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Research Articale

Corrosion and Wear Behavior of Ultra-hard Ni-Cr Electrodeposits on CK45 Steel Substrate Obtained from Cr (III) Based Baths

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ABSTRACT

In recent years, attempts have been made to put aside the hard chromium coating due to environmental damage to its plating baths. Due to their low toxicity, the Cr, Ni-Cr, and Cr-Ni coatings produced in the baths containing Cr^{3+} ions are perfect substitutes for the hard chromium coatings. In this study, Ni-Cr coatings were created using electroplating, and the effect of formic acid concentration as complexing agents was investigated. Cyclic voltammetry tests studied the electrodeposition mechanism of coatings. The SEM and XRD methods were used to investigate the coatings' microstructure. The pinch-on-disk and potentiodynamic polarization tests were used to study coatings' wear and corrosion behavior. The results of the cyclic voltammetry test showed that increasing the concentration of formic acid resulted in increasing deposition of chromium ions during electrodeposition. Increasing the formic acid concentration in the bath to 30 g/L increased the micro-hardness of coatings to values similar to that obtained for the conventional hard chromium coating. It was due to the formation of chromium carbides during the electrodeposition process, as revealed in XRD patterns of coatings. In this case, the chromium content of the coating increases to 86 weight percent, and the grain size of the coatings is reduced to 40 nm. The coatings' best corrosion and wear resistance was obtained at 30 g/L formic acid in the bath due to the coatings' high hardness and crack-free microstructure.

1. Introduction

Hard chromium plating is one of the valuable technologies for improving the wear resistance of industrial parts in automobile manufacturing, aircraft manufacturing, steel manufacturing, and oil and gas industries. Hard chromium coatings are widely used in mold applications, anti-wear parts, and surgical equipment. These coatings also have high corrosion resistance and bright appearance, making them attractive decorative coatings [1, 2, 3, 4, 5]. However, chromium plating methods with Cr^{6+} have created many environmental and health hazard concerns. In particular, toxic and carcinogenic water and Cr^{6+} ions fumes are released during chrome plating. This release is a severe risk to the health of operators and the environment [6, 7, 8]. Due to their low toxicity, hardness, and wear resistance, the Ni-base nano-structured coatings can be a good substitute for the hard chromium coatings. However, the hardness of the nano-structured nickel base coatings is still less than that of the hard chromium coatings. So, applying nano-structured Ni coatings in applications requiring high wear resis-

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tance still has problems. In recent years, many research activities have been conducted to find a better alternative to hard chromium coatings based on electroplating chromium coating from baths containing Cr^{3+}ions with lower toxicity [6, 7, 8]. The most commonly used Cr^{3+} plating electrolytes which contains $CrCl_3$ or $Cr_2(SO_4)_3$ salts [7]. When these salts are dissolved in water, they form Cr (III) ions at the $[Cr(H_2O)_6]^{3+}$ complex [3, 7, 9, 10, 11]. Because of the high stability of the $[Cr(H_2O)_6]^{3+}$ complex, the coating formation is almost impossible. In order to destabilize the complex and reduce the Cr^{3+} ions, complexing agents are added to the electrolytes to form some other complexes of chromium ions [9, 10, 11]. Organic acids such as formic acid, ammonium format, acetic acid, and oxalic acid are the most common complexing agents used in Cr (III) plating processes [12, 13, 14, 15, 16, 17, 18]. Carbon from these organic substances could be reduced along with metallic chromium and form a chromium carbide coating after heat treatment of these coatings [11, 17, 18, 19]. The formation of carbides in these coatings improves the coating's hardness after heat treatment at about 600 °C. However, such a thermal process can lead to distortion and decreasing substrate hardness due to annealing microstructure. In addition, the need for heat treatment can limit the application of these coatings for low melting point substrates such as aluminum. Some studies reported achieving ultra-high hardness in Cr coatings in baths containing trivalent chromium ions without subsequent heat treatment. They attributed this to the formation of crystals with a diamond-like structure during electroplating [6]. However, such an event has not been observed for Ni-base coatings. Facilitating the formation conditions of carbides during electrodeposition will improve the industrial application of Ni-base coatings, especially in severe wearing conditions. One of the other ways that can further improve the hardness of Ni-base coatings is by decreasing grain size. This decrease can be obtained with increasing current densities and alloying Ni coatings with other metals. In this relation, efforts have been made to produce Ni-Cr coatings with a hardness close to that of hard chromium coatings. A better understanding of the Cr^{3+} ions electrodeposition mechanism can help us find a solution to improve reducing Cr^{3+} ions during electroplating. However, studies on the electrochemical deposition mechanism of Ni-Cr coatings are rare.

