Effect of current density and deposition time on Ni-W alloy coating and evaluation of corrosion and wear resistance

Shaik Shajahan, A. Basu*

Department of Metallurgical and Materials Engineering, National Institute of Technology, Rourkela, Odisha, India – 769008

basua@nitrkl.ac.in

Abstract

The current work investigated effect of current density and plating time of electrodeposited Ni-W coating on their structure-properties. Ni-W alloy coatings were obtained by DC electro-codeposition technique with varying current density and deposition time from a new deposition bath followed by evaluation of surface-mechanical (microhardness and wear) and electro-chemical properties of the coated samples. Phase formation, microstructural changes of Ni-W alloy coating with deposition current density and deposition time were analyzed by XRD and SEM study respectively. Apart from phase identification, from XRD peak broadening, fineness of the structure was calculated. Microstructure analysis revealed change in coating morphology with change in current density and deposition time. Hardness and wear studies were also taken up and it was observed that with increasing coating time or current density, surface-mechanical properties exhibit better results due to higher W content and fine structure. Corrosion study of coated samples was carried out by potentiodynamic polarization test in 3.5 wt.% NaCl solution. Results indicated better corrosion resistance for samples deposited with higher current density and deposition time.

Keywords: Ni-W coating, electrodeposition, wear, corrosion

1. Introduction

Nickel–Tungsten (Ni-W) alloy coatings on conductive substrates are widely used in various industrial applications such as aerospace, automobiles and petroleum industries due to their enhanced properties such as corrosion resistance [1-3], wear resistance [4-6], high hardness, magnetic properties [7-8], oxidation resistance etc. compared to virgin metal coatings. Due to excellent corrosion and tribological properties of Ni-W alloy coatings, their demand increased in recent years. Lowe et al. [9] reported approximately three times higher hardness Ni-W alloys compared to pure Ni coating [10]. It is well known that W cannot be electroplated from aqueous solution containing only sodium tungstate, whereas, after introducing Ni compound such as $NiSO_4$ into the electroplating bath, Ni-W alloy deposit can be formed. Usually, W content in Ni-W deposition is in the range of 15-40 weight % (in conventional plating bath) [11]. In order to increase tribological, oxidation and thermal stability, it is necessary to increase the W content of alloy coatings [12]. There are some possible ways/routes to enhance the W content (up to 50-70 weight % range) in the alloy coatings such as pulse current route [13-14] and eliminating NH_3 from the plating bath with citrate as an addendum ligature. The elimination of NH_3 and using citrate method was investigated by Gileadi and co-workers [15-18]. By using pulse current method (PC), it can also reduce the residual stress and grain size in the alloy coatings [13-14].

Ni-W coatings are widely synthesized by electrodeposition technique because of higher deposition rate, lower wastage and higher production rate with uniform coating [19-20]. In order to improve the corrosion resistance and oxidation resistance properties further, secondary dispersive particles like SiO_2 [21], TiO_2 [22] are added into Ni-W based coatings. Electrodeposition can be performed by direct current and pulse current in electrolytic solution bath [23]. Morphology, composition and structure of Ni-W coatings can be controlled by operational parameters such as current density, deposition time, electrolytic composition, Temperature, pH etc. [24-26]. So far, few literatures contributed on Ni-W coatings, and still there is scope of investigation of Ni-W coatings.

In the current work, Ni-W alloy coatings were obtained by alloy deposition technique (DC) with varying current density and deposition time from a new deposition bath followed by phase analysis, surface-mechanical (microhardness and wear) and corrosion property evaluation of the coated samples to study the outcome of deposition time and current density of these properties with this new electrolyte bath.

