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Original Research

Nanoparticle Concentration and Heat Treatment Effects on Microstructure and Tribological Behavior of the Ni-P Nanocomposite Coating

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ABSTRACT

The aim of this study was to create electroless Ni-P-SiO_2-MoS_2 nanocomposite coating and investigate the effect of the concentration of nanoparticles and heat treatment on its structure and tribological behavior. To achieve this purpose, MO40 steel specimens were coated at the temperature of 90°C in electroless nickel-phosphorus coating baths containing different concentrations of 3, 7, 11, and 15 g/L of SiO_2 and MoS_2 reinforcement nanoparticles with pH 6.4 for 60 minutes. Then, the coated sample containing 7 g/L of nanoparticles was subjected to heat treatment of 400°C for 60 minute. To investigate the microstructure, tribological behavior, elements' weight percent and phases in the coatings, FE-SEM images were observed and wear test, EDS and XRD analysis were performed, respectively. Results showed that by increasing the concentration of nanoparticles in the coating bath, the weight percent of the reinforcement elements in the coating increases. Exceeding concentration of nanoparticles from certain value leads to the agglomeration of the coating particles and creation of porosity which results in a non-uniform coating with low protecting properties. Therefore, the appropriate concentration of nanoparticles in the coating bath was chosen 7 g/L, because the results show a uniform coating of the amorphous nickel phase and the SiO_2 and MoS_2 nanoparticles. Subsequently, the heat treatment results showed that the amorphous nickel phase formed in the coating became into two crystalline nickel and Ni_3P phases after heat treatment that leads to increase wear resistance.

KEYWORDS Electroless Ni-P coating, Nanocomposite, Nanoparticle concentration, Wear resistance.

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INTRODUCTION

Different coating methods are used to increase the wear resistance, hardness and corrosion resistance of components in various industries such as aerospace, automotive, petrochemical, etc. One of the most important of these methods is electroless coating.[1,2] This process was invented by Berner and Riedel in 1946 to meet industrial needs. In electroless coating, using a chemical bath without using electric current, the chemical reactions inside the bath create a uniform coating of the metal on the surface of the components.[3,4] Among different types of electroless coatings, nickel is very popular because of its ability to provide a hard and wear resistant surface. According to the studies, these coatings are generally divided into three major groups of pure nickel, alloy and composite electroless coatings, which among them the composite coatings are one of the suitable industrial methods to increase the efficiency and properties of nickel electroless coatings.[5-7] In these coatings, the solid particles immersed in the electroless bath are coprecipitated with the matrix coating on the surface of the work piece. In the process of nickel electroless coating various types of ceramic particles such as oxides, carbides and hard compounds like diamond have been known as a factor in increasing wear resistance and hardness. Also, various types of soft particles including PTFE and MoS_2 have been used as lubricants in the nickel composite structure.[8-10] Improving the wear resistance parameter in these coatings can make their application wider and more appropriate. One of the basic methods to enhance the wear properties of nickel coatings is their heat treatment in the temperature range of 300-600°C. In this temperature range, heat treatment at 400°C for 1 hour is the most common cycle which results in the maximum hardness in the nickel electroless coatings.[11-13] Although there have been many reports about pure and alloy nickel electroless coatings, very little researches have been performed on the creation of composite and nanocomposite nickel coatings to replace with the traditional methods used in the industry. Therefore, the aim of this study was to create a new coating of nickel-phosphorus nanocomposite by using both reinforcement and lubricant particles on steel substrate by electroless method and to investigate the effect of nanoparticle concentration and heat treatment on the structure and tribological behavior of these coatings.

