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Studying the Effect of the Concentration of PTFE Nanoparticles on the Tribological Behavior of Ni-P-PTFE Composite Coatings

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Abstract

In the past 30 years, electroless nickel (EN) plating has grown to such proportions that these coatings and their applications are now found underground, in outer space, and in a myriad of areas in between. Moreover, in order to further improve the mechanical and tribological properties of the nickel-phosphorous (Ni-P) coatings, Ni-P/PTFE composite coatings can be obtained, which provides even greater friction behavior and lubricity than the one naturally occurring in the nickel-phosphorous alloy deposit. In this paper, The Ni-P-PTFE coating was deposited on mild carbon steel surface via electroless deposition process. The friction behavior and wear mechanisms of Ni-P-PTFE nanocomposite coating were studied at different concentrations of PTFE. Frictional behavior was examined using a pin on disk wear test method. Surface morphology and worn surface was evaluated using field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS) analysis. The results showed that the incorporation of PTFE nanoparticles can reduce the wear rate of Ni-P coating from 33.07×10^{-6} mm^3/Nm to 12.46×10^{-6} mm^3/Nm for the Ni-P PTFE containing 10 g/l PTFE and decrease the friction coefficient from 0.64 to 0.2. Thus the tribological behavior of Ni-P coating is much improved in the presence of PTFE nanoparticles and 10 g/l is the optimized concentration of PTFE in the electroless bath.

Keywords: Composite Coating, Nickel Electroless, Nano-PTFE, Wear, Friction Coefficient

1. Introduction

Electroless nickel-phosphorous coatings are widely used in many of industrial applications for the unique properties, including high wear resistance, high corrosion resistance, high hardness and toughness properties, and good lubrication (Grosjean, et al. 2001; Wang, et al. 2008). By combining nanosized particles as a reinforcing phase into Ni–P matrix to form functional nanometer composite coating via electroless co-deposition process, the properties of Ni–P coating can be greatly improved and some new features are entirely added to the coating performance (Tian, et al. 2010). For this purpose, different nanoparticles such as nano-SiC, WC, Al_2O_3, TiO_2, and ZnO as hard particles and PTFE, MoS_2, and graphite as lubricating particles are added to the coatings (Tian, et al 2010; Dong, et

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al. 2009). Among these nanoparticles, PTFE has attracted tremendous interest due to its properties such as a low friction coefficient, being non-stick, dry lubricity, anti-fouling properties, and very good wear and corrosion resistance (Ger, et al. 2002; Zhao, et al. 2002, Ramalhoa, et al. 2005). Ni-P-PTFE can be used as an anti-stick coating. Condensed fluorine atoms in the outer layer of these molecules are the main cause of the physical properties of PTFE such as low surface energy and very low friction coefficient (Ramalhoa, et al. 2005). By co-deposition of PTFE in the matrix of the coating, the properties of Ni-P and PTFE can be used simultaneously. PTFE has excellent anti-stick properties due to the low surface energy of PTFE polymer (18.6 mN/m). Therefore, another potential application of Ni-P-PTFE is the reduction of fouling. For example, the formation of limestone on the surfaces of heat exchangers or heat elements is a serious problem. The sediments are one of the natural problems with the design and operation of various production equipment and processes. Unwanted sediments can affect the equipment in two ways:

- The low thermal conductivity of the formed sediments can increase resistance to heat transfer, and therefore reduces the efficiency of heat exchangers.
- Fouling on the ducts reduces the cross-sectional area of the fluid path and increases the friction, which causes an increase in pressure drop across the system.

Any methods for reducing these sediments can decrease the costs. It is found that the adhesion of the formed sediments on the surfaces with low surface energy is poor. For this purpose, various polymeric coatings have been used. The low thermal conductivity, low wear resistance, and poor adhesion to the substrate of the polymer coatings have limited their industrial applications. Since Ni-P-PTFE coating is metal based, its thermal conductivity, mechanical strength, and wear-resistant properties are much better than PTFE coatings, while it has a low surface energy.

