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Novel investigation on tribological properties of Ni–P–Ag–Al_2O_3 hybrid nanocomposite coatings

S. Alirezaei [a,*], S.M. Monirvaghefi [a], A. Saatchi [a], M. Ürgen [b], K. Kazmanlı [b]

[a] Department of Materials Engineering, Isfahan University of Technology, 8415683111 Isfahan, Iran
[b] Department of Metallurgical and Materials Engineering, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

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ABSTRACT

In this research, silver and alumina particles were co-deposited within Ni–P matrix to obtain Ni–P–Ag–Al_2O_3 hybrid coating. The structure of coatings was analyzed by X-ray diffraction and the tribological properties of deposits were evaluated by pin on disc tribometer. 3D optical profiler and scanning electron microscopy were used to study wear rate and worn surfaces. The results showed that Ni–P–Ag and Ni–P–Ag–Al_2O_3 coatings have the self-lubrication property and maximum hardness (~1310 HV) and wear resistance were obtained for Ni–P–Al_2O_3 coating. Also, Ni–P–Ag–Al_2O_3 hybrid nanocomposite coating had higher wear resistance than Ni–P and Ni–P–Ag coatings. Moreover, the best conditions was achieved for heat treated hybrid coating in the concentration of 30 mg/L silver and 150 mg/L alumina in the plating solution.

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1. Introduction

Electroless composite coatings have been widely used in sliding contact conditions over the past decades [1–4]. They have been categorized into lubricant and wear resistant coatings with two kinds of soft and hard particles [5–8]. In some applications, lubrication and wear resistance are required simultaneously and in recent years, attention has turned to hybrid composite coatings [9–11]. Not only, hybrid coatings can improve the coefficient of friction, but also they can increase the wear resistance. Several methods have been developed to produce hybrid coatings. Gui and Kang studied the structure of aluminum hybrid composite coatings including SiC and graphite particles by plasma spray [12]. Mulligan evaluated the self-lubricant characteristics of CrN–Ag hybrid coatings produced by magnetron sputtering [13]. Drees et al. discussed the hybrid processes as short case studies [14]. Wu found that co-deposition of PTFE-SiC or C (Graphite)–SiC particles within Ni–P coating can modify lubrication and wear resistance of composite coatings [15,16]. Silver as a new and significant lubricant material is a good candidate for lubrication at low and high temperatures [13]. Although, a few works have been done on electroless hybrid coatings [15–18], but there is no information on Ni–P–Ag–Al_2O_3 hybrid nanocomposite coating. The aim of this research is to investigate the structure, mechanical and tribological properties of Ni–P composite coatings with silver and/or alumina particles by electroless plating.

2. Experimental procedure

The substrate was prepared from AISI 1045 steel as a disc shape with 4 cm in diameter and 5 mm in thickness. Before plating, surface preparation of the samples was performed by grinding up to 600-grade SiC paper, degreasing in 10 wt% NaOH alkaline bath and acetone with intermediate deionized water rinsing process, respectively. A commercial Ni–P electroless solution (MacDermid NiKlad ELV 811) was used containing 6 g/L nickel (as sulfate solution), 30 g/L NaH_2PO_2 and suitable amounts of additive and stabilizer. The plating bath was agitated at stirring rate of 350 rpm, using a magnetic stirrer and a PTFE coated magnet with 80 mm length and 10 mm in diameter. The electroless deposition process was carried out in a 1000 mL double wall beaker connected to a thermostated circulating water system and the deposition conditions were presented in Table 1. Before addition of silver particles (2–7 μm size) and alumina nanoparticles (average size 80 nm) into the plating solution, the particles were well dispersed in some electroless solution with suitable amounts of surfactant (Cetyl Trimethyl Ammonium Bromide (CTAB)) and an ultrasound treatment of one hour. Co-deposition of particles was done for 2 h. Heat treatment of coatings was carried out isothermally at 400 °C for one hour. The hardness of the coatings was measured by Leitz Wetzlar microhardness tester with a Vickers diamond indenter under a 50 g applied load. X-ray diffraction (XRD) analysis was performed using Cu K_α radiation in 40 kV to study the

* Corresponding author. Tel.: +98 312 5243532; fax: +98 311 3912752.
E-mail addresses: shahram79ir@yahoo.com, s.alirezaei@ma.iut.ac.ir (S. Alirezaei).

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Table 1
Deposition conditions for electroless plating.

