MATERIALS ENGINEERING | RESEARCH ARTICLE

Heat treatment and quenching effects on wear of electroless nickel–phosphorous plating
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Abstract: This work aims to evaluate the effect of post-heat treatment and quenching on the hardness, coating thickness, morphology, wear, and microstructure of the coatings made on steel travelers. The test result shows that all the quenched samples have similar hardness. Wear tests of the specimens show that Type-I oil quenched specimens have better wear resistance compared to other specimens. Atomic force microscope results reveal that Type-I oil-quenched travelers have a smoother surface than water and air-cooled travelers. Scanning electron microscope images show that the distribution of plating on the substrate is not uniform. After baking, the coating becomes uniform. However, some small voids are present in the coating due to improper surface activation before the plating process.

Subjects: Mechanical Engineering; Heat Transfer; Materials Science

Keywords: electroless plating; microhardness test; heat treatment; mechanical properties

1. Introduction

Electroless plating involves a reduction reaction in an aqueous solution that results in an amorphous layer deposition on the substrate surface. This process is used to develop surfaces with corrosion resistance, excellent wear characteristics, and hardness. It is also possible to improve the coating’s magnetic behavior and catalytic properties on the substrates, such as metal or plastics. There is no need for electrical supply to the chemical bath, unlike electroplating (Zhang et al.,

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Dr. B. Shivamurthy is an associate professor in the department of mechanical and manufacturing engineering at Manipal Institute of Technology, Manipal, India. He has received a Ph. D. from the department of metallurgical and materials engineering, NITK Surathkal, India. He has more than 10 years of industrial experience in the field of polymer processing and research. For the last 20 years, he has been involved in teaching and research. His key area of research such as structure property of polymer nanocomposites, tribology, ballistic materials, EMI shielding materials, sensors and transducers, special coatings and surface engineering. The present investigation is on surface engineering of ring and traveler assembly of textile machine part, although it is very minute in appearance, it plays a vital role in the spinning operation. It has a direct effect on the quality of yarn produced. So the present investigation has wider application in yarn industries.

PUBLIC INTEREST STATEMENT
Ring and the traveler assembly in the textile machine is a critical unit. Though it is very minute in appearance, it plays a crucial role in the spinning operation. It has a direct effect on the quality of yarn produced. High hardness, high surface finish, and wear resistance are the required properties of travelers used in the yarn industry. Surface engineering is a secondary process followed while manufacturing travelers. This process enhances the required surface properties of travelers. Electroless plating is selected in this process and the post-plating heat treatment effect on the hardness, surface roughness, and wear resistance is significant from the quality of yarn production.
The most common electroless plating is electroless nickel plating. The Ni\(^{2+}\) ions in the solution are reduced by chemical reduction into Ni metal, which develops as a uniform layer on the substrate surface. It acts as a catalyst for further deposition. Sodium hypophosphite and formaldehyde are commonly used reducing agents (Zhang et al., 2014). The thickness of the layer deposited due to electroless plating is uniform and has a linear relationship with the process duration. Compared to conventional plating, electroless Ni plated surface is challenging to remove chemically; it is hard and has good wettability. The plating process can be applied to both conductive and non-conductive substrates. However, it is also associated with certain disadvantages, such as sophisticated bath control, low efficiency, and higher operating costs. Electroless nickel-phosphorus coatings are widely used in many areas such as engineering and functional coating for various applications. It has been used as wear-resistance and self-lubricating surface, corrosion-resistance, protective or decorative coatings, and functional coating in electronics, chemical, oil and gas, aerospace, and automobile industries (Maretić et al., 2017).

