

## Effect of heat treatment on the tribological performance of electroless quaternary nickel alloy

M. Zaimi<sup>1</sup>, M. N. Azran<sup>1</sup>, M. S. Kasim<sup>1</sup>, M. R. M. Kamal<sup>1</sup>, I. S. Othman<sup>1</sup>,  
N. Mohamad<sup>1</sup>, K. T. Lau<sup>1</sup>, T. D. Widodo<sup>2</sup> and A. H. Sofian<sup>3</sup>

<sup>1</sup>Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka,  
Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

\*Email: mdzaimi@utem.edu.my

Phone: +6011-14310750; Fax: +609424222

<sup>2</sup>Department of Mechanical Engineering, Brawijaya University,  
Malang, Street Mayjend Haryono 167 Malang 65145 Indonesia.

<sup>3</sup>Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang,  
26300, Gambang, Kuantan, Pahang, Malaysia.

### ABSTRACT

Heat treatment of nickel-based alloy can increase the alloy's hardness as well as the wear resistance properties. Nevertheless, the effect of heat treatment on the quaternary Ni alloy coating properties produced from electroless deposition bath is less known due to its composition uniqueness. In this study, Cu and Co are added in the Ni-P alloy matrix using hypophosphite-based Electroless Ni deposition method on mild steel substrate in acidic and alkaline bath. The coatings are then heat treated at 623 K for 3600s. The coatings hardness is measured using microVickers hardness tester and the surface morphology of the coatings are studied using both Scanning Electron Microscope (SEM) and X-ray diffraction (XRD) analysis. X-ray fluorescence (XRF) measurement is used to measure the coatings compositions. The wear behavior of the coatings is also investigated before and after heat treatment using ASTM G-99. The coatings from acidic-based bath produces Ni-Cu-Co-P alloy coating while the alkaline-based bath produces Ni-Co-Cu-P alloy based on XRF analysis. Results show that the hardness increases more than 20% for acidic-based bath and 40% for alkaline-based bath coating. The highest increment is the Ni-Co-Cu-P alloy, from 553.3 HV to 991.3 HV after heat treatment. The grain refinement of the coatings can be observed after heat treatment in SEM observation. This is proved by the XRD measurement results where polycrystalline Ni (111) formation is seen after heat treatment overshadowing the Cu (111) and Co (111) peaks. Ni phosphide species are also formed after the heat treatment. The polycrystalline Ni and the Ni phosphide formation, as well as the existence of Co and Cu in the alloy deposits reduces the wear rate significantly after the heat treatment.

**Keywords:** Electroless Ni deposition; quaternary Ni alloy; tribology; heat treatment; wear rate.

## INTRODUCTION

The autocatalytic reaction in the electroless nickel deposition provides uniform deposition on a various type and complex shape of substrate. This made electroless nickel deposition become one of the common deposition method in various field such as electronic, automotive and chemical [1]. Ni-P alloy can be formed by hypophosphite-based bath which provide superior mechanical and tribological properties compare to pure Ni itself. Moreover, the plating bath can be modified by adding other metal ions such as Cu, Co and W, to further enhanced the abovementioned properties. The improvement of the mechanical and tribological properties of the Ni alloys also makes the coating potential to be used as a cutting tool. Conventional cutting tool inserts usually uses tungsten carbide as a substrate and multiple layers Ti-based alloy deposited by pressure vapor deposition which is quite expensive in terms of coating equipment investment and, it's limitations.

Coatings for cutting tools also can be made from abrasive coatings. The formation of composite Ni coatings also can be achieved by adding abrasive particle such as SiC, which significantly increases its hardness more than 30% [2]. However, the deposition method requires surfactant to stabilize the deposition reaction, where the existence of foreign particle inside the plating bath solution will destabilize the deposition reaction itself [2]. Light metal composite such as MgSiCp reinforced aluminium alloy also has the potential to be used as abrasive materials [3]. Nevertheless, the process to form the composite requires superheating the aluminium alloy at 750°C which made the forming process expensive, dangerous and sensitive to normal atmosphere. The ternary and quaternary Ni alloy could be the cheaper alternative to coat on a less hard and cheap materials like mild steel. Balaraju et. al. proved that the as-plated Ni-Cu-P, Ni-W-P and Ni-Cu-W-P alloy have at least 5% increment of hardness compare to Ni-P alloy [4]. With heat treatment at 400°C, the hardness of all as abovementioned Ni alloy improve significantly, almost double compare to the as-plated coatings [4]. The Ni alloy coatings hardness after heat treatment is near to 900 HV, comparable to conventional high-speed steel hardness in between 740 to 870 HV for non-cobalt based and 870 to 1000 HV for cobalt based steels [5]. The heat treatment temperature for the Ni-P to gain maximum hardness is between 300°C to 400°C [6].

