

The Effect of Simultaneous Incorporation of PTFE Nanoparticles and Carbon Nanotubes on the Tribological Behavior of Ni-P Coating

Hamid Rahmati and Farzad Mahboobi*

Department of Mining and Metallurgy Engineering, Amirkabir University of Technology, Tehran, Iran

Received: June 09, 2015; *revised:* July 04, 2015; *accepted:* July 05, 2015

Abstract

In some engineering fields, wear resistance and a low friction coefficient are required at the same time. In this research, PTFE nanoparticles and carbon nanotubes were co-deposited within Ni-P matrix to obtain an Ni-P-PTFE-CNT hybrid coating for wear resistance and a low friction coefficient. The tribological properties of the deposits were evaluated by pin on disc tribometer. The morphology of the coatings and worn surface was evaluated by scanning electron microscopy. However, the results showed that the addition of PTFE nanoparticles to the Ni-P electroless coating caused the friction coefficient to decrease to values lower than 0.2, which led to an improvement in friction behavior because of its self-lubricity properties; it, however, decreased the strength of coating due to polymeric and soft structure of the molecules. The simultaneous incorporation of PTFE nanoparticles and carbon nanotubes can provide the properties of both molecules and increased the strength of coating with a low friction coefficient and self-lubricity properties. Therefore, the wear rate and the degradation of surface were decreased during the wear process.

Keywords: Coating, Nickel electroless, PTFE, CNT, Wear

1. Introduction

Tribology is the science of interacting surfaces in relative motion. When two interacting surfaces move against each other, two undesirable phenomena occurs: friction and wear. The development of new materials to deal with these two issues has always been a critical purpose for researchers. Surface engineering and surface finishing are two fields that provide new methods and techniques for the prevention of friction and wear. New coatings have been designed and developed to protect various parts used in different fields ranging from industrial machines to medical equipment and prosthetic components. Electroless nickel coating is one of these methods and is widely used in various industries (Shahoo et al., 2012). Electroless nickel coatings have unique properties such as high wear resistance, high corrosion resistance, high hardness, and good lubricity and toughness (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 coatings via an 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, nanoparticles such as SiC, WC, Al₂O₃, TiO₂, and ZnO as hard particles and PTFE and graphite as solid lubricant nanoparticles are added to the coating

* Corresponding Author:
Email: mahboubi@aut.ac.ir

(Huang et al., 2003). Among these composite coatings, Ni-P-PTFE has come under focus because of the properties such as very low friction coefficient, lubricity, anti-stick, and anti-fouling properties and good wear and corrosion resistance (Ger et al., 2002; Zhao et al., 2002; Ramalho et al., 2005); however, the polymeric nature of polytetrafluoroethylene causes a decrease in the hardness and strength of the coating. Nowadays, complex composite coatings containing both hard and lubricating particles are receiving more and more interest, and, in recent years, attention has turned to hybrid composite coatings. Several methods have been developed to produce hybrid coatings. Guo and Kong studied the structure of aluminum hybrid coatings containing SiC particles and graphite, which was created by the plasma spray (Gui et al., 2001). Mulligan evaluated the self-lubricating properties of CrN-Ag hybrid composite coatings produced by the magnetron sputtering (Mulligan et al., 2005). Straflinie et al. studied the wear behavior of Ni-P-PTFE-SiC coatings (Straflinie et al., 1999). Although a few works have been reported on electroless hybrid coatings (Wu et al., 2005; Wu et al., 2006; Huang et al., 2003; Suiyuan et al., 2012), but there is no information on Ni-P-PTFE-CNT hybrid nanocomposite coatings.

However, the extraordinary properties of carbon nanotubes such as high length to diameter ratio, strength, flexibility, elastic modulus, hardness, conductivity, chemical stability, etc. provide very beneficial improvements in the Ni-P matrix. In this study, the effect of simultaneous incorporation of PTFE nanoparticles and carbon nanotubes on the tribological properties of Ni-P coatings was investigated and compared with Ni-P-PTFE and Ni-P coatings.

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. After that, 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, the sample was 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 15 μm .

