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COMPARATIVE ANALYSIS ON MICROHARDNESS OF THE ZNO, AL_2O_3 AND SIC PARTICLES REINFORCED ELECTROLESS NI-P DUPLEX COATINGS

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Abstract
Functional performance of components can be increased by the surface coating techniques. Most of the industries need to improve the components performance using several coating techniques. To improve the mild steel surface hardness duplex Ni-P-ZnO/Ni-P-SiC and Ni-P-Al_2O_3/Ni-P-SiC coatings were tried on it in this investigation. In this study by using dual electroless bath multi-layer coatings is developed. Microhardness of duplex coating measured with assistance of the Vickers microhardness tester. The above mentioned coatings subjected to heat treatment at a temperature of 400^{o}C to enhance the microhardness of the deposit. A comparative study was carried out between both the coatings to know the better alternative to achieve good surface hardness. Results confirm that Ni-P-SiC outer layer duplex coating offers good microhardness. After Heat treatment process, microhardness of the deposit has been increased because of Phase transmission occurs to hard Ni_3P from unstructured to structured hard Ni_3P.
Key words: Duplex coating, nano particles, Microhardness, Heat treatment.

Introduction
Brenner and Riddell developed electro-less Ni plating in 1946 and widely used in several industries since the early 1980s.Composite coatings without electricity i.e., Ni-P, Ni-B arewidely used in various industries like automobile, chemical, marine, aerospace, mining, oil and gas due to its superior characteristics like hardness, surface finish, adhesion, wear, corrosion resistant and thickness uniformity over intricate shapes [1-3].By co-depositing the soft and hard particles, composite coatings of Ni-P were produced. Tribological and mechanical properties related to the Ni-P plating can be enhanced by reinforcing the second phase particles of different sizes i.e., Nano, macro and micron. Improvement in the properties like resistance to corrosion, resistance to wear and hardness can be achieved by depositing the various hard ceramic second phase particles[4-6].Particles co-deposition rate, phosphorus concentration and thermal treatment also affects the coatings microhardness. Ni-P coating hardness on the mild steel is increased by 13%, by reinforcing Nano Al_2O_3into Ni-P matrix.[7].A process of thermal treatment carried at 400^{o}C for Ni-P-Al_2O_3 coating confirms that the 135% improvement in microhardness due to the formation of hard crystalline Ni and Ni_3P structure. Increase in hardness results decrease in exact wear proportion of the coat [8,9].Partial capacity of the coating matrix to hold maximum amount of secondary particles, which results lower microhardness to the composite coating fabricated at maximum concentration of SiC particles. Therefore to obtain maximum microhardness value Ni-P-SiC coating was fabricated at optimum concentration of SiC particles [10,11].Microhardness of Ni-P composite coating is increased by 42% compared to the Ni-P coating by reinforcing CNT particles in the Ni matrix [12].Ni-P-rGO coat on low carbon steel having low carbonenhances the resistance hardness at micro level of the substrate and the corresponding value of 761 HV is witnessed for Ni-P-rGO coatobtained from the electroless immersion having 50 mg/L oxide of grapheme (rGO) [13]. Incorporation of TiN particles in the Ni lattice increases the hardness at micro level of the Ni-P coating at 33 %. After heat treatment process, 90% improvement in the microhardness is witnessed

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for Ni-P-TiN coatings [14].Optimum concentration (0.5 g/L) of Zinc Oxide constituent part in electroless immersion results 60% improvement in microhardness of Ni-P-ZnO coat on mild steel compared with substrate which is uncoated [15].Compared to SiC particles, CNTs are having maximum load transfer resistance and self-lubricating properties. So, in the composite coating maximum hardness achieved by depositing the CNTs (Ni-P)