Type of coating	Ni–P	Ni–P–Ag	Ni–P–Al_2O_3	Ni–P–Ag–Al_2O_3
pH	4.8 ± 0.1	4.8 ± 0.1	4.8 ± 0.1	4.8 ± 0.1
T (°C)	90 ± 2	90 ± 2	90 ± 2	90 ± 2
Nickel sulfate (g/L)	6	6	6	6
Sodium hypophosphite (g/L)	30	30	30	30
Al_2O_3 content in electroless solution (mg/L)	–	–	0–500	150
Ag content in electroless solution (mg/L)	–	0–100	–	30

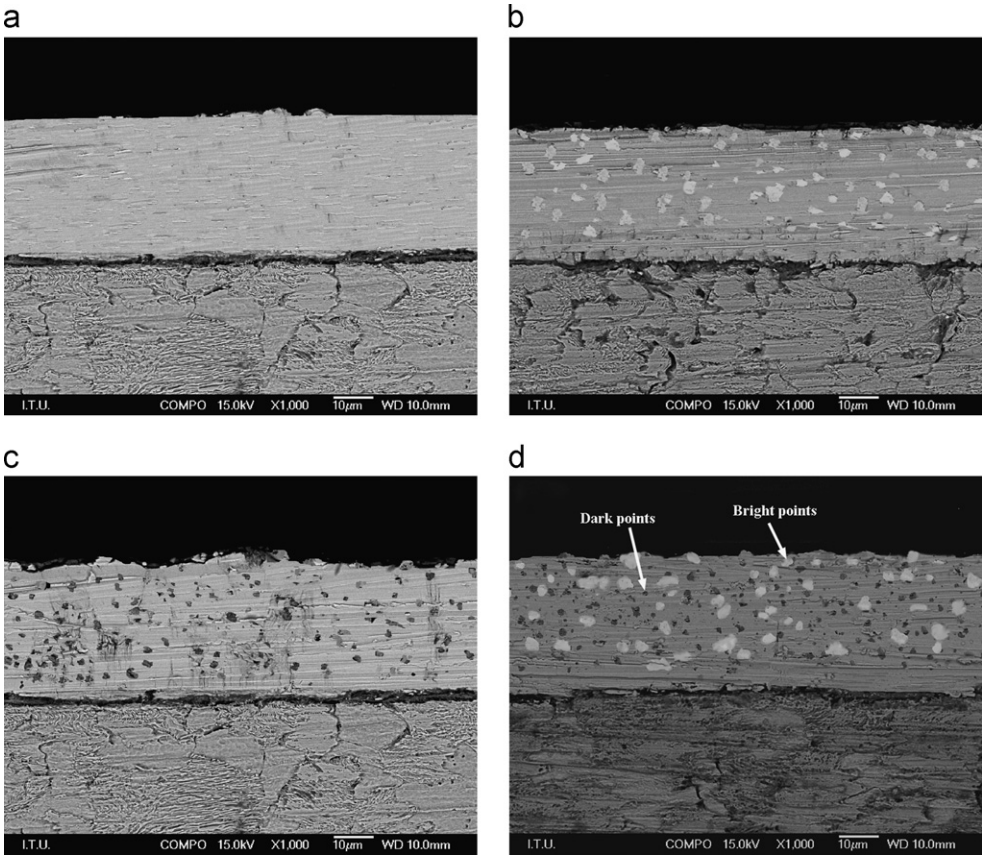

Fig. 1. SEM cross-section images of (a) Ni–P, (b) Ni–P–Ag (30 mg/L), (c) Ni–P–Al_2O_3 (150 mg/L) and (d) Ni–P–Ag (30 mg/L)–Al_2O_3 (150 mg/L) coatings.