Pristine CVD-grown multi-walled carbon nanotubes, 30-50 μm in length and 5-15 nm in diameter, with a special surface area (SSA) of about 233 m^2/g were purchased from Iranian Nanomaterials Pioneers Company. The nano-PTFE particle size was between 100-200 nm (produced by AHC-Surface (RIAG) Company, Germany). After preparing the Ni-P bath, a portion of the bath was selected and a suspension of PTFE nanoparticles (60 wt.%) at a concentration of 10 gr./L was added to it. For producing Ni-P-PTFE-CNT hybrid composite coatings, PTFE nanoparticle at a concentration of 10 gr./L and carbon nanotubes at a concentration of 2 gr./L were added to a portion of electroless nickel bath. In order to prevent the agglomeration of PTFE particles and CNT's in the bath and obtain a uniform distribution, the cetyl trimethyl ammonium bromide (CTAB) was added to the bath (20-30 mg/L) as the surfactant. The surfactant not only increases suspension stability by increasing the wettability and the surface charge of particles suspended in solution, but also increases the electrostatic absorption of particles on the cathode by increasing the positive electrical charge on the particles (Ming et al., 2002). Finally, this part was added to the electroless nickel bath, and the final solution was stirred for 5 hrs using a magnetic stirrer at 1000 rpm and then for 30 minutes by

ultrasonic stirrer followed by the coating process. Additionally, mechanical stirring was used to keep particles from sediment during the coating process.

The surface morphology and the worn surfaces were studied using a scanning electron microscopy (SEM model Philips XL30).

Pin-on-disk tests were used to determine the wear resistance and the dynamic friction coefficient of the coatings; the weight loss was measured by a microbalance. The results were recorded as the friction coefficient variations versus the sliding distance. The wear rate of the coating was also computed and reported.

3. Results and discussion

3.1. Coating surface morphology

Figures 1 and 2 depict the SEM micrographs corresponding to the surface morphology of the electroless Ni-P-PTFE and Ni-P-PTFE-CNT coated samples respectively. The simultaneous incorporation of PTFE nanoparticles and carbon nanotubes can be seen in Figure 2. As can be seen, PTFE nanoparticles are in the form of black dots and carbon nanotubes are in the form of fine white lines. The PTFE nanoparticles and CNT's are uniformly embedded in the Ni-P matrix as seen in the SEM images.

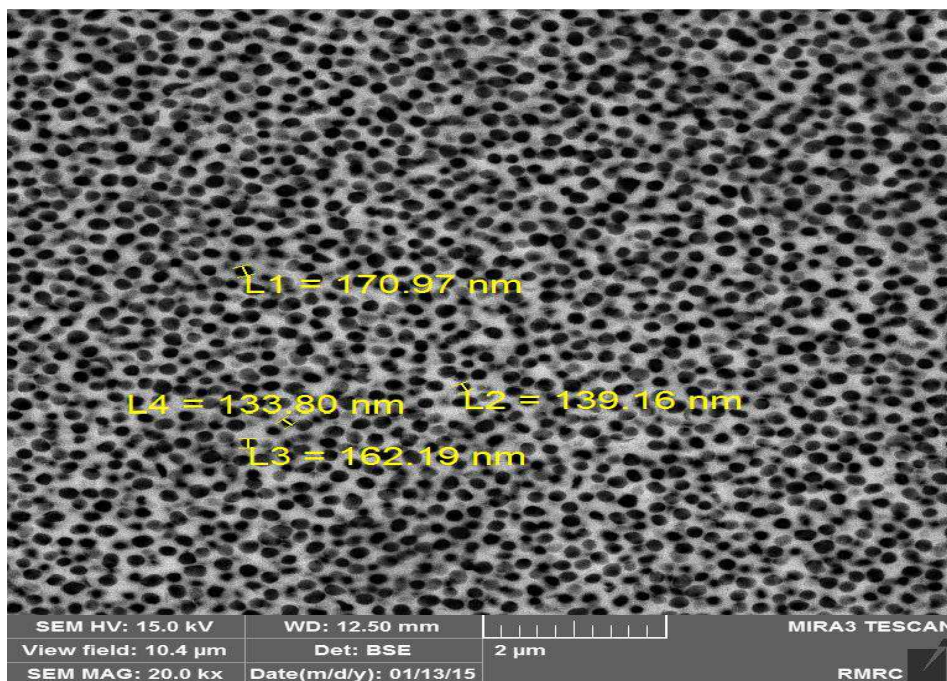


Figure 1
Surface morphology of Ni-P-PTFE nanocomposite coatings.

