Novel investigation on nanostructure Ni–P–Ag composite coatings

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ABSTRACT

In this research, silver particles with different contents were co-deposited within Ni–P coating on AISI 1045 steel samples by electroless plating process and then Ni–P–Ag composite coatings were heat treated at 400 °C for 1 h. The concentration of silver particles in Ni–P metallic matrix was determined by using scanning electron microscopy (SEM) and image analysis software. The phase transformation of deposits was analyzed by X-ray diffraction (XRD) and differential thermal analysis (DTA). Also, the mechanical properties of coatings were evaluated by microhardness and indentation tests. The results showed that the content of silver particles and heat treatment have the great effects on hardness and mechanical properties of Ni–P–Ag electroless composite coatings. Also, heat treatment can lead only to phase transformation in metallic matrix of nanostucture Ni–P–Ag composite coatings.

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1. Introduction

Electroless plating process is a common method for the formation of the composite coating by which different particles could be uniformly dispersed in a metal matrix. In the past decades, various studies have been performed on the synthesis and characterization of electroless composite coatings [1–6]. Although, electroless Ni–P coatings have developed for different applications such as corrosion and wear resistance, lubricity, etc. [7–9], but electroless composite coatings have better capabilities than usual electroless coatings for sliding contact conditions [10,11]. Not only Ni_3P phases by precipitation hardening mechanism increase the hardness and wear resistance of composite coatings, but also dispersion hardening mechanism by hard particles can improve tribological properties. The physical and mechanical properties of particles, hydrodynamic conditions of plating bath such as temperature, pH, stirring rate and also selected strategy for composite plating are the main factors to achieve more uniform coatings [12,13]. Also, cationic or anionic surfactants have great influences on the uniformity of particles in the composite coatings [14,15]. At recent years, most of investigations have been focused on hard and soft inert particles such as ceramics and polymers [16–20], but there is a little information about composite coatings including lubricant metallic particles [21–23]. Silver as a special lubricant material at low and high temperature sliding contact applications have been paid more attention in recent years [24–30]. In the present study, co-deposition of

silver particles, mechanical properties and phase transformation of nanostructure Ni–P–Ag electroless composite coatings have been investigated.

2. Experimental details

The substrate materials were selected from AISI 1045 steel as the disc shape samples with 4 cm in diameter and 5 mm in thickness. Surface preparation of the samples was performed using 600-grade SiC paper, degreasing in an alkaline bath and acetone with intermediate water rinses, respectively. The commercial Ni–P electroless solution (MacDermid NiKlad ELV 811) containing 6 g/l nickel (as sulfate solution), 30 g/l NaH_2PO_2 and suitable amounts of additive and stabilizer was used. The stirring rate of plating bath was about 350 rpm, using a magnetic agitation system and a PTFE coated magnet with 8 cm length and 10 mm in diameter. The plating process was carried out in a 1000 ml double wall beaker attached to a thermostated circulating water bath whereas experimental conditions are presented in Table 1. Before entering silver powders (2–7 μm in size) into the plating bath, the particles were well dispersed in some electroless solution within suitable amounts of wetting agent (Cetyl Trimethyl Ammonium Bromide (CTAB)) by using an ultrasound for 1 h. Co-deposition of silver particles with concentration of 10–100 mg/l in plating bath was done for 2 h. Isothermal heat treatment was carried out at 400 °C for 1 h to improve the mechanical properties of nanostructure Ni–P–Ag composite coatings. The hardness of the coatings was measured using Leitz Wetzlar microhardness tester with a Vickers diamond indenter under a 50 g load. Also indentation test was done by using Fischer indentation equipment to evaluate the mechanical

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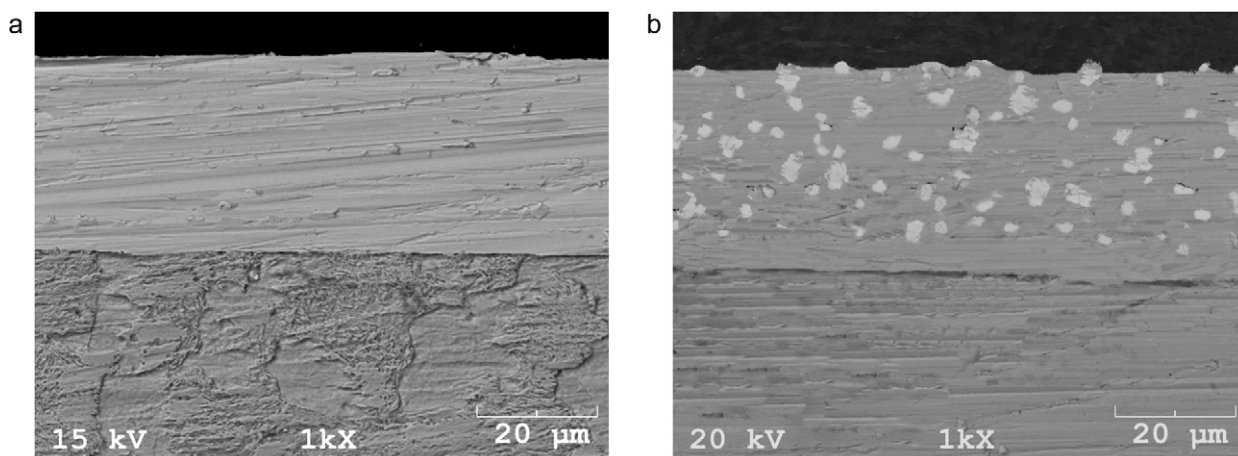E-mail address: shahram79ir@yahoo.com (S. Alirezaei).