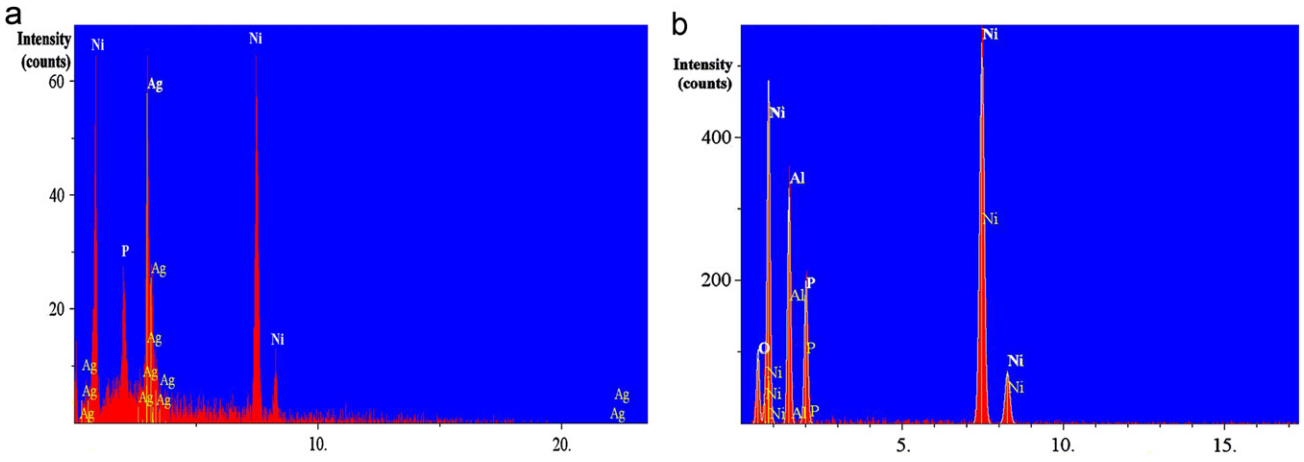

Fig. 2. EDS analysis of (a) bright and (b) dark points whereas indicated by arrow in Fig. 1.

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structure of Ni–P composite deposits. The percentage of silver and alumina particles in the coatings was also determined by using electron micrographs and image analysis. Pin-on-disc wear tests were implemented by using CSM standard tribometer at normal load of 10 N and sliding speed of 0.05 m/s to evaluate the tribological properties of the coatings. The wear tests were done against AISI 52100 high-carbon chromium steel pins (10 mm diameter and hardness of 62 HRC) without any lubrication at room temperature and in an air with 40% relative humidity. Wyko 1100NT 3D optical profiler was used to evaluate wear tracks and volume loss of the coatings. The cross-section of composite coatings and worn surfaces were analyzed by Scanning Electron Microscopy (JEOL JSM-5410 SEM and JEOL JSM-7000F FESEM) equipped with EDS analysis.

3. Results and discussion

3.1. Structure of the coatings

As shown in Fig. 1, silver and alumina particles were well entrapped in Ni–P metallic matrix. Particles present in the electroless solution can easily move to the surface of substrate during mechanical agitation of the solution and then they are co-deposited within Ni–P matrix to form a composite coating. As shown in Fig. 2, EDS analysis from bright and dark points (as indicated by arrow in Fig. 1) confirmed the presence of silver and alumina particles in the composite coatings, respectively. The percentage of particles in Ni–P–Al_2O_3 and Ni–P–Ag coatings depends on the particle content in plating bath as shown in Fig. 3. There are two different optimum values in the curves showing the maximum content of co-deposited particles in the matrix. The optimum value for alumina was 150 mg/L, higher than that for silver particles that was 30 mg/L. These values were also used for the deposition of Ni–P–Ag–Al_2O_3 hybrid nanocomposite coatings. Although the size of alumina particles is so smaller than silver particles, but silver micro-sized powder has much more electric surface charge rather than inert aluminum oxide nano-sized particles in electroless solution. So, the reduction of positive nickel ions can rapidly occur on the surface of silver particles during co-deposition process. The type, size, shape and zeta potential of the particles can have the great influences on the entrapment of the particles in the coating. Surfactants can also improve the electric surface charge and uniform dispersion of the particles in the composite coating without agglomeration [19,20]. Although CTAB as a cationic surfactant can easily disperse silver and alumina particles in the plating bath, but a few agglomerated alumina nanoparticles can be observed in Ni–P–Al_2O_3 and Ni–P–Ag–Al_2O_3 coatings. Balaraju believes that the agitation of plating solution is a key factor in determining particle incorporation [5]. While the fluid flow of electroless solution can be kept in laminar–turbulent transition region, the particles can be attracted to the substrate and high incorporation of the particles in Ni–P matrix can occur during the growth of electroless deposits [21]. This mechanism has also been mentioned by Abdel Hamid [22]. The co-deposition process has also been related to Langmuir physical adsorption and Temkin chemical adsorption as reported by Balaraju et al. [23]. In addition, the density of powder materials can affect the kinetic energy of particles in the solution and the mechanical interlocking of particles into the metallic matrix. From this viewpoint, silver particles can be embedded easier than alumina particles into the composite coating because of higher electric surface charge and higher density of silver particles. On the other hand, if the concentration of particles in the plating bath exceeds the optimum values, the number of collisions between the particles increases and subsequently, lower quantities of particles can be incorporated in the coating. According to the mentioned parameters including type, size, shape, density and concentration of particles, the formation mechanism of a hybrid coating with soft and hard particles has more complexity. It seems that total concentration of particles and competition between soft and hard particles for the entrapment are main factors to affect the quantity of co-deposited particles. Spot EDS analysis of composite coatings shows that Ni–P matrix can be classified as high