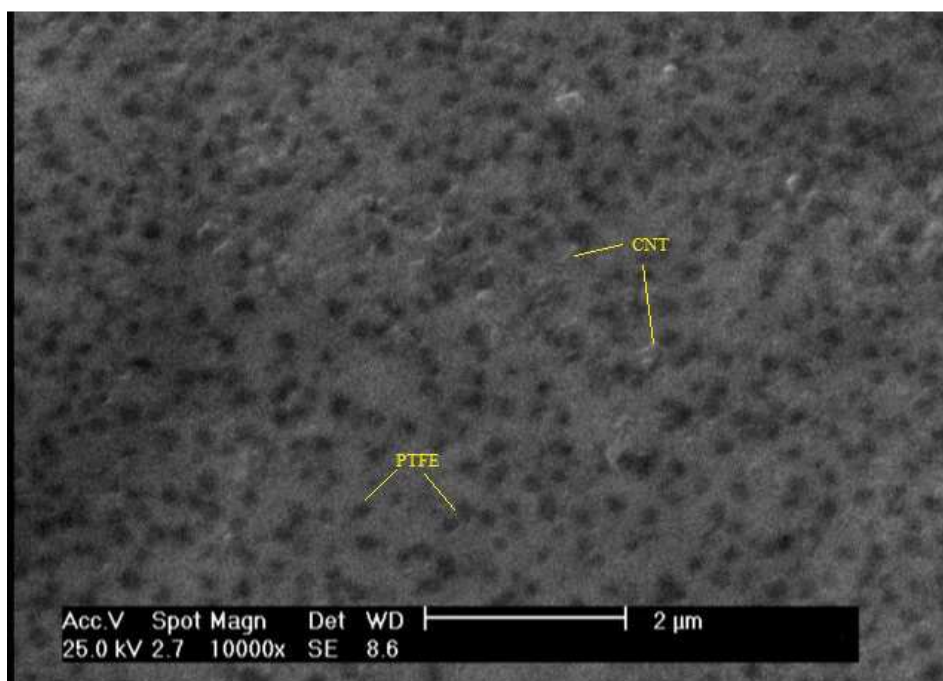


Figure 2
Surface morphology of Ni-P-PTFE-CNT nanocomposite coatings.

3.2. Wear resistance

Figure 3 shows the effects of adding PTFE nanoparticles and the simultaneous incorporation of carbon nanotubes and PTFE nanoparticles on the friction coefficient of the Ni-P coating. It can be seen that adding PTFE nanoparticles to Ni-P matrix, and thus self-lubricating properties of these particles, has significantly reduced the friction coefficient of the composite coating compared to the Ni-P coating. On the other hand, a significant reduction in the coefficient of friction in the presence of carbon nanotubes has been reported by Alishahi et al. (Alishahi et al., 2012). Therefore, the reduction of the coefficient of friction in the simultaneous incorporation of PTFE nanoparticles and carbon nanotubes can be explained as follows:

- The presence of PTFE nanoparticles in the Ni-P coating reduced the coefficient of friction because of the self-lubrication properties of these particles. PTFE molecules have 13 to 15 chemical repeating units, have no branches, and are not considered as bulky molecules. This causes the molecule to have a smooth profile. The smooth molecular profile and the easy formation of a PTFE transfer film between the coating and pin ball during the wear sliding decrease the coefficient of friction (Huang et al., 2003; Wu et al., 2006; Ramalhoa et al., 2005).
- The cylindrical shape and unique structure of carbon nanotubes and their low coefficient of friction (0.09 in horizontal orientation) reduce the coefficient of friction of the coating. In addition, with increasing the sliding distance, thereby increasing the material lost, some CNT's were placed in the worn surface. Strong bonding between the carbon atoms results in the high strength of CNT's to the extent that they can withstand pressures up to 55 GPa without the destruction of their cylindrical shape (Yang et al., 2005; Hilding et al., 2003). Therefore, it seems that the CNT's can easily slip between the sliding surfaces due to their cylindrical shape, which consequently leads to further reduction in the coefficient of friction.