Fig. 1. Cross-section SEM micrographs of Ni–P and Ni–P–Ag coatings.

properties of the deposits under a 100 mN constant force. X-ray diffraction (XRD) analysis was performed using Cu Kα radiation in 40 kV to study the structure of Ni–P–Ag composite coatings. Differential thermal analysis (DTA) measurements using Perkin Elmer Diamond DTA equipment were carried out to confirm the XRD results. DTA measurements were carried out on the same samples with initial weight of 5 mg and the tests were done in alumina crucibles with a heating rate of 10 °C/min from room temperature to 700 °C in a flowing (100 ml/min) argon gas media. The content of silver particles in coating was also determined by using an image analysis software and Scanning Electron Microscopy (JEOL JSM-5410 SEM) micrographs.

3. Results and discussion

3.1. Structural characterization of the coatings

As shown in Fig. 1, silver particles have been well dispersed in Ni–P matrix as shiny zones in SEM micrographs. Silver particles have high atomic number and high electrical conductivity and the surface electric charge of the particles in the plating bath is so greater than other non metallic particles such as ceramics and polymers. They can attract nickel ions rapidly and subsequently, reduction of nickel can be occurred. Some surfactants such as CTAB can decrease and change the surface electric charge of the particles and also they can influence on uniformity of particles distribution in metal matrix. Fig. 2 indicates that there is an optimum value for co-deposition of particles within Ni–P coating. This trend has also been observed in other electroless composite coatings [29]. When concentration of silver in plating bath increases to 30 mg/l, the particles content in matrix of coating will be reached to a maximum value of 20 vol.%. XRD analysis showed a wide and broad peak in as plated deposits. It can be an evident of an amorphous structure in Ni–P–Ag composite coatings (Fig. 3). Also, spot EDS analysis from Ni–P matrix in composite coating indicated the high value of phosphorus content (more than 10 wt.%) (Fig. 4). So, this coating can be categorized as high phosphorus electroless coating and then, it is evident to obtain an amorphous structure in as plated conditions [30,31]. Heat treatment of the Ni–P–Ag composite coatings led only
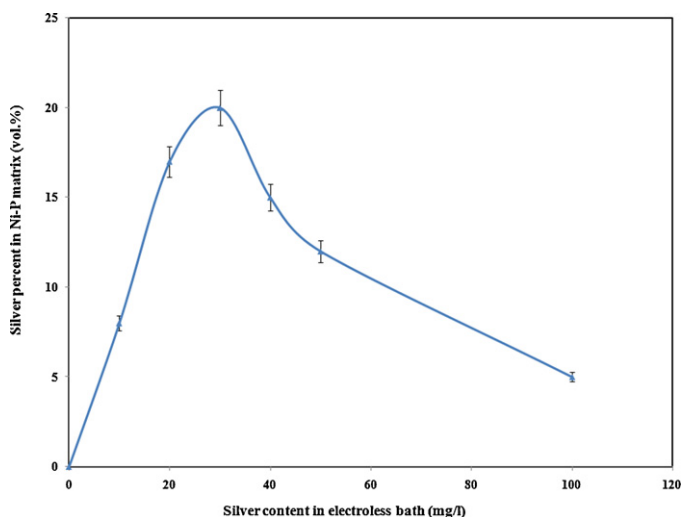

Fig. 2. The volumetric percent of co-deposited particles within Ni–P matrix at different concentrations of Ag particles in electroless bath.