2.Experimental procedure
2.1 Electrodeposition of Ni-W alloy coatings
In this study, mild steel sample was used as a substrate with a size of 14 mm x 20 mm x 5 mm each. Substrate was metalogrphically prepared by grinding with different grades of emery papers, followed by 1µm diamond paste polishing. Polished substrate was cleaned with soap water, dried and again was cleaned by acetone. A pure nickel plate was used as an anode and the prepared substrate as cathode. These two electrodes were vertically dipped into the electrolyte solution bath and the solution was under continuous magnetic stirring. Direct current (DC) electroplating technique was employed with different plating parameters as shown in table 1. The new composition of the bath was decided by consulting the available literatures to optimise the stress in the coatings, current efficiency and W deposition rate. Mainly ammonia chloride (NH_4Cl) and tri-sodium citrate-di-hydrate ($Na_3C_6H_5O_7.2H_2O$) amounts were changed from conventional one. Coatings were carried out with varying current density (20, 40 and 60 mA/cm^2) and deposition time (15, 30, 60 min). The pH value was maintained at around 7 by minor addition ammonium hydroxide or acetic acid. After completion of the deposition process, coated samples were cleaned with distilled water and dried for characterizations.

2.2 Characterization of Ni–W coatings
Ni-W coated samples were characterized by XRD (X-ray diffraction) by using Bruker D8 Advanced diffractometer fitted with Cobalt K alpha (λ=1.79^{o}A) target to determine the phase formations. Morphology of the coated surface was analyzed by SEM (scanning electron microscope) (JEOL JSM- 6084LV). Composition of Ni-W alloy coatings was done by Energy Dispersive Spectroscopy (EDS) fitted with SEM/FESEM instrument. Hardness of Ni-W alloy coated samples was determined by Vickers microhardness tester (Model: LECO LM700) with application of 10 g load for 10 sec. Corrosion behaviour of coatings was studied by polarization technique with a VERSASTAT3-400, PAR equipment. Test was conducted with 3.5 wt. % NaCl solution in a three electrode cell. During the experiment, silver chloride (in KCl) and platinum wire mesh were used as reference and counter electrode respectively and a scanning rate of 0.1666 mV/s was employed. Wear test of Ni-W deposits was carried out by ball-on-the plate type wear tester (DUCOM TR-208-M1) under 5 N load for 5 mins at 10 rpm in dry sliding conditions. Hardened steel ball (grade: SAE 52100) of 2 mm dia. was used as the counter body and was rotated on a track diameter of 10 mm.

Table1: Deposition parameters of Ni-W alloy coatings

Bath chemicals	Amount (g/L)	Other plating parameters
$NiSO_4.6H_2O$	26.3	Current density: 20, 40, 60 mA/cm^2
$Na_2WO_4.2H_2O$	98.96	Deposition time: 15, 30, 60 min
$Na_3C_6H_5O_7.2H_2O$	147.05	*pH*: ~7
NH_4Cl	26.7	Temperature: 70°$\pm$2° C
NaBr	20.4	

3. Results and Discussion
3.1 SEM analysis
Surface morphology of Ni-W alloy coatings obtained with various operational conditions is shown in figure1. The coatings are crack free and uniform in appearance with spherical and ellipsoidal morphology. In some cases, clustered appearance is also there. It is clear that the surface morphologies of Ni-W coatings are greatly influenced by operational parameters such as plating time and current density. Microstructure of Ni-W coating at 20 mA/cm^2 for 15 min is shown in Fig. 1(a); the obtained microstructure exhibited very fine and spherical/ellipsoidal shaped morphology. With increase in deposition time (30 min, 60 min) at the same current

