

Wear behavior of carbon steel electrodeposited by nanocrystalline Ni-W coating

A. Amadeh^{1*}, M. Harsij sani² and H. Moradi³

School of Metallurgy and Materials Engineering, Faculty of Engineering, University of Tehran, P.O.Box 11155-4563, Tehran, Iran

Abstract

Ni-W coatings, compared to pure nanocrystalline Ni, exhibit higher hardness and wear resistance. In some cases, these coatings are considered as environmental friendly alternatives for hard chromium coating. Till now, most of Ni-W coatings have been produced by direct current electrodeposition from alkaline baths. In this study square pulse current was used for deposition of Ni-W precipitates from Watts bath. The effect of current density and duty cycle on morphology and wear behavior of nano-structured Ni-W coatings was investigated. The structure and morphology of the coatings were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques, respectively. Mechanical and tribological properties of the deposits were also investigated by means of microhardness and pin-on-disk wear tester. The results showed that a decrease in current density and duty cycle increased the W content of Ni-W coating. This increase led to an increase in hardness and improved the wear resistance of nanocrystalline coatings.

Keywords: Nanocrystalline coatings, Ni-W alloys, Watts bath, Pulse electrodeposition.

1. Introduction

Hard chromium coating is widely used on steel for protection against wear and corrosion. Because chromium plating solution is based on environmentally hazardous hexavalent chromium ions, Ni-W electrodeposits were developed as an alternative for hard chromium plating^{1,2}. Although it is well established that W can not be electrodeposited from aqueous electrolytes, it can be co-deposited with iron group metals such as nickel to form an alloy³. This phenomenon is known as induced co-deposition and its detailed mechanism is still not fully understood³⁻⁵. The most widespread hypothesis assumes that the Ni-W alloy deposition is the result of two main cathodic reactions; namely, a reduction of nickel ions (usually as ammonium complexes) and a depolarization of tungsten and/or mixed nickel-tungsten complexes^{4,6}. Generally, Ni-W alloys are known to exhibit higher hardness, higher heat resistance and better corrosion and tribological behavior in comparison to pure Ni⁶⁻⁸. For further improvement in microhardness and wear resistance of Ni-W coating, it is sometimes desirable to increase its tungsten content^{9,10}. Unfortunately, this has been found difficult, even when the concentration of WO_4^{2-} ions in electrolyte solution is in large excess compared to Ni^{+2} ions⁹.

One possible way to increase the tungsten concentration in the alloy is the application of pulse current, which in turn also increases the throwing power and the deposition rate, and improves the properties of the deposit^{2,4,10,11} (e.g. reduces the residual stresses and porosity, refines the grain size, improves the wear resistance, etc.). Different baths with various complexing agents such as maleic, glycine, gluconic, hydroxyl acetic, triethanolamin (TEA), citric and tartaric acid have been found useful for satisfactory electrodeposition of Ni-W coatings^{8,12}. Unfortunately, the traditional baths for Ni-W plating containing citrate and ammonia as complexing agents are characterized by low current efficiency and poor stability of the pH value^{4,8,10}. In this study acidic Watts bath (pH = 3.5) free of complexing agents and organic additives, was used for application of nano-structured Ni-W deposits on mild steel and the effect of pulse current density, duty cycle and agitation rate on morphology and wear behavior of the coatings was investigated.

2. Experimental

Ni-W coating was electrodeposited from a typical Watts bath using a square pulse current. The composition of the bath was presented in Table.1. The solution temperature was maintained at 50 °C. The pH of the bath was adjusted at 3.5 using the drops of dilute ammonia or sulfuric acid. Mild steel plates with 12 cm² surface area were used as the substrate. A pure nickel (99.99%) sheet was used as the anode. Prior to electrodeposition, the steel cathodes were boiled for 1 minute in an aqueous solution containing 30% NaOH and 70% distilled water, rinsed in distilled water and activated for 20

** Corresponding author:*

Tel: +9821-82084090 Fax: +9821-88006076

E-mail: amadeh@ut.ac.ir

Address: School of Metallurgy and Materials Engineering, Faculty of Engineering, University of Tehran, P.O.Box 11155-4563, Tehran, Iran.