Composite coatings of Ni-B were developed by means of co-depositing the oxides, carbides and nitride elements in the matrix of nickel to enhance the resistance to corrosion, resistance to wear and hardness. Co-deposited SiC [17] and Si_3N_4 [18] retains the anodic dissolution reaction by reducing its actual metallic zone, susceptible to corrosion, improvementin the resistance to corrosion of the Ni-B composite plating. To get optimal properties, researchers [19-21] investigated with the Ni-P-Ni-B multi pass plating with double bath. Microhardness and resistance to wear of the multi-pass Ni-B-Ni-P coating is lesser than the Ni-B plating and higher than the Ni-P coating. Ni-B as an inner layer and high Phosphorus content in Ni-P as an outermost layer results enhanced corrosion resistance compared to the coatings made of Ni-P and Ni-B. Development of crystalline Ni_3P in Ni-P and Ni_3B in Ni-B after thermal treatment process further increases the hardness and resistance to corrosion of the duplex coating [22-24].Hardness at micro level of the Ni-P inner layered Ni-Co-Al_2O_3(60g/L) coat is 20% greater than the coating of Ni-Co-Al_2O_3(60g/L) single layered coat. Related to Ni-Co-Al_2O_3 (60g/L) coating, duplex Ni-Co-Al_2O_3 (60g/L) plating by Ni-P as internalcoating offers improved resistance against corrosion [25]. Resistance to hardness at micro level of the multipass Ni-P/Ni-P-W coatings is greater than the ternary coat of Ni-P-W and Ni-P. Corrosion protection ability of the samples follows the subsequent order i.e., Ni-P < Ni-P-W < Ni-P/Ni-P-W [26].Resistance against Corrosion of the high boron- medium level of phosphorus duplex coat in presence of electrolyte related to sulphuric acid is greater than the Ni-P mono layer coating. After treating thermally same corrosion behavior is witnessed in the multi-pass coatings [27].Very few researchers were focused on influence of secondary particles concentration in the electroless bath on mechanical and tribological properties of the Ni-P-Ni-B dual coatings. Therefore, Present investigation Ni-P-ZnO/Ni-P-SiC and Ni-P-Al_2O_3/Ni-P-SiC coatings are fabricated on mild steel substrate at various concentrations of SiC, $Al_2O_3$and ZnO nanoparticles. Present study mainly focus on surface hardness of the duplex coating developed at different concentrations of nanoparticles is analyzed clearly.

Methodology

Methodology adopted to execute the present investigation chosen from the past literature.Steps followed in the coating process are schematically representation in the Figure 1.

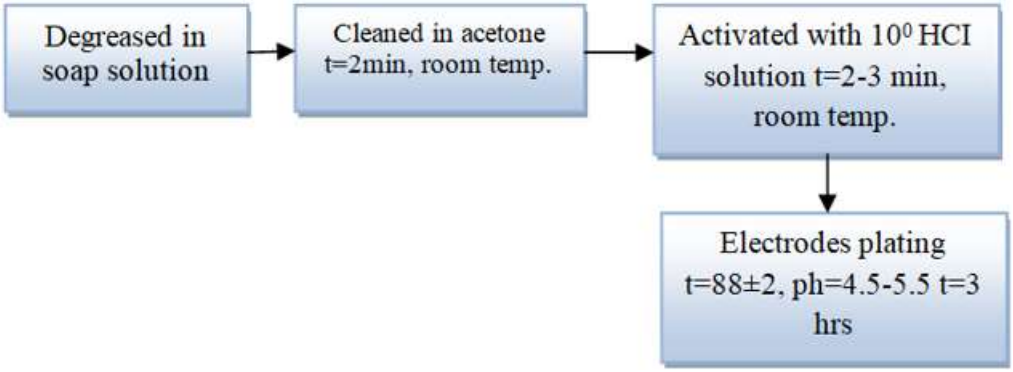

Figure-1: Steps followed in the electro less coating

Selection of Materials: Mild steel with 20 x 20 mm^2 are consider as a substrate materials for the present investigation. Electroless duplex coating process has following three phases (i) Preparation of substrate (ii) Preparation chemical bath and (iii) Coating.

Substrate Preparation: Prior to the pretreatment process substrate was mechanically polished with SiC papers of grade 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 sec to improve the adhesion of the deposit

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Table -1: Electroless bath composition for duplex

Coating Composition	Concentration (g/L)
Nickel-chloride	40
Sodium-hypophosphite	20
Tri sodium-citrate	25
Ammonia-chloride	50
CTAB	0.8
ZnO, Al_2O_3 and SiC nanoparticles	1, 2 and 3
pH	4.5 to 5.5
Temperature	88 ^oC (±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 hotplate was used. Solution temperature continuously monitor by using thermocouple attached PID controller. Entire deposition process constant solution volume 150 ml was maintained. Pen type 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 ^oC temperature. Procedure mentioned above is adopted to fabricate multi pass Al_2O_3 and SiC reinforced Ni-Pcoatings. Microhardness of the coating surfaceis examined by using Vickers hardness tester. 100g of load is applied with dwell time of 10 sec to examine the thin film microhardness. Average of five readings isconsidered to report the microhardness of the coating.To know the affect of heat treatment temperature all the coated substrate materials are heated at optimum temperature 400 ^oC by using muffle furnace.