MATERIALS & METHODS

In this research, samples of MO40 steel sheet with dimensions of 1.5 × 1.5 × 3 cm^3 were prepared. The chemical analysis of this steel is shown in Table 1. The samples were polished by sandpaper and 0.3 µm abrasive alumina particles. They were then washed and degreased by alkaline sodium solution at 70-85°C for 1 to 3 minutes and finally deoxidized and activated by hydrochloric acid solution at ambient temperature for 30 to 40 seconds. After this step, the samples were immediately transferred to the pre-prepared coating baths. In order to create the coating, four Nickel-Phosphorus SLOTONIP 70A electroless baths and SiO_2 and MoS_2 powders with different concentrations of 3, 7, 11 and 15 g /L were used. Samples were immersed in these baths at a constant temperature of 90°C and pH of 6.4 for 60 minutes and then were brought out. Field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) analysis were employed to investigate the microstructure, elements, and phases in the created coatings, respectively. To investigate the effect of heat treatment on the structure, the nanocomposite coating with a concentration of 7 g/L was heat treated at 400°C for 60 min, then the heat treated coating was investigated by FE-SEM images and XRD analysis. Finally, in order to comparing wear resistance of coated and uncoated samples, pin wear test on a radial plate with pin radius of 4 mm, rotating speed of 200 rpm, force of 30 N and maximum cycles of 5000 performed. Samples wear resistances were evaluated by measuring friction coefficient and weight reduction.

Table 1: The chemical composition of MO40 (Wt. %).

Fe	C	Si	Mn	Cr	Mb	S
Base	0.42	0.25	0.75	1.10	0.22	0.035

RESULTS & DISCUSSION

Analysis of Lubricant and Hard Particles

The FE-SEM images of SiO_2 and MoS_2 particles used in the coating have been depicted in the previous article.[14] The MoS_2 lubricant particles are plate-shaped and the thickness of the plates is in nanometer scale. These particles are added to the coating due to their suitable lubrication property, stability at high temperatures, and to reduce friction coefficient.[8] The SiO_2 particles are nano-sized and agglomerated. The presence of these particles improves the hardness and wear resistance of the coatings.[9]

Nanoparticle Concentration Effect on Coating Structure

As it is shown in Fig. 1, in order to investigate the effect of MoS_2 and SiO_2 nanoparticle concentrations on the coating structure and also select the appropriate amount of them, coatings containing different amounts of MoS_2 and SiO_2 were created. Fig. 1a shows the coating prepared in the bath containing 3 g/L of each MoS_2 and SiO_2 nanoparticles. As can be seen, the surface has a relatively uniform morphology, whereas the reinforcement particles on the surface of coating are non-uniformly distributed. Figs. 1b and c show the coatings created in the bath containing 7 and 11 g/L of nanoparticles, respectively. As it is seen, the coating is uniform and the hard particles and lubricant show suitable stability in the coating. However, in Fig. 1c, porosities, marked with an arrow, appeared on the surface of the coating which is due to the increase of the available surface area resulted from the excessive MoS_2 and SiO_2 particles in the coating. In Fig. 1d, the concentration of the nanoparticles in the coating bath is 15 g/L and the morphology is non-uniform and a completely porous coating is obtained. In this coating, concentration of the lubricant and hard particles is the highest value. It can be noted that by increasing the amount of MoS_2 and SiO_2 particles, the number of collisions between the particles increases and despite the presence of these particles on the surface, the empty spaces appear at the interface of these coatings. Therefore a non-uniform and agglomerated coating is composed.

