Tribological characterization of electroless Ni-P-Cu-TiO₂ coatings

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Abstract

Present research work aims to describe the deposition of electroless quaternary Ni-P-Cu-TiO₂ coating on mild steel substrate and its tribological characterization. Energy dispersive x-ray analysis confirms the presence of all four elements within the coating. Tribo-testing at different sliding velocity revealed wear depth is high but stable at high sliding velocity whereas the coefficient of friction increased linearly with sliding velocity.

Keywords: Quaternary coating, Electroless, Ni-P-Cu-TiO₂, Wear, Friction

1. Introduction

The emphasis on electroless composite coatings for superior micro-hardness, corrosion, friction and wear resistance properties dates back to the notable works of few scientists with evidence [1, 2]. Payder and Araghi concentrated on the micro-hardness of the composite and so for its increase went for the incorporation of boron in the form of B₄C to form Ni-P-B₄C composite [3]. As a result, there was an increased wear resistance of AZ91D alloy substrate significantly in the presence of hard B₄C composites. Leon et al. reported excellent friction and wear resistance found in the Ni-P-BN(h) composite coatings [4]. Bozzini heat-treated the Ni-P/diamond composite layers and found out an increased hardness along with an increased Young’s Modulus [5]. The incorporation of diamond particles and heat treated up to 400°C showed results of fantastic higher hardness, corrosion resistance and wear resistance. To gain improved micro-properties, uniform incorporation of particles in matrices was required and hence Sol-Gel technique was developed. The technique of very modern day over electroless coating for uniform agglomeration of particles in composites and Chen used it in his Ni-P-TiO₂ matrix [6]. The experimental results confirmed that the wear resistance and micro-hardness of the sol-gel TiO₂ coatings were higher as compared to conventional TiO₂ coatings. At later stages Jappes used X-Ray Diffraction method and heat treatment technique for the measurement of wear resistance of Ni-P deposits in reference to different temperatures [7]. It was observed that at 350°C the coating showed higher wear resistance than at 500°C. His work was a confirmation of the technique used by Chen [6]. Few authors observed improvements in the tribological properties of the composites when there is a change in the orientation of the specimen (say from vertical to horizontal). Even electroless nickel with polymer matrix showed an improved result too as an effect of the addition of soft particles. The work of Mohammadi and Ghorbani on EN-PTFE-MoS₂ showed better experimental results relative to wear resistance with respect to any other incorporated soft particles to improve wear resistance, corrosion resistance [8]. Other than that, with the incorporation of certain hard particles like SiC, Ni composites showed a prospect of high micro-hardness and high Friction co-efficient. These were the works performed by Zarebidaki and Allahkaram [9] and prior to them it was the observation of Grosjean [10] as well. There was a decrease in the corrosion resistance of Ni-P-SiC as well due to the porosity and agglomeration of nano-particles. It improved when heat treated at annealing temperature of 400°C for 1 hour. With that result, Mallafati [11] observed that due to the reduction in the exposed area of metallic matrix as by the presence of SiC particles coated layer, the Ni-P alloy showed an improvement in the corrosion properties.
Above discussion ensures that, with an increased crystallinity, low porosity and decreased residual stresses, elements like Al₂O₃, B₄C, SiC, ZrO₂, TiO₂ are able to provide the degree of hardness required. Thus, the aim of this work is to develop and characterize electroless coated Ni-P-Cu-TiO₂ composite coatings where, Copper and Titania acts as a ternary and quaternary components respectively. The coatings have been deposited using hypophosphite bath. The effects of sliding speed on the tribological behavior of this composite coating have been studied at close proximity.