The wear profile of a cutting tool is highly related to temperature during turning, however, it requires special tools to measure the temperature. The estimated temperature during turning of a mild steel substrate is less than 100°C, hence, the use of Ni alloy coating for cutting is considered feasible without significant change of the coating microstructure [7]. The Ni-W-P alloy (~500 HV) deposited tungsten carbide cutting tool insert cutting performance was done by Sanusi et. al. for cutting tool recycling [8]. However, the results showed the coating is completely removed after one minute, thus, the wear analysis of the Ni alloy coating as a cutting tool in either milling or turning are not feasible for relatively soft coatings. Therefore, the method of pin-on-disk is suitable to be used to evaluate Ni alloy coatings as per ASTM G-99-05(2010) [9]. In the previous studies, the addition of Co (II) and Cu (II) ions in the hypophosphite-based electroless Ni deposition bath can produces a quaternary Ni-Cu-Co-P and Ni-Co-Cu-P alloy depending on plating bath pH [10–12]. The abovementioned coating is potential to be used as a hard coating with high corrosion resistance in neutral media. Still, the wear properties of the coatings before and after heat treatment are yet to be studied.

In this study, the quaternary Ni alloy is deposited using hypophosphite-based electroless Ni deposition bath. The Cu (II) and Co (II) ions are added in the bath. The deposition time is set to 3600 s with magnetic bar agitation at  $358 \pm 2$  K. The substrate used is mild steel, etched with diluted hydrochloric acid. The coated sample is then heat-treated at 623 K for 3600 s. Comparison is made between the non-heat-treated and heat-treated samples in terms of surface morphology, hardness and wear properties. The composition analysis is based on the previous research [10–12]. The surface morphology and crystallinity are studied using scanning electron microscope (SEM) and X-ray diffraction (XRD) measurement respectively. The hardness of the sample is measured using microVickers hardness tester. Using pin-on-disk machine, the wear properties of the coatings are studied.

## METHODS AND MATERIALS

Mild steel (20 mm × 20 mm × 0.5 mm) is used as substrates for electroless quaternary Ni alloy deposition. The mild steel substrates are polished using emery paper until #1200 to produce a mirror-like surface. The substrates are then degreased with ethanol in ultrasonic bath before rinsed with distilled water. Surface activation of the substrates is done using diluted HCl aqueous solutions (HCl, 17.5%) for 30 s. After surface activation, the substrates are rinsed heavily with distilled water again before immersing into electroless quaternary Ni alloy deposition bath with composition shown Table 1. The electroless deposition parameter is stated in Table 2. The coated substrates are rinsed with distilled water and ethanol before testing. The detailed plating procedure is shown in Figure 1. Similar mild steel samples with 50 mm diameter are also undergone similar electroless deposition procedure for pin-on-disk testing. Cu (II) and Co (II) ions are used as metal ion additives. The Cu (II) ion is used lesser than other metal ions is due to its reaction inhibitor properties as per discussed in previous study [12].

Table 1. Plating bath composition of electroless quaternary Ni alloy deposition conditions on mild steel.

Plating bath composition	Concentrations
Nickel Sulfate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ )	0.10 M
Sodium Hypophosphite Dihydrate ( $\text{NaH}_2\text{PO}_2 \cdot 2\text{H}_2\text{O}$ )	0.28 M
Trisodium Citrate Dihydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ )	0.20 M
Ammonium Sulfate ( $(\text{NH}_4)_2\text{SO}_4$ )	0.50 M
Cobalt Sulfate ( $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ )	0.01 M
Copper(II) Sulfate Pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ )	0.001 M

Table 2. Plating parameters of electroless quaternary Ni alloy deposition conditions on mild steel.

Parameters	Conditions
Plating bath pH	4.50, 4.75, 5.00, 8.50, 9.00, 9.50
Bath temperature	358 ± 2K
Deposition time	3600 s
Agitation speed (magnetic bar)	500 rpm

The compositions of the electroless quaternary Ni alloy coating is measured using XRF (X-Supreme 8000, Oxford Instruments, United Kingdom). As for annealing, using a vacuum furnace, the temperature is increased from room temperature to 623 K in 900 s and maintained 623 K for 3600 s. The temperature is then reduced to ambient normally. SEM (SEM EVO 50, Carl Zeiss SMT, United Kingdom) is used to observe the surface morphology of the coated substrates before and after annealing. The hardness and the wear behaviour of the coated substrate before and after annealing are studied using ASTM E92 MicroVickers Hardness Tester (HM-20 Series, Mitutoyo, Japan) and ASTM G-99 Pin-on-Disk Tester (TR-20LE, Bangalore) respectively. The hardness test uses 0.1 kg force producing five indentations. As for the pin-on-disk test, 10 N loading is used on 6 mm diameter CR6 steel ball to rotate at 10 mm constant track radius with speed of 200 rpm for 3600 s. The schematic diagram for pin-on-disk testing is shown in Figure 2. The calculation of the wear rate (mm<sup>3</sup>/min) is based on the Equation (1) as per ASTM G-99. The XRD analyses is done on the coated substrate to investigate the effect of annealing on the surface crystallinity using glancing angle method with CuK $\alpha$  incident angle of 0.5°, scanning from 10° to 90°.