Because of its wide application range, many research studies reported the influence of various reducing agents and concentrations, bath temperature, pH value, and heat-treatment methods and temperature on electroless plating performance (Zhang et al., 2014). Wang et al. (2017) reported improved hardness and young’s modulus of electroless Ni–P coated surface on API X100 pipeline steel due to the crystalline structure of nickel and nickel phosphide phases obtained by heat-treatment. However, the toughness was lower than as-plated samples due to the amorphous status of the as-plated Ni–P surface. Sribalaji et al. (2015) found improvement in wear resistance property of Ni–P coated surface on steel substrate due to heat treatment at a higher temperature. They reported this was due to the formation of a passivation layer (NiO) which protects the P enriched layer, and the absence of an interdiffusion layer from the substrate to coating. Chang et al. (2013) recommended pH 5 bath solution and heat-treatment at 350°C, pH 8 bath solution, and heat-treatment temperature of 300°C are the best parameters to achieve better wear resistance and hardness of Ni–P plating surface on S 45 C carbon steel substrate. Maretić et al. (2017) found remarkably increased hardness (429–853 HV) of an electroless Ni–P coated surface of austenitic stainless-steel due to the heat treatment at 500°C for 60 min in an air atmosphere. They concluded that the heat-treatment results in the formation of the Ni3P phase on the coated surface are responsible for enhancing hardness. Goettems & Ferreira (2017) found that electroless Ni–P deposits with post-heat-treatment at 320°C (9 h) and 400°C (1 h) have shown a better wear resistance than electroplated hard chromium coating. They also concluded that this is due to the formation of nickel crystallites and nickel phosphides (Ni5P2). Shen et al. (2012) investigated the hardness and associated plastic deformation in as-deposited and as-annealed nickel-phosphorus (Ni–P) coatings. They found that th as-deposited Ni–P coating was deformed appreciably through the shear-band mechanism.

Figure 1 shows the schematic representation of the ring and the traveler assembly in the textile machine. This combination is effectively a twisting and winding mechanism and is used in textile mills to process yarn. Although it is very minute in appearance, it plays a vital role in the spinning operation. It has a direct effect on the quality of yarn produced. High hardness, high surface finish, and wear resistance are the required properties of travelers used in the yarn industry. Our study’s main objective is to determine the effect of post-plating heat treatment on the hardness, surface roughness, and wear resistance of the electroless plated steel traveler specimens.

2. Methods and materials

2.1. Electroless nickel plating

Electroless nickel plating was carried out in Rimtex Engineering Pvt. Ltd., Gujarat. The solutions used for electroless plating were obtained from Atotech Company. A steel specimen of a particular grade is used as the substrate onto which electroless nickel coating is deposited. First, the specimens are cleaned in a solution containing alkaline cleaner and demineralized water (DM) at a temperature of 60°C for 10 min, followed by rinsing in DM water at room temperature. Then
they are subjected to ultrasonic cleaning for 3 min at 60°C followed by DM water rinse. A water rinse is carried out to avoid the flow of contamination from one stage to another. To improve the adhesion between the substrate and the plating activation process is carried out. It is carried out by dipping the components in sulfuric acid for 30 seconds. Next, the samples are preheated by dipping the components in DM water at 60°C for 1 to 2 min. The plating process is carried out by dipping the components in a solution containing Nickel and Phosphor. The process used here is mid-phosphor plating, which contains about 5% phosphorous. The primary bath solution contains Nickel ion, Phosphorous ion, along with some additives. Components are dipped in the primary bath solution for 20 to 25 min at a temperature of 85°C to 88°C. A plating thickness of about 3 to 4 µm is obtained. The solution is continuously agitated using air so that all the chemicals are uniformly distributed, and the temperature is maintained uniformly throughout the solution. After the plating process, the component is rinsed in warm water and dried using a centrifugal dryer. Some of these samples were taken as an as-plated condition. These plated components are baked at 285°C for 3 h in a furnace to improve the bond between the substrate and plating. The components are covered in aluminium wrap to avoid oxidation. After baking, some specimens were left for air cooling, some specimens were water quenched, and some were oil quenched by using two types of oil, namely, Type-I oil and Type-II oil.

2.2. Characterization and testing methods
The microhardness of all the samples was measured using the Matsuzawa micro-hardness testing machine (MMT-X7A, Japan) by applying 200 g of load on the diamond cone point indenter for about 15 s. The Vickers micro-hardness of each sample was determined as the average of five test results obtained with the Vickers tester.

Surface morphology, surface roughness, and 3D images of all the sample surfaces were investigated using an Innova SPM Atomic Force Microscope (AFM). The tip of an AFM is traded over the electroless nickel-plated surface with constant force to give a three-dimensional picture of a surface and its features. The tip is moved across the surface using piezoelectric motors, the force between the tip and the surface is kept constant by measuring the position of the tip using light reflected from it.
The microstructure analysis of the electroless nickel plating layers was carried out with a scanning electron microscope (ZEISS, SEM EVO-M18) coupled with XRD. The sliding adhesive wear test was carried out for all the samples using a pin-on-disc machine (Ducom, India).