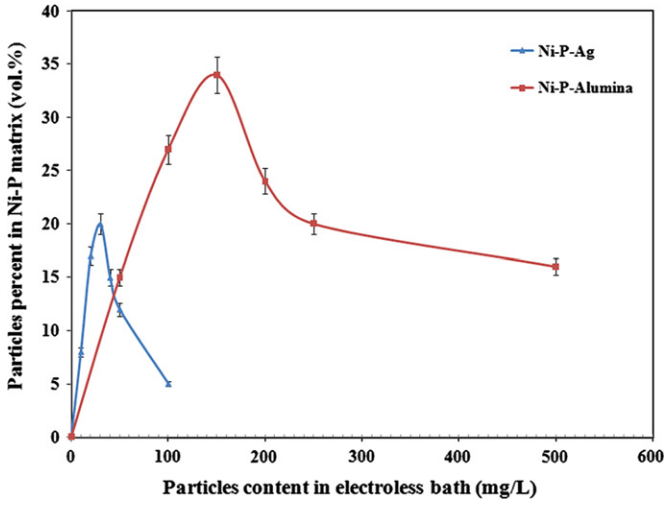

Fig. 3. The variation of embedded particles vs silver and alumina concentrations in electroless bath.

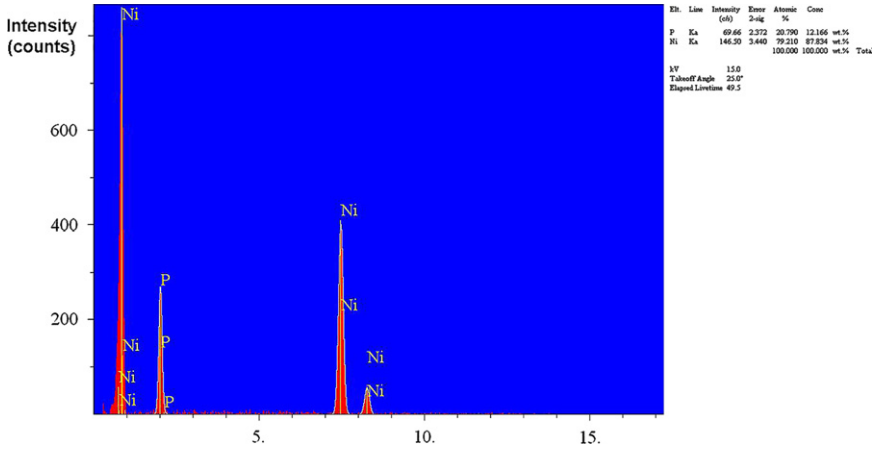

Fig. 4. Spot EDS analysis of Ni–P matrix coating.

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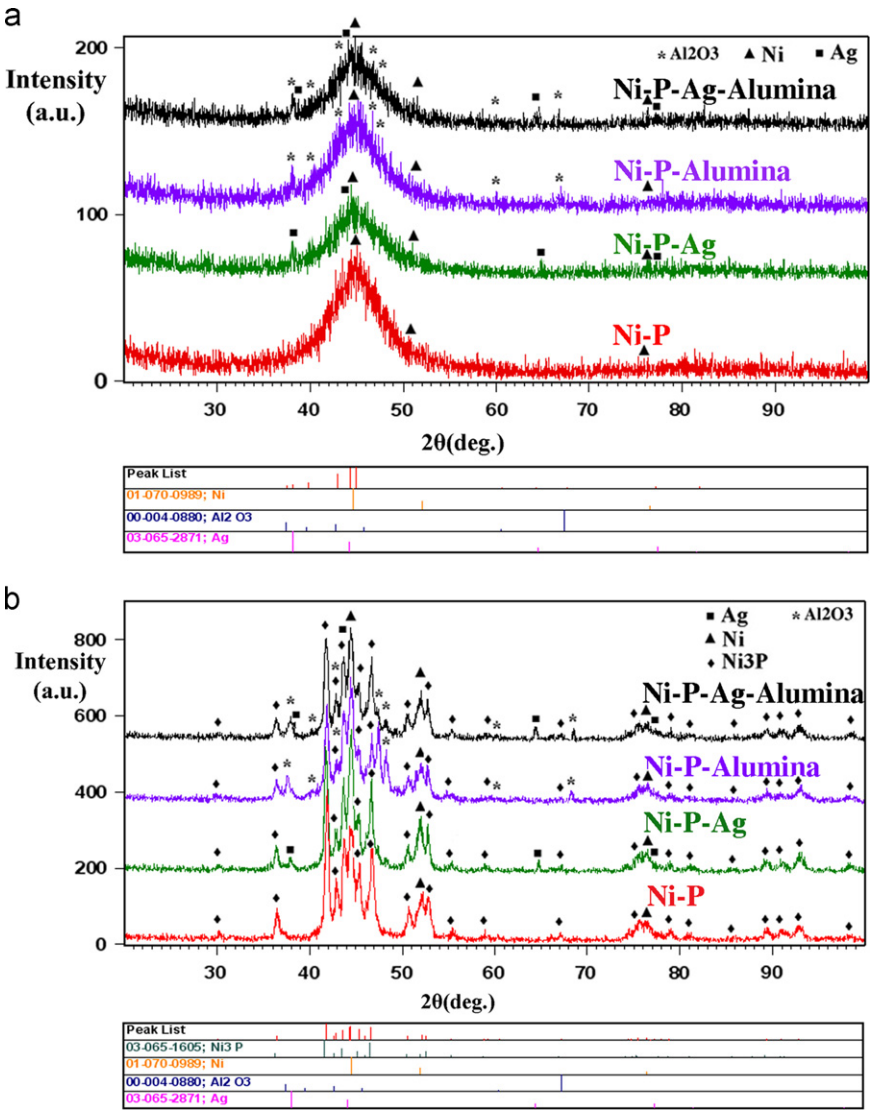