density (20 mA/cm^2), the size does not show any remarkable change, but shape becomes more spherical. Similar observation is also noticed with 40 mA/cm^2 current density as displayed in Fig.1(d-f). In comparison, the coating obtained at 60 mA/cm^2, with 15 min deposition time (Fig. 1(g)) showed small cauliflower like structure. With increase of deposition time (to 30-60 min) at same current density (60 mA/cm^2), the size of the flower was increased with denser appearance (Fig. 1(h, i)).
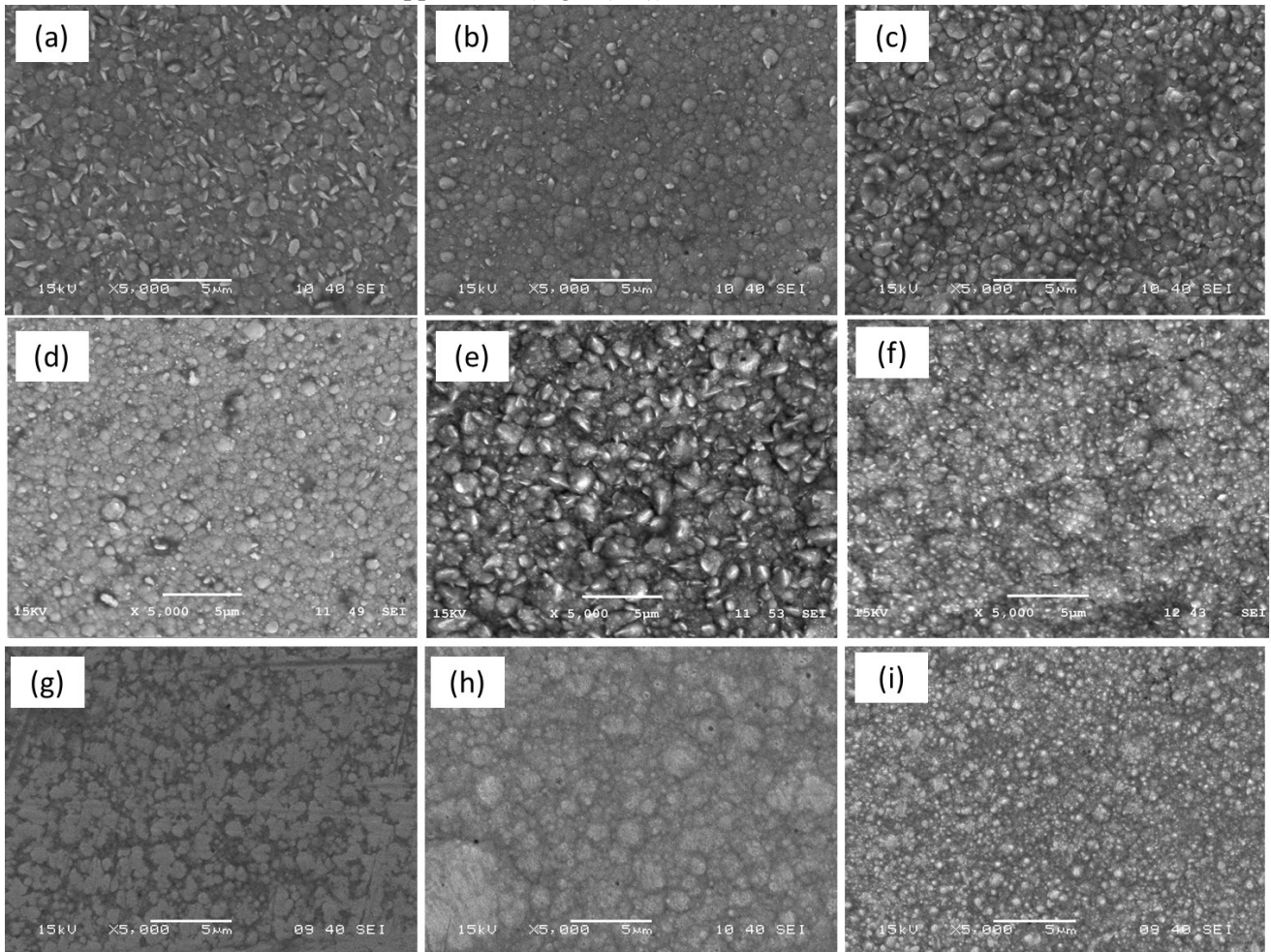
Fig. 1. SEM micrograph of Ni–W alloy coatings obtained from different parameters: (a) 15, (b) 30, and (c) 60 min with 20 mA/cm^2; (d) 15, (e) 30 and (f) 60 min with 40 mA/cm^2;(g) 15, (h) 30 and (i) 60 min with 60 mA/cm^2.
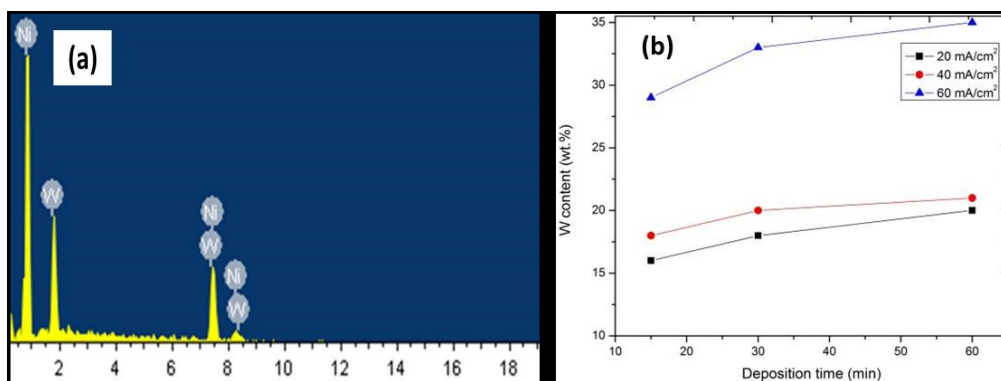