Researches show that when the surface energy of the substrate is in the range of 20-30 mN/m, the microbial adhesion is minimal. The surface energy of stainless steel 304 is about 40 mN/m, which is much more than the optimum values (Zhao, et al. 2004). Another property of this coating is that it can be used in a wide temperature range from cold conditions to 290 °C, which is suitable for many of heating elements and heat exchangers.

As explained before, the good wear resistance of Ni-P-PTFE composite coatings due to PTFE nanoparticles caused them wide industrial applications. The aim of this study is to investigate the tribological properties of Ni-P-PTFE nanocomposite coatings with different concentrations of PTFE and to determine the optimized concentration of PTFE nanoparticles.

2. Materials and methods

Carbon steel disc-shaped samples with a diameter of 20 mm and a thickness of 8 mm were used as the substrate. The surface preparation of the samples was as follows:

The substrate was ground using SiC abrasive papers and then degreased with an electrolytic degreasing solution for 15 minutes at 75-55 °C. Then, the samples were immersed in a Ferro-clean solution to remove surface oxides for 4-5 minutes. Finally, in order to neutralize and activate the surface of the samples, they were immersed in a solution of sulfuric acid (10 wt.%) for 15 seconds. The as-pretreated substrate was electroless deposited in a thermostatically controlled bath and were coated to a thickness of 15μm.

After preparing the Ni-P bath, a portion of the bath was selected and a suspension of PTFE nanoparticles (60 wt.%) with a particle size of 100-200 nm and different concentrations of 5, 10, and

15 g/l was added to it. The PTFE suspension was purchased from AHC-Surface (RIAG) Company. In order to prevent the agglomeration of PTFE particles in the bath and uniformly distribute them, the cetyl trimethyl ammonium bromide (CTAB) was added to the bath (20-30 mg/l) as the surfactant. The surfactant, not only increases the stability of the suspension by enhancing the wettability and surface charges of the suspended particles in the solution, but also improves the electrostatic adsorption of the particles on the surface of the cathode by the enhancement of a positive electrical charge on the particles (Ger, et al. 2009). Finally, this part of the bath was added to the electroless nickel bath and then the final solution was stirred for 5 hours using a magnetic stirrer at a speed of 1000 rpm; next, it was mixed by an ultrasonic stirrer for 30 minutes followed by the coating process.

The surface morphology and the worn surfaces were studied using a field emission scanning electron microscopy (Mira 3-XMU, Philips). Energy dispersive spectroscopy (EDS) analysis was used for the determination of the chemical composition of the coatings and the worn surfaces.

To study the tribological behavior, wear test was accomplished by the pin on disk method using a 52100 steel pin with a hardness of 64RC and a movable disk with a 5 N vertical force and at a speed of 0.1 m/s. During the wear test, the diagram of the friction coefficient to distance was drawn by the device.

3. Results and discussion

3.1. Surface morphology of the coating

Figure 1 shows the SEM images of the surface morphology of Ni-P-PTFE nanocomposite coatings containing PTFE (10 g/l). According to Figure 1, the PTFE particles are uniformly distributed in the Ni-P coating matrix. Figure 2 shows the map of the fluorine atoms. Since PTFE molecules are composed of fluorine atoms, the distribution of fluorine atoms represents the distribution of the PTFE nanoparticles in the coating. According to Figure 2, a homogeneous distribution of the PTFE nanoparticles can be observed in the nickel metal matrix.