1. Professor

2. M.Sc

3. M.Sc

seconds in 20% HCl. Both electrodes were kept in a vertical position and the solution was agitated at three agitation rates (180, 230, 350 rpm) using a magnetic stirrer. The current density varied from 2.5 to 10 A/dm² and the duty cycle (d.c. = $T_{on} / T_{on} + T_{off}$ in which T_{on} and T_{off} denote the on-time and off-time periods, respectively) varied from 30 to 90 %.

After deposition, the morphology of the coatings was studied by scanning electron microscope (SEM). The hardness of selected deposits was measured on metallographic cross-sections by means of Vickers microhardness tester under a load of 80 g. The content of W in the coating was determined by EDS elemental analyzer. The grain size of the coatings was calculated from XRD patterns using Scherrer equation:

$$d = 0.9\lambda / \beta \cos\theta \quad (1)$$

where λ , β , θ are the wavelength of CuK_{α} radiation (1.5406 Å), the full-width of the nickel (111) peak at its half maximum (FWHM) and the diffraction angle, respectively. Sliding wear tests were carried out at room temperature in unlubricated conditions using a pin-on-disc sliding wear tester under the load of 1 N, total sliding distance of 200 m and the speed of 0.75 m/s. The coated steel specimens were used as the disk and the pin was made of DIN 52100 tool steel. The disk specimens were weighed before and after wear test to a precision of 0.1 mg and the weight change was considered as wear weight-loss. The worn surfaces were also studied by SEM.

Table 1. Chemical composition of electroplating bath.

NiSO ₄ .6H ₂ O	300 g/l
NiCl ₂ .6H ₂ O	45 g/l
H ₃ BO ₃	45 g/l
Na ₂ WO ₄	3 g/l

3. Results and discussion

3.1. Effect of pulse current density and duty cycle

Figure.1. presents the surface morphology of as-deposited coatings at various current densities.

This figure demonstrates a colony-like structure. Each colony consists of several grains. By increasing the current density, the size of the colonies increases but the surface morphology becomes smoother and more homogeneous. Figure. 2. shows the XRD patterns of pure Ni and Ni-W deposits produced at $i = 5$ A/cm². This pattern illustrates the characteristic peaks of fcc nickel. Because tungsten is in the form of solid solution in nickel, its peaks have not appeared in XRD pattern. The calculation of the grain size using equation 1 indicates that the deposited alloy at the mentioned current density consists of nanocrystalline grains of about 32 nm. The composition of the deposits at different current densities has been presented in Table.2. The results of EDS analysis

shows that the content of tungsten in the deposited layers decreases with the increase in current density. This evolution disagrees with the observations of other authors for Ni-W deposition^{5,9}.

However, it should be taken into account that firstly, the electroplating bath used in this research is acidic and therefore, rich of hydrogen ions; and secondly, the content of tungsten in the electrolyte is much lower than that of nickel and the tungsten deposition most probably proceeds under diffusion control.