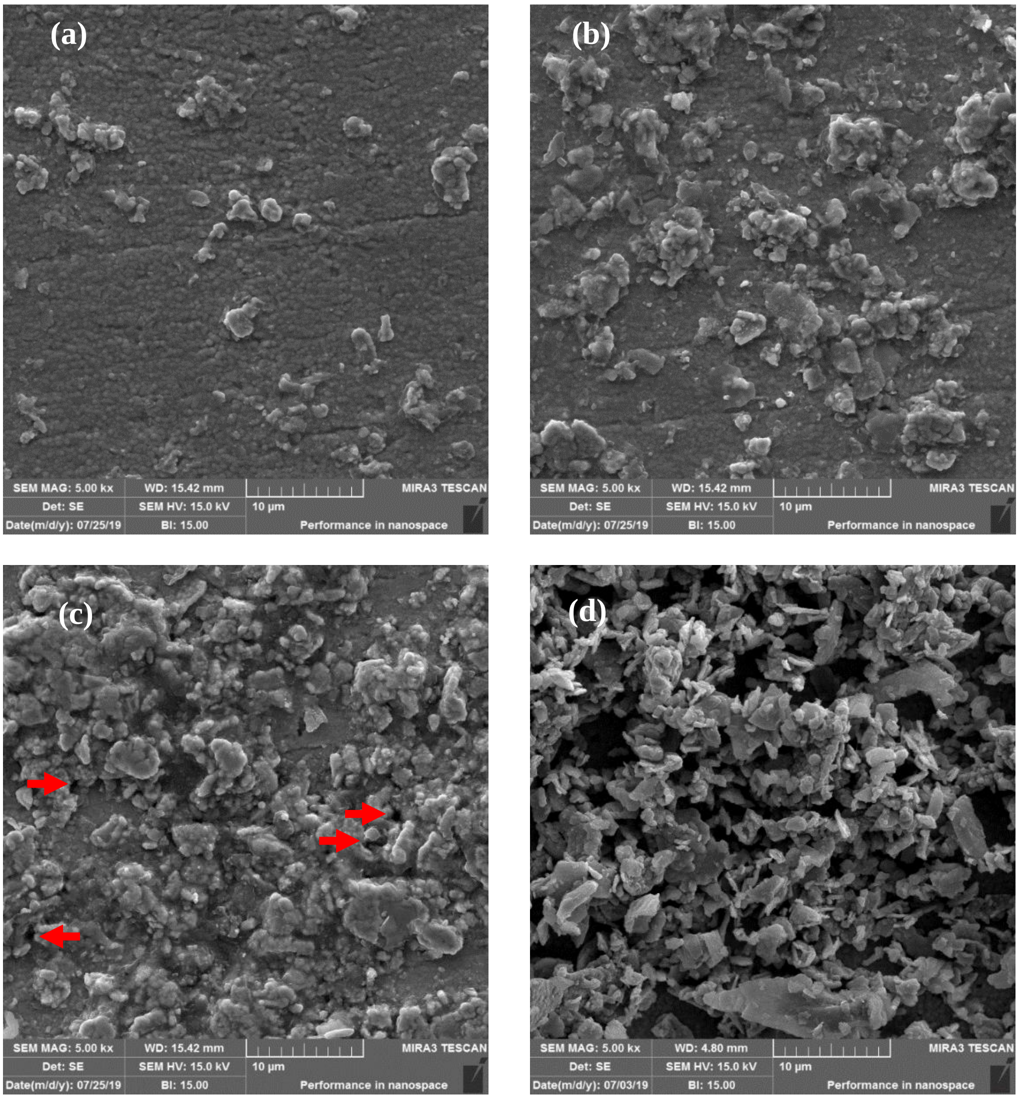

Fig. 1: Morphology of Ni-P-SiO_2-MoS_2 nanocomposite coating composed in bath containing of MoS_2 and SiO_2 with concentration of a) 3, b) 7, c) 11, and d) 15 g/L.

EDS elemental analysis was performed on the coatings containing 3, 7, 11, and 15 g/L of reinforcement particles. Results of this analysis, given in Fig. 2, show that by increasing the amount of composite particles in the coating bath, the weight percentage of the constituent elements of the particles increases while the amount of Nickel and Phosphorus in the coating decreases. Moreover, Fig. 3 shows the trend of the weight percentage of MoS_2 and SiO_2 elements in the coating by increasing the concentration of these particles in the coating bath. It is observed that the content of MoS_2 particles in the coating increases more rapidly in comparison to the SiO_2 particles, which is due to their geometrical structure. The plate-like structure of MoS_2 particles results in the preferential placement of these particles on the surface of coating. By investigating FE-SEM images and EDS analysis, it can be concluded that the increase of the concentration of composite particles in the coating provides the conditions for the formation of a lubricant and hard layer to improve the wear properties, but when the concentration exceeds a certain value the particles agglomerate which results in the creation of porosity and increase the particle size. These factors reduce the protective properties of the coating, including wear resistance, adherence, corrosion resistance, etc. Therefore, in this paper, the optimum amount of reinforcement particles was considered 7 g/L to create a uniform coating.