$$\text{Wear volume, } V = 2\pi R \left[ r^2 \sin^{-1} \left( \frac{d}{2r} \right) - \left( \frac{d}{4} \right) \left( 4r^2 - d^2 \right)^{\frac{1}{2}} \right] \text{ [mm}^3\text{]} \quad (1)$$

$R$  = wear track radius [mm],  $r$  = pin end radius [mm], and  $d$  = wear track width [mm]

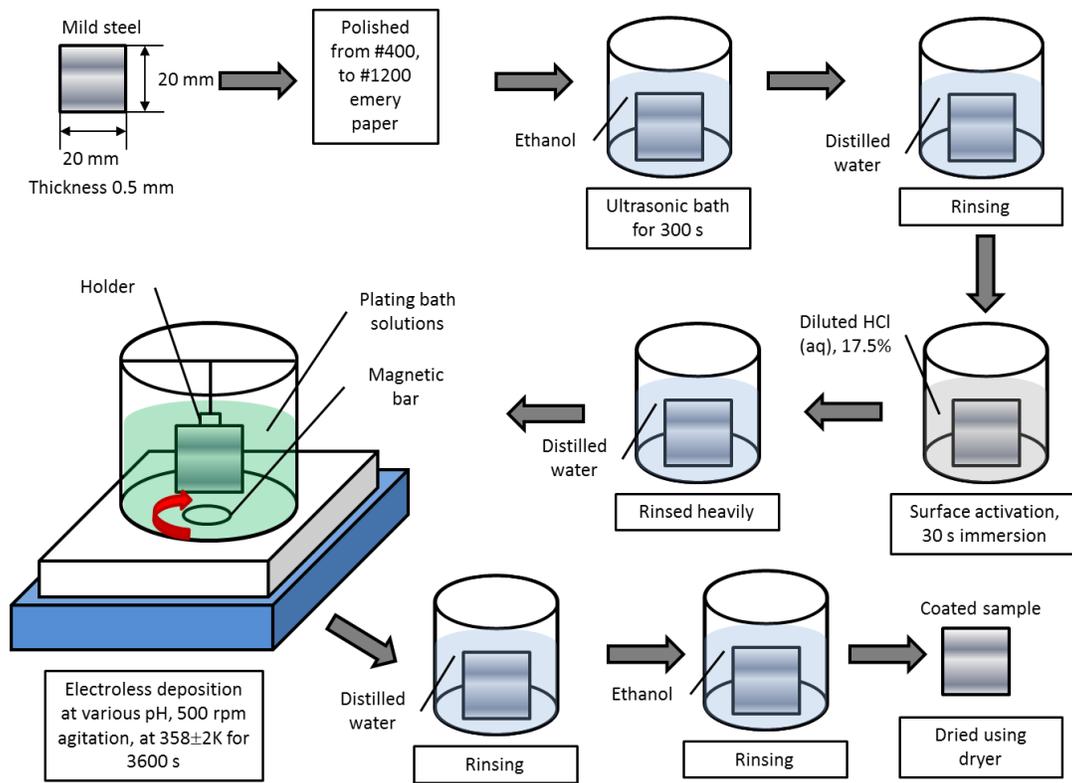


Figure 1. Electroless deposition on mild steel procedure.

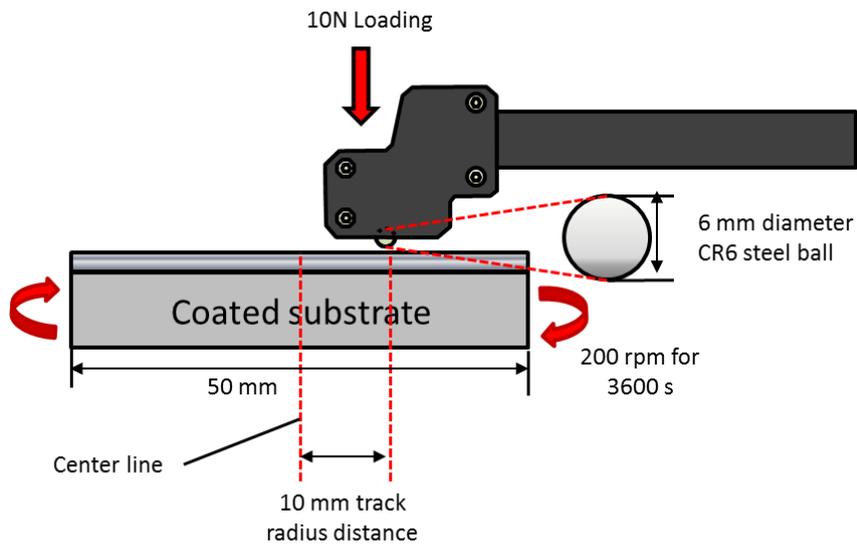


Figure 2. Pin-on-disk test.

