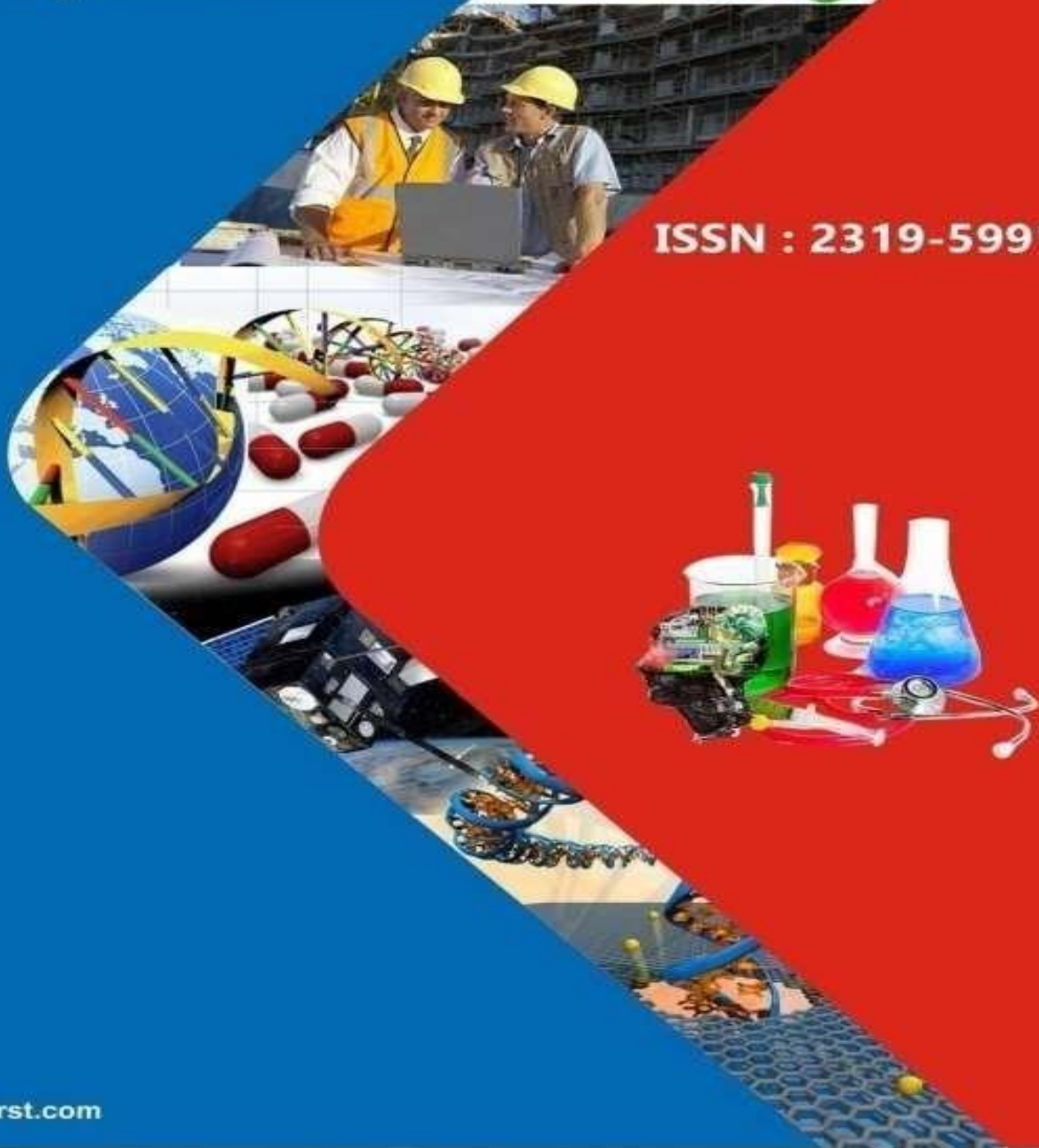


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Investigation on the Micro Hardness of Electroless Ni-P Duplex Coatings Reinforced with ZnO, Al₂O₃, and SiC Particles

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Abstract

Coating methods on components' surfaces may improve their functional performance. A variety of coating processes are required by the majority of industries in order to enhance the performance of components. In this experiment, Ni-P-Al₂O₃/Ni-P-SiC and Ni-P-ZnO/Ni-P-SiC duplex coatings were tested on mild steel in an effort to increase its surface hardness. The researchers in this work created multi-layer coatings by using a dual electroless bath. The Vickers microhardness tester was used to assess the microhardness of the duplex coating. In order to increase the deposit's microhardness, the aforementioned coatings were heated to 400 °C. We compared the two coatings to find out which one was superior for getting a firm surface. The findings demonstrate that the microhardness of the Ni-P-SiC outer layer duplex coating is satisfactory. Phase transition from unstructured to structured hard Ni₃P increases the microhardness of the deposit after heat treatment. Microhardness, heat treatment, duplex coating, nanoparticles