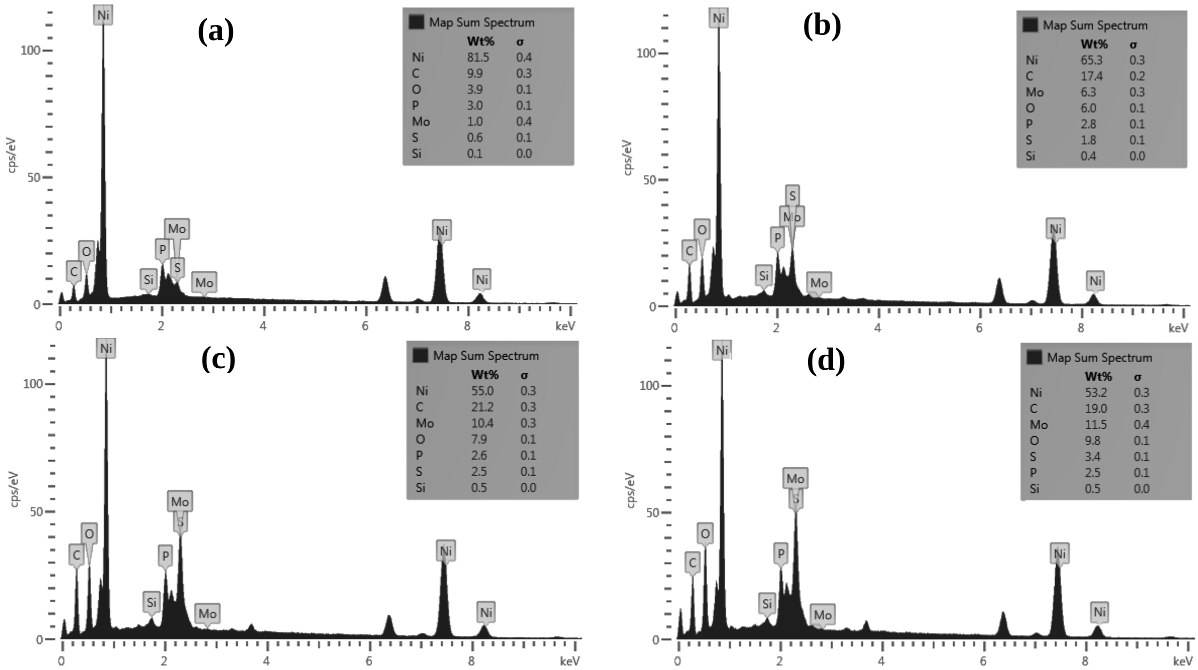

Fig. 2: EDS analysis of composed coating in bath containing of MoS_2 and SiO_2 with concentration of a) 3, b) 7, c) 11, and d) 15 g/L.

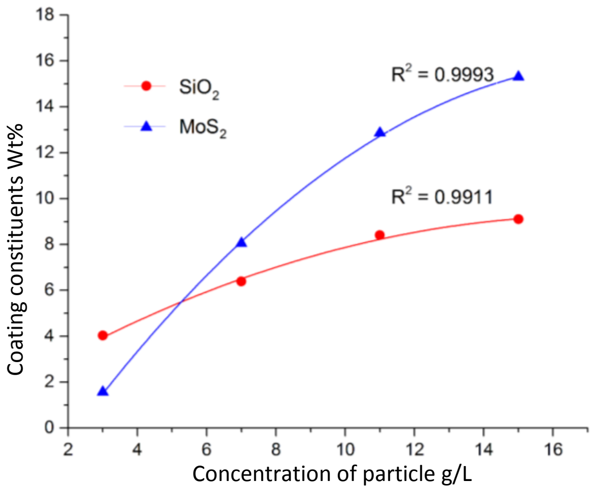

Fig. 3: Weight percent of coating constituents versus concentration of MoS_2 and SiO_2 particles in the coating bath.