Fig. 2. (a) EDS spectra of 60 mA/cm^2, 60 min sample, (b) comparisons of the W content as a function of deposition time at different current densities.

From EDS analysis both Ni and W was observed on the coated surface. Fig. 2(a) shows one such representative spectra obtained from coating prepared with 60 mA/cm^2 current density and 60 min deposition time. Semi-quantitative analysis of all such spectra was recorded and the composition of all Ni-W coatings under various

operational parameters was displyed in Fig. 2(b). From this figure it can be noticed that at a particular current density, W content was increased with increasing deposition time. Moreover, it could also be noticed that at a fixed deposition time, higher current density led to higher W content. High current density may have increased the mobility of W ion in the modified plating bath.

3.2 XRD analysis

Fig. 3 displays X-ray diffraction profiles of Ni-W coatings of various deposition parameters. From Fig. 3(a) (20 mA/cm^2 coatings), it is clear that there exist Ni, W and Ni-W solution peaks. At higher deposition time, merging of nearby Ni and W (W at $2\theta = 51.89^o$ and Ni at $2\theta = 53.69^o$) peaks is observed. Moreover, decrease in intensity of individual peaks (like Ni) is also observed with higher deposition time. These represent formation of Ni-W solid solution at high deposition time or accumulation stress/strain. Solid solution formation is possible due to modified strain condition prevailing at higher deposition time. Moreover, relatively higher (70°C) plating temperature could also help in achieving this. Similar trend is also observed at other current densities (Fig. 3(b, c)).
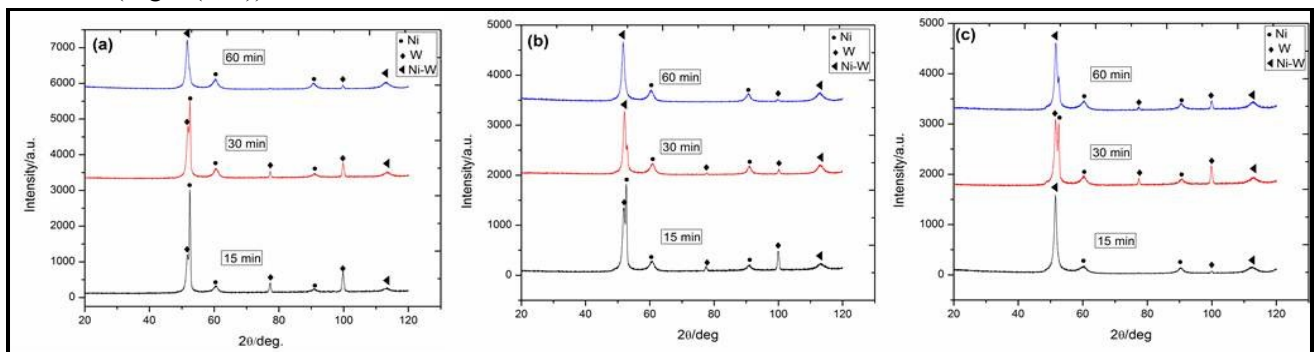