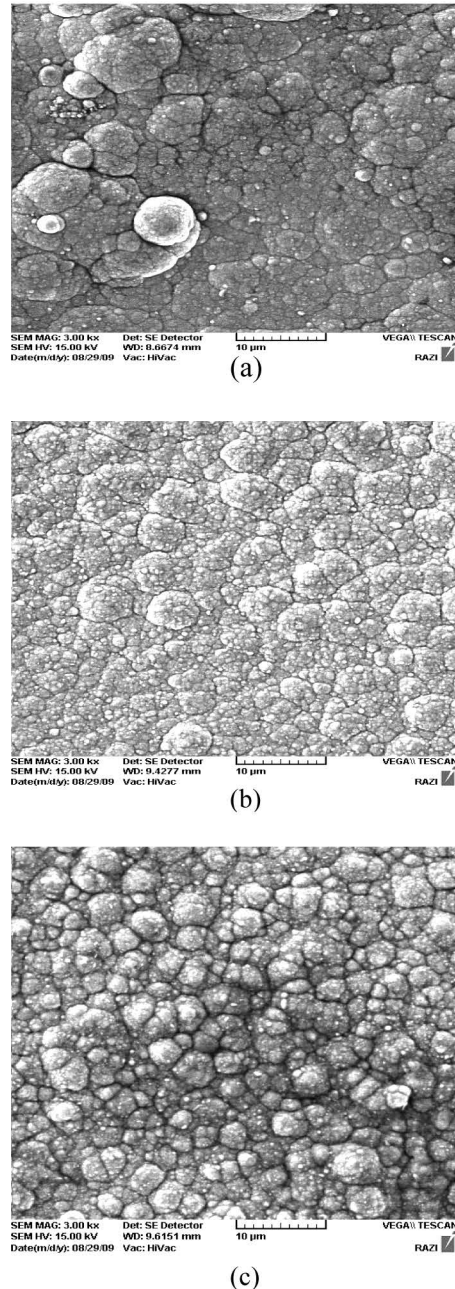
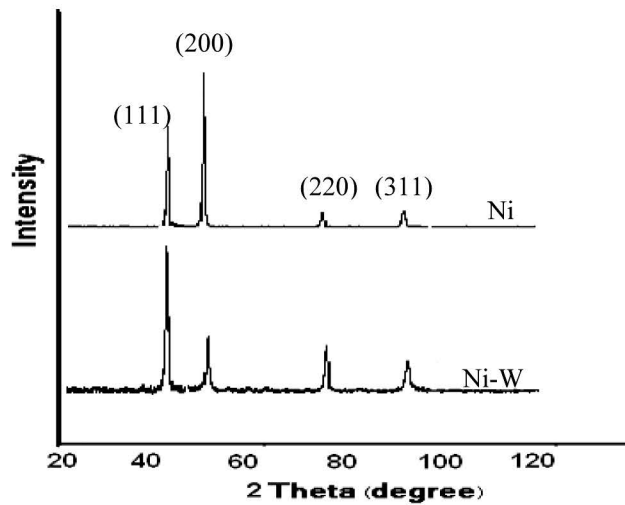


Fig. 1. Surface morphology of Ni-W coatings at $d.c.=30\%$, agitation rate=230 rpm and various current densities: a) 2.5, b) 5, c) 10 A/dm².

Table 2. Chemical composition of coatings that obtained from EDS analysis.

Current density (A/dm^2)	Ni (wt.%)	W (wt.%)
2.5	97.65	2.35
5	97.87	2.13
10	97.98	2.02

Fig. 2. XRD patterns of pure Ni and Ni-W deposits produced at $i = 5 A/cm^2$.

The effect of agitation rate on the morphology and tungsten content of the coatings at $i = 5 A/dm^2$ has been shown in Figure. 3. It can be seen that the increase in the agitation rate leads to an increase in the tungsten content of the deposits. This evolution verifies that tungsten deposition proceeds under diffusion control. It was also reported, for Ni-Mo and Co-W coatings, that increasing the overpotential of hydrogen reduction, decreases the reduction of tungstate and molybdate ions by hydrogen and so decreases the content of tungsten and molybdenum in the deposit^{12,13}. Figure. 4. depicts the surface morphology and EDS results of Ni-W coatings

obtained at different duty cycles. It can be observed that an increase in duty cycle from 30 to 90% decreases the tungsten content in the deposit. This evolution is probably due to the fact that the loss in metallic ions concentration in double layer is compensated during the off-time period or the increase in electrochemical reduction of tungsten ions during the off-time period, by the hydrogen reduced during the on-time period¹². Moreover, the coating morphology changes from pyramidal structure at the duty cycle of 90% to colony-like structure at the duty cycle of 30%.