- The presence of carbon nanotubes—which are considered as one of the hardest materials in the nature—along with PTFE nanoparticles helped these particles to play the role of a barrier in the coating. As a result, the direct contact between steel pin and the surface (and thus the direct contact of iron and nickel, which have a high solubility in each other) became limited and the coefficient of friction was decreased (Huang et al., 2003).
- In addition, PTFE and CNT's form a mechanically mixed PTFE-rich layer on the worn surface, which contains both PTFE and CNT. This layer acts as lubricant layer and reduces the coefficient of friction. Similar results were observed by Huang et al. (Huang et al., 2003).
- Given the high thermal conductivity of the nanotubes used in the coating, they could quickly transfer the heat produced during the sliding process to the substrate and prevent the formation of severe conditions in the contact surfaces, and they consequently reduced the coefficient of friction.

The wear rate of each coating was calculated by using Equation 1. In this equation, W_r (mm^3/Nm) is the wear rate, and Δm (mg) is the weight loss; ρ (gr/cm^3) represents density, and l (m) and F (N) are the sliding distance and the applied force respectively.

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

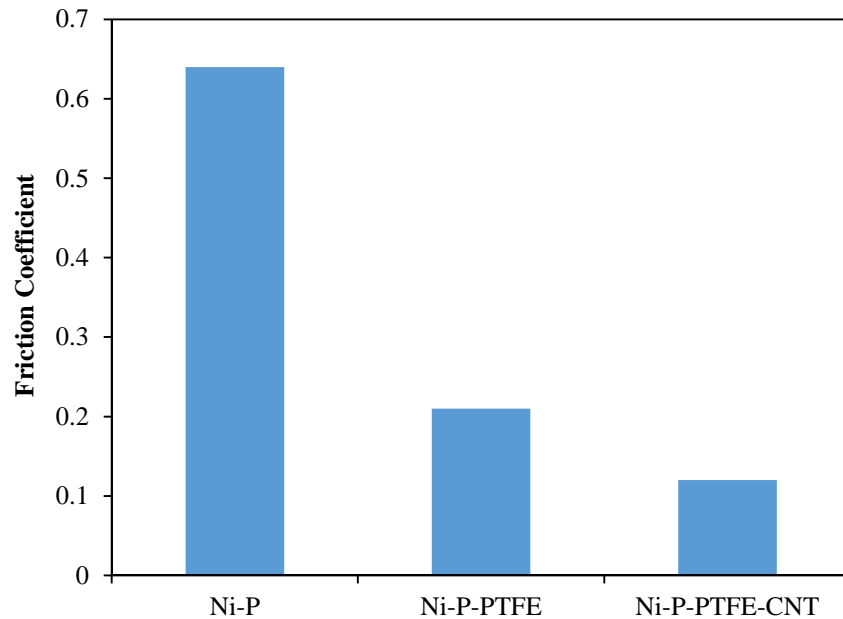


Figure 3

The effect of the simultaneous incorporation of PTFE nanoparticles and CNT's on the friction coefficient.

3.2. Analysis of worn surfaces

Figures 4-6 show the SEM images of the worn surfaces of Ni-P, Ni-P-PTFE, and Ni-P-PTFE-CNT coatings respectively. Studying the surface of the Ni-P coating (Figure 5) showed that this surface is mainly composed of longitudinal grooves and partial irregular pits along the sliding direction. A more detailed view of the wear track (at a higher magnification) reveals that not only scuffing and peeling-off are occurred, but also micro-cracks are emerged on the worn surface. Additionally, a serious plastic deformation is taken place. These observations indicate that the wear mechanism in the Ni-P

coating is featured as severe adhesive and abrasive wear, which are established for electroless Ni–P sliding against steels (Liu et al., 1996; Palaniappa et al., 2008; Staia et al., 1996). On the other hand, the presence of uneven corrugated holes increased the possibility of the delamination wear mechanism along with adhesive wear mechanism. High solubility of nickel and iron in each other caused the transmission and diffusion of atoms in the interface of wear surfaces, and created a strong adhesive connection between them. 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 it eventually destructs the surfaces (Ashrafi et al., 1995).