The present study aims to electroplate ultra-hard Ni-Cr coatings in a bath containing Cr^{3+} ions and formic acid. In this condition, high values of current densities were used. It is believed that increasing the concentration of formic aside can release the content of carbon atoms into coatings. High content of carbon atoms besides high values of current densities may facilitate the formation of chromium carbides during electrodeposition. Formation of the Ni-Cr coating containing Cr carbides can dramatically enhance the coatings' hardness without a supplementary heat treatment process. This enhancement can improve the anti-wear properties of Ni-base coating.

2. Materials and Methods

2.1. Electroplating process

A DC power supply with a maximum output current of 50 A and an accuracy of 0.01 A was used. A 300 ml beaker was used as the electroplating bath. The electrolyte volume used for plating was 200 ml. A simple hot plate was used to heat and agitate the electrolyte. A digital pH meter with a precision of 0.01 was utilized to measure pH. A graphite anode (5×3×1 cm) was prepared. Flat specimens of CK45 steel (3×3×0.2 cm) were prepared as working electrodes. The distance between the anode and the cathode was 3 cm. The chemical composition of the substrate is shown in Table 1.

One substrate side was meticulously covered entirely with transparent polyethylene glue for insulating purposes. The electroplating time for all Ni-Cr, a crucial detail, was precisely set at 50 minutes.

2.2. Preparation and electroplating of samples

The surface of the samples was subjected to the following surface preparation:

- Mechanical polishing of the sample's surface with sandpaper grit 100 to 1200.
- Washing the samples using a detergent for initial de-acidification.
- Degreasing in 40 g/L NaOH solution at 80°C for 20s and then rinse with distilled water.
- Chemical activation in 20% sulfuric acid solution.
- Electroplating of Ni-Cr coatings immediately after the latter step.

The present study investigated the effect of the formic acid concentration as a complexing agent on the electrodeposition mechanism, microstructure, mechanical properties, wear, and corrosion behavior of Ni-Cr coatings. Electroplating baths were prepared according to Table 2. and using pure Merck materials. pH was measured at about 1, and temperature was kept constant at 25°C. The current density was selected at 80 A/dm^2.

Table 1. Chemical composition of CK45 substrates measured by quantometric test.

Element	C	Si	Mo	S	P	Ni	Cr	Mn	Cu	Fe
Wt. %	0.452	0.225	0.007	0.030	0.004	0.063	0.078	0.795	0.028	Balance

Table 2. The composition of the baths used in this study for electrodeposition of the Ni-Cr coating.

Bath Code	Concentration of salts and additives (g/L)				
	Nickel Chloride ($NiCl_2.6H_2O$)	Chromium Chloride ($CrCl_3.6H_2O$)	Formic Acid (HCOOH)	Boric Acid (H_3BO_3)	Amonium Chloride (NH_4Cl)
1	20	80	0	30	80
2			15		
3			30		
4			45		

2.3. Electrochemical studies of the deposition process of Ni-Cr coatings

The cyclic voltammetry (C.V) method was used to investigate the deposition mechanism of Ni-Cr coatings in various concentrations of formic acid in the bath. An Autolab corrosion testing device (AUT 84091 model) was used for electrochemical studies. Steel substrates with a cross-section of $4cm^2$ were used as a cathode, and graphite as an anode. All potentials in this study were compared to the Ag/Ag Cl electrode potential. All experiments were performed at ambient temperature (25 °C) and with scan rates of 10 mV/s. The potential range was -500 to -1500 mV versus open circuit potential.

2.4. Phase and morphological studies

X-ray diffraction (XRD) tests were performed by PhilipsX'pert pro equipment with $Cu_{k\alpha}$ (λ=1.542 A). A Philips scanning electron microscope (XL 30 model) was utilized to investigate the coatings' surface morphology, measure their thickness, and study the worn surfaces after a wear test. The scanning electron microscope was equipped with an X-ray energy spectrometry (EDS) system to evaluate the coatings' chemical composition.

2.5. Micro-hardness

Micro-hardness testing was carried out on the cross-sections of the samples using a HXD-10000 micro-hardness tester. Micro-hardness tests were carried out at a load of 50g and during 10s in the middle of the coating thickness.