Fig. 5. XRD patterns of (a) as-plated and (b) heat treated Ni–P coatings with or without Ag (30 mg/L) and/or Al_2O_3 (150 mg/L) particles.

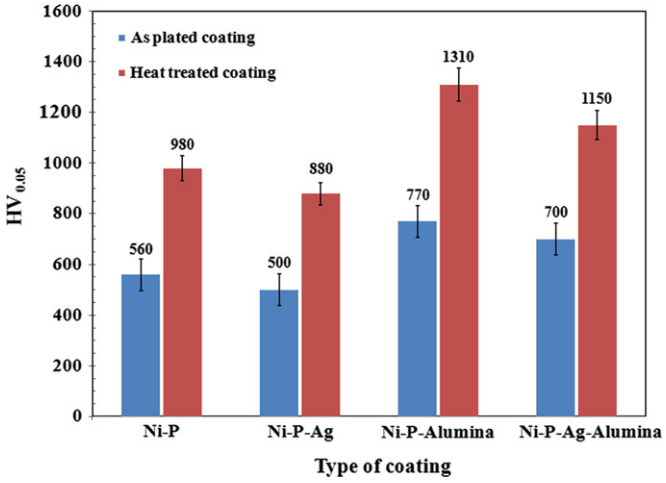

Fig. 6. The microhardness of as plated and heat treated composite coatings.

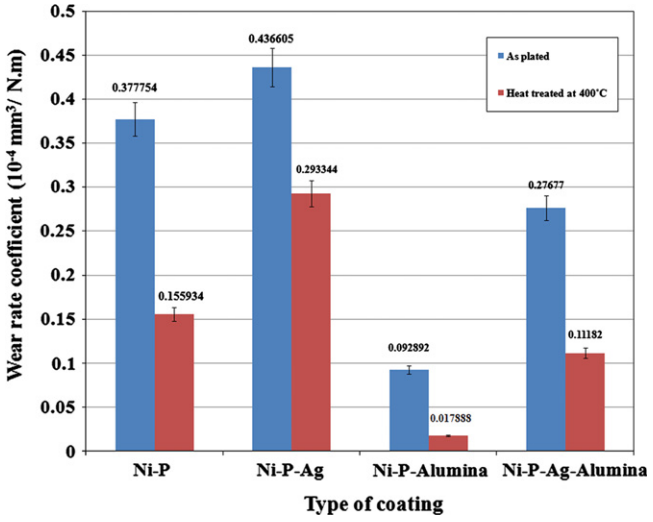

Fig. 7. The wear resistance of Ni–P coatings with or without of silver and/or alumina particles.

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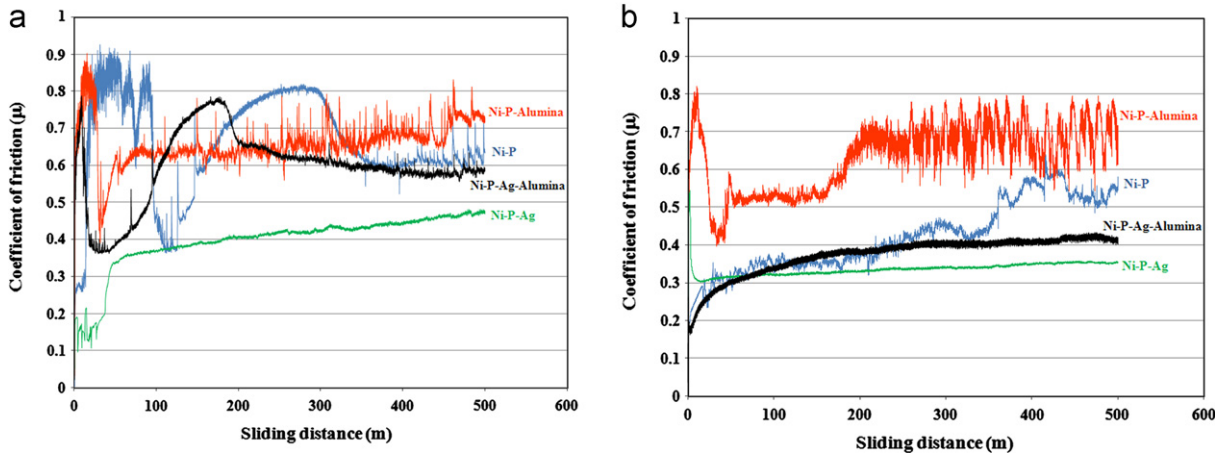