3. Results and discussion

3.1. Microhardness

The microhardness of different specimens is given in Table 1. It can be seen that the hardness of raw samples (uncoated) is significantly less as compared to others. It is noticed from the results that, due to the electroless nickel-phosphorus coating, the hardness increased. Further, while heat treatment, the microstructure of the coated surface (Ni–P coatings) at about 220–260 °C starts changing from amorphous to crystalline (Buchtík et al., 2019). In this research, it is found from the EDAC investigation that the coating consists of a medium quantity of phosphorus; hence the metastable phases NiP₂ and Ni₁₂P₅ may form and enhances the hardness (Buchtík et al., 2019).

The hardness of all the coated specimens is in the same range irrespective of the type of quenching method employed. However, the air-quenched samples showed slightly higher hardness and more consistent results as compared to other samples.

Table 1. Micro hardness test results of different specimens

| Sample Type       | VHN 220 | VHN 226.2 | VHN 221.8 | VHN 224.7 | VHN 230.2 | VHN 230.2 | VHN Average |
|-------------------|---------|-----------|-----------|-----------|-----------|-----------|--------------|
| Raw               | 220     | 226.2     | 221.8     | 224.7     | 230.2     | 230.2     | 224.5        |
| As-plated         | 510     | 515.2     | 522       | 558       | 500       | 500       | 521          |
| Air-cooled        | 535.4   | 539.2     | 531.5     | 532.1     | 540       | 540       | 535.6        |
| Water-quenched    | 515.3   | 519.2     | 511.9     | 506.1     | 522.1     | 522.1     | 514.9        |
| Type I oil-quenched | 535.6   | 531.2     | 533.2     | 532       | 527       | 527       | 531.8        |
| Type II oil-quenched | 526.2   | 532.9     | 530.2     | 558       | 500       | 500       | 529.4        |

Figure 2. Atomic force microscope 3D images of electroless nickel plating surface (a) air-quenched (b) water-quenched (c) Type-I oil-quenched and (d) Type-II oil-quenched.
Table 2. Ra values of the different quenched specimens

| Samples                        | Ra Value (nm) |
|-------------------------------|---------------|
| Air-cooled Sample             | 16.7          |
| Water-quenched Sample         | 16.6          |
| Type I oil-quenched Sample    | 14.4          |
| Type II oil-quenched Sample   | 21.7          |

3.2. Atomic force microscope (AFM) analysis

AFM is used to give a visible picture of a surface. AFM-3D images of all heat-treated different types of post quenched specimens are given in Figure 2(a-d).

All the images are taken under 10 µm magnification. The Ra values of all the electroless nickel-plated air-cooled, water-quenched, type-I, and type-II oil-quenched samples are given in Table 2. AFM results show that the Ra value of Type I oil quenched samples is low compared to other types of samples.

3.3. Thickness of plating

The thickness of the coating is measured using an optical microscope. In all types of samples, five specimen cross-sections were prepared. Further, the specimen was kept under an optical microscope, and the thickness of the coating of each sample was measured. The coating thickness of all types of specimens is given in Table 3. The results show that the average coating thickness of all the specimens is above 3 µm.

3.4. Morphology and chemical composition

The scanning electron microscope (SEM) equipped with an EDS system is used to investigate the morphology and chemical analysis of the cells in the samples over a broad range of magnification.

The SEM images of the uncoated traveler sample, electroless Ni-P plated sample, and electroless Ni-P plated, and heat-treated post quenched samples are shown in Figure 3(a-f). The EDS results of as-plated and heat-treated samples are given in Figure 4(a,b). It has been observed nonuniform distribution of the plating on the substrate in the case of as-plated sample 3(b). The electroless Ni–P coating is in the form of amorphous layers on the substrate. The distribution of the plating will become uniform, and crystalline structure formation takes place after the heat treatment followed by air-quenched which is shown in Figure 3(c), water-quenched as mentioned in Figure 3(d), Type-I oil-quenched in Figure 3(e), and Type-II oil quenched as shown in Figure 3(f).