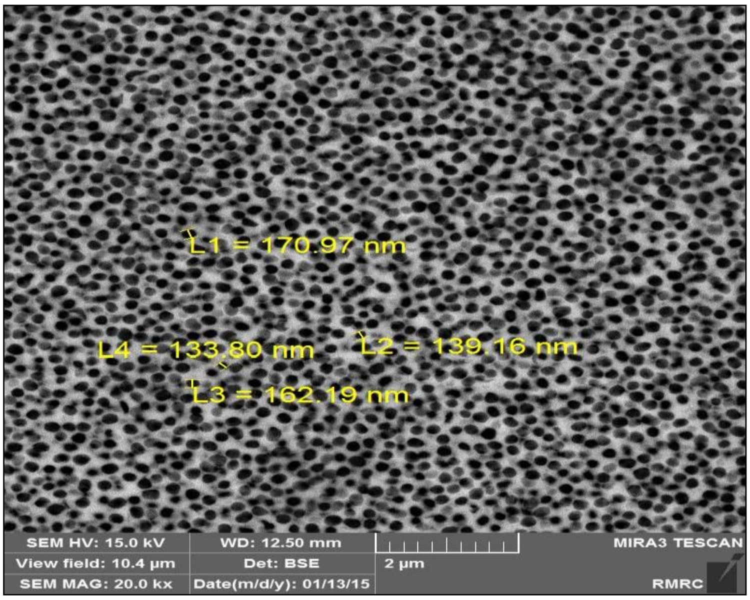


Figure 1
Surface morphology of nanocomposite coating.

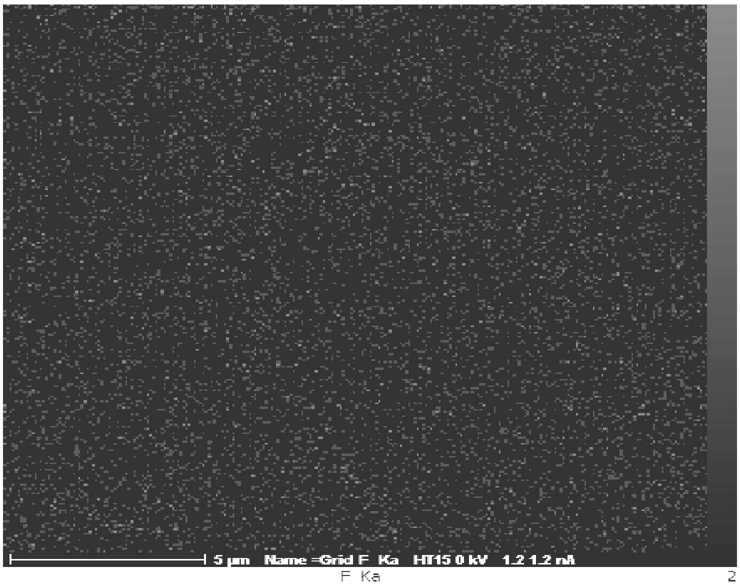
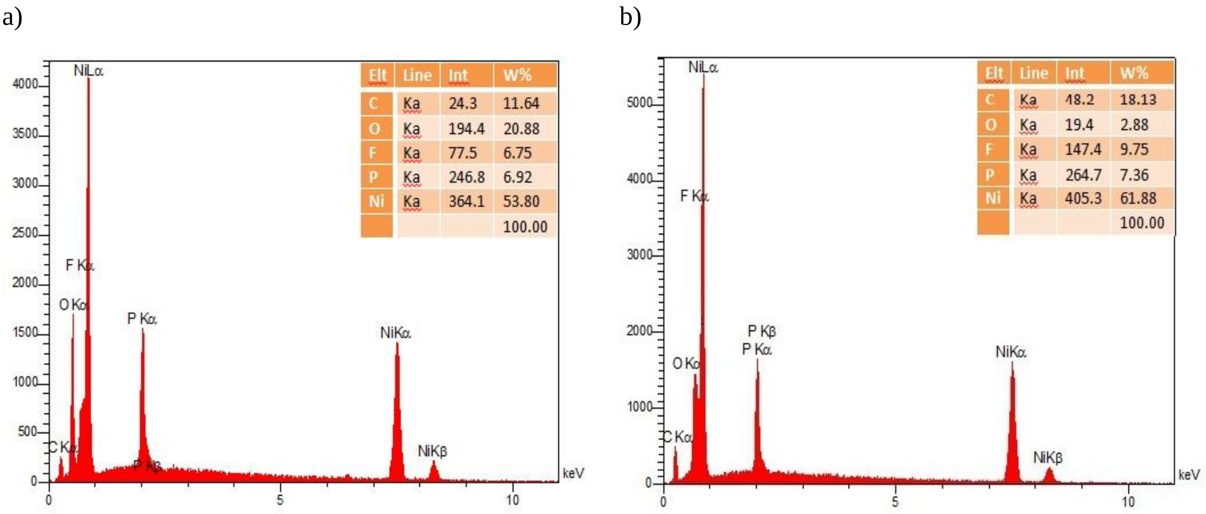