2. Experimental details

The chosen substrate for the purpose of coating in this paper is Mild Steel (AISI 1040). As per the size stringency, to fit in the pallet comfortably for further analytical tests the pin-type samples with specifications of 30 mm length and 6 mm diameter were used. The pin-type samples were degreased for the experiment by the process as mentioned. Three different beakers were taken containing dilute hydrochloric acid solution (50% HCL and 50% distilled water), Distilled water (deionized water), palladium solution respectively (PdCl₂). The sample was stringed carefully for the preliminary chemical treatment for activating the substrate for deposition. The sample was dipped in deionized water and then into dilute HCL solution, then after a few moments into palladium solution (warmed up to a few degrees above room temperature). The specimen activated for coating deposition was then immersed (dipped) into the hot electroless bath composed of Nickel sulphate (NiSO₄) 35 g/l, Sodium Hypophosphite (NaPO₂H₂) 20 g/l, Trisodium citrate (Na₃C₆H₅O₇) 15 g/l, Sodium acetate (C₂H₃NaO₂) 5 g/l, Copper sulphate (CuSO₄) 0.5 g/l, Sodium Dodecyl sulphate (NaC₁₂H₂₅SO₄) 0.2 g/l and Titanium Oxide (TiO₂) 5 g/l. The bath was kept at constant temperature of 85°C for 3 hours. To achieve higher thickness the coated samples were immediately placed into a fresh bath for next 3 hours. The baths were continuously stirred by a magnetic stirrer to keep the TiO₂ particles in suspension. After coating the samples were taken out of the bath and washed in distilled water and dried. Energy dispersive x-ray analysis was performed to confirm the presence of four elements. The tribological study of the as-deposited electroless Ni-P-Cu-TiO₂ coated pin-type samples was performed on a multi-tribotester (DUCOM-TR-20LE) with a pin-on-disc configuration. The test on the pin samples were performed in dry (non-lubricated) condition. The tests were performed at a normal room temperature under a normal load of 10 N. The speed was varied for four different samples ranging from 2 to 8 m/s for a sliding distance of 600 m. The test data was captured by associate software beside this the ware volume was also measured.

3. Results and discussion

3.1. Composition analysis

Energy dispersive x-ray analysis confirms the presence of all the four components of the coating. The EDX spectrum is shown in Figure 1. Table 1 shows the range of wt% of those four components at different test points.

|        | Minimum value (wt.%) | Maximum value (wt.%) |
|--------|---------------------|---------------------|
| Nickel | 48.94 %             | 82.62 %             |
| Phosphorus | 4.99 %             | 12.7 %             |
| Copper | 3.96 %              | 13.40 %            |
| Titanium | 0.97 %            | 36.67 %            |
3.2. Tribological test

Wear depth and frictional force were captured by allied software during test. Coefficient of friction was calculated from the friction force. Wear depth and coefficient of friction as a function of sliding distance for different sliding velocities are shown in Figure 2.

It is clear from figure 2 (a) that the wear depth jumps to a high value when, sliding velocity increased from 2 m/s to 4 m/s but a small increase in coefficient of friction was observed in this case (figure 2 (b)). However at higher speed, wear depth is high but stable with sliding distance but coefficient of friction...
increased with the sliding distance. In order to have a close observation on tribological behavior, a correlation between wear coefficient (Eq. 1) and frictional power (Eq. 2) was established.

\[
\text{Wear coefficient} = \frac{V_w}{F_n \times s} \quad (1)
\]

\[
\text{Friction power} = F_f \times v \quad (2)
\]

Where, \( V_w \) is the wear volume, \( F_n \) is normal force, \( s \) is sliding distance, \( F_f \) is friction force and \( v \) is sliding velocity.

The ambiguity of Figure 2(a) can be understood clearly from Figure 3. It shows that wear coefficient or wear volume follows same pattern with respect to friction power and sliding velocity respectively. Both wear parameters reach at maximum value while sliding with 6 m/s and remain almost constant or a little bit decreased while sliding with next higher speed of 8 m/s. In both cases friction coefficient is seen to be increased gradually in a linear way. Thus a stable wear can be achieved at higher sliding speed.

![Figure 3: (a) Wear coefficient and Coefficient of friction vs. Friction power, (b) Wear volume and Coefficient of friction vs. sliding velocity](image)

4. Conclusion

The paper describes the successful deposition of electroless Ni-P-Cu-TiO2 composite quaternary coating over mild steel substrate and characterizes the effort with EDXA and tribotesting. The subject comprises with vast scope of futuristic research work relative to microstructure study, hardness, anti-corrosion properties and many more. Hence, such futuristic researches should be carried out on electroless Ni-P coatings in lieu of its existence in automobile, aerospace to alloy industries.

Acknowledgement

Authors are grateful for financial support provided by CSIR-HRDG, India, vide sanction letter no.: 22(0804)/19/EMR-II dated 25/07/2019, to carry out this work.

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