Structure of Coating Containing 7 g/L Nanoparticles

Before Heat Treatment

In order to do more accurate study on the effect of the particles used in the coating, secondary electron microscopy (SE) images at different magnifications of Ni-P-SiO_2-MoS_2 coating surface containing 7 g/L nanoparticles were taken. Fig. 4a shows the surface of a uniform nanocomposite coating consisting of reinforcement nanoparticles and a dome-shaped Ni-P coating and Fig. 4b shows the structure at the magnification of 70,000x. As it is seen, the images show well the formation of small Nickel-Phosphorus islands on available surfaces, i.e. the substrate and the particles.[15, 16] The arrows also show the plate-like structure of the MoS_2 and the agglomerated structure of SiO_2. Fig. 5 shows the XRD analysis of the nanocomposite coating surface containing of 7 g/L nanoparticles prior to the heat treatment. As can be seen, the coating consists of the phases of SiO_2, MoS_2, and Ni. Also, the peak width at the angle of 2θ=45 is mainly due to the amorphous structure of the coating. From this point of view, the results of the XRD patterns are in agreement with the results of other researchers regarding the electroless Nickel-Phosphorus coatings without heat treatment.[17, 18]

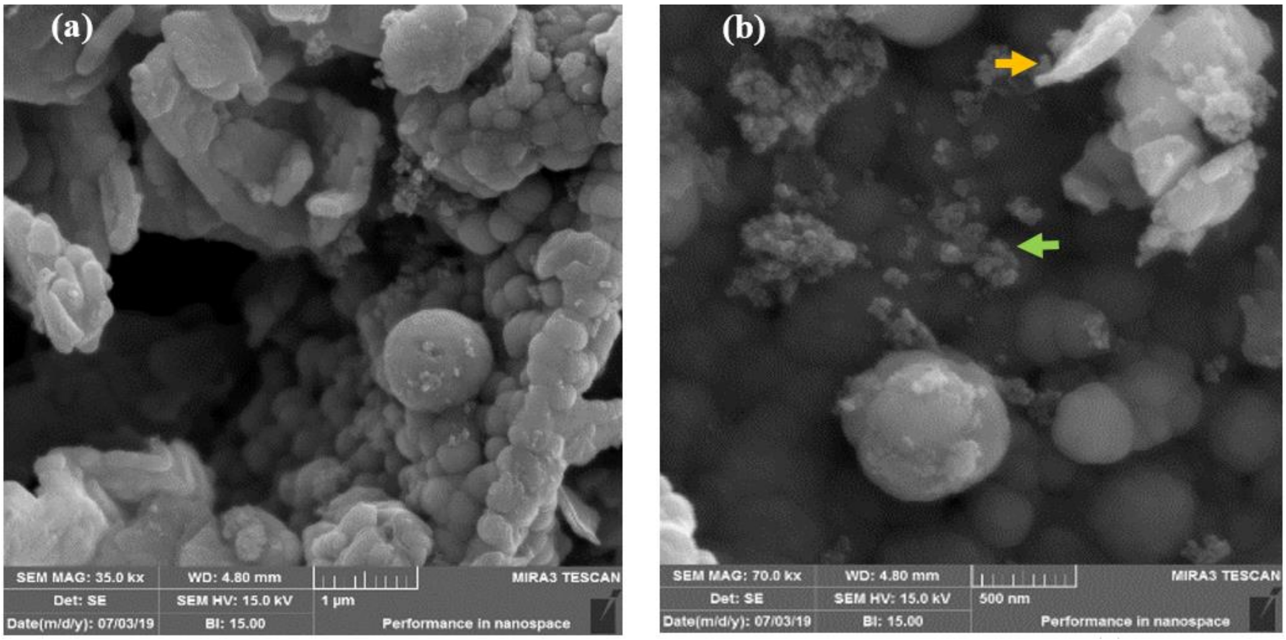

Fig. 4: SEM images from Ni-P-SiO_2-MoS_2 nanocomposite coating surface with concentration of 7 g/L before heat treatment at magnification of a) 35 kx, b) 70 kx.