2.6. Wear test

A pin-on-disk apparatus was used to study the wear behavior of the samples. The rotational speed was 300 rpm, and the sliding distance was 200m, ensuring a comprehensive analysis. The diameter of the wear path was 2 cm. Alumina ceramic pins with a hardness of about 3500 Hv were applied as counter faces. The normal load was 5N.

2.7. Corrosion test

Potentiodynamic polarization tests were used to study the coatings' corrosion behavior. Corrosion tests were carried out using a 3.5% saline solution by an Autolab device (AUT 84091 model). All potentials were compared to the saturated calomel electrode (SCE) potential. The samples were kept in the corrosion test medium for 30 min before the corrosion tests. All experiments were performed at ambient temperature and with scan rates of 2 mV/s. The potential range was -700 to 1000 mV versus open circuit potential.

3. Results and Discussion

3.1. Cyclic Voltammetry

Fig. 1. shows the diagrams of cathodic cyclic voltammetry for the baths with different amounts of formic acid. Scanning was conducted in a potential range of -500 to -1500 mV in all the baths from the Ag/AgCl reference electrode. Increasing cathodic potential resulted in increasing cathodic current density. This increase can be related to increasing the reduction of Ni^{2+}, Cr^{3+}, and H^+ ions by increasing the cathodic potential. Increasing the formic acid concentration in the electroplating bath from 0 to 30 g/L enhances the cathodic reactions and shifts the cathodic branch to the higher cathodic potentials. Shifting cathodic potentials to a higher value can be related to forming a complex between formic acid and chromium ions. It can facilitate the reduction of chromium ions and increase the rate of cathodic reactions. However, by increasing the amount of formic acid from 30 to 45 g/L, the cathodic cyclic voltammetry curve shifted to a lower current density. It happened likely due to the formation of insulating particles. At high concentrations of the complexing agents, the formation of chromium hydroxide

compounds has already been reported [9]. It is believed chromium hydroxide is insoluble in water, and covering the surface of the cathode decreased the deposition rate and thus decreased the cathode current density.

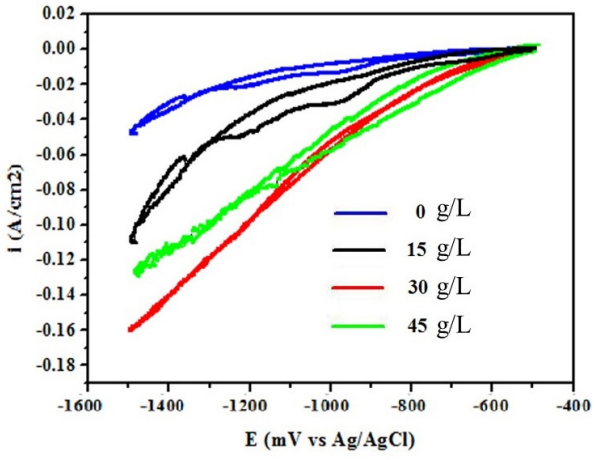

Fig. 1. Cyclic voltammetry curves were obtained at various concentrations of formic acid in the bath at 25°C, 10 mV/s, and a potential range of -500 to -1500 mV.

3.2. Morphology, phase analysis, and micro-hardness results

Fig. 2. shows the surface morphology of Ni-Cr coatings at various concentrations of formic acid. The coating produced without formic acid (Fig. 2a.) has cauliflower structures in some places, forming relatively coarse raised particles perpendicular to the surface. Increasing the formic acid concentration in the bath to 15 and then 30 g/L (Figs. 2b to 2c.) decreases the size of raised surface colonies, making the surface morphology smoother. The finer micro-structure of the coatings can indicate it. Adding formic acid in the bath as a complexing agent probably increases the electrodeposition rate of metallic ions near the cathode surface. This process can promote the nucleation rate and obtain a finer micro-structure during electrodeposition. Increasing the amount of formic acid from 30 to 45 g/L resulted in micro-cracks forming within the coating (Figs. 2d and 2e.). This formation can be attributed to the high amounts of carbon and increasing internal stresses in the coating [6]. In addition, the size of raised particles increased due to the prevailing growth rate of the nucleation rate.