to phase transformation in Ni–P matrix and changing the structure of coatings from amorphous to nanocrystalline structure. DTA data also confirmed that there was one phase transformation at about 350 °C (Fig. 5). Although, Ag–P binary phase diagram shows thermodynamically that there are some intermetallic compounds such
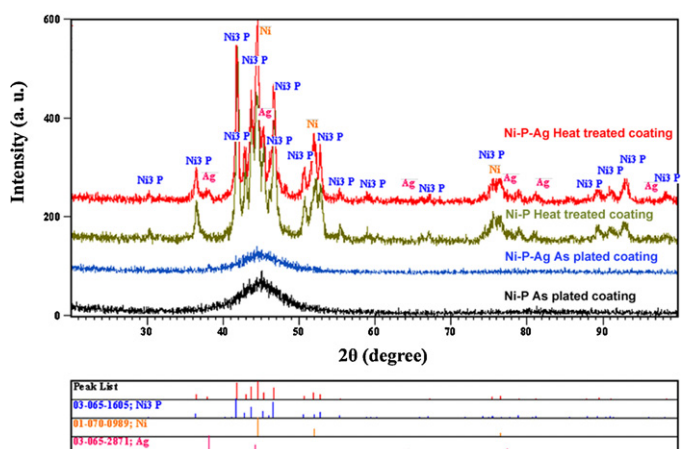
Table 1
Deposition conditions for electroless coating.

pH	4.8 ± 0.1
T	90 ± 2 °C
Stirring rate	350 rpm
Ag content in bath	0–100 mg/l

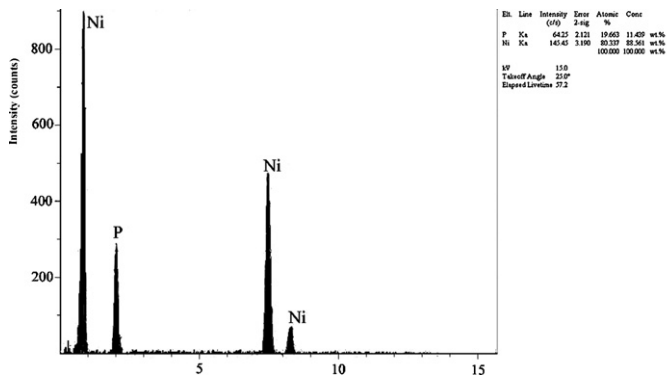Fig. 3. XRD patterns of as plated and heat treated Ni–P and Ni–P–Ag coatings.

Fig. 4. EDS analysis of Ni–P matrix in Ni–P–Ag composite coating.

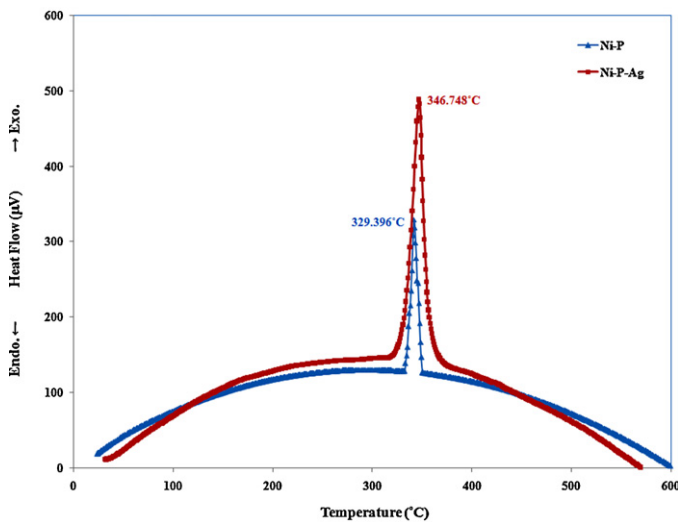**Fig. 5.** DTA curves of Ni–P and Ni–P–Ag coatings.

as AgP$_2$ (Fig. 6) [32], but there were only Ni, Ni$_3$P and Ag phases in XRD pattern of heat treated Ni–P–Ag composite coatings. From the viewpoint of thermodynamics, Gibbs free energy value for the formation of Ni$_3$P is more negative than AgP$_2$ [33], so it seems that Ni$_3$P is more stable and there will be no chance for the formation of AgP$_2$ intermetallic compound.
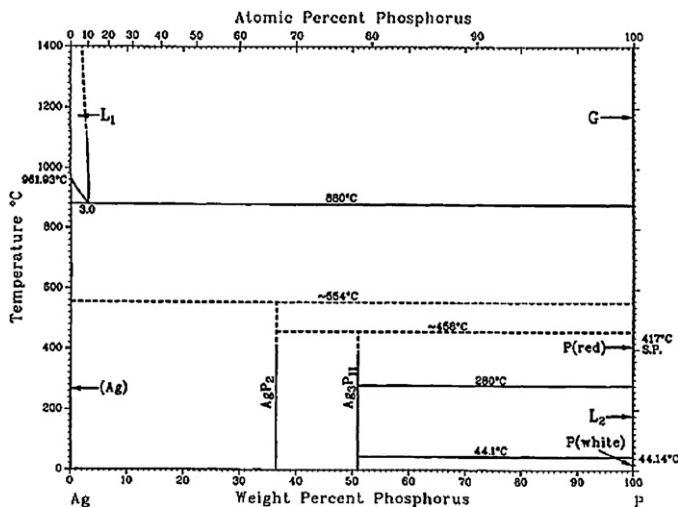