Fig. 8. The variation of friction coefficient of (a) as plated and (b) heat treated of Ni–P based composite coatings containing silver and/or alumina particles.

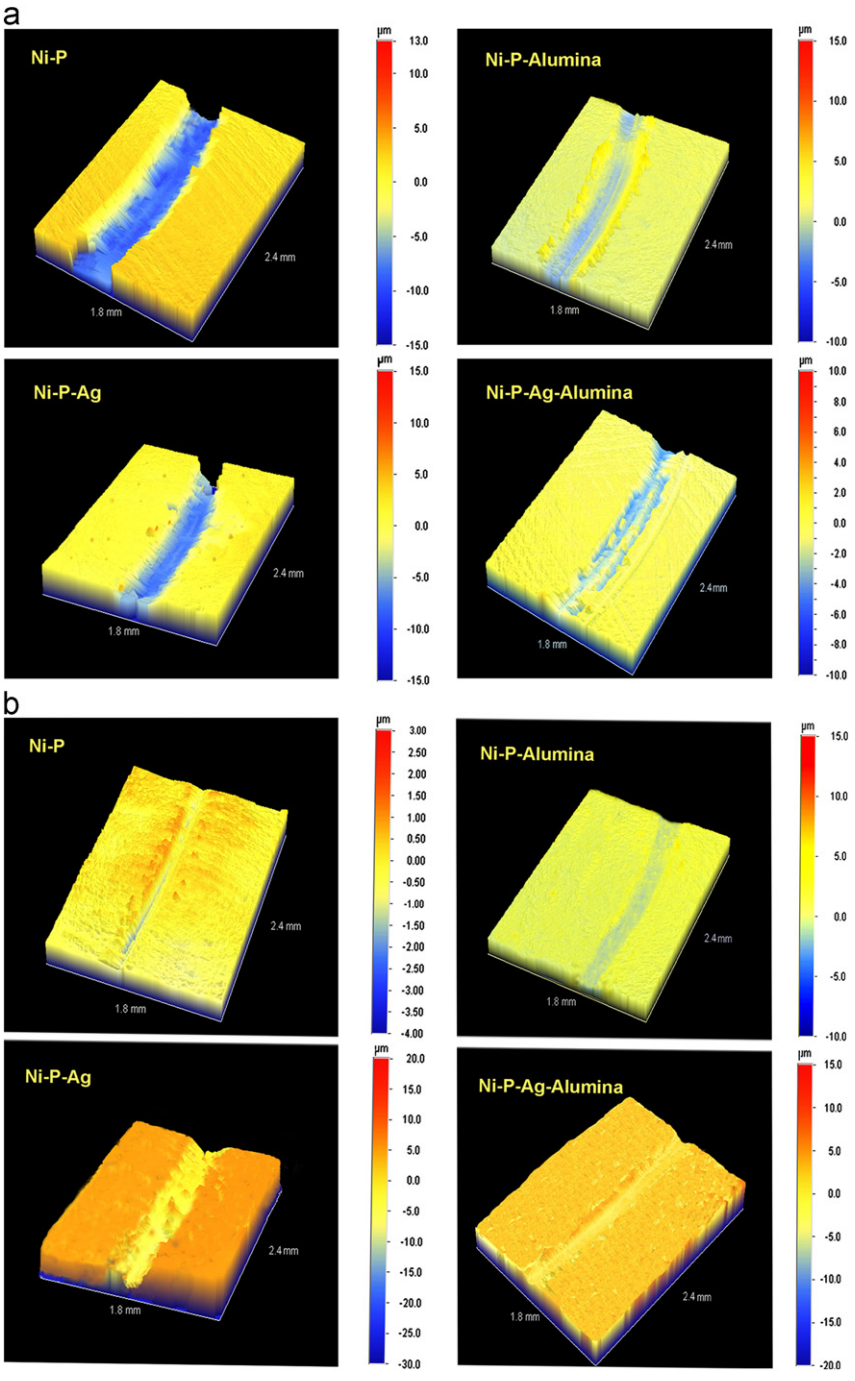

Fig. 9. 3D optical images of worn tracks of (a) as plated and (b) heat treated coatings.