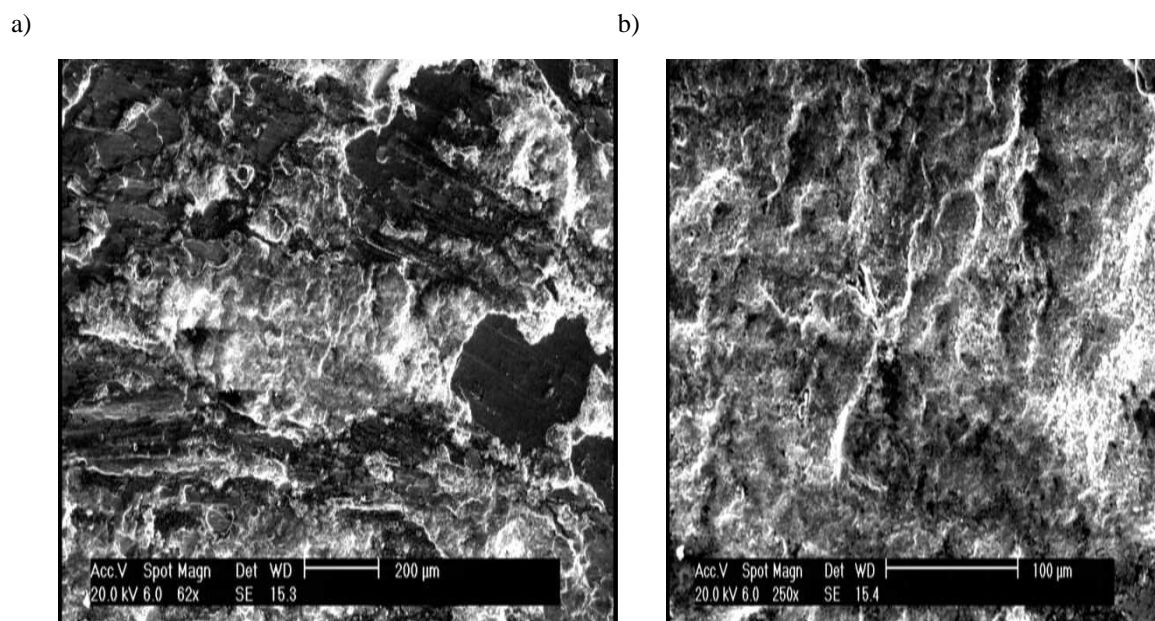


Figure 4

The SEM images of the worn surface of the Ni-P coating at a magnification of: a) 62x and b) 250x.