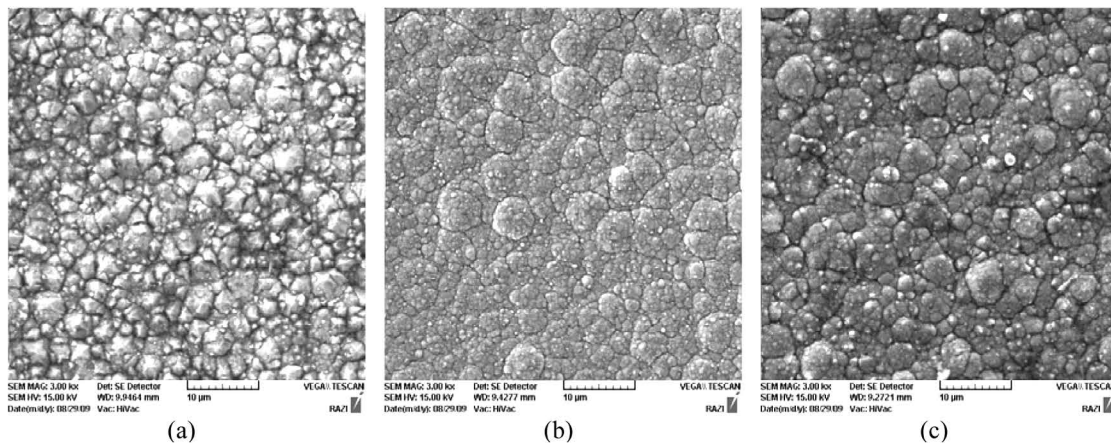


Fig. 3. Effect of agitation rate on morphology and tungsten content of the coatings at $i = 5 A/dm^2$, d. c. = 30%: a) 180 rpm, $W = 1.10$ wt.%, b) 230 rpm, $W = 2.13$ wt.%, c) 350 rpm, $W = 3.22$ wt.%.

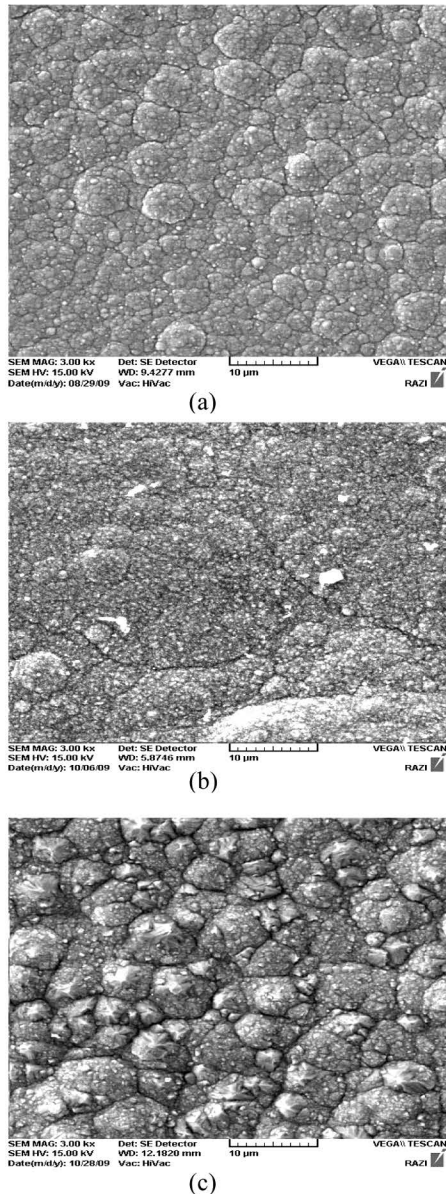


Fig. 4. Surface morphology and EDS analysis of Ni-W coatings obtained at $i=5\text{A/dm}^2$, agitation rate = 230 rpm and different duty cycles: a) 30%, $W=2.13$ wt.%, b) 50%, $W=1.31$ wt.%, c) 90%, $W=1.10$ wt.%.

3.2. Microhardness and wear behavior

The evolution of microhardness and wear weight loss of Ni-W coatings electrodeposited at various current densities and duty cycles have been shown in Figures 5 and 6, respectively. The microhardness and wear resistance of Ni-W coatings increases with a decrease in current density and duty cycle due to an increase in W content of the deposits. The hardness of the coatings varies from 495 to 554 HV while that of pure nickel deposit is about 280 HV. Thus, the microhardness of Ni-W deposits is nearly twice as

much as that of pure nickel. This confirms the role of W in increasing the hardness of nanocrystalline nickel-tungsten alloy coatings. The highest hardness (554 HV) was obtained for the sample with the highest tungsten content (3.22 wt.%). The electroplating condition of this sample was the current density of 5A/dm^2 , duty cycle of 50% and the bath agitation rate of 350 rpm. Siraman et al.⁸⁾ found a maximum hardness of 638 HV for Ni-W coating obtained from an additive containing bath.