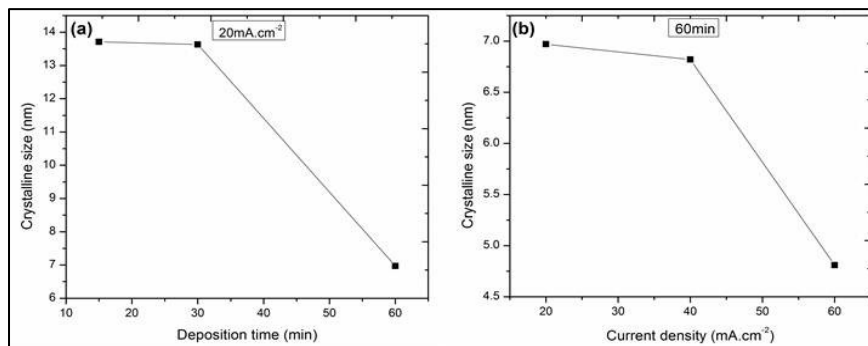Fig. 3. XRD profiles of Ni–W coatings obtained with (a) 20, (b) 40 and (c) 60 mA/cm^2 at different deposition times.

Fig. 4. Crystallite size of coatings obtained with (a) 20 mA/cm^2 (15, 30 and 60 min) and (b) 60 min (20, 40 and 60 mA/cm^2).

In all the XRD peaks, considerable peak broadening was observed. So, full width half maxima of selected peaks were measured and from Scherrer equation crystallite size was measured. Fig. 4(a, b) shows the measurement of crystalline size of Ni-W alloy coatings synthesized from various coating times and current densities. The plots exhibit nanometric crystallite size of all the coatings. Due to limitations of applicability of Scherrer equation, the numerical values of the crystallite size may not be so accurate, but the values typically fallow a trend which is similar to the peak broadening trends as seen in Fig. 3.

Fig. 4(a) show that with increase in deposition time the crystallite size of Ni-W alloy coatings decreases. Higher deposition time leads to higher coating depth and this may provide differential effect from subsurface to near surface region of the coatings due to accumulated stress/strain condition during long deposition time (mainly at 60 min). In case of fixed deposition time, higher current density also reduces the crystallite size (Fig. 4(b)). Higher current density may lead to better nucleation process of the coatings leading to finer structure.

3.3 Microhardness study

Fig. 5(a, b) shows the microhardness values of Ni-W alloy coatings for varying deposition times and current densities. From Fig. 5(a) it was noted that, with increase in deposition time the microhardness values also increase, it is indicating that increase in W content in the Ni-W alloy enhanced their microhardness due to solid solution formation. Moreover, this can also be attributed to fine crystallite size at higher deposition time as observed in Fig. 4(a). Similar effect was also observed with current density variations at a constant deposition time; with an increase in current density the microhardness value increases as observed in Fig. 5(b). The possible reasons for rise in hardness is an increment in W content and decrease in crystallite size resulting in solid solution hardening and grain refinement.
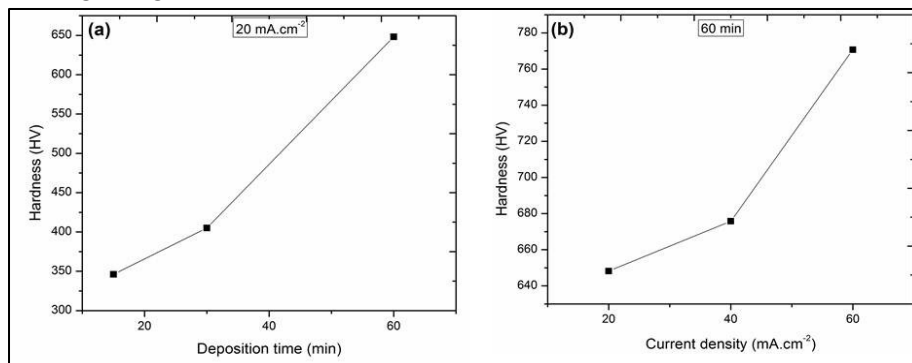