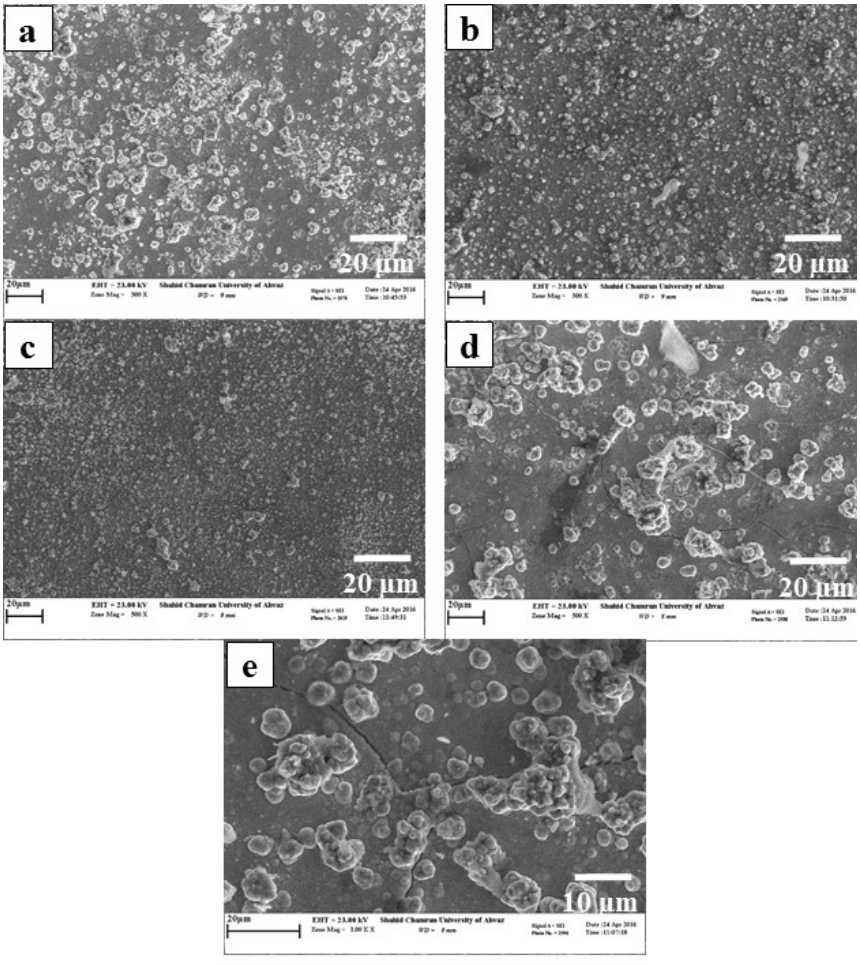

Fig. 2. The surface morphology of Ni-Cr coatings produced at different concentrations of formic acid, a) 0, b) 15, c) 30, and d) 45 g/L (higher magnification).

Fig. 3. illustrates the X-ray diffraction patterns of the Ni-Cr coatings produced at 0, 15, and 30 g/L formic acid in the bath. It is clear that at 0 g/L formic acid concentration in the bath, the XRD pattern of the coating shows fcc micro-structured, which is related to the presence of the Ni-Cr solid solution phase. Increasing formic acid concentration to 15 and then 30 g/L causes the broadening of peaks of the Ni-Cr phase and the appearance of the Cr-Ni phase with the bcc micro-structure. In this case, the broadening of the peak is a sign of the decreasing grain size of the micro-structure. Obviously, in a 30 g/L concentration of formic acid in a bath, the Ni-Cr phase is still the dominant phase of the microstructure. In addition, in this formic acid concentration in the plating bath, the chromium carbide phases ($Cr_{23}C_6$) peak appeared at XRD patterns.