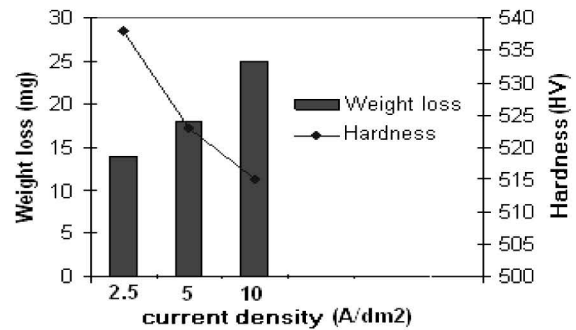


Fig. 5. Evolution of microhardness and wear weight loss of Ni-W coatings as a function of current density.

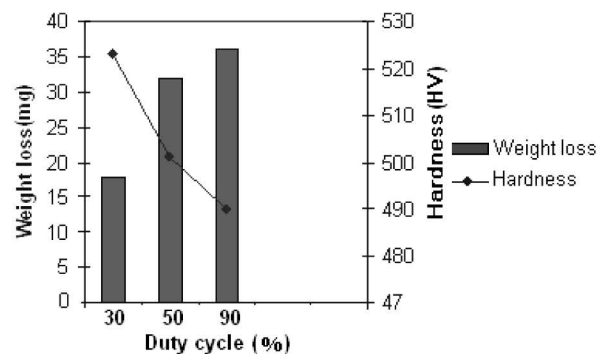


Fig. 6. Microhardness and wear weight loss of Ni-W coatings electrodeposited at different duty cycles.

Eliasz et al.⁹⁾ mentioned that the hardness of as-deposited Ni-W alloys at 30-70 °C is typically in the range of 450-768 HV. Figures 7 and 8 present the SEM images of worn surfaces of Ni-W coatings applied at different current densities and duty cycles. The presence of many scratches and adhesive tearing and plough lines along the sliding direction indicates the combined abrasive and adhesive wear mechanisms of these coatings. It is also clear from these figures that the increase in the hardness of the coatings, consequent to the increase in W content, the width of the scratches and the depth of plough line become shallower, which improve the wear resistance of nanocrystalline Ni-W coatings.

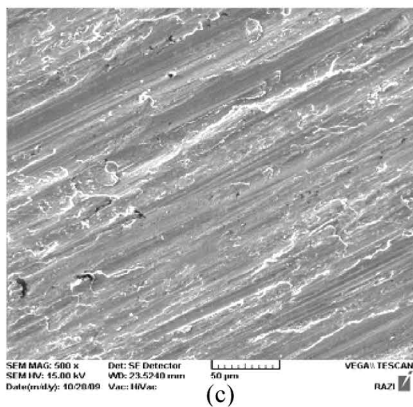
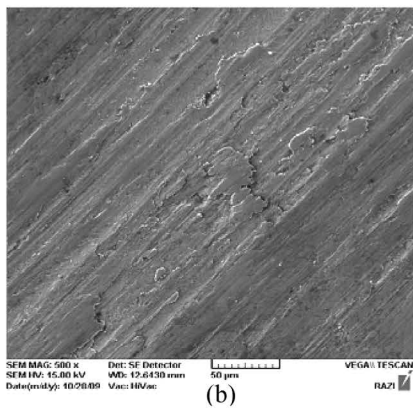
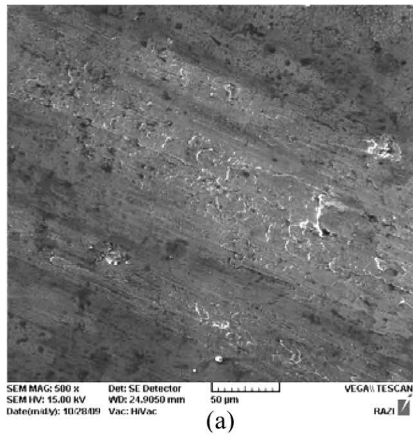


Fig. 7. SEM micrographs of worn surfaces of Ni-W coatings applied at different current densities: a) 2.5, b) 5, c) 10 A/dm².