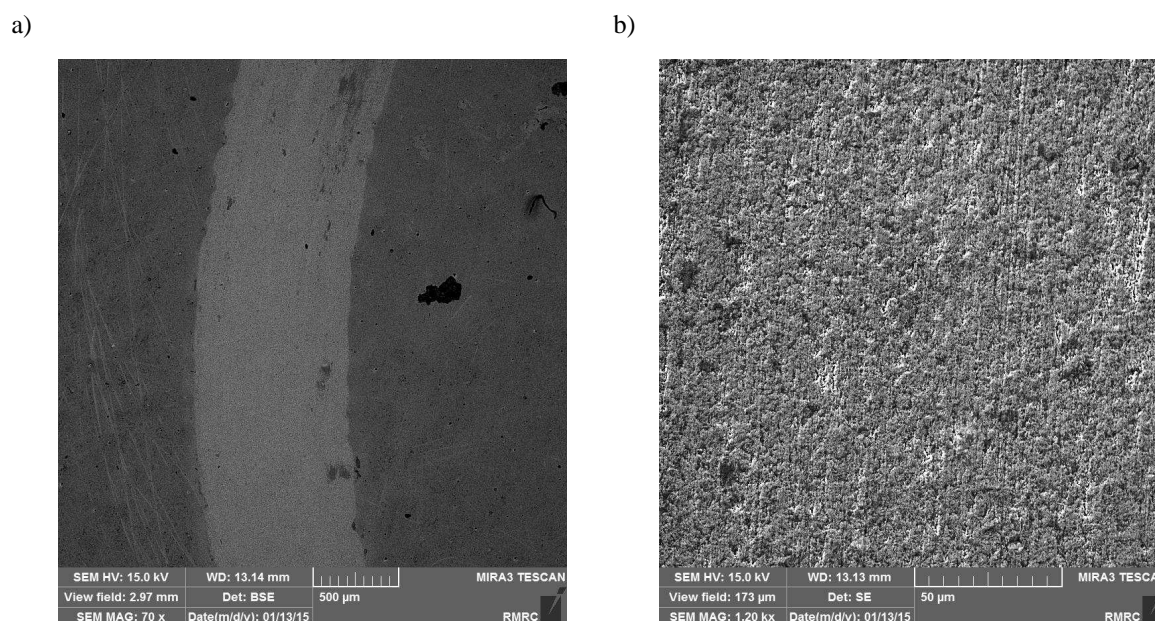
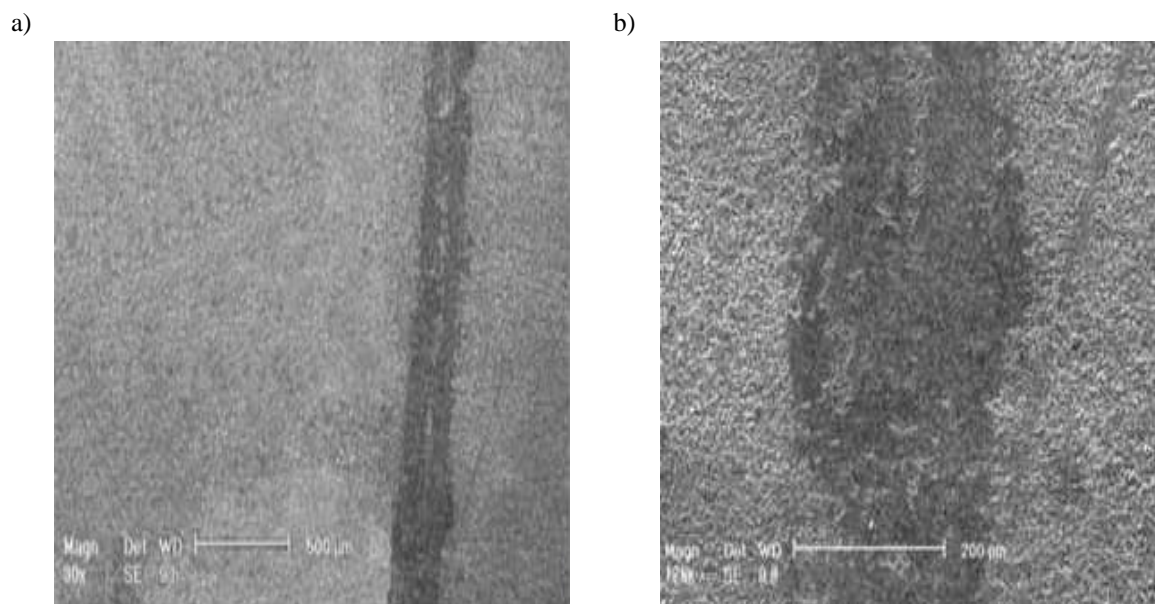


Figure 5

The SEM images of the worn surface of Ni-P-PTFE coating at a magnification of: a) 70x and b) 1.20kx.

**Figure 6**

The SEM images of the worn surface of the Ni-P-PTFE-CNT coating at a magnification of: a) 30x and b) 125x.