Figure 2
Map of fluorine atoms.

3.2. EDS analysis

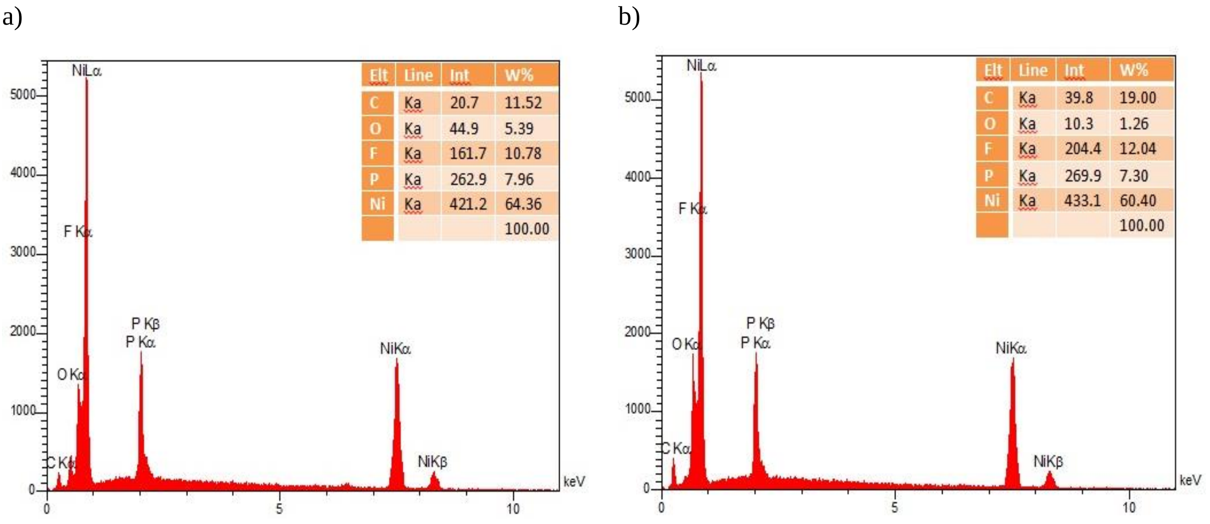
The results of EDS analysis of the coatings and worn surfaces are shown in Figures 3, 4, and 5. The approximate weight percent (wt.%) of the PTFE particles in the coating was calculated by the weight percent of fluorine and is presented in Table 1. As it can be observed, an increase in the concentration of the nanoparticles in the bath improves their incorporation into the coating. Increasing the PTFE concentration in the bath leads to an increase in the flux of these particles around the surface of the sample and thereby enhancing the physical interactions between the nanoparticles and the surface of the sample. This fact causes the possibility of the particles trapping in the mechanical locks of the surface and the coating to rise, and therefore enhances the incorporation of the PTFE into the composite coating. The incorporation of Si_3N_4 into the Ni-P-Si_3N_4 composite coating is also reported similarly elsewhere (Balaraju, et al. 1998; Alishahi, et al. 2012).


a) b)

Elt	Line	Int	W%
C	Ka	24.3	11.64
O	Ka	194.4	20.88
F	Ka	77.5	6.75
P	Ka	246.8	6.92
Ni	Ka	364.1	53.80
			100.00

Elt	Line	Int	W%
C	Ka	48.2	18.13
O	Ka	19.4	2.88
F	Ka	147.4	9.75
P	Ka	264.7	7.36
Ni	Ka	405.3	61.88
			100.00

Figure 3
EDS analysis of Ni-P-PTFE (5) coating; a) worn surface and b) surface morphology.