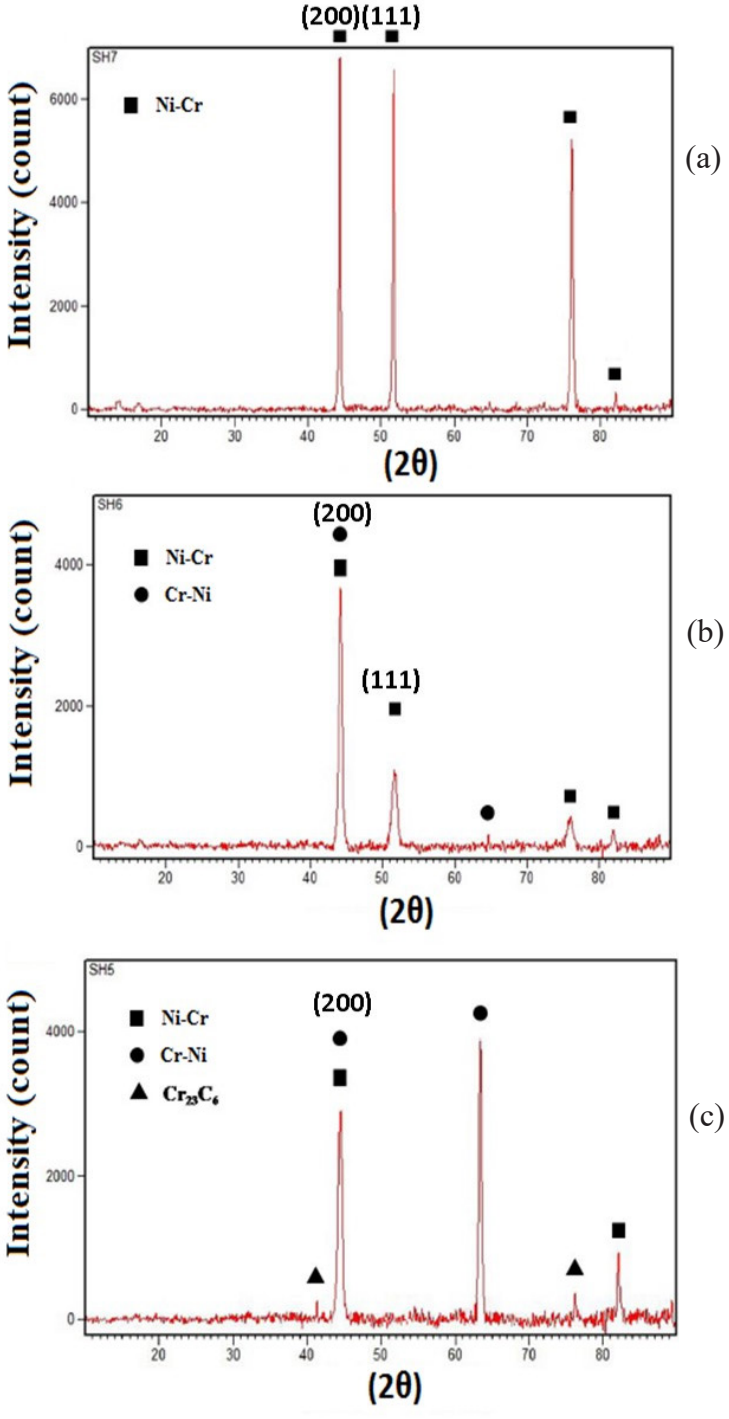

Fig. 3. The XRD patterns of the Ni-Cr coatings produced at a) 0, b) 15, and c) 30 g/L formic acid in the plating bath.

The effect of formic acid concentration on the weight percent of nickel and chromium, grain size, and micro-hardness of the coatings is shown in Fig. 4. The chromium content in the coating produced in the formic-free bath is negligible. This process is due to the lower ability of chromium ions to be reduced compared to nickel ions during the electroplating process. Increasing formic acid concentration in the plating bath will promote the weight percentage of chromium in the coatings. This process can be due to the formation of complexes of Cr ions in the presence of formic acid. Increasing the concentration of formic acid from 30 to 45 g/L leads to a slight reduction in the percentage of chromium. This process can be attributed to an increase in the amount of chromium hydroxides or carbon atoms in coatings. As mentioned above, carbon atoms may also be reduced, leading to decreased chromium content in the coating.

According to Fig. 4. increasing the formic acid to 30 g/L reduced the grain size of the coating to 35 nm. The interference of adsorbed nickel and chromium atoms at growing surfaces disturbed grains' growth and promoted the nucleation rate [21]. This interference can result in a decrease in the grain size. Further increases in formic acid concentration and grain size are increasing to about 50 nm, possibly due to decreasing Cr adsorbed ions on the surface and decreasing its disturbing effects.

As can be seen in Fig. 4. increasing formic acid concentration from 0 to 15 g/L increases the micro-hardness from 480 to 660 HV. This increase can be attributed to the role of chromium atoms in the solution hardening of the Ni-Cr coating and decreasing grain size of the micro-structure [20]. Further increasing formic acid to 30 g/L dramatically increased the coatings' micro-hardness from 660 to 1020 HV. Forming chromium carbides at higher concentrations of formic acid can significantly improve micro-hardness. An increase in the amount of formic acid from 30 to 45 g/L slightly reduced the micro-hardness of the coating. This reduction can be due to carbon atoms or metal hydroxide deposition, which softens the coatings.