Results and Discussions

Microhardness

Microhardness of both the duplex Ni-P-ZnO/Ni-P-SiC and Ni-P-Al_2O_3/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 1g/L to 2g/L in the bath increases the deposit microhardness value. Higher hardness value is identified in both the deposits fabricated at nanoparticles concentration 2g/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 3g/L concentration of particles. Particle agglomeration in coating solution at higher concentration results lower deposition of particles into the coating matrix. At greater particle concentration, conglomeration of the particles in the coating solution negatively

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affects the multi pass coating hardness. So, minimum microhardness value quoted for both the coating fabricated at 3g/L concentration of nanoparticles [30-32].

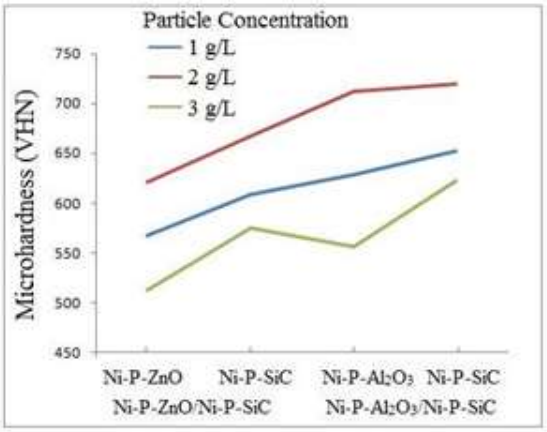

Figure-2: Microhardness comparison between the Ni-P-ZnO/Ni-P-SiC and Ni-P-Al_2O_3/Ni-P-SiC Coatings

At all the particle concentrations, the Ni-P-SiC external layer coating's microhardness is superior to the Ni-P-ZnO and Ni-P-Al_2O_3 external layer. Compared to Al_2O_3 and ZnO nanoparticles load carrying capacity of the SiC nanoparticles is higher, which restricts the deformation in coating matrix. Therefore, multilayer coating with Ni-P-SiC layer offers better microhardness value. Higher softening nature of the ZnO nanoparticles results lower microhardness value to the Ni-P-ZnO external layer coatings [33].

Duplex coating heat treated at optimum heat treatment temperature 400 oC significantly improves its microhardness. After the thermal process microhardness of the coatings developed at different amounts of nanoparticles is represented in Figure 3. After heat treatment process microhardness of both the coating is significantly improved. Formation of hard crystalline phase from amorphous phase after annealing process is the main cause for enhancement in microhardness [34, 35]. Ni-P-Al_2O_3/Ni-P-SiC coating developed at 2g/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 same level. Hard crystalline Ni_3P phase formation in Ni-P-Al_2O_3/Ni-P-SiC coating issuperior to the Ni-P-ZnO/Ni-P-SiC coating. Therefore hardness at micro-level of Ni-P-Al_2O_3/Ni-P-SiC coating is superior to Ni-P-ZnO/Ni-P-SiC coating after annealing process.

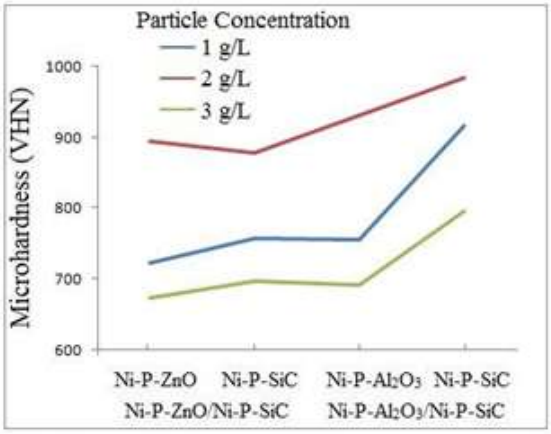

Figure-3: Microhardness of the Ni-P-ZnO/Ni-P-SiC and Ni-P-Al_2O_3/Ni-P-SiC coatings after heat treatment process.

Conclusions

Dual electroless bath is used to develop multi passNi-P-SiC/Ni-P-ZnO and Ni-P-Al_2O_3/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.

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

At the same concentration of nanoparticles microhardness of the Al_2O_3 and SiC reinforced duplex coating is higher than the ZnO and SiC reinforced duplex coating. Both the coatings higher microhardness value observed at 2g/L particle concentration. Maximum microhardness value 720 VHN observed in the Ni-P-SiC external layer Ni-P-Al_2O_3/Ni-P-SiC duplex coating.

After heat treatment process further improvement in hardness was identified in all the coatings. Formation of hard crystalline Ni_3P after thermal process significantly improves the microhardness of the coating. Maximum hardness value 985 VHN observed in the Ni-P-Al_2O_3/Ni-P-SiC coating developed at 2g/L particle concentration. Which is 11 % higher than the Ni-P-ZnO/Ni-P-SiC coating formed at same level.

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