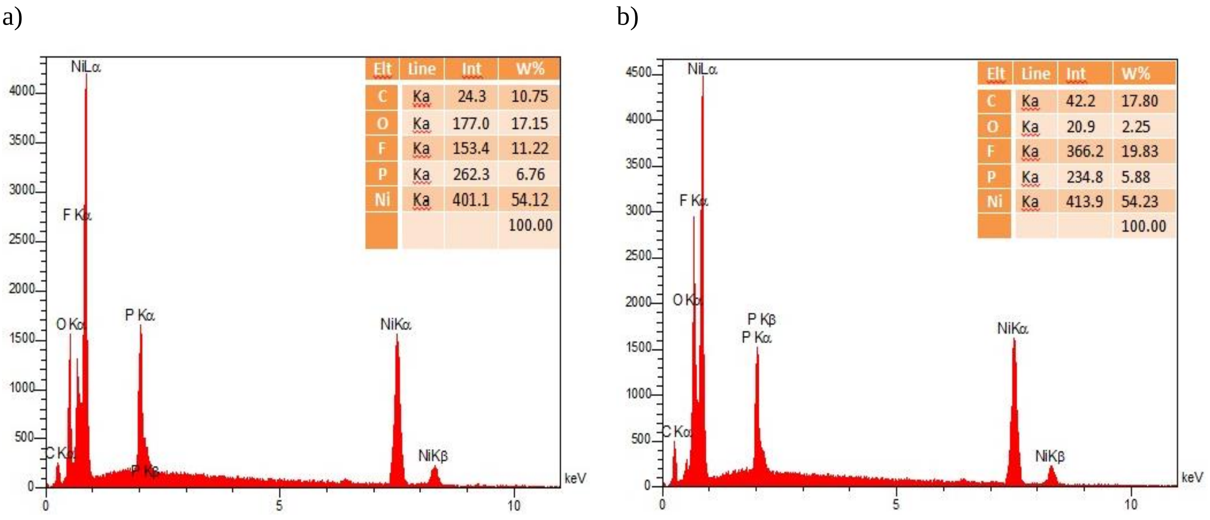

a)

Elt	Line	Int	W%
C	Ka	20.7	11.52
O	Ka	44.9	5.39
F	Ka	161.7	10.78
P	Ka	262.9	7.96
Ni	Ka	421.2	64.36
			100.00

b)

Elt	Line	Int	W%
C	Ka	39.8	19.00
O	Ka	10.3	1.26
F	Ka	204.4	12.04
P	Ka	269.9	7.30
Ni	Ka	433.1	60.40
			100.00

Figure 4
EDS analysis of Ni-P-PTFE (10) coating; a) worn surface and b) surface morphology.


a)

Elt	Line	Int	W%
C	Ka	24.3	10.75
O	Ka	177.0	17.15
F	Ka	153.4	11.22
P	Ka	262.3	6.76
Ni	Ka	401.1	54.12
			100.00

b)

Elt	Line	Int	W%
C	Ka	42.2	17.80
O	Ka	20.9	2.25
F	Ka	366.2	19.83
P	Ka	234.8	5.88
Ni	Ka	413.9	54.23
			100.00

Figure 5
EDS analysis of Ni-P-PTFE (15) coating; a) worn surface and b) surface morphology.

Table 1
EDS analysis of the coatings and the worn surfaces.