So far, most coatings produced in baths containing trivalent chromium ions have shown their highest hardness after heat treatment. In this case, the hardness of the coatings reaches the hardness of the conventional hard chromium coatings. The reason for this is the precipitation of chromium carbide at high temperatures during the heat treatment of the coatings, which causes a significant increase in hardness. Unlike most previous reports, the chromium carbide was deposited during the electrodeposition process in the current studies. This process has increased the hardness of the Ni-Cr coating immediately after electroplating to the amount reported for the conventional hard chromium coatings. Chromium carbide precipitation during electroplating can be related to the high current density and high concentration of formic acid in the bath. The electroplating current density of the present study is 80 A/dm^2, which is significantly higher than that of the previous research (about 30 A/dm^2). In some studies, it has been reported that the high current density of the electrodeposition process, due to a high potential gradient in the vicinity of the electrical double layer, causes the deposition of new metallic grains with high temperatures on a microscopic scale [20]. Instantaneous high temperatures, besides high concentrations of carbon atoms, can lead to chromium carbide precipitation during electrodeposition. It is believed that the higher concentration of carbon in the coating due to the higher amount of formic acid in the bath causes a greater thermodynamic tendency to form chromium carbide. However, the small grain size of Ni-Cr coatings increases the hardness of coatings. Since the heat capacity of the solution and the substrate metal is much higher than these points with high temperatures, the system's average temperature does not show much difference compared to the ambient temperature, and the temperature of these points decreases quickly. Achieving high hardness without needing heat treatment is a great practical success, especially for applications requiring high wear resistance, because it reduces costs and removes defects caused by heat treatment, such as distortion, oxidation, or melting of the substrate.

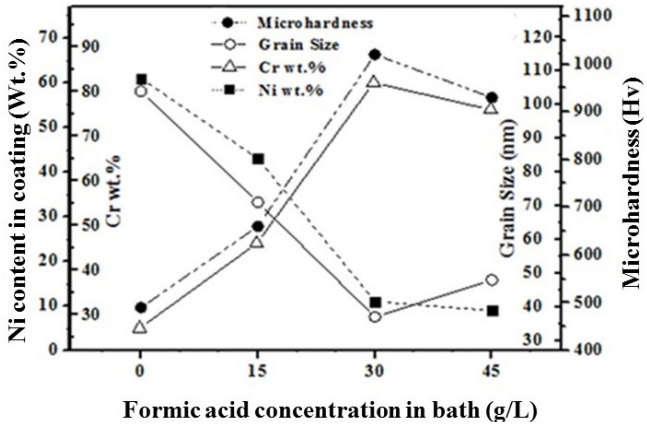

Fig. 4. Effect of formic acid concentration on Ni and Cr weight percent, grain size, and micro-hardness of the Ni-Cr coatings.

3.3. Evaluation of wear behavior

Fig .5. shows the effect of formic acid concentration on the wear weight loss and the average friction coefficient of electroplated Ni-Cr coatings. As can be seen, adding formic acid to the value of 30 g/L significantly decreased the friction coefficient and the wear rate of the coatings. This decrease indicates an improvement in the wear resistance of the coatings. The best wear resistance is obtained at a concentration of 30 g/L. According to Archard's theory, increasing the hardness will increase the materials' wear resistance [21]. Therefore, the decreasing the wear weight loss in this case is related to the increasing the hardness of the coatings. The decreasing friction coefficient is related to the increase in hardness, thus decreasing the ability of the plastic to deform the surface roughness. Reducing the plastic deformation of the surface roughness results in decreasing cold welding between contact surfaces, thus reducing the adhesion between them. So, decreasing adhesion between contact surfaces leads to a decrease in the friction coefficient of the coatings. The slight increase in wear weight loss with the increase in formic acid concentration from 30 to 45 g/L can be related to surface micro-cracks, which facilitate the creation of wear debris and, as a result, further weight loss.

