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PULSE ELECTRO CO-DEPOSITED Ni/MWCNT COATINGS ON Al 6061 SUBSTRATE USING PULSE ELECTROPLATING

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ABSTRACT

The excellent mechanical properties of multiwall carbon nanotubes (MWCNTs) like high modulus of elasticity, strength, modulus and fracture strain, they are substitution benefits as reinforcement materials in metallic thin coatings. In this work, a composite coating of Nickel and carbon nanotube (CNT) deposited on aluminum (Al 6061) using pulse electrodeposition (PED) engaged in a nickel watts bath. Surface topography, microhardness, and microstructure and wear resistance of CNT composite coatings were studied. In the composite coating, the carbon nanotubes prohibited the columnar shape growth of the nickel caused resulting in fragile texture. From the experimental result, it can be observed that, the Ni-CNT composite coating on aluminum significantly enhanced microhardness of 567 ± 15 HV. Pure nickel coatings showed the hardness value of 302 ± 15 HV. The wear test experiment result indicated that, the reinforcement of CNTs significantly enhance the wear resistance of the MWCNT-NI-Al composite coatings.

Key Words: MWCNT, Pulse electrodeposition (PED), Aluminum 6061, coating thickness, microhardness

INTRODUCTION

Various coating technologies are employed in metal substrates to prevent corrosion and improve the hardness and microstructure. Over other surface coating processes, pulse electrodeposition (PED) brings a new era in the electrodeposition of metals, alloys, and metal matrix composites. PED technique has a higher flexibility in terms of varying basic electrodeposition parameters, such as pulse current on time, peak current density and pulse current off time resulting in a unique combination of composition and microstructure in deposited coatings. An average current density can be obtained from the pulse current on time and off time through the combinations of different peak current densities.[1] Pulse electrodeposition process used for the synthesis of coatings with controlled thicknesses, compositions, and microstructures by regulating pulse elector parameters. This process is one of the efficient method, which is used for altering the values of two different series of equal duration pulses, polarity, and amplitude separated by zero current.[2]

Ni-TiO_2 composite coatings by electro-co-deposition process were conducted. TiO_2 and nickel composite coating was prepared by a direct current deposition process on a steel substrate. Watt's bath was used for this investigation. Below 100 nm $TiO_{2\ was}$ dispersed uniformly in the nickel matrix. This work concluded that addition of TiO2 increase the microhardness and wear resistance.[3] Ni-P composite coating was fabricated using electroplating and electroless plating on magnesium alloy substrate. In this work zinc and copper were immersed on Mg alloys using direct electroless by chemical conversion detail. In this work, a brief discussion on recent developments on magnesium alloy (AZ 91 and AZ 31) was investigated.[4] Al reinforced Ni / Cu composite was fabricated using accumulative roll bonding and an electroplating method. Microstructure evaluation and mechanical properties of the fabricated Al + Ni + Cu composite showed that, when the number of cycles was increased, elongation and tensile strength of the composite was increased.[5] Electrodeposited Ni–Al composite coating on steel substrate was made. The conclusion from this work showed that the corrosion resistance of the composite coating was increased by 3.5% while NaCl solution was used also an increase in the microhardness was seen.[6] Electro brush plating method was used to deposit