Figure 6 shows the worn surface of Ni-P-PTFE coating. As seen, wear resistance is much better than that of the Ni-P coating, and low wear damage is observed. There are only a few effects of smearing on the coating and no cracks are seen. The sufficient and appropriate incorporation of the nanoparticles in the coating leads to the disconnection of the direct contact of iron and nickel and thereby a low coefficient of friction; therefore, an improvement in the wear resistance is obtained. Given the presence of the soft polymer phase of PTFE, the reduction of the coefficient of friction was combined with the reduction of the coating strength. As seen in Figure 6, no peeling-off is occurred, but there are longitudinal grooves in the sliding direction, which indicates the abrasive wear mechanism.

Figure 7 shows the worn surface of the Ni-P-PTFE-CNT coating. In this sample, the amount of wear damage is reduced. The presence of carbon nanotubes increased the strength of the coating and reduced the plastic deformation and damaged to the surface. The presence of carbon nanotubes also prevented the growth of cracks, longitudinal grooves, and removing of the coating from the surface. A low coefficient of friction combined with sufficient strength caused by the simultaneous incorporation of self-lubricant PTFE nanoparticles and high-strength carbon nanotubes reduced the plastic deformation, the possibility of connection between the coating and the counter surface, and the delamination phenomenon during the wear process. On the other hand, the increased heat transfer coefficient of the coating in the presence of carbon nanotubes caused the quick transfer of the heat produced during the sliding process to the substrate and prevented the formation of severe conditions on the worn surfaces. All these factors improved the tribological behavior of the Ni-P-PTFE-CNT composite coating.

4. Conclusions

A Ni-P-PTFE-CNT hybrid nanocomposite coating was successfully applied on the steel substrate for the first time. After the heat treatment of the coating to obtain optimum wear properties, the tribological behavior of the coating was evaluated and the following results were obtained:

Adding PTFE lubricant nanoparticles to the Ni-P matrix reduced the coefficient of friction and the wear rate of the coating; therefore, the wear resistance of the Ni-P coating was improved.

The decrease in strength caused by adding the soft polymer phase of PTFE resulted in longitudinal grooves in the direction of sliding.

The simultaneous incorporation of self-lubricant PTFE nanoparticles and carbon nanotubes increased the strength of the coating, which consequently reduced the damage caused by the wear process. In this method, the plastic deformation and removing of the coating decreased; the wear rate and the coefficient of friction is lower than the Ni-P and Ni-P-PTFE coatings, and, as a result, the tribological behavior of the coating is highly improved.

Nomenclature

CTAB	: Cetyl trimethyl ammonium bromide
CNT	: Carbon nanotube
PTFE	: Polytetrafluoroethylene
SEM	: Scanning electron microscopy