Fig. 6. shows the SEM image of the worn surfaces of Ni-Cr coatings produced at different values of formic acid in the bath. The coating surface produced in the bath without formic acid is rough. In addition, wavy lines of plastic deformation can be seen on worn surfaces. This process indicates the occurrence of an adhesive wear mechanism. This issue agrees with the observation of high wear weight loss and high friction coefficient for this coating. The low hardness of this coating has led to severe plastic deformation of the contact surface and a higher amount of cold welding between them. The cold welding between contact surfaces will lead to an increase in the friction coefficient. After cold welding, the relative movement of the wear surfaces relative to each other causes wear debris formation and increases the wear weight loss of the coatings [22]. The worn surface became smoother by increasing the formic acid concentration in the bath to 30 g/L. Only shallow groove lines can be seen in the direction of wear, indicating a mild abrasive wear mechanism. This shallow groove can be due to the coatings' increasing micro-hardness, which decreases surface roughness's plastic deformation and weakens cold welding between contact surfaces. This process led to decreasing wear weight loss and mean wear coefficient, which agrees with the observed minimum wear weight loss and is the best wear resistance for this coating.

According to Fig. 6d. some micro-cracks can be seen on the worn surface of the coatings produced at a concentration of 40 g/L formic acid in the bath, which agrees with observing an increase in the wear rate of this coating. The presence of these micro-cracks can be due to the higher brittleness of this coating and also the presence of inherent micro-cracks for this coating. Brittleness and inherent micro-cracks are thought to cause a delamination wear mechanism.

3.4. Evaluation of corrosion behavior

Fig. 7. shows the potentiodynamic polarization curves of Ni-Cr coatings produced at different concentrations of formic acid in the plating bath. All curves show active corrosion behavior. However, pseudo-passive behavior is observed for coating produced at a 30 g/L formic acid concentration in the bath. Observing pseudo-passive behavior can be related to forming hydrated oxide layers with higher stability at higher chromium concentrations in the coatings. For a closer look, corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic (β_a) and cathodic (β_c) line slope, polarization resistance, and corrosion rate of the coatings are shown in Table 3.

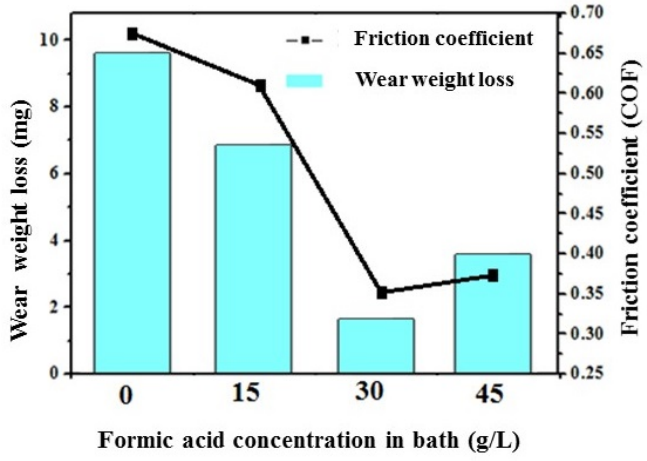

Fig. 5. The wear weight loss and mean friction coefficient of the Ni-Cr coatings electroplated at different concentrations of formic acid in the bath.