### RESULTS AND DISCUSSIONS

The chemical composition by XRF analyses of the electroless quaternary Ni alloy coating on the mild steel is shown in Table 3. Average density of the coating is calculated based on the chemical composition. Using weight difference method, the weight difference of the substrates before and after electroless deposition are measured, divided by the surface area and average density to gain calculated thickness of the quaternary Ni alloy coating after 3600 s the electroless deposition. From Table 3, it can be observed that the deposition rate of the quaternary Ni alloy increases with the increase of plating bath pH. The Cu content is relatively higher in coatings from acidic bath compare to alkaline bath due to Cu is easily deposited in acidic condition [12]. However, Co is much deposited in alkaline bath compare to Cu since Cu (II) ions act as inhibitor for the electroless deposition in alkaline condition due to more stable complex ion in alkaline compare to acidic condition [12].

Table 3. Chemical composition by XRF and calculated thickness of electroless quaternary Ni alloy coating on mild steel from various plating bath pH [11].

Bath pH	4.50	4.75	5.00	8.50	9.00	9.50
Ni (wt%)	68.55	82.09	74.42	83.53	88.73	91.09
Co (wt%)	1.32	1.39	1.52	11.60	7.54	5.79
Cu (wt%)	27.80	14.11	22.11	3.43	2.68	2.13
P (wt%)	2.33	2.42	1.96	1.44	1.06	1.00
Average density, $\rho$ (g/cm <sup>3</sup> )	8.76	8.74	8.78	8.82	8.83	8.84
Calculated thickness ( $\mu\text{m}$ )	3.29	4.18	5.60	24.97	35.54	43.61

Table 4 exhibit the average hardness of the electroless quaternary Ni alloys before and after heat treatment. From the acidic bath, the Ni-Cu-Co-P alloy coatings on mild steel have the hardness comparable to its mild steel substrate at approximately 200 HV. This low hardness value is mainly contributed by the low coating thickness less than 6  $\mu\text{m}$ . The heat treatment of the coatings from the acidic bath increase the hardness of the coatings gradually as the increase of the coatings from plating bath pH 4.50 to pH 5.00. The alkaline bath pH in otherwise, produces coatings higher than 20  $\mu\text{m}$ . The increase of coatings thickness increases the coatings hardness, after heat treatment, the hardness increases more than 40% than the as-plated coatings. The highest of them all is the coatings from pH 9.50 with the hardness of 991.3 higher than conventional high speed steel materials and even SiC embedded Ni-P coatings [2, 5]. Hence, the coatings can be considered to be used as a cutting tool insert coatings.

Table 4: Average micro hardness (HV) for the electroless quaternary Ni alloy on mild steel.

Ni Alloy	pH	Hardness before heat treatment, HV	Hardness after heat treatment, HV
Ni-Cu-Co-P	4.50	210.7	254.6
	4.75	218.0	286.0
	5.00	233.6	325.5
	8.50	444.9	820.0
Ni-Co-Cu-P	9.00	521.1	901.5
	9.50	553.3	991.3

The Figure 3 depicts the effect of heat treatment on the microstructure of the quaternary Ni alloys coatings. From the figure, the surface refinement of the coatings can be seen after heat treatment. The blackish lines on the surface of the coatings before heat treatment is alcohol residue after cleaning that appears during SEM observations. Other than that, all the coatings have uniform surface, absence of pit and without nodular-like structure as in Ni-P alloy [13].

Before the quaternary Ni alloy coatings undergo heat treatment, the XRD measurement results of all coatings show low intensity and broad peaks, resembling an amorphous-like structure in between 40° to 50° (Figure 4). Unlike electrodeposition method, the autocatalytic reaction of the electroless Ni alloy deposition produces uniform deposits on the substrate surface, and the Co, Cu and P elements dispersed almost uniform distribution across the surface. This element distribution can be confirm using energy dispersive X-ray (EDX) mapping analysis as shown in electroless Ni-Cu-Zn-P [14,15] and Ni-Cu-W-P alloy [4] deposits.

	<b>BEFORE ANNEALING</b>	<b>AFTER ANNEALING</b>
<b>Ni-Cu-Co-P pH 4.50</b>	<p>Before Heat Treatment</p> <p>2µm</p>	<p>After Heat Treatment</p> <p>2µm</p>
<b>Ni-Cu-Co-P pH 4.75</b>	<p>2µm</p>	<p>2µm</p>
<b>Ni-Cu-Co-P pH 5.00</b>	<p>2µm</p>	<p>2µm</p>
<b>Ni-Co-Cu-P pH 8.50</b>	<p>2µm</p>	<p>2µm</p>
<b>Ni-Co-Cu-P pH 9.00</b>	<p>2µm</p>	<p>2µm</p>
<b>Ni-Co-Cu-P pH 9.50</b>	<p>2µm</p>	<p>2µm</p>

Figure 3. SEM micrograph of the electroless quaternary Ni alloy from various bath pH before and after annealing [20].