References

- Alishahi M., Monirvaghefi S. M., Saatchi A., and Hosseini S. M., The Effect of Carbon Nanotubes on the Corrosion and Tribological Behavior of Electroless Ni-P-CNT Composite Coating, *Applied Surface Science*, Vol. 258, p.2439-2446, 2012.
- Ashrafi, F. and Salehi, M., *Surface Metallurgical and Tribology*, Vol. 1, Science Association and Surface Technology of Iran Publication, 1995.
- Ger, M. and Hwang, B., Effect of Surfactants on Codeposition of PTFE Particles with Electroless NiP Coating, *Materials Chemistry and Physics Journal*, Vol. 76, p. 38-45, 2002.
- Grosjean, A., Rezrazi, M., and Takadoun, J., Hardness, Friction and Wear Characteristics of Nickel-SiC Electroless Composite Deposits, *Surface Coating and Technology Journal*, Vol. 92, No. 6, p. 137-142, 2001.
- Gui, M. and Kang, S. B., Aluminum Hybrid Composite Coatings Containing SiC and Graphite Particles by Plasma Spraying, *Materials Letters Journal*, Vol. 51, p. 396-401, 2001.
- Hilding, J., Grulke, E. A., Zhang, Z. G., and Lockwood, F., Dispersion of Carbon Nanotubes in Liquids, *Journal of Dispersion Science and Technology*, Vol. 24, No. 1, p. 1-41, 2003.
- Huang, Y. S., Zeng, X. T., Annergren, I., and Liu, F. M., Development of Electroless NiP-PTFE-SiC Composite Coating, *Surface and Coatings Technology*, Vol. 167, p. 207-211, 2003.
- Liu, Y. and Tandon, K. N., Effect of Temperature on the Wear of an Electroless Nickel Coating under Lubricated Reciprocating Sliding Conditions, *Tribol. Lett.*, Vol. 2, p. 263-272, 1996.
- Ming, D. G. and Bing, J. H., Effect of Surfactants on Codeposition of PTFE Particles with Electroless Ni-P Coating, *Materials Chemistry and Physics journal*, Vol. 76, p. 38-45, 2002.
- Mulligan, C.P. and Gall, D., CrN-Ag Self-lubricating Hard Coatings, *Surface and Coatings Technology Journal*, Vol. 200, p. 1495-1500, 2005.
- Palaniappa, M. and Seshadri, S. K., Friction and Wear Behavior of Electroless Ni-P and Ni-W-P Alloy Coatings, *Wear*, Vol. 265, p. 735-740, 2008.
- Ramalhosa, A. and Miranda, J. C., Friction and Wear of Electroless NiP and NiP/PTFE Coatings, *Wear Journal*, Vol. 259, p. 828-834, 2005.
- Sahoo, P., Tribological Performance of Electroless Ni-P Coatings, Jadavpur University, India

- Staia, M. H., Castillo, E. J., Puchi, E. S., Lewis, B., and Hintermann, H. E., Wear Performance and Mechanism of Electroless Ni-P Coating, *Surface Coating Technology*, Vol. 86, p. 598-602, 1996.
- Straffelini, G., Colombo, D., and Molinari, A., Surface Durability of Electroless Ni-P Composite Deposits, *Wear Journal*, Vol. 179, p. 236, 1999.
- Suiyuan C., Ying S., Hong F., Jing L., Changsheng L., and Kai S., Synthesis of Ni-P-PTFE-nano- Al_2O_3 Composite Plating Coating on 45steel by Electroless Plating, *Journal of Composite Materials*, Vol. 46, p. 1405-1416, 2012.
- Tian, J., Liu, X., Wang, J., Wang, X., and Yin, Y., Electrochemical Anticorrosion Behaviors of the Electroless Deposited Ni-P and Ni-P-PTFE Coatings in Sterilized and Unsterilized Seawater, *Materials Chemistry and Physics*, Vol. 124, p. 751-759, 2010.
- Wang, R., Ye, W., Ma, C., and Wang, C., Preparation and Characterization of Nanodiamond Cores Coated with a Thin Ni-Zn-P Alloy Film, *Mater Character Journal*, Vol. 108, No. 11, p. 59-65, 2008.
- Wu, Y., Liu, H., Shen, B., Liu, L., and Hu, W., The Friction and Wear of Electroless Ni-P Matrix with PTFE and/or SiC Particles Composite, *Tribology International Journal*, Vol. 39, p. 553-559, 2006.
- Wu, Y., Liu, L., Shen, B., and Hu, W., Study of Selflubricant Ni-P-PTFE-SiC Composite Coating, *Journal of Materials Science* Vol. 40, p. 5057-5059, 2005.
- Wu, Y., Shen, B., Liu, L., and Hu, W., Thetribological Behavior of Electroless Ni-P-Gr-SiC Composite, *Wear*, Vol. 261, p. 201-207, 2006.
- Yang, Z., Xu, H., Shi, Y. L., Li, M. K., Huang, Y., and Li H. L., The Fabrication and Corrosion Behavior of Electroless Ni-P-Carbon Nanotube Composite Coatings, *Materials Research Bulletin*, Vol. 40, p. 1001-1009, 2005.
- Zhao, Q., Liu, Y., Mu'ller-Steinhagen H., and Liu, G., Graded Ni-P-PTFE Coatings and their Potential Applications, *Surface and Coatings Technology Journal*, Vol. 155, p. 279-284, 2002.