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the layer of SiC / Cu composites on 5 m pure copper sheet. Optical microscope and scanning electron microscope was used to study the structural characterizations of SiC /Cu composite coating. The findings from this work were that the density of the current (3 A/dm^2) increase the coating thickness. The hardness was depended on the SiC content.[7] Plasma sprayed alumina coating was prepared by Nickel electro-deposition process. By using SEM the porosity was analyzed. Crack propagation and hardness were analyzed using Vickers hardness testing machine. The damage mechanism including wear have been analyzed. This work concluded that the electrodeposition of nickel is a sealing treatment for sprayed alumina coatings. As result of sealing hardness and the wear resistance was found to be increased.[8] Sediment electro co-deposition (SECD) method was used to coat nickel (Ni) composite on mild steel wok piece. These composite coatings reviled that, the coefficient of friction was reduced and wear resistance increased when associated with Ni coatings. Nickel Calcium Fluoride composite coatings offered a very low coefficient of friction and wear.[9] Copper composed with Nb coating was employed using co-electro deposition process. The conclusion from this work was that this process is capable of distribution of Nb particles was based on stirring rate and amount of the particles presented in the salt bath. Also, the corrosion resistance of Cu-Nb composite was more when compared with pure copper coating.[10] Nanocrystalline cobalt deposited by electroplating was conducted. The cobalt sub-micron structures were made by an electrodeposition process. This work concluded that the electrodeposited workpieces offered good mechanical strength. Size-dependent softening with shrinking sample dimensions were noticed.[11]

Nowadays CNTs used for improving the mechanical (impart strength, toughness and wear / corrosion resistance), thermal and electrical properties of metal, ceramic and polymeric materials.[12] The reinforcement of carbon nano tubes with metallic materials improve the strength and wear resistance, which is chosen in various structural applications.[13] Hot pressing, hot extrusion, rapid solidification, sintering and plasma spray are the different processes used for carbon nano tube (CNT) reinforced MMCs.

Plasma spray coating and sintering process were used to improve the mechanical properties of the composite coating.[14] Thermal and electrical properties are enhanced and reduction in saturation magnetic was obtained by using rapid solidification technique.[15] Fabrication of metal matrix composites (MMCs) fabricated by hot pressing showed improvement in mechanical and electrical properties. This was obtained because of inhomogeneous dispersion of carbon nano tubes (CNTs) in the metal substrates.[16] Conventional forming process and powder metallurgy were used to fabricate bulk CNT reinforced MMCs. Very few earlier works showed the limitation of the work.[17]

Recent work focused on reinforcing Al_2O_3, ZrO_2 and SiC ceramic substrates. Nickel (Ni) is used for improving the mechanical and electro catalytic properties. The various applications of nickel include circuit boards and switches.[18,19]

From the previous work, it was observed that pulse electrodeposition of carbon nano tubes on aluminum is scanty. In this work combination of Nickel and MWCNTs are coated on aluminum substrates using pulsed electrodeposition process. Two types of coatings. (i) Pure Ni coatings (ii) Combination of (Ni–CNT) coatings deposited on Al 6061 substrates using pulsed electrodeposition (PED) process.

EXPERIMENTAL

Pretreatment of MWCNTS

The one-dimensional semi-static multiwall CNT is for the most part accessible in packaged shape on account of solid Vander dividers connections between the tube dividers[19]. The manufacture of CNT strengthened composite coatings is identified with the no uniform scattering of CNTs in the composite materials is testing. In this examination, the MWCNTs were obtained from the nearby market for manufacturing the composite covering. Figure-1 demonstrates the SEM pictures of MWCNTs utilized for beat electrodeposition process.

To enhance the scattering of carbon nano tubes (CNTs) into the electrodeposited Ni– CNT covering, surface treatment was completed utilizing nitric corrosive. The nitric corrosive surface medications frame carboxylic corrosive gatherings on CNTs and help in the uniform scattering of CNTs with no extra scattering added substance.[20,21] In the present examination, 1 gram of CNTs was included into 900 mL of 8M HNO3 in a container. The blend was hence sonicated in an ultrasonic shower at 30-500 C for nearing

3 hours. The blend was weakened with 1000 mL deionized water and afterward vacuum separated utilizing a 0.5 µm polytetrafluoroethylene channel. The got strong blend was washed with deionized water on the channel until the point when the filtrate was unbiased. The filtrate was impartial at pH 7, which was checked with a pH meter. After this, got CNTs were scattered in the electrolyte without expansion of any scattering specialist. Figure-2 demonstrates the shower arrangement process for beat electro statement.