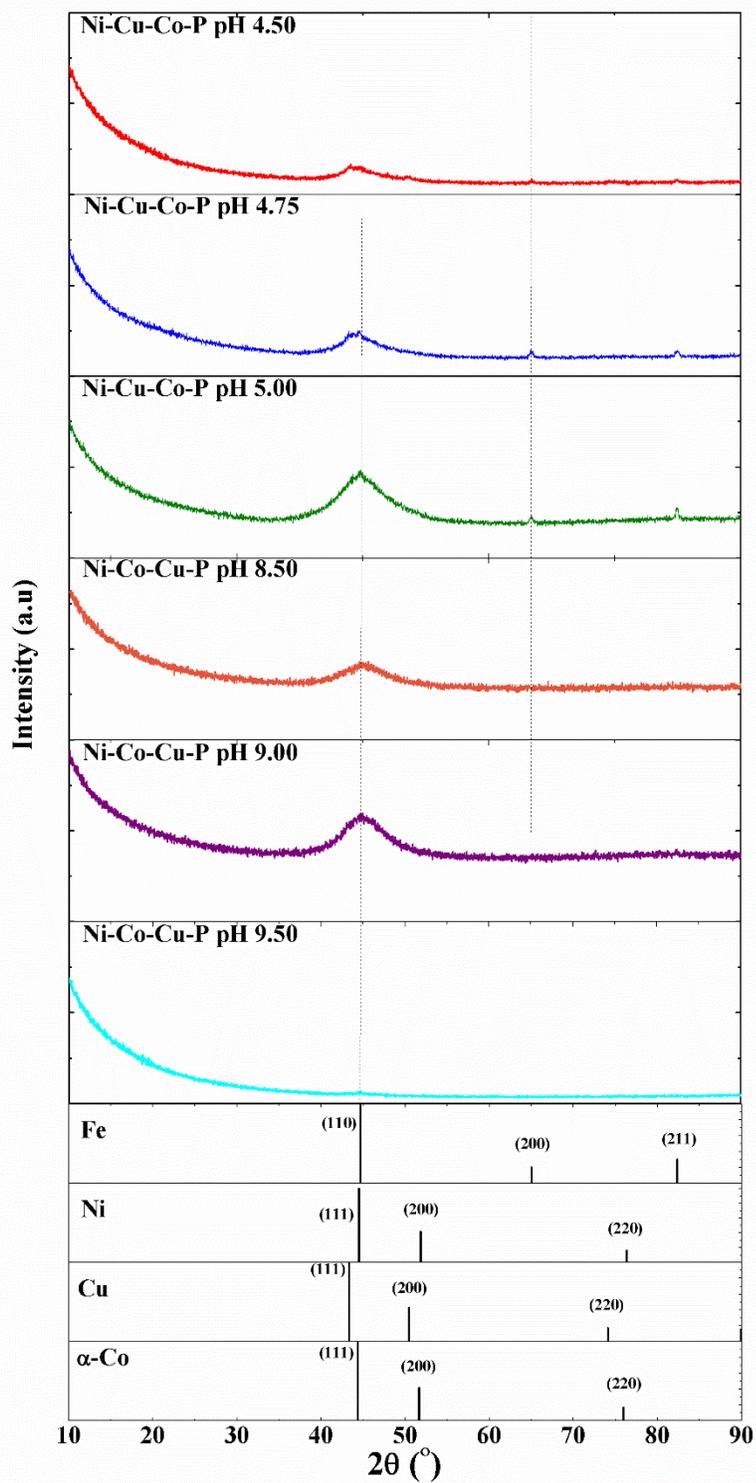


Figure 4. XRD analysis of electroless quaternary Ni alloy deposits before heat treatment.