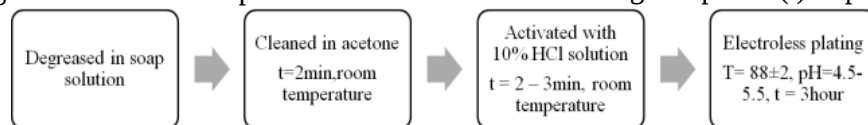
Introduction: In 1946, Brenner and Riddell created electro-less Ni plating, which has been used extensively across several sectors since the early 1980s. Many industries rely on composite coatings made of non-electric materials, such as

Ni-P and Ni-B. These coatings have many advantages, including superior hardness, surface finish, adhesion, wear resistance, corrosion resistance, and thickness uniformity over complex shapes [1-3]. Using a combination of soft and hard particles, composite Ni-P coatings were created. Thickening the second phase with particles of varying sizes (Nano, macro, and micron) improves the tribological and mechanical characteristics of Ni-P plating. The different hard ceramic second phase particles may be deposited to improve features such as hardness, wear resistance, and corrosion resistance [4-6]. Microhardness of coatings is influenced by heat treatment, phosphorus content, and particle co-deposition rate. Reinforcing the Ni-P matrix with Nano Al₂O₃ increases the coating hardness on mild steel by 13%. [7]. The creation of hard crystalline Ni and Ni₃P structures, as confirmed by a thermal treatment procedure performed at 400°C for Ni-P-Al₂O₃ coating, accounts for the 135% increase in microhardness. As the hardness of a material increases, the precise wear percentage of a coat decreases [8,9]. A coating matrix's partial ability to store the greatest quantity of secondary particles, resulting in a composite coating with reduced microhardness when the SiC particle concentration is maximised. Hence, the ideal concentration of SiC particles was used to create the Ni-P-SiC coating in order to achieve the

greatest microhardness value [10,11]. Ni-P composite coatings, which include carbon nanotube (CNT) reinforcements in the Ni matrix, have a microhardness 42% higher than Ni-P coatings alone [12]. A hardness value of 761 HV was observed for the Ni-P-rGO coat that was generated via the electroless immersion process with 50 mg/L of oxide of grapheme (rGO) [13]. This coating is applied to low carbon steel, which improves the substrate's resistant hardness at the micro level. Adding TiN particles to the Ni lattice makes the Ni-P coating 33% harder at the micro level. The microhardness of Ni-P-TiN coatings is increased by 90% after the heat treatment method [14]. When electroless immersion is performed with a zinc oxide component portion at an optimal concentration of 0.5 g/L, the microhardness of a Ni-P-ZnO coating on mild steel is 60% higher than that of the uncoated substrate [15]. The self-lubricating qualities and maximal load transfer resistance of CNTs make them superior to SiC particles. Depositing CNTs (Ni-P) into the composite coating results in the highest possible hardness.

To improve the corrosion resistance, wear resistance, and hardness of nickel, composite coatings of Ni-B were created by co-depositing oxides, carbides, and nitride components in the nickel matrix. The corrosion resistance of the Ni-B composite plating is improved by co-deposited SiC [17] and Si₃N₄ [18], which maintain the anodic dissolution process by decreasing the real metallic zone that is vulnerable to corrosion. Using the Ni-P-Ni-B multi pass plating with double bath, researchers [19-21] studied to acquire ideal characteristics. Compared to Ni-B plating, the multi-pass Ni-B-Ni-P coating has lower microhardness and

Methodology: Methodology adopted to execute the present investigation chosen from the past literature



re. Steps followed in the coating process are schematically representation in the Figure 1.

Figure-1: Steps followed in the electroless coating

Selection of Materials: Mild steel with 20x20mm² are considered as substrate materials for the present