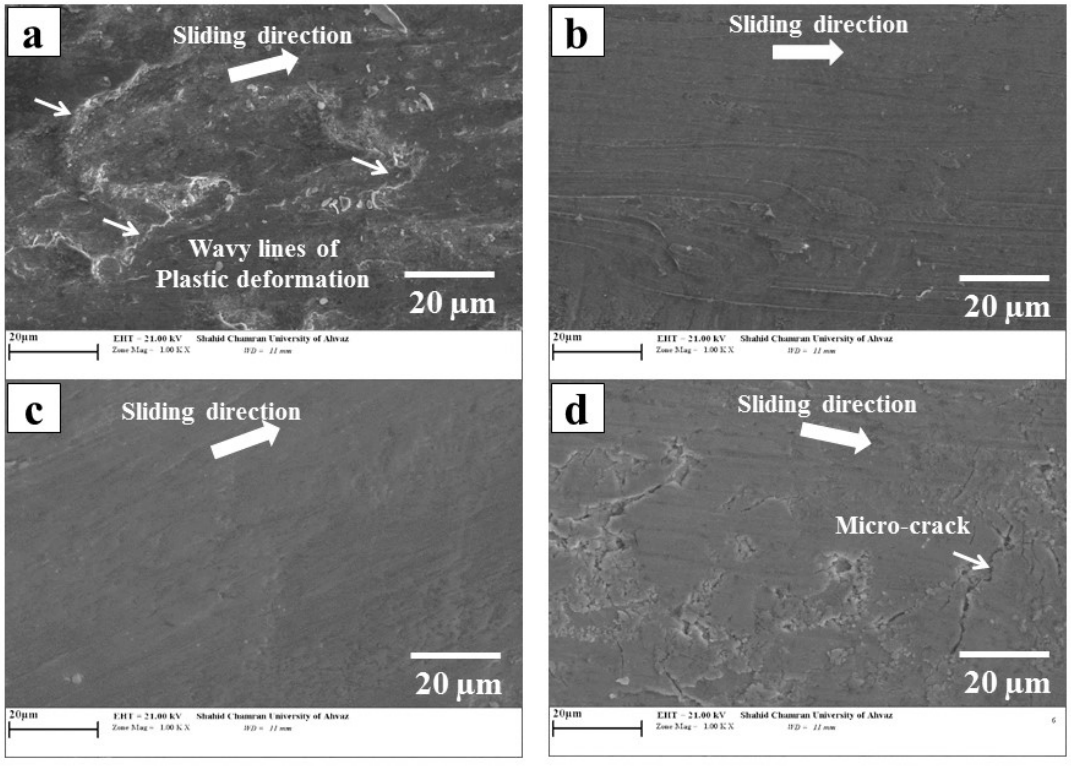

Fig. 6. The worn surfaces of Ni-Cr coatings were electroplated at different concentrations of formic acid in the bath: a) 0 g/L, b) 15 g/L, c) 30 g/L, and d) 45 g/L.

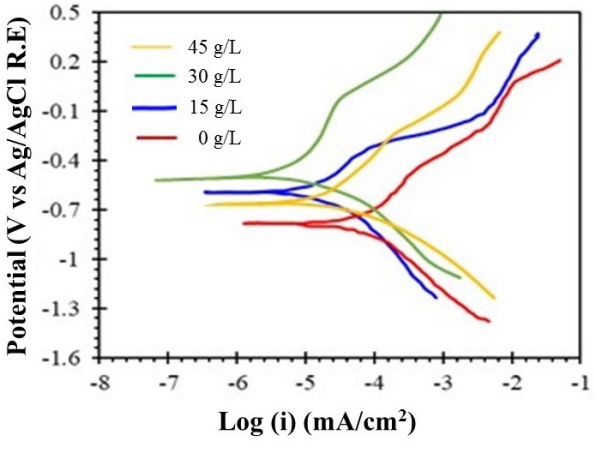

Fig. 7. The potentiodynamic polarization curves of the coatings produced at different concentrations of formic acid in the bath.

Table 3. Results of potentiodynamic polarization tests on the coatings electroplated at different concentrations of formic acid in the bath.

Concentration of formic acid in plating bath (g/L)	E_{corr} (mV)	I_{corr} (µA/cm^2)	β_a (mV/dec)	β_c (mV/dec)	R_p (kΩ)	Corrosion rate (mm/year)
0	-0.787	6.80	43.44	33.702	1.21	0.152
15	-0.670	4.90	45.33	37.56	7.65	0.132
30	-0.589	1.02	49.41	39.175	9.62	0.022
45	-0.690	4.15	47.51	36.20	79.55	0.125

It is clear that the addition of formic acid concentration in the bath from 0 to 30 g/L increases the corrosion potential of Ni-Cr coatings from -0.777 to -0.589 V and decreases the corrosion current density from 6.80 to 1.02 μA/cm^2. These changes show that increasing formic acid concentration in the plating bath to 30 g/L increases Ni-Cr coating corrosion resistance. It can be due to the increasing chromium content of the coatings. It is believed that increasing the chromium content of the coatings increased the stability and resistance of the passive layer and decreased the corrosion rate. However, increasing formic acid to 45 g/L has increased the corrosion current density and reduced the corrosion potential. The reason for this can be related to the inherent micro-cracks of this coating, which causes easier penetration of the corrosive species into the coating and increases the corrosion current rate. The above results showed the best corrosion resistance for the coatings produced at 30 g/L formic acid in the bath. As mentioned above, this coating also showed the best wear resistance, so it is the best option for industrial applications that require simultaneous high wear and corrosion resistance.

4. Conclusions and Suggestions

- Increasing the formic acid concentration in the plating bath improves the reduction of chromium ions, increases the coating's chromium content, and reduces the grain size.
- Due to the high current density applied in the bath, formic acid formed chromium carbide particles in the coating during the electrodeposition process. In this case, the coating's micro-hardness increased significantly without heat treatment.
- The Ni-Cr coatings with the best wear and corrosion resistance were obtained in the plating bath at a 30 g/L formic acid concentration.

5. Acknowledgements

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