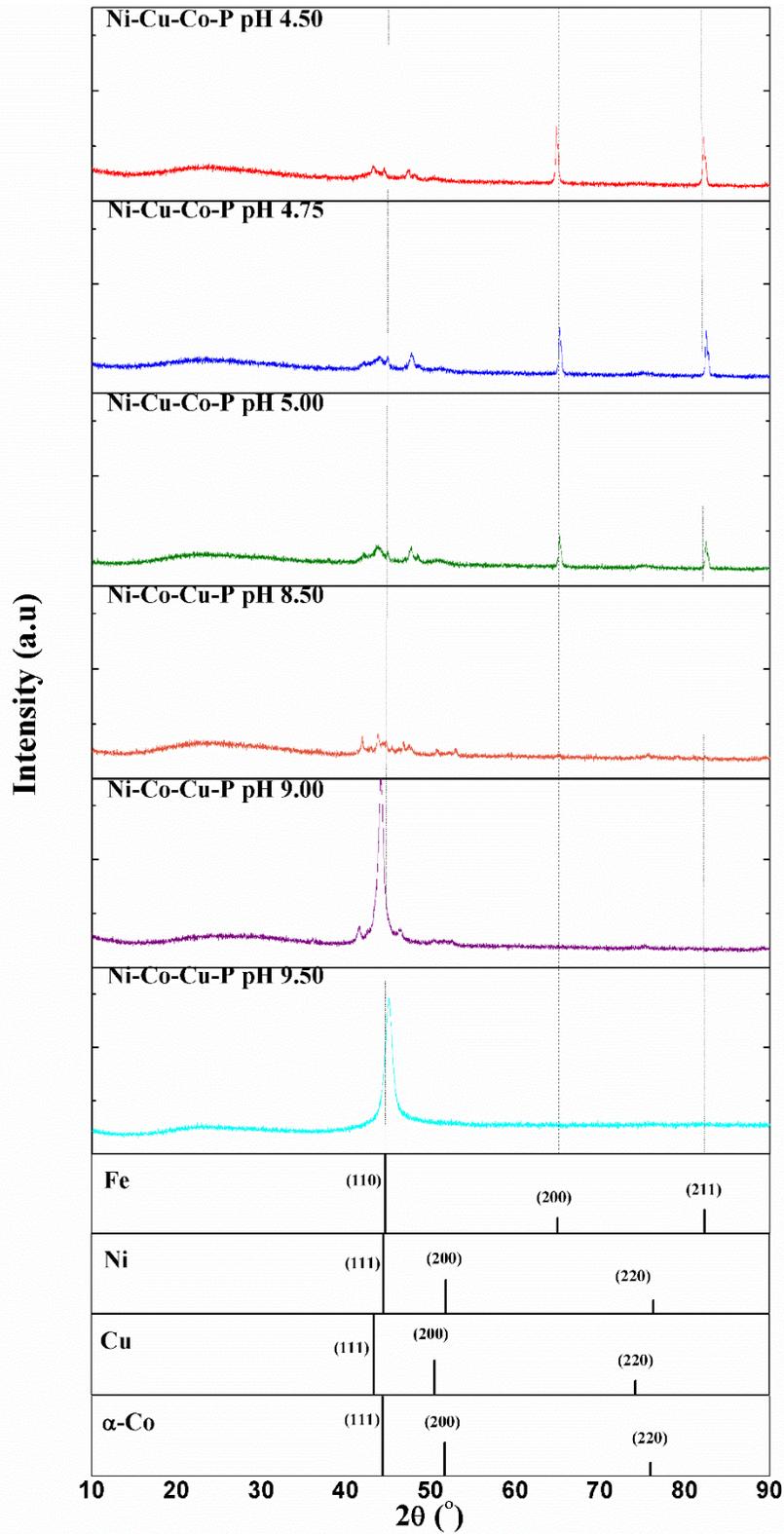


Figure 5. XRD analysis of electroless quaternary Ni alloy deposits after heat treatment.

As the Ni quaternary Ni alloy heated at 623 K, the elements in the coatings began to vibrate and segregate, producing higher crystallinity structure compare to non-treated coatings as shown in Figure 5. Since Ni content is the major content in all quaternary Ni alloy coatings, it can be suspected that during heat treatment at 623K, the originally amorphous-like structure of the quaternary Ni alloy surface as the XRD results in Figure 4, changed into polycrystalline Ni (111) near  $44.48^\circ$  (standard pattern ICDD/PDF:01-071-4654) [16]. Nevertheless, the quaternary Ni alloy coatings the acidic bath has lower than  $6\ \mu\text{m}$  thickness, the Fe (111) peaks from the mild steel substrate are detected at  $44.67^\circ$  merging with Ni (111) peaks, as well as the other two peaks of Fe (200) and Fe (211) at  $65.02^\circ$  and  $82.33^\circ$  respectively (ICDD/PDF:00-006-0696). Moreover, the peaks before and after the Ni (111) peak can be considered as Ni phosphide species,  $\text{Ni}_3\text{P}$ ,  $\text{Ni}_2\text{P}$  and  $\text{Ni}_{12}\text{P}_5$  alloy [17]. The peaks of the Ni phosphide species are being considered instead of copper phosphide and cobalt phosphide species due to the phosphorous is much co-deposited near Ni atom and Ni is the majority element in the coating itself [18, 19]. The quaternary Ni alloy from the alkaline bath exhibits the similar Ni phosphide species peaks, except the peaks are gradually disappear when the deposit thickness becomes higher than  $25\ \mu\text{m}$ . At plating bath pH 9.50, the high thickness of the electroless quaternary Ni alloy deposits cause more polycrystalline Ni (111) to be formed. The Cu (111) and Co (111) are less to be observed due to its  $2\theta$  value is very near to Ni (111) peak, thus, overshadowed by the Ni (111) peak.