greater resistance to wear. Improved corrosion resistance compared to Ni-P and Ni-B coatings is a consequence of using Ni-B as an inner layer and Ni-P with a high phosphorus concentration as an outermost layer. The duplex coating's hardness and corrosion resistance are further enhanced by the development of crystalline Ni₃P in Ni-P and Ni₃B in Ni-B after the heat treatment method [22–24]. Comparing the Ni-P inner layered Ni-Co-Al₂O₃(60g/L) coat to a Ni-Co-Al₂O₃(60g/L) single layered coat reveals a 20% increase in micro hardness. Duplex Ni-Co-Al₂O₃ plating with Ni-P as an internal coating provides enhanced corrosion resistance, which is related to Ni-Co-Al₂O₃ (60g/L) coating [25]. Multipass Ni-P/Ni-P-W coatings are more resistant to microhardness than ternary Ni-P-W and Ni-P coatings. The capacity of the samples to prevent corrosion is arranged in the following sequence, namely, Ni-P < Ni-P-W < Ni-P/Ni-P-W [26]. Compared to a Ni-P monolayer coating, a high-boron-medium-phosphorus duplex coat offers better corrosion resistance when exposed to an electrolyte containing sulfuric acid. The corrosion behaviour of multi-pass coatings remains unchanged after heat treatment [27]. A small number of studies examined how the concentration of secondary particles in the electroless bath affected the tribological and mechanical characteristics of Ni-P-Ni-B dual coatings. So, in this study, mild steel substrates are coated with Ni-P-Al₂O₃/Ni-P-SiC and Ni-P-ZnO/Ni-P-SiC at different concentrations of SiC, Al₂O₃, and ZnO nanoparticles. In this work, the surface hardness of duplex coatings created with varying nanoparticle concentrations is examined in detail.

Investigation. Electroless duplex coating process has following three phases (i) Preparation of substrate

(ii) Preparation of chemical bath and (iii) Coating.

Substrate Preparation: Prior to the pretreatment process substrate was mechanically polished with SiC papers of grad numbers 100, 220, 320 and 420 to obtain smooth surface. Refined substrate was rinsed

with acetone and deionized water to accomplish oil and dirt free face. After that substrate was stimulate

in the 10% HCl solution for 60 seconds to improve the adhesion of the deposit

Table-1: Electroless bath composition for duplex

Coating Composition	Concentration (g/L)
Nickel-chloride	40
Sodium-hypophosphite	20
Trisodium-citrate	25
Ammonia-chloride	50
CTAB	0.8
ZnO, Al ₂ O ₃ and SiC nanoparticles	1, 2 and 3
pH	4.5 to 5.5
Temperature	88°C (±2)

Chemical Bath Preparation: Chemical components required for the preparation of electroless solution is chosen from past literature. Electroless bath composition and experimental condition required to fabricate multi layer coating is shown in Table 1

Coating Process: To fabricate Ni-P-SiC outer layer coating, initially chemically treated substrate material is dipped into the ZnO particles mixed solution for 90 minutes to develop Ni-P-ZnO layer. Ni-P-ZnO deposited substrate is immersed into the SiC added solution for 90 minutes to form an external Ni-P-SiC layer. To develop Ni-P-ZnO extreme layer coating initially polished surface submerged into the SiC chemical solution for 90 minutes. Afterwards substrate was immersed into the SiC nanoparticles added solution. An ultrasonic agitation technique was used to disperse the nanoparticles uniformly in the chemical solution. Electroless solution distribution of nanoparticles is more uniform in the ultrasonic method compared to other agitation technique [19 and 20]. To maintain constant coating solution temperature oil bath and hot plate

was used. Solution temperature continuously monitored by using thermocouple attached PID controller. Entire deposition process constant solution volume 150 ml was maintained. Pentype pH meter is used to check the pH value of solution. To know the effect of temperature on properties of the duplex deposit thermal treatment carried at 400°C temperature. Procedure mentioned above is adopted to fabricate multi pass Al₂O₃ and SiC reinforced Ni-P coatings. Microhardness of the coating surface is examined by using Vickers hardness tester. 100g of load is applied with dwell time of 10 seconds to examine the thin film microhardness. Average of five readings is considered to report the microhardness of the coating. To know the effect of heat treatment temperature all the coated substrate materials are heated at optimum temperature 400°C by using muffle furnace.

Results and Discussions:

Microhardness:

Microhardness of both the duplex Ni-P-ZnO/Ni-P-SiC and Ni-P-Al₂O₃/Ni-P-SiC

deposit is analyzed by changing the nanoparticles concentration. Results confirm that particle concentration in the coating solution significantly affects the coating microhardness. Hardness of both the coated surfaces fabricated at different concentrations of nanoparticles are shown in Figure 2. Increase in particle concentration from 1 g/L to 2 g/L in the bath increases the deposit microhardness value. Higher hardness value is identified in both the deposits fabricated at nanoparticles concentration 2 g/L. The highest amount of secondary particles is reinforced into the coating matrix uniformly. Under loading, plastic deformation of alloy matrix is prevented by uniformly

reinforced nanoparticles results in better microhardness [28, 29]. A lower microhardness value was observed in the duplex films developed at 3 g/L concentration of particles. Particle agglomeration in coating solution at higher concentration results in lower deposition of particles into the coating matrix. At greater particle concentration, conglomeration of the particles in the coating solution negatively affects the multi-pass coating hardness. So, minimum microhardness value quoted for both the coatings fabricated at 3 g/L concentration of nanoparticles [30-32].