Fig. 5. Microhardness of coatings obtained with (a) 20 mA/cm^2 (15, 30 and 60 min) and (b) 60 min (20, 40 and 60 mA/cm^2).

3.4 Electrochemical characterization

Potentiodynamic polarization curves of different coatings are presented in Fig. 6. From the plots, corrosion potential (E_{corr}) values were recorded and from Tafel extrapolation technique corrosion current density values (I_{corr}) were measured. The obtained outputs are listed in table 2 and 3. Fig. 6(a) shows the potentiodynamic curves of Ni-W coatings obtained with 20 mA/cm^2 current density and varying coating time. From the figure it was noted that, corrosion resistance of Ni-W coating was increased with deposition time due to higher tungsten content in the coating with deposition time. Hui et al. [27] suggested the importance of tungsten to improve the corrosion resistance. Tungsten can be migrated to the surface and form an oxide layer leading to better corrosion resistance.
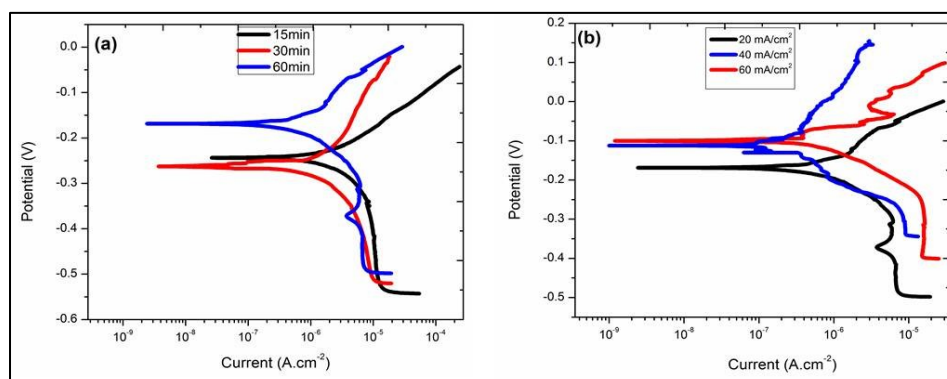

Fig. 6. Potentiodynamic polarization curves of the coatings obtained with (a) 20 mA/cm^2 (15, 30 and 60 min) and (b) 60 min (20, 40 and 60 mA/cm^2) in 3.5 wt.% NaCl solution.

Table 2: Summery of corrosion data (samples deposited with 20 mA/cm^2)

Deposition Time (min)	E_{corr}/V	$I_{corr}/A.cm^{-2}$
15	-0.244	1.86×10^{-6}
30	-0.264	8.57×10^{-7}
60	-0.168	6.46×10^{-7}

Apart from minor variation in E_{corr} value of 30 min sample, E_{corr} and I_{corr} values in table 2 show almost similar trend as observed in Fig. 6(a). Similar effect was observed in the case of current density variation as displayed in Fig. 6(b). The obtained results displayed that, corrosion resistance of Ni-W coating was increased with current density, because of increment of tungsten content with current density. Corresponding E_{corr} and I_{corr} values in table 3 show almost similar trend apart from minor variation in I_{corr} value of 60 mA/cm^2 sample.