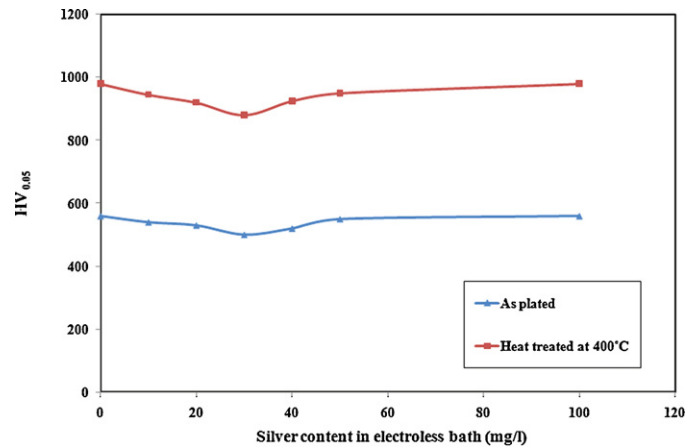**Fig. 6.** Binary phase diagram of Ag–P [32].

Fig. 7. Microhardness values of as plated and heat treated Ni–P and Ni–P–Ag coatings.

3.2. Mechanical properties

Microhardness data of Ni–P–Ag coatings demonstrated that by increasing of silver particles in composite coating, the hardness decreases (Fig. 7). Low hardness of soft Ag particles rather than Ni–P matrix in both as plated and heat treated conditions could be the main reason for the reduction of hardness in composite deposits. While phase transformation occurs in Ni–P metallic matrix by heat treatment, Ni$_3$P phases nucleate and grow and so, the matrix will be harder by precipitation hardening mechanism. On the other hand, when the silver concentration in the composite coating increases, according to the rule of mixtures in composite materials [34], the total hardness of Ni–P–Ag composite coating will decrease. This trend has been observed in other composite coatings with soft particles such as MoS$_2$ and PTFE [35,36]. Indentation results were the same as microhardness data (Fig. 8). In some cases such as Ma et al., it has been reported the increment in hardness by increasing in silver nanoparticles [21]. It seems that silver nano size particles may show this behavior. There are several reports that the existence of soft particles in Ni–P coating lead to decrease the hardness of composite coatings [24,29,36]. Silver micron size particles may affect
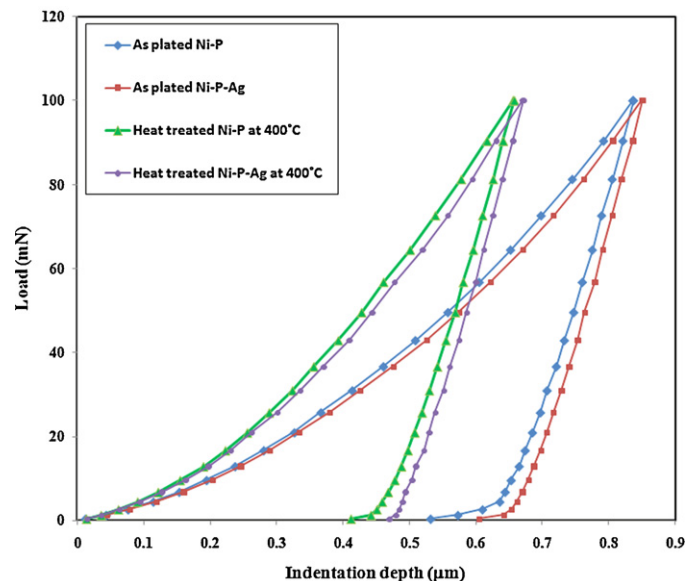

Fig. 8. Load–displacement indentation curves for Ni–P and Ni–P–Ag coatings.

the reduction of hardness of Ni–P–Ag composite coatings but this reduction is not too high.

4. Conclusions

Silver particles can be easily embedded in Ni–P electroless matrix by using CTAB cationic surfactant to create Ni–P–Ag electroless composite coatings. The maximum silver content in Ni–P–Ag composite coating obtained about 20 vol.% in the concentration of 30 mg/l particles in plating solution bath. Heat treatment leads to phase transformation from amorphous to nanocrystalline structure and formation of Ni_3P phases from supersaturated nickel lattice, as well as the existence of Ni and Ag phases. Also, No evidence was obtained for the formation of any other phases. Microhardness of Ni–P–Ag composite coatings decreased by the increment in silver content in the composite coating. Not only, hardness of Ni–P–Ag composite coatings influenced by silver particles content, but also heat treatment at 400 °C could increase the hardness of Ni–P–Ag electroless composite coatings due to the phase transformation in Ni–P metallic matrix.

Acknowledgements