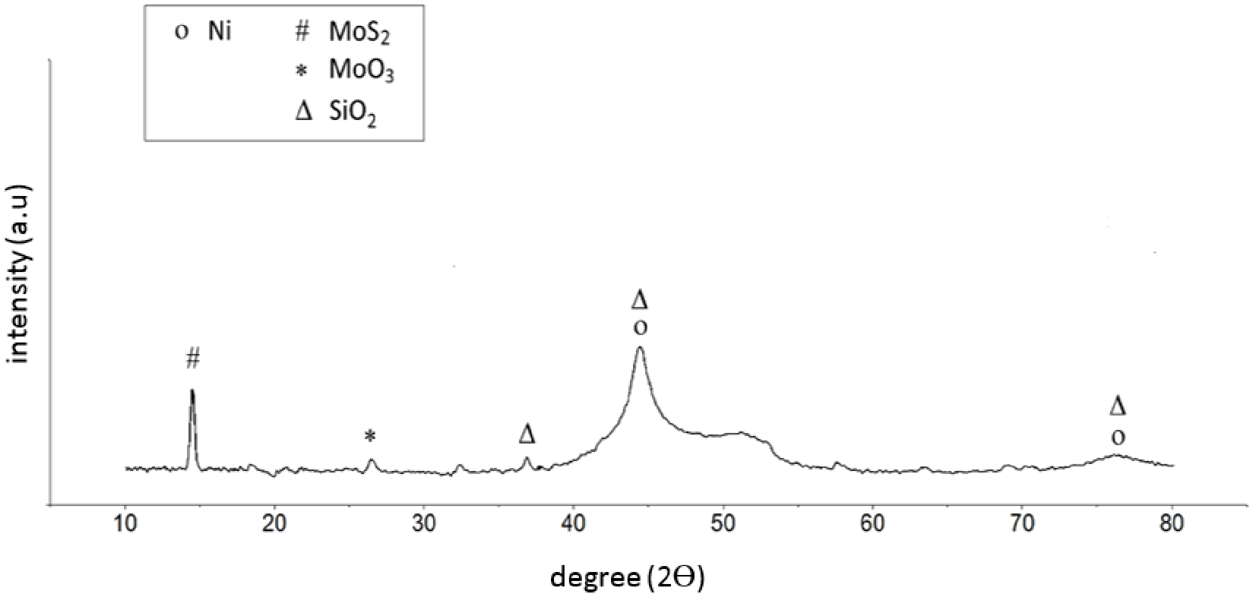

Fig. 5: XRD analysis of Ni-P-MoS_2-SiO_2 nanocomposite coating containing of 7 g/L MoS_2 and SiO_2 nanoparticles before heat treatment.

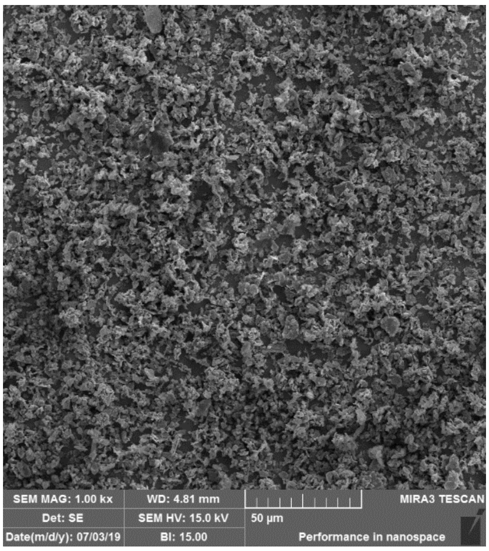

Fig. 6: FE-SEM image of Ni-P-MoS_2-SiO_2 nanocomposite coating containing of 7 g/L MoS_2 and SiO_2 nanoparticles after heat treatment.