Coating	Weight percent of fluorine atoms in the coating	Weight percent of fluorine atoms in the worn surface	PTFE weight percent in the coatings	PTFE weight percent in the worn surfaces
NiP-PTFE (5)	9.75	6.75	12.82	8.88
NiP-PTFE (10)	12.04	10.78	15.84	14.18
NiP-PTFE (15)	19.83	11.22	26.09	14.76

3.3. Wear test results

Figure 6 shows the effect of the PTFE concentration on the friction coefficient of Ni-P-PTFE composite coating. It is obvious that the incorporation of PTFE nanoparticles in the nickel matrix, due to the self-lubricating properties of these particles, leads to a significant reduction in the friction coefficient of the coating. PTFE molecules have 13 to 15 repeated units and no branches and are not considered as bulky molecules; this causes the molecules to have a flat profile. The flat and smooth profile of the PTFE molecules causes a low friction and forms a thin film on the contact surface during the wear process. The wear rate of the coatings was calculated using Equation 1.

$$W_r = \frac{\Delta m}{(\rho \times l \times F)} \qquad (1)$$

where, W_r is the wear rate (mm^3/Nm) and Δm stands for the weight loss (mg); ρ, l, and F represent the density (g/cm^3), the distance (m), the vertical force (N) respectively. Using this equation, the wear rates for Ni-P, Ni-P-PTFE (5), Ni-P-PTFE (10), and Ni-P-PTFE (15) coatings were obtained to be 49.9×10^{-6}, 41.5×10^{-6}, 26.5×10^{-6}, and 35.2×10^{-6} respectively.

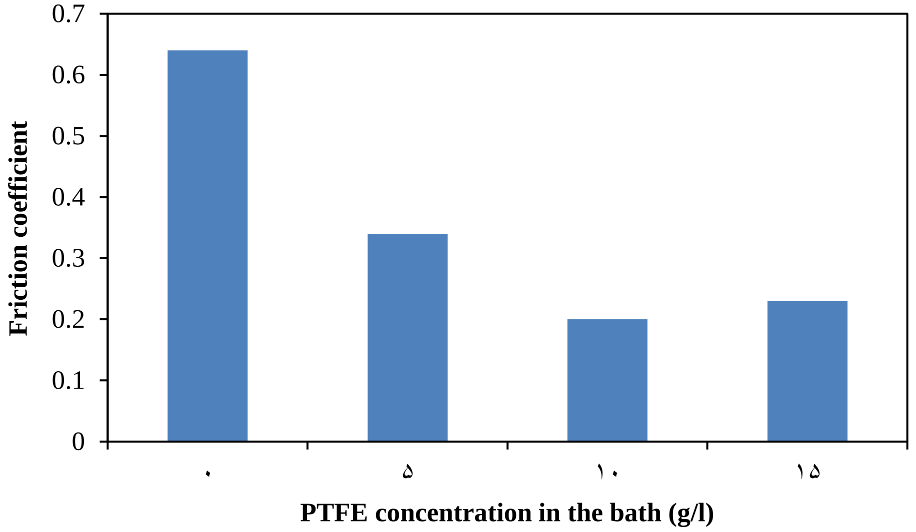


Figure 6

Variation of the friction coefficient against PTFE concentration in the bath.