Table 3. The thickness of coating of different specimen

| Sample                      | Thickness of coating trials (µm) | Average thickness (µm) |
|-----------------------------|---------------------------------|------------------------|
| As-plated                   | 3.21, 3.35, 3.2, 3.57, 3.86     | 3.43                   |
| Air-cooled                  | 3.39, 3.56, 3.55, 3.72, 3.85     | 3.61                   |
| Water-quenched              | 3.72, 3.54, 3.89, 3.55, 3.45     | 3.63                   |
| Type I oil-quenched         | 3.96, 3.55, 3.46, 3.19, 3.92     | 3.61                   |
| Type II oil-quenched        | 3.23, 3.55, 3.76, 3.89, 3.55     | 3.59                   |
Figure 3. SEM images of (a) Uncoated, (b) Ni–P plated and untreated (c) Ni–P heat-treated air-quenched (d) Ni–P heat-treated water quenched (e) Ni–P heat-treated Type-I oil-quenched and (f) Ni–P heat-treated type-II oil-quenched sample.

Figure 4. EDS results of (a) as-plated Ni–P and (b) heat-treated, followed by type-I oil quenched samples.

Figure 4(a,b) shows the EDS results of the as-plated sample and type-I oil quenched sample. It indicates the presence of Ni–P on the substrate. A small amount of iron and carbon were also present, which may be due to improper activation of the surface before coating.

3.5. Wear test
The sliding wear test was conducted for all the as-plated, air-cooled, water-quenched, type-I, and type-II oil-quenched specimens as per ASTM-G99-12 (ASTM 2012). Specimens of 8 mm diameter and 30 mm height were prepared and coated using an electroless nickel process with an average coating thickness of 4 µm. The disc’s rotation speed was set at a constant 200 rpm and a time duration of 30 min for all the samples. A 20 N load normal to the disc’s surface, was applied to all the samples during testing. Three trials were taken for each specimen. The weight of the specimen
before and after the test was measured, and the weight difference is noted and reported in Table 4. The schematic representation of the wear test regarding the application of load, the direction of rotation of the disc, contact surface of the specimen, and the disc is shown in Figure 5.

The purity of electroless nickel deposition (generally 92% nickel and 8% phosphorus) is less than the electrodeposition method (99% Nickel). The phosphorus content in the electroless Ni–P coating has a significant effect on the properties. In the case of electroless nickel plating, it is possible to obtain 3% to 12% of P. Based on the P content, one can classify the coatings as low (2–5% P), medium (6–9% P), and high (10–13% P) phosphorus coating. The content of P also influences corrosion resistance, wear resistance, friction coefficient, and hardness of the coating (Buchtík et al., 2019). Further, the content of P is also influenced by the internal residual stress in the coated film. The high content of P leads to compressive stress, while the low content creates tensile residual stress in the coated film. The microstructure of the electroless Ni–P is amorphous in as-plated conditions, and it converts into a fine grain structure after proper heat treatment. This structure also influences the wear resistance of the electroless Ni–P. It has been reported in the literature that, due to Ni–P coating on steel, improved tremendous wear resistance after heat treatment at 320°C and 400°C (Samuel & Zoppas, 2017; Uday Venkat Kiran et al., 2019).

Table 4. Loss of material due to wear

| Type of specimen | Initial Weight | Final Weight (g) | Weight Loss (g) | Wear (g) |
|------------------|----------------|------------------|-----------------|---------|
| As-plated        | 8.645          | 8.632            | 0.013           | 0.013   |
|                  | 8.683          | 8.669            | 0.014           |         |
|                  | 8.650          | 8.638            | 0.012           |         |
|                  | 8.782          | 8.772            | 0.01            |         |
| Air-quenched     | 8.785          | 8.776            | 0.009           | 0.009   |
|                  | 8.783          | 8.773            | 0.01            |         |
|                  | 8.683          | 8.676            | 0.007           |         |
| Water-quenched   | 8.686          | 8.677            | 0.009           | 0.008   |
|                  | 8.684          | 8.675            | 0.009           |         |
|                  | 8.728          | 8.723            | 0.005           |         |
| Type-I oil-quenched | 8.726      | 8.722            | 0.004           | 0.004   |
|                  | 8.730          | 8.726            | 0.004           |         |
|                  | 8.645          | 8.632            | 0.008           |         |
| Type-II oil-quenched | 8.683     | 8.673            | 0.007           | 0.007   |
|                  | 8.650          | 8.639            | 0.008           |         |
It is noticed from the wear loss results from the table that higher wear loss of as-plated samples as compared to heat-treated quenched samples. This change is confirmed from the EDAC results that the hardness of as-plated samples is less than the heat-treated quenched samples because of the amorphous structure in as-plated samples. This difference leads to higher wear loss. The 3D image and surface roughness results reveal that the type-I oil quenched samples have a smooth surface compared to other samples. This difference leads to mild deformation at the junction of asperities in type-I oil quenched sample, which results in shallow wear loss. In addition to this, EDAC results reveal that the content of P, which has solid lubricant behavior in the coated samples, is low in the as-plated sample compared to heat-treated samples. This aspect is responsible for lower wear loss in heat-treated samples and higher wear loss in as-plated samples. Thus, it is found that the synergistic effect of higher hardness, crystalline structure, excellent bonding developed between the coating and substrate, and moderate content of P helps in marginal reduction of wear in type-I oil quenched samples as compared to other samples.