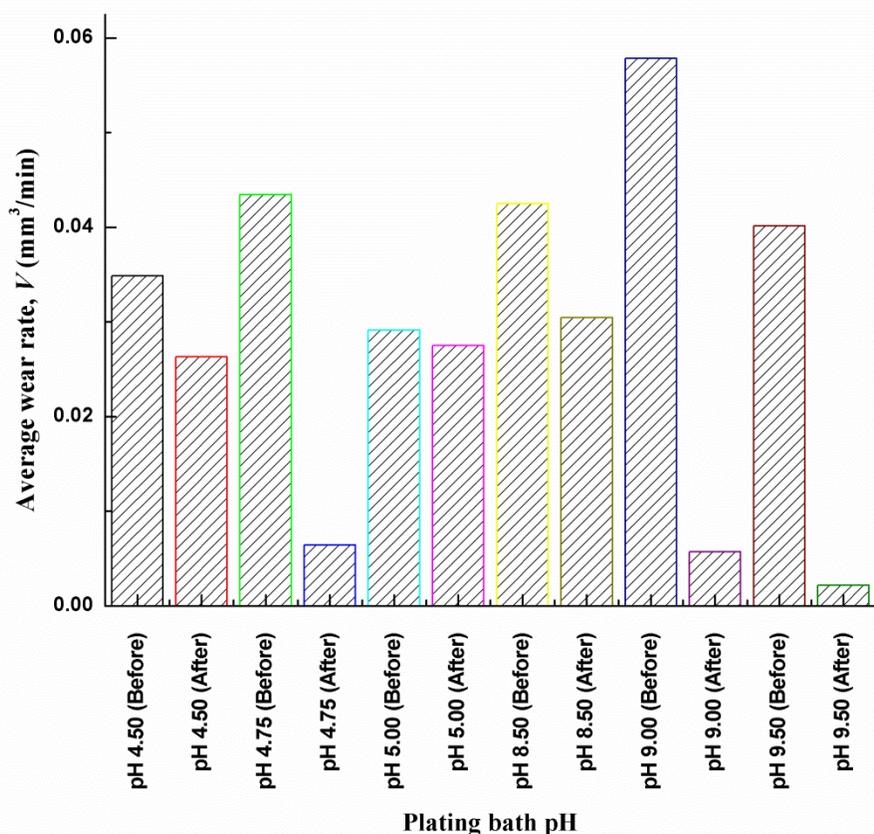


Figure 6. Average wear rate of electroless quaternary Ni alloy coatings before and after heat treatment.

As in Figure 6, the wear rate of the as-plated and the heat treated electroless quaternary Ni alloy deposits are calculated using Equation (1) after pin-on-disk measurement. The hardness of the electroless quaternary Ni alloy can be related with its wear rate. The as-plated alloy deposits in respective of its plating bath pH is less harder than the heat-treated alloy deposits, hence, the wear rate of the alloy is reducing drastically, especially the deposits from plating bath pH 9.00 and pH 9.50. It also can be suggested the thicker deposits, and the higher Ni content in the alloy has the best improvement after heat treatment. Hence, the formation of the polycrystalline Ni (111) and Ni phosphide species as well as the Cu and Co addition can be the contributing factor in the improvement of wear rate. The alloy deposits from pH 9.50 bath shows promising wear resistance performance comparable to Ni-P/SiC alloy composite [2].

Figure 7 and 8 are showing the coefficient friction of the electroless quaternary Ni alloy deposit surface before and after heat treatment. The as-plated quaternary Ni alloy deposits from the acidic bath shows lower coefficient friction compare to the alkaline bath (Figure 7). The higher coefficient friction of the alloy deposits from the alkaline bath is due to its higher thickness and hardness of the the deposits. After the heat treatment, the coefficient friction of the electroless quaternary Ni alloy with high Ni content in respective acidic and alkaline bath have the lowest value. Although in general, the coefficient friction of electroless Ni alloy is expected lower than  $0.50 \mu$ , the surface polishing during the initial process and the surface flatness may has influenced the coefficient friction, thus, higher value can be observed. Nevertheless, the coefficient friction between the samples before and after heat treatment still in between  $0.50$  to  $1.00 \mu$ , except the range between maximum and minimum value of the coefficient friction are significantly reduced after heat treatment. Originally, the electroless deposition provides a very uniform coating with uniform element distribution. The coefficient friction is expected to reduce approximately in between  $0.02$  to  $0.03$  after heat treated at  $573$  K for W-Co alloy [21], and in between  $0.10$  to  $0.20 \mu$  for Ni-W-P alloy [22]. Hence, the formation of polycrystalline Ni (111) formation after heat treatment at  $623$  K has very slight improvement of coefficient of the quaternary Ni alloy deposits surface.