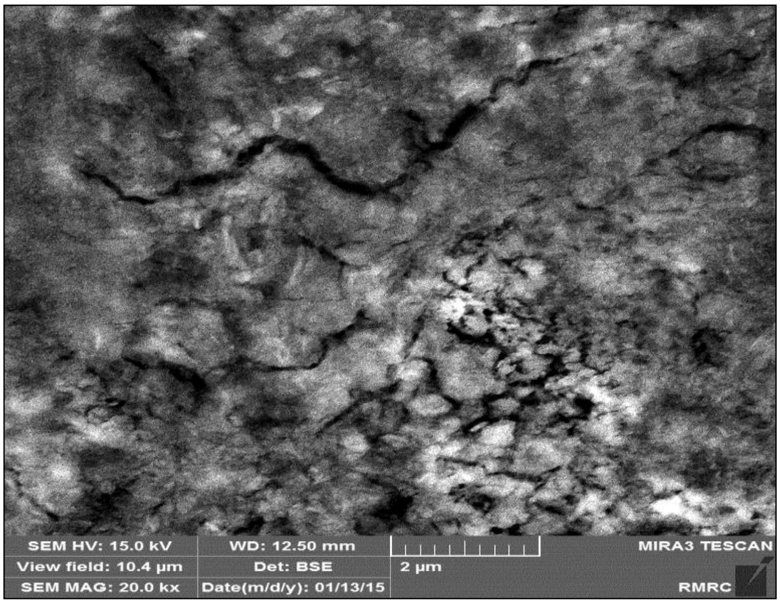
According to Figures 3, 4, and 5 and Table 1, a concentration of 10 gr/l for PTFE can be regarded as the optimum concentration, since higher concentrations of PTFE nanoparticles cause increased encounters between them. On the other hand, an increase in the interactions of PTFE nanoparticles, and thus the higher tendency of PTFE particles to agglomerate in the solution, causes the particles to agglomerate and move toward the top of the bath before the coating process. In addition, the adsorption probability of PTFE on the surface of the samples increases at high concentrations of the nanoparticles and consequently some active parts of the surface covered by nanoparticles become inactive. This reduces both the adhesion of the coating to the substrate and the cohesion between the components of the composite coating. Thus the coatings have lower wear resistance, and consequently the wear rate increases. The presence of large amounts of oxygen in the EDS analysis of the worn surfaces indicates the separation of the coating from the surface and the oxidation of the substrate.

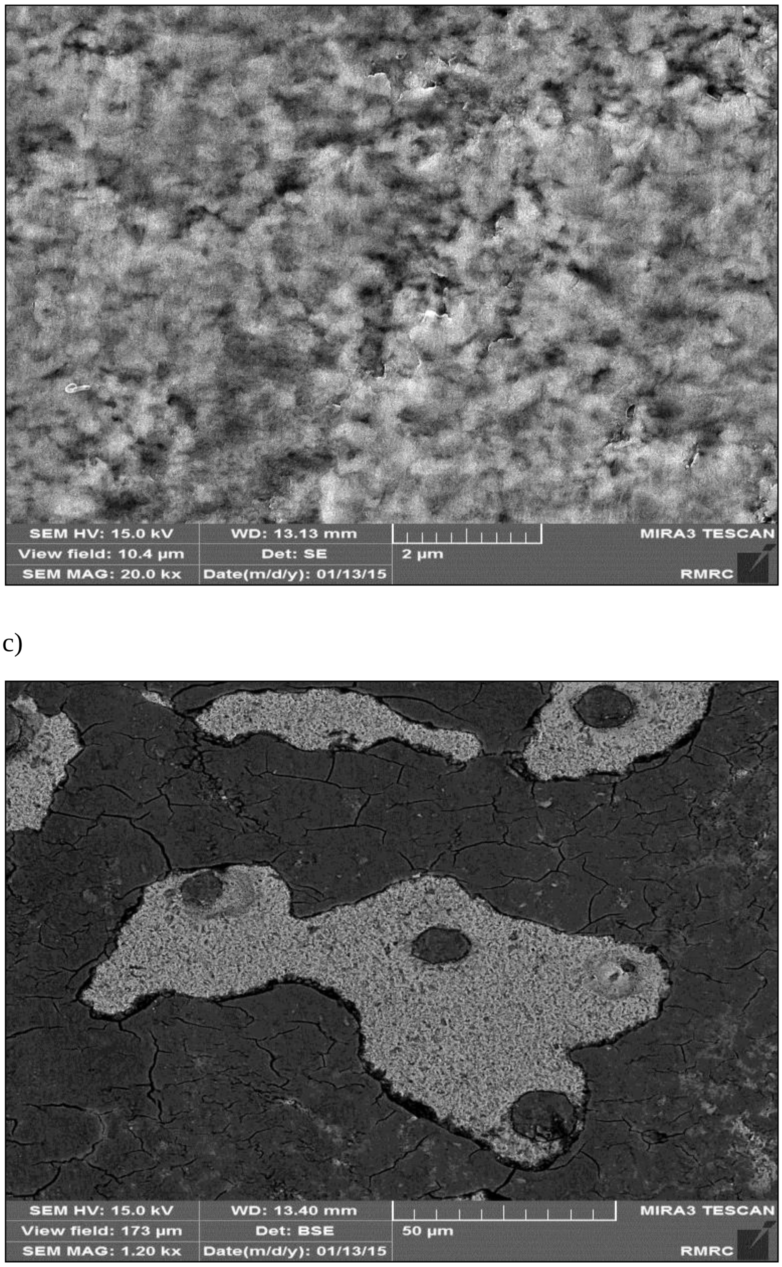
According to these results, it can be concluded that the Ni-P-PTFE (10) coating offers better wear properties. The Ni-P-PTFE (5) coating has a higher friction coefficient because of the lower incorporation of the PTFE lubricant nanoparticles in the coating matrix. Therefore, the wear rate and the rate of weight loss increase. In the case of Ni-P-PTFE (15) coating, despite the increase in the concentration of the PTFE nanoparticles in the bath, the friction coefficient is similar to Ni-P-PTFE (10) coating. However, because of the excess concentration of PTFE nanoparticles in the bath, and therefore agglomeration, the adhesion strength between the nickel matrix and the nanoparticles is weakened; therefore, the nanoparticles are removed from the coating matrix and placed on the worn surface. As a result, the wear rate increases and the coating is removed from the surface over a shorter distance.