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phosphorus electroless coating (Fig. 4). As shown in Fig. 5, a broad peak is observed in XRD pattern at ~45° confirming amorphous structure of as plated composite coatings. Heat treatment of composite coatings at 400 °C gives the phase transformation in Ni–P matrix and changing the structure of coatings from amorphous to nanocrystalline structure. It was found that there are only Ni, Ni_3P, Ag and Al_2O_3 phases in XRD patterns of heat treated composite coatings. Formation of Ni_3P intermetallic compounds from supersaturated nickel phase was predictable by heat treatment at 400 °C as reported in other heat treated electroless composite coatings [3,19,24].

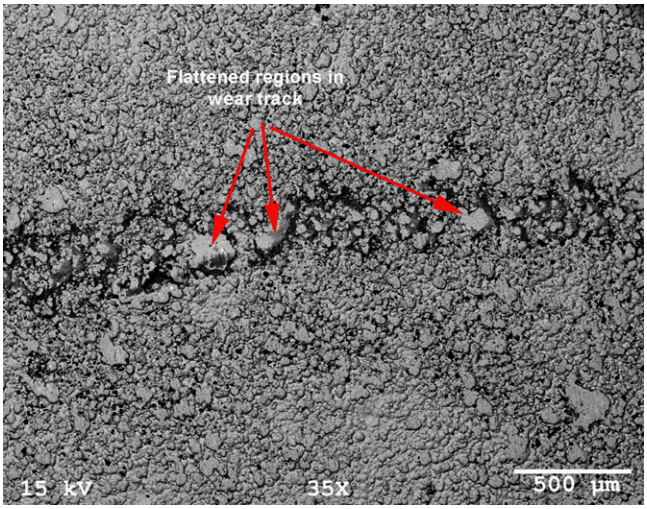

Fig. 10. SEM image of worn surface in Ni–P–Ag–Al_2O_3 hybrid nanocomposite coating.

3.2. Hardness and wear resistance

A comparison between the hardness of Ni–P, Ni–P–Ag, Ni–P–Al_2O_3 and Ni–P–Ag–Al_2O_3 coatings in as plated and heat treated conditions has been reported in Fig. 6. It demonstrates that as plated Ni–P–Ag coating has the least hardness value (~500 HV) and heat treated Ni–P–Al_2O_3 coating has the highest hardness (~1310 HV). According to the rule of mixtures in composite materials [25] and low hardness of silver particles, it was predictable that the lowest hardness is related to as plated Ni–P–Ag coating. In some cases such as Ma et al., it has been reported the increment in hardness by increasing in silver nanoparticles [26,27]. It seems that silver nano-sized particles may show this behavior. There are several reports to present the reduction of hardness with the existence of soft particles in Ni–P composite coatings [5,18,28]. Silver micron-sized particles can decrease the hardness of Ni–P–Ag composite coatings, but this reduction is not too high. On the other hand, attachment of hard alumina particles into the metallic matrix can enhance the hardness via dispersion hardening mechanism. Heat treatment can cause the formation of Ni_3P secondary phases in Ni–P matrix and subsequently, the hardness increases by precipitation