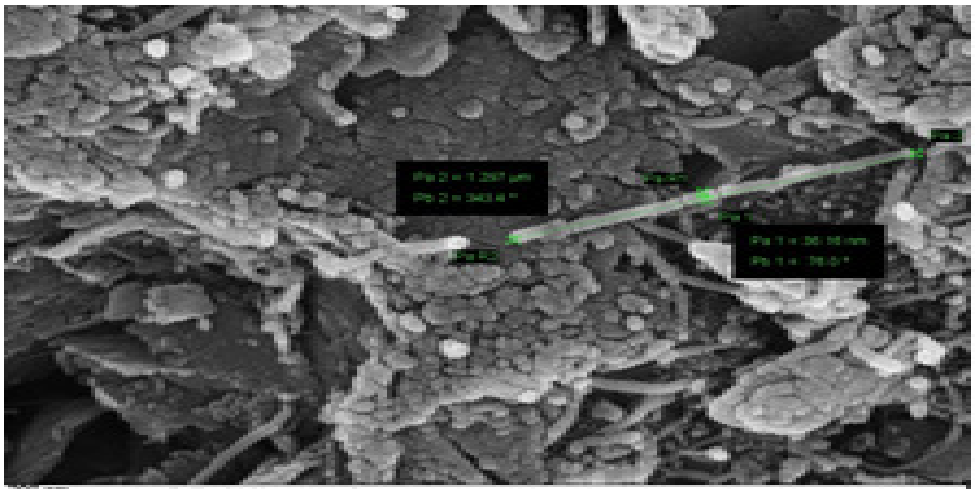


Fig.-1: SEM image of MWCNTs used for pulsed electrodeposition process

Fig.-2: Pretreatment of CNTs

Pulse Electrodeposition of Ni and Ni–CNT Composite Coatings

In this work the plating shower utilized for beat electro statement procedure of Ni– CNT composite coatings was standard watts arrangement. The creation of the electroplating arrangement and the plating parameters for keeping unadulterated nickel coatings are introduced in Table-1.

Table-1: Electroplating solution composition

Composition of Electrolyte	
Nickel sulfate	260 g L^{-1}
Nickel chloride	45 g L^{-1}
Boric acid	15 g/L
Saccharine	0.5 g/L

For Ni– CNT composite coatings, 1 g of multiwall CNTs were blended in 1 litter of essential electrolyte. The CNTs utilized have outside distance across of 30- 50 nm, inside width of 5- 15 nm and length of 10-20 mm. The schematic of the trial set-up appears in Fig.-2.