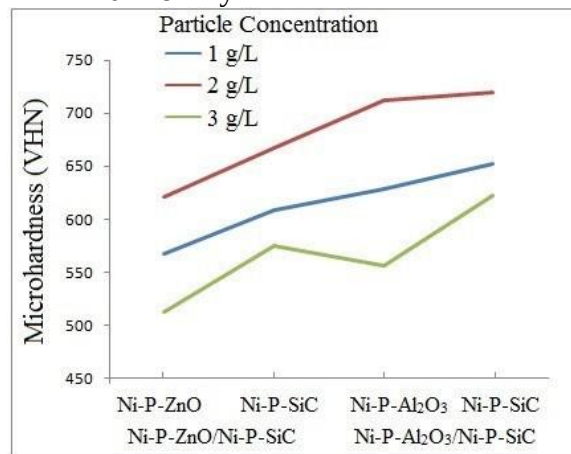


Figure-2: Microhardness comparison between the Ni-P-ZnO/Ni-P-SiC and Ni-P-Al₂O₃/Ni-P-SiC coatings

At all the particle concentrations, the Ni-P-SiC external layer coating's microhardness is superior to the Ni-P-ZnO and Ni-P-Al₂O₃ external layer. Compared to Al₂O₃ and ZnO nanoparticles, the load-carrying capacity of the SiC nanoparticles is higher, which restricts the deformation in the coating matrix. Therefore, multilayer coating with Ni-P-SiC layer offers better microhardness value. Higher softening nature of the ZnO nanoparticles results in lower microhardness value than the Ni-P-ZnO external layer coatings [33].

Duplex coating heat treated at optimum heat treatment temperature 400 °C significantly improves its microhardness. After the thermal process, microhardness of the

coatings developed at different amounts of nanoparticles is represented in Figure 3. After the heat treatment process, microhardness of both the coatings is significantly improved. Formation of a hard crystalline phase from an amorphous phase after the annealing process is the main cause for enhancement in microhardness [34, 35]. Ni-P-Al₂O₃/Ni-P-SiC coating developed at 2 g/L particle concentration shows a maximum hardness value of 985 VHN. Which is 11% higher than the Ni-P-ZnO/Ni-P-SiC coating fabricated at the same level. Hard crystalline Ni₃P phase formation in Ni-P-Al₂O₃/Ni-P-SiC coating is superior to the Ni-P-ZnO/Ni-P-SiC coating. Therefore, hardness at the micro-level of Ni-P-Al₂O₃/Ni-P-SiC coating is superior to Ni-P-ZnO/Ni-P-SiC coating.

after annealing process.

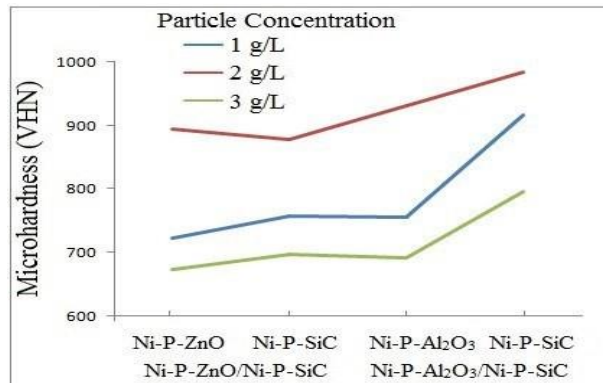


Figure-3: Microhardness of the Ni-P-ZnO/Ni-P-SiC and Ni-P-Al₂O₃/Ni-P-SiC coatings after heat treatment process.

Conclusions:

Dual electroless bath is used to develop multiple Ni-P-SiC/Ni-P-ZnO and Ni-P-Al₂O₃/Ni-P-SiC coatings. Microhardness of the coatings developed at various concentrations of nanoparticles is compared. Based on the comparative study following conclusions are summarized.

Particle concentration in the coatings solution considerably influences the coating properties. Microhardness of all the coatings increases up to 2 g/L particles concentration. Particle agglomeration in the coatings solution at 3 g/L particle concentration lowers the microhardness of the coating.

At the same concentration of nanoparticles microhardness of the Al₂O₃ and SiC reinforced duplex coating is higher than the ZnO and SiC reinforced duplex coating. Both the coatings higher microhardness value observed at 2 g/L particle concentration. Maximum microhardness value 720 VHN observed in the Ni-P-SiC external layer Ni-P-Al₂O₃/Ni-P-SiC duplex coating.

After heat treatment process further improvement in hardness was identified in all the coatings. Formation of hard crystalline Ni₃P after thermal process significantly improves the microhardness of the coating. Maximum hardness value 985 VHN observed in the Ni-P-Al₂O₃/Ni-P-SiC coating developed at 2 g/L particle concentration. Which is 11 % higher than the Ni-P-ZnO/Ni-P-SiC coating formed at same level.

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