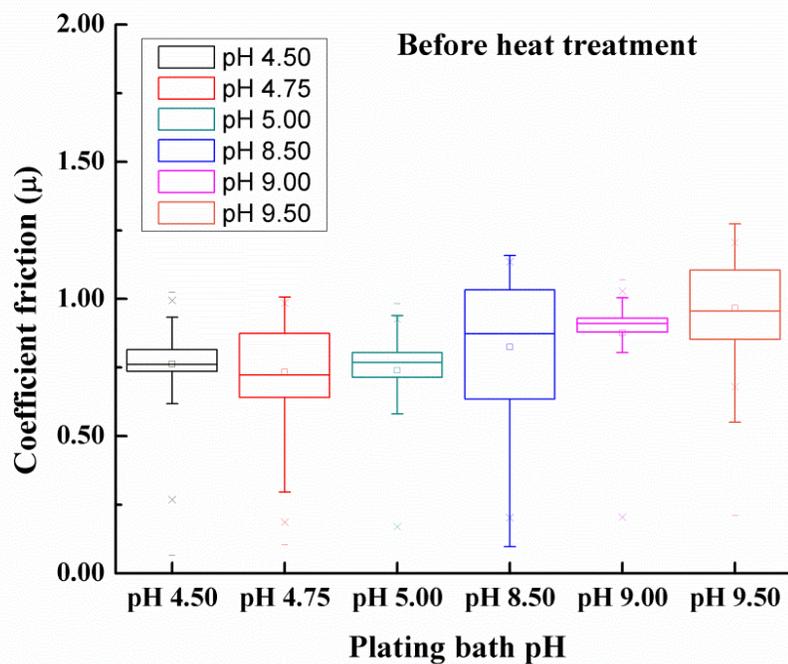


Figure 7. Coefficient friction of the electroless quaternary Ni alloy surface before heat treatment.

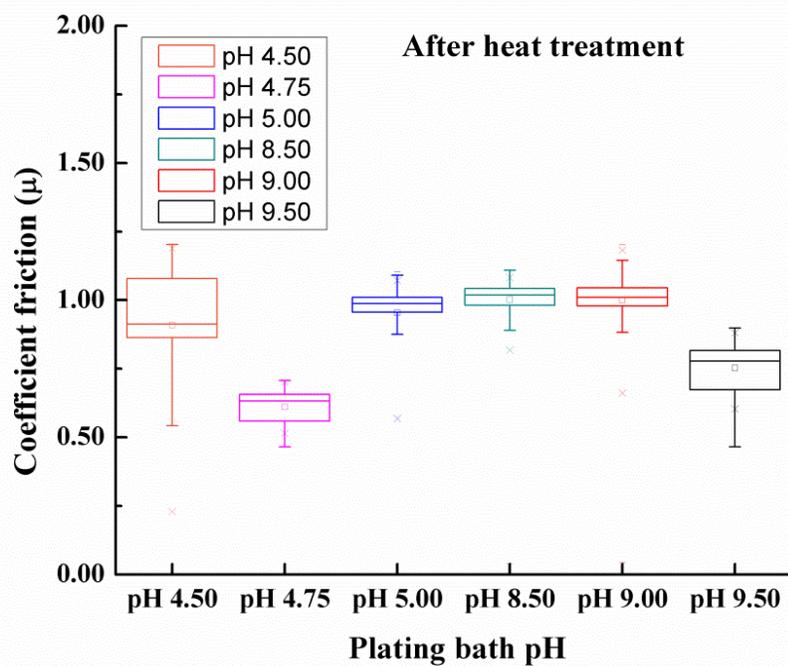


Figure 8. Coefficient friction of the electroless quaternary Ni alloy surface after heat treatment.

## **CONCLUSIONS**

The acidic bath produces a quaternary Ni-Cu-Co-P alloy deposits, while the alkaline bath produces Ni-Co-Cu-P alloy deposits based on the XRF measurement results. The surface micro hardness of the as-plated electroless quaternary Ni alloy deposit increases gradually as the plating bath pH increases. The heat treatment of the quaternary Ni alloy improves the micro hardness significantly, at least 20% improvement for the alloy deposits from the acidic bath and more than 40% improvement of the alloy deposits from the alkaline bath. The micro hardness of the quaternary Ni alloy deposits from pH 9.50 is 991.3 HV, can be considered better than conventional high-speed steel micro hardness. The grain refinement was observed in electroless quaternary Ni alloy deposits after heat treatment at 623 K for 3600 s. The as-plated alloy deposits shows a broad and low intensity peaks near Ni (111) peak. The heat treated alloy deposits exhibits sharper polycrystalline Ni (111) peak along with Ni phosphide species peaks. The Cu (111) and Co (111) peaks are overshadowed by the majority content of Ni (111) peaks. The wear resistance of the electroless quaternary Ni alloy deposits improves significantly after heat treatment, especially the alloy deposits from pH 9.00 and 9.50 bath. Hence, the polycrystalline Ni and Ni phosphide species formation, as well as the Co and Cu content, have significant effect on the wear rate reduction. The coefficient friction of the alloy deposits is less affected by the heat treatment, but more affected by the Ni content, polycrystalline Ni of the alloy deposits. From these results, it can be suggested that the quaternary Ni alloy deposits can be considered as a cutting tool hard coating.

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