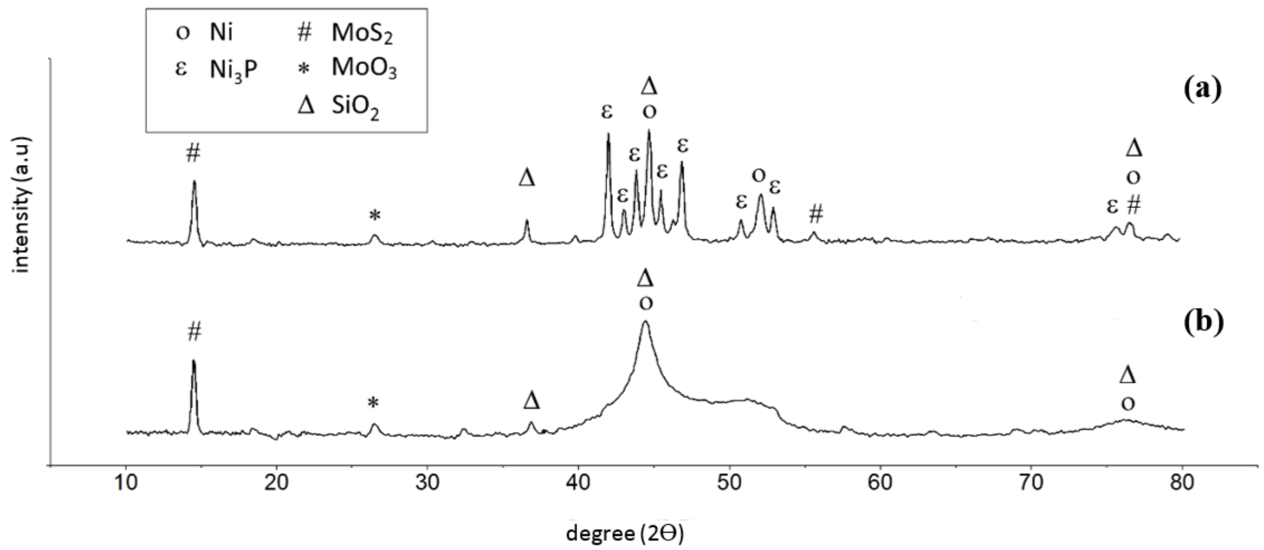

Fig. 7: XRD analysis of Ni-P-MoS_2-SiO_2 nanocomposite coating containing of 7 g/L MoS_2 and SiO_2 nanoparticles a) after heat treatment and b) before heat treatment.

After Heat Treatment

Electron microscopy image of the coating structure containing of 7 g/L nanoparticles after heat treatment is shown in Fig. 6. Employing heat treatment plays a significant role in the variations of the material's microstructure.[19] According to Fig. 6, microstructure of the coating shows that the islands of Nickel-Phosphorus became finer and the reinforcement nanoparticles are distributed uniformly on the surface of the coating. Fig. 7 illustrates the X-ray diffraction pattern of the coating after heat treatment at 400°C for one hour. By comparing the XRD patterns of the nanocomposite coatings before and after heat treatment, it can be inferred that due to the heat treatment the structure of the amorphous Nickel layer is converted to crystalline Nickel and Ni_3P intermetallic phase. Therefore, it can be concluded that the wear resistance of the coating increases in this case. Because the main reason of the hardness increase of Nickel-Phosphorus coatings by heat treatment is their crystallization, namely the conversion of amorphous Nickel phase to Ni grains and hard Ni_3P particles.[20, 21]

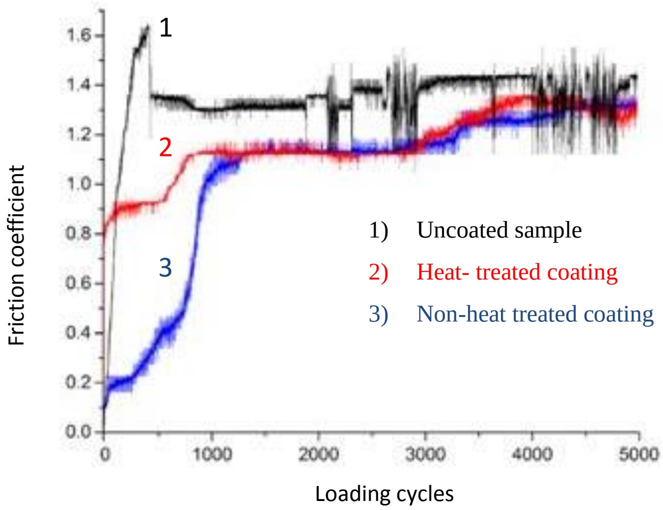

Fig. 8: Friction coefficient of samples versus loading cycles.