4. Conclusions

- It was shown that the increase in tungsten content of Ni-W alloy coatings can be realized either through high agitation rate of the electrolyte, or by using lower pulse current density and duty cycle.
- The maximum tungsten content achieved was 3.22 wt.% which is rather low. Nevertheless, the presence of tungsten in Ni-W coatings, even at these low concentrations, increases their hardness and improves their wear resistance. The maximal hardness of 554 HV, obtained for the sample with the highest tungsten content, is about twice as high as pure nickel deposit.

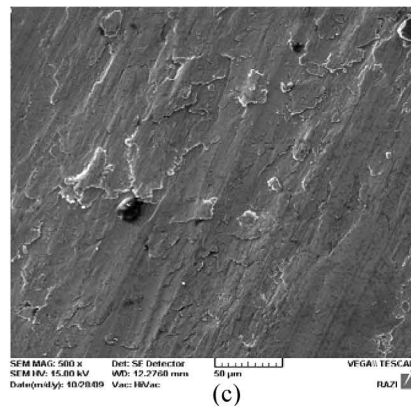
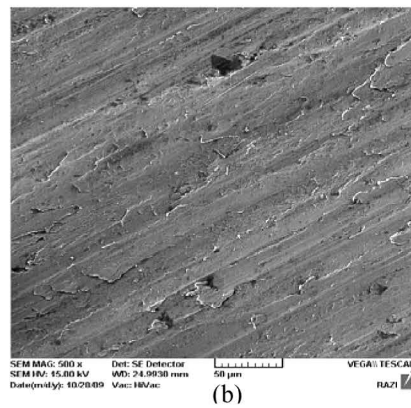
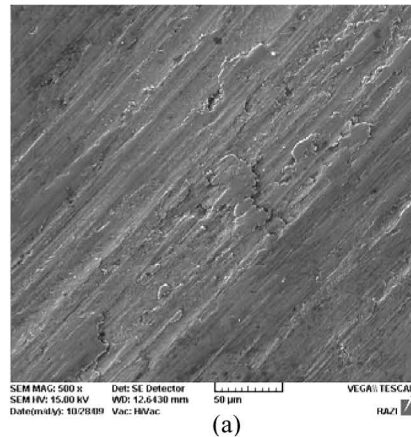


Fig. 8. SEM images of worn surfaces of Ni-W coatings applied at different duty cycles: a) 30, b) 50, c) 90%.

References

- [1] R.M. Krishnan, C. Josephkenedy, S. Jayakrishnan, S. Sriveeraraghavan, S.R. Nataraja and P.G. Venkatakrishnan: Metal Finish., 93 (1995), 33.
- [2] M. Donten, H. Cesiulis and Z. Stojek: Electrochim. Acta, 45 (2000), 3389.
- [3] Brenner: Electrodeposition of alloys, Academic Press, New York, (1963).
- [4] O. Younes-Metzler, L. Zhu and E. Gileadi: Electrochim. Acta, 48 (2003), 2551.
- [5] E. Slavcheva, W. Mokwa and U. Schnakenberg: Electrochim. Acta, 45 (2000), 5573.

- [6] H. Iwasaki, K. Higashi and T.G. Nieh: Scripta Materialia, 50 (2004) 395.
- [7] I. Mizushima, P.T. Tang, H.N. Hansen and M.A.J. Somers: Electrochim. Acta, 50 (2005) 888.
- [8] K.R. Siraman, S.G.S. Raman and S.K. Seshardri: Mate. Sci. Eng. A, 418 (2006) 303.
- [9] N. Eliaz, T.M. Sridhar and E. Giladi: Electrochim. Acta, 50 (2005) 2893.
- [10] I. Mizushima, P.T. Tang, H.N. Hansen and M.A.J. Somers, Electrochimica Acta, 51(2006) 6128.
- [11] M.S. Chandrasekar and M. Pushpavanam, Electrochi. Acta, 53 (2008) 3313.
- [12] M.D. Obradovic, G.Z.Bosnjakov, M. Stevanovic M.D. Maksimovik and A.R. Despic: Surf. Coat. Tech., 200 (2006) 4201.
- [13] M.A.M. Ibrahim, S.S, Abdelrahim and S.D. Moussa: Appl. Electrochem., 33 (2003), 627.