3.4. The surface of abrasion analysis

Figures 7-A, B, and C show the SEM images of the worn surface. According to Figure 7-A, the presence of the microcracks and microcavities and the surface plastic deformation regions indicates the adhesive wear mechanism. The low incorporation of PTFE nanoparticles, the contact and interaction of nickel and iron atoms, and their high solubility in each other cause the transmission and diffusion of the atoms through the interface and as a result a strong adhesive connection is created. The relative movement of the surfaces leads to the rupture and cutting of these connections and the transmission of material from one surface to another and eventually results in the destruction of surfaces. According to Figure 7-B, very low wear damage is seen and there are only a few signs of smearing on the coating; also, no cracks or holes are seen. The sufficient and appropriate incorporation of the nanoparticles into the coating results in the disconnection of the direct contact of iron and nickel and leads to a low friction coefficient; therefore, the wear resistance is improved. As shown in Figure 7-C, the high concentration of the nanoparticles in the bath causes agglomeration. As mentioned before, in this case, due to the poor adhesion between the nanoparticles and the nickel matrix and the weak connection between the coating and the substrate because of surface inactivation, the coating detaches from the surface.

a)




b)

c)

Figure 7
SEM images of worn surfaces; a) Ni-P-PTFE (5); b) Ni-P-PTFE (10); and c) Ni-P-PTFE (15).

4. Conclusions

The results showed that the presence of Nano-PTFE solid lubricant in the matrix of electroless nickel coating lead to further improvement of the coating wear behavior. The investigation of the SEM images of the worn surface and the wear test results showed that:

- The uniform distribution of the PTFE nanoparticles in the coating gives the lowest friction coefficient (2.0) with the minimal wear damage;

- The incorporation of PTFE reduces the wear rate of Ni-P coating from 33.07×10^{-6} mm^3/Nm to 12.46×10^{-6} mm^3/Nm at a PTFE nanoparticle concentration of 10 g/l in the bath;
- The optimum concentration of PTFE nanoparticles to obtain the best tribological behavior is 10 g/l.

Nomenclature

CTAB	: Cetyl trimethyl ammonium bromide
EDS	: Energy dispersive spectroscopy
FESEM	: Field emission scanning electron microscopy
PTFE	: Polytetrafluoroethylene
SEM	: Scanning electron microscopy

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