Tribological Behavior

Fig. 8 shows the tribological behavior of the samples. In this figure, friction coefficient of samples versus loading cycles is illustrated. As it is seen, uncoated sample has highest friction coefficient among samples. This result expresses that repeated destruction and deforming of surface will be followed by fluctuation in tribological behavior. In other hands, coated samples, before and after heat treatment, have lower fluctuation and friction coefficient average. It can be concluded, in non-heat treated nanocomposite, sliding mechanism is activated by MoS_2 lubricant nanoparticles to 1000 cycles. However, surface layer after heat treatment resists wear better by hard Ni_3P and SiO_2 abrasive agents.

After this step, friction coefficient of both samples reach a steady state. Finally, adherent wear mechanism increases surface friction coefficient and intensifies the wear process. These two behaviors are two different mechanisms in wear subject that substantially depends on structure of coating. The wear resistant of heat treated sample has improved by composing hard layer, while activating sliding mechanism decreases friction coefficient of non-heat treated sample and postpones the wear process. Also, Fig. 9 shows weight reduction of samples versus loading cycles. It is seen that weight reduction of coated samples, before and after heat treatment, are much lower than uncoated sample. Therefore, obtained results express that heat treated coating has the lowest weight reduction. In other words, heat treated coating has the best tribological properties and wear resistant.

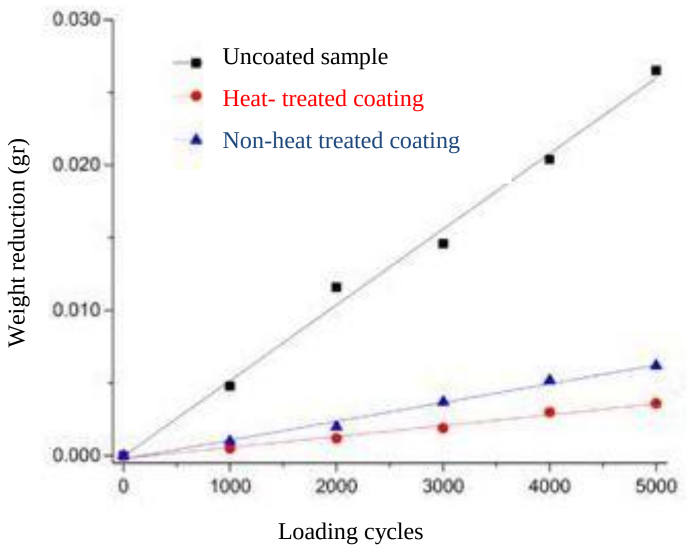

Fig. 9: Weight reduction of samples versus loading cycles.

CONCLUSION

Based on results of this work, the remarkable achievements could be evaluated for concluding part. First, electroless Nickel-Phosphorus nanocomposite coating containing different concentrations of hard SiO_2 nanoparticles and MoS_2 lubricant was successfully created on MO40 steel. Second, by increasing the concentration of composite nanoparticles in the coating bath, the content of MoS_2 particles increased more rapidly than that of SiO_2 particles. However, exceeding the concentrations from certain value results in the creation of porosity. This factor reduces the protective properties of the coatings. Third, in order to provide a uniform coating, the optimum amount of reinforcement particles was determined 7 g/L. Fourth, the coating is contained of SiO_2, MoS_2 and amorphous Ni phases. Heat treatment at 400°C for one hour leads to the conversion of the amorphous nickel phase to the crystalline phase and creation of the hard Ni_3P intermetallic phase. And finally, the wear resistance of heat treated sample has improved by composing hard Ni_3P and SiO_2 phase, while activating sliding mechanism by MoS_2 phase decreases friction coefficient of non-heat treated sample.

DISCLOSURE STATEMENT

The author(s) did not report any potential conflict of interest.

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