Table 3: Summery of corrosion data (sample deposited for 60 min)

Current density (mA/cm^2)	E_{corr}/V	I_{corr}/A.cm^{-2}
20	-0.168	6.46×10^{-7}
40	-0.112	1.99×10^{-7}
60	-0.100	4.68×10^{-7}

3.5 Wear study

Fig. 7(a) shows comparable wear loss plots of Ni-W coatings (wear depth/vertical penetration vs. time) with varying deposition time (deposited at 20 mA/cm^2). The wear depth has crossed the coating thickness but their comparative values corresponding to different samples are indicative. With higher deposition time wear loss decreases due to better W content and fine crystallite size. Similar behaviour was also found case of varying current density with fixed deposition time (60 min) as shown in Fig. 7(b) *i.e.* wear resistance of Ni-W coatings was increased with current density due to the same reasons mentioned above. Wear study displays similar trend as that was observed in hardness study.
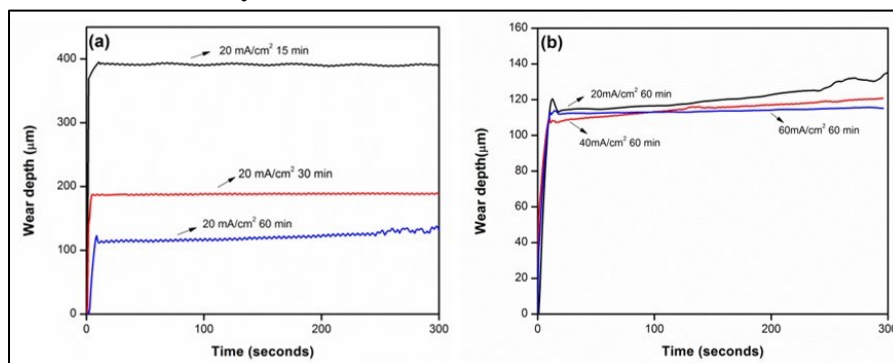

Fig. 7. Wear depth vs. time plots of Ni–W coatings obtained with (a) 20 mA/cm^2 (15, 30 and 60 min) and (b) 60 min (20, 40 and 60 mA/cm^2).

4. Conclusions

Ni-W coatings were successfully synthesized using a DC power source with various deposition time and current densities from a new deposition bath. The obtained results showed following outcomes:

(i)   Higher deposition time at a constant current density increases W content in the coating along with solid solution formation and finer crystallite size leading to higher hardness, improved wear and corrosion resistance

(ii) With increasing current density at a particular deposition time, W content increases along with solid finer crystallite size leading to higher hardness, better wear /corrosion resistance.

References

[1]   M. Obradovic, J. Stevanovic, A. Despic, R. Stevanovic, J. Stoch, Characterization and corrosion properties of electrodeposited Ni-W alloys, J. Serb. Chem. Soc. 66 (2001) 899-912.

[2]   M. Obradovic, J. Stevanovic, A.R. Despic and R. Stevanovic, Electrochemical deposition and phase

structure of electrodeposited NiW alloys, J. Serb. Chem. Soc. 64 (1999) 245-257.

[3]   D.R. Gabe, The role of hydrogen in metal electrodeposition processes, J. Appl. Electrochem. 27 (1997) 908-915.

[4]   O. Younces, E. Gileady, Electroplating of Ni/W alloys I. ammoniacal citrate baths, J. Electrochem. Soc. 149 (2002) C100-C111.

[5]   E. Slavcheva, W. Mokwa, U. Schnakenberg, Electrodeposition and properties of NiW films for MEMS application, Electrochim. Acta, 50 (2005) 5573-5580.

[6]   I. Mizushima, P. Tang, H. Hansen, M. Somers, Development of a new electroplating process for Ni-W alloy deposits, Electrochim. Acta, 51 (2005) 888-896.

[7]   T. Yamasaki, P. Schlossmacher, K. Ehrlich, Y.Oginoi, Formation of amorphous electrodeposited Ni-W alloys and their nanocrystallization, NanoStruct. Mater. 10 (1998) 375-388.

[8]   T. Yamasaki, High-strength nanocrystalline Ni-W alloys produced by electrodepostition and their embrittlement behaviors during grain growth, Scripta Mater. 44 (2001) 1497-1502.