4. Conclusions
The microhardness test result shows that all the quenched samples have similar hardness. The thickness of the coating obtained is around 3 μm. Wear tests of the specimens show that Type I oil quenched specimens have better wear resistance than other specimens. Analysis of AFM results shows that the Type I oil quenched travelers have a smoother surface morphology than that of water- and air-cooled travelers. SEM images show that the distribution of plating on the substrate is not uniform in as-plated conditions. After baking, the coating becomes uniform on the substrate. However, there are some small voids present in the coating. These voids are formed due to improper surface activation before the plating process.

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References
Buchlik, M., Krystynová, M., Mášilko, J. & Wasserbauer, J. (2019). The effect of heat treatment on properties of Ni-P coatings deposited on a A291 magnesium alloy. Coatings, 9(7), 661. https://doi.org/10.3390/coatings9070661
Chang, S. H., Chang, C. C., & Electroless Ni-P, L. C. (2013). Plating and heat treatments on S45C carbon steel. IOP Conference Series: Materials Science and Engineering, 46, 1. https://doi.org/10.1088/1757-899X/46/1/012003
Goettems, F. S., & Ferreira, J. Z. (2017). Wear behavior of electroless heat treated Ni-P coatings as alternative to electroplated hard chromium deposits. Materials Research, 20(5), 1300–1308. https://doi.org/10.1590/1980-5373-MR-2017-0347
Maretić, M., Smoljan, B., & Iljić, D. (2017). Heat treatment of electroless Ni-P layers on an austenitic stainless-steel substrate. Material in Technology, 51(3), 413–417. https://doi.org/10.17222/mit.2016.010
Samuel, G. F., & Zappas, F. J. (2017). Wear behaviour of electroless heat treated Ni-P coatings as alternative to electroplated hard chromium deposits. Materials Research, 20(5), 1300–1308. https://doi.org/10.1590/1980-5373-MR-2017-0347
Shen, Y. F., Liu, W. N., Sun, X., Xue, W. Y., Wang, Y. D., Zuo, L., & Llow, P. K. (2012). Plastic deformation in an amorphous Ni-P coating. Metallurgical and Materials Transactions A, 43(5), 1610–1620. https://doi.org/10.1007/s11661-011-0989-0
Sribalaji, M., Arunkumar, P., Babu, K. S., & Keshri, A. K. (2015). Crystallization mechanism and corrosion property of electroless nickel phosphorus coating during intermediate temperature oxidation. Applied Surface Science, 355, 112–120. https://doi.org/10.1016/j.apsusc.2015.07.061
Uday Venkat Kiran, K., Arora, A., Ratna Sunil, B., & Dampala, R. (2019). Sliding wear characteristics of as-deposited and heat-treated electroless Ni-P coatings against AISI ES2110 steel ball. Materials Research Express, 6(3), 03640. https://doi.org/10.1088/2053-5078/aaf2f9
Wang, C., Farhat, Z., Jarrouja, G., Hassan, M. K., Abdulllah, A. M., & Foyad, E. M. (2017). Investigation of fracture behavior of annealed electroless Ni-P coating on pipeline steel using acoustic emission methodology. Surface and Coatings Technology, 326, 336–342. https://doi.org/10.1016/j.surfcoat.2017.07.067
Zhang, H., Zou, J., Lin, N., & Tang, B. (2014). Review on electroless plating Ni-P coatings for improving surface performance of steel. Surface Review and Letters, 21(3), 1430002. https://doi.org/10.1142/S0218625X14300020