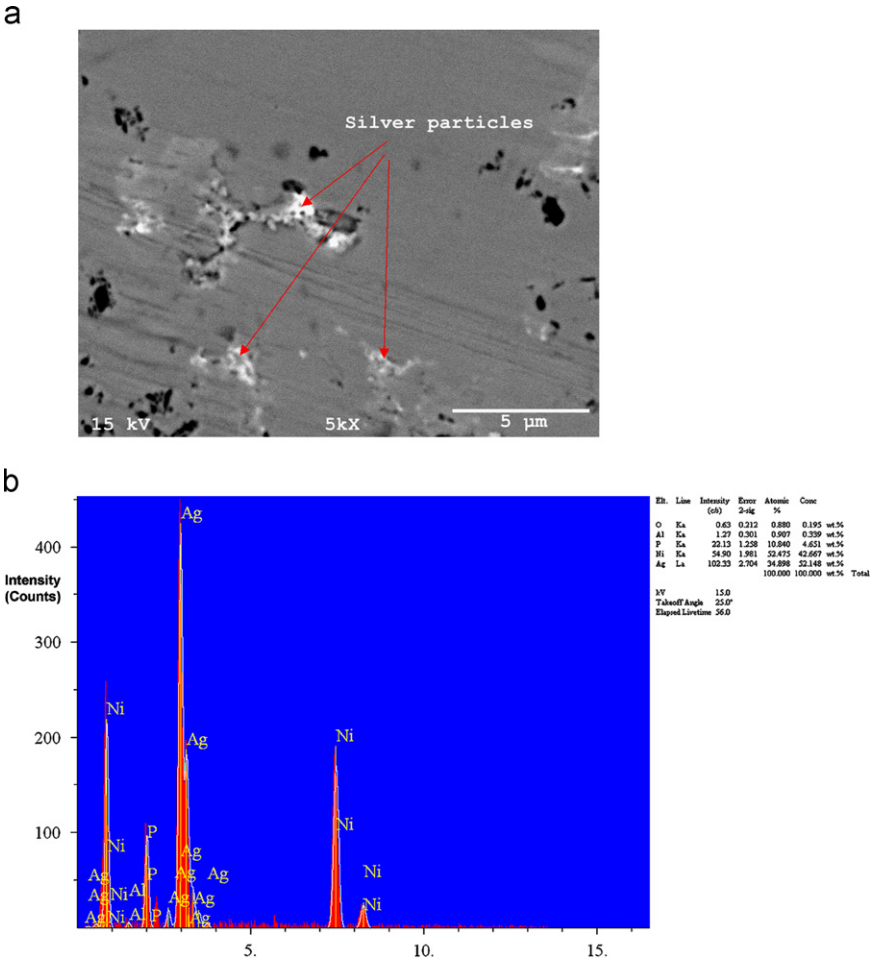

Fig. 11. (a) Electron micrograph and (b) spot EDS analysis from flattened regions of worn surface in Ni–P–Ag–Al_2O_3 coating.

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hardening mechanism. Thus, heat treated Ni–P–Al_2O_3 coating will have the highest hardness value among all the above mentioned coatings. As shown in Fig. 7, the maximum wear resistance has also been achieved in heat treated Ni–P–Al_2O_3 composite coating. Similar to hardness results, Ni–P–Ag–Al_2O_3 hybrid nanocomposite coating had a lower wear resistance than Ni–P and Ni–P–Al_2O_3 coatings, but higher wear resistance than that of Ni–P–Ag coating. In addition, the friction coefficient of Ni–P–Ag–Al_2O_3 hybrid deposit was lower than Ni–P and Ni–P–Al_2O_3 coatings, but it was more than Ni–P–Ag coating (Fig. 8). This twofold behavior has also been observed in Ni–P–Gr–SiC and Ni–P–PTFE–SiC hybrid composite coatings [16,17]. Slight fluctuations in the curve of friction coefficient imply the effective lubrication behavior of Ni–P–Ag–Al_2O_3 hybrid coating. The evaluation of worn surfaces confirmed a relatively lower deterioration of hybrid coatings after sliding (Fig. 9). Similar variations of hardness and wear resistance indicate the activation of abrasive wear mechanism in heat treated coatings. It has been reported that abrasion wear is a dominant wear mechanism in degradation of Ni–P–Al_2O_3 coatings [29–31]. SEM micrographs of worn surfaces demonstrated flattening of some regions in Ni–P–Ag–Al_2O_3 hybrid coating (Fig. 10). Further investigations by EDS analysis and higher magnification images confirmed the existence of silver in these regions (Fig. 11). Silver can spread on wear scare during sliding and then lubrication can improve. Moreover, aluminum oxide nanoparticles cause a reduction of plastic deformation in the coating and consequently, the wear resistance of Ni–P–Ag–Al_2O_3 hybrid coating increases.

4. Conclusions

In this study, Ni–P–Ag–Al_2O_3 hybrid nanocomposite coatings were prepared by electroless plating. The optimum values for incorporation of silver and/or alumina particles in Ni–P composite coatings were 30 mg/L and 150 mg/L. The maximum hardness (about 1310 HV) and wear resistance were obtained for heat treated Ni–P–Al_2O_3 coatings and the lowest coefficient of friction was achieved for heat treated Ni–P–Ag deposits. The wear resistance of Ni–P–Ag–Al_2O_3 hybrid nanocomposite coating was so higher than Ni–P and Ni–P–Ag coatings, but lower than that of Ni–P–Al_2O_3 coating. Conversely, the friction coefficient of hybrid coating was lower than Ni–P coating with or without alumina nanoparticles. Flattening and extension of silver particles in the sliding path can cause the self-lubrication property of hybrid coating. Furthermore, heat treatment at 400 °C could also enhance the hardness and wear resistance via precipitation hardening mechanism by the formation of Ni_3P secondary phases.

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