[9]   H. Lowe, W. Ehrfeld and J. Diebel, Ultraprecision micro electroforming of metals and alloysProc. SPIE. 168 (1997) 3223-3226.

[10] V.B. Singh, L.C. Singh and P.K. Tikoo, Studies on electrodeposition of Nickel-Cobalt-Tungsten alloys, J. Electrochem. Soc. 127 (1980) 590-596.

[11] Information on http://www.enthone.com PWA 36975: Electroplated NiW—thin deposit (Enloy Ni-500).

[12] O. Younes, E. Gileadi, Electroplating of high tungsten content Ni/W alloys, Electrochem. Solid-State Lett. 3 (2000) 543-545.

[13] L. Namburi, Electrodeposition of NiW Alloys into Deep Recess, M.Sc. Thesis, Louisiana State University, December (2001).

[14] M. Donten, Z. Stojek, H. Cesiulis, Formation of nanofibers in thin layers of amorphous W alloys with Ni, Co, and Fe obtained by electrodeposition, J. Electrochem. Soc. 150 (2003) C95-C98.

[15] O. Younes, L. Zhu, Y. Rosenberg, Y. Shacham- Diamand, E. Gileadi, Electroplating of amorphous thin films of Tungsten/Nickel alloys, Langmuir. 17 (2001) 8270-8275.

[16] O. Younces, E. Gileady, Electroplating of Ni/W alloys I. ammoniacal citrate baths, J. Electrochem. Soc. 149 (2002) C100-C111.

[17] L. Zhu, O. Younes, N. Ashkenasy, Y. Shacham- Diamand, E. Gileadi, STM/AFM studies of the evolution of morphology of electroplated Ni/W alloys, Appl. Surf. Sci. 200 (2002) 1-14.

[18] O. Younes-Metzler, L. Zhu, E. Gileadi, The anomalous codeposition of tungsten in the presence of nickel, Electrochim. Acta. 48 (18) (2003) 2551-2562.

[19] J.L. Stojak, J. Fransaer, J.B. Talbot, Review of Electrodeposition, Adv. in Electrochem. Sci. and Engg. 7 (2001) 193-223.

[20] R.K. Saha, T.I. Khan, Effect of applied current on the electrodeposited $Ni-Al_2O_3$ composite coatings, Surf. Coat. Technol. 205 (2010) 890-895.

[21] Y. Wang, Q. Zhou, K. Li , Q. Zhong, Q. B. Bui, Preparation of $Ni-W-SiO_2$ nanocomposite coating an evaluation of its hardness and corrosion, Ceramics Int. 41 (2015) 79–84.

[22] K. A. Kumar, G. P. Kalaignan, V.S. Muralidharan, Direct and pulse current electrodeposition of $Ni-W-TiO_2$ nanocomposite coatings, Ceramics Int. 39 (2013) 2827–2834.

[23] M. Zemanova, M. Krivosudska, M. Chovancova, V. Jorık, Pulse current electrodeposition and corrosion properties of Ni–W alloy coatings, J. Appl. Electrochem. 41 (2011) 1077–1085.

[24] H. Cesiulis, E.J.Podlaha-Murphy, Electrolyte considerations of electrodeposited Ni-W alloys for microdevice fabrication, Materials Science (Medziagotyra), 9 (2003) 329-333.

[25] T.Yamasaki, P.Schloβmacher, E.Erlich, Y.Ogino, Formation of amorphous electrodeposited Ni-W alloys and their nanocrystallization, NanoStructured Mater., 10(3) (1998) 375-388.

[26] T.Yamasaki, High strength nanocrystalline Ni-W alloys produced by electrodeposition, Mater.Phys.Mech. 1 (2000) 127-132.

[27] W.H. Hui, J.J. Liu, Y.S. Chaug, A study of the corrosion resistance of brush-plated Ni-Fe-W-P films Surf. Coat. Technol. 68/69 (1994) 546–551.