17.5	36.6	42.7
Co	56.0	47.2	41.5
W	26.5	16.2	15.8
Ni-29 at.% W			
O	12.9	52.0	37.2
Ni	61.9	36.5	47.1
W	25.2	9.4	15.7
P	–	0.8	–
Al	–	1.3	–
Fe-31 at.% W			
O	17.9	40.5	55.2
Fe	57.9	40.9	28.3
W	24.2	0.4	1.5
Cr	–	11.6	7.1
Mn	–	0.9	–
Ni	–	5.7	7.8

4. CONCLUSIONS

Tribocorrosion evaluation of the following electrodeposited ultra-nanocrystalline W-rich alloys: Co–32 at.% W, Ni–29 at.% W and Fe–31 at.% W were performed. All investigated as-deposited alloys are in active state under tribo-corrosion conditions. The dissolution of W and iron group metals along with the formation of oxide containing wear debris on the contact surface has been determined. The tribo-corrosion resistance in 0.5 M Na₃PO₄ at 10 N load decreases in a sequence: Co–32 at.% W>Ni–29 at.% W>Fe–32 at.% W.

5. ACKNOWLEDGMENT

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