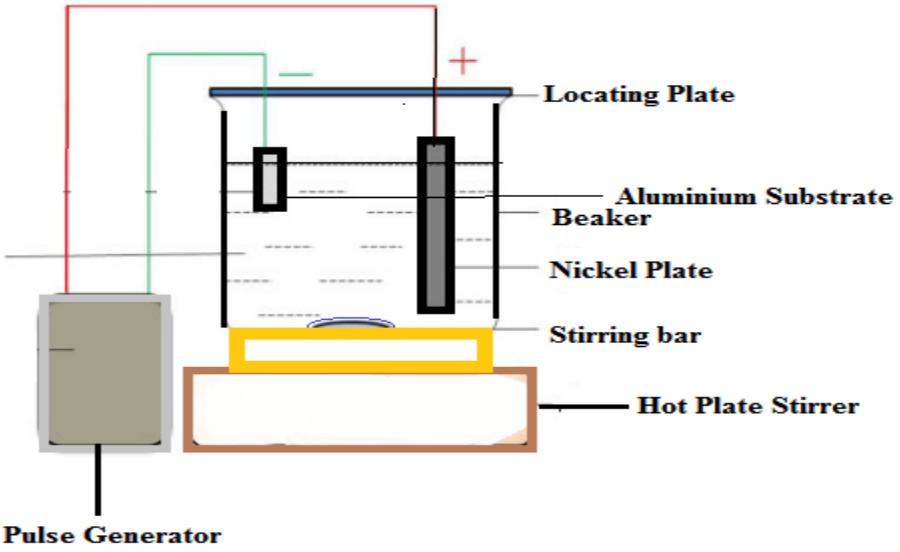


Fig.-3: Schematic diagram of PED system

Pulsed Electro Deposition (PED) PROCESS

Before beat electro statement, the plating shower was sonicated in an ultrasonic cleaner for one hour at room temperature took after by mixing for 5 hours. The underlying pH of the shower was 3.0. The pH of this shower was changed in accordance with 4.0 by the legitimate expansion of NaOH. Aluminum bar and an unadulterated nickel plate with a territory of 20 cm2 were utilized as cathode and anode individually. Aluminum substrates were mechanically cleaned utilizing an arrangement of 200, 400 and 600 work emery papers took after by a grouping of cleanings $(CH_3)_2CO$, ethanol and deionized water) to set up the substrate surface for electrodeposition. The low carbon steel substrate was then enacted in 25% H2SO4 solution. The electrodeposition was done with obligation cycle of 20% and heartbeat recurrence of 10 Hz. The present thickness of 5 A/dm2 was kept up all through the electrodeposition procedure by keeping TON equivalent to 20 min and TOFF equivalent to 80 min. the beat parameters utilized as a part of the present examination are found to give follower composite coatings. Comparative administrations of heartbeat parameters are additionally announced in the writing on PED of coatings. After electrodeposition for 30 min, the composite covering was washed and cleaned with deionized water. Table-2 clarified the parameters utilized for this PED procedure. Fig.-4 clarifies the covering morphology of beat electro affidavit of CNT on Al6061 substrate.

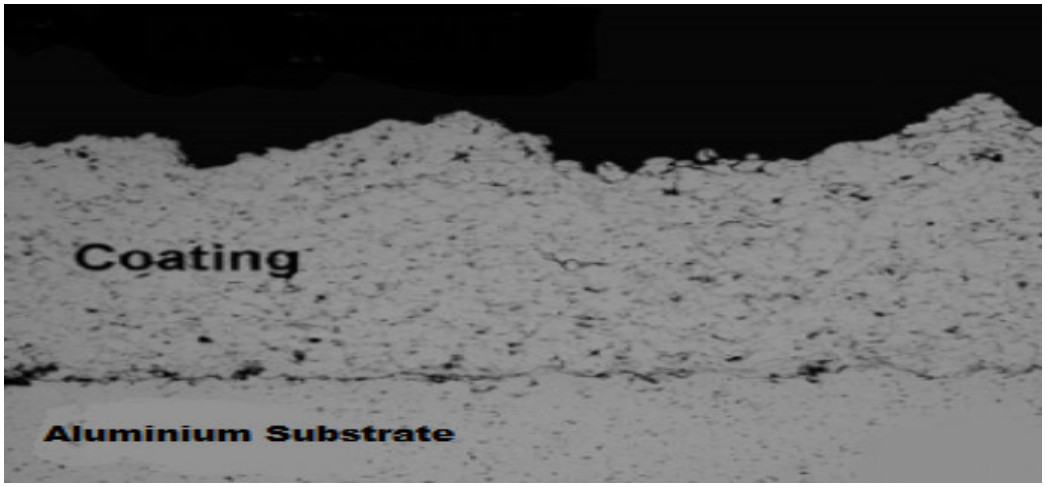


Fig.-4: SEM images of coating on Al 6061 substrate

Table-2: Pulsed Electro Deposition parameters

Current density	4 A /dm^2
pH	5.0
Temperature of the bath	26 ^{0}C
coating time	33 min
Electrolyte agitation	200 rev / min
Duty cycle percentage	20 %
Frequency	12 Hz
Anode material	Nickel (Ni)
Cathode material	Aluminum 6061

Characterization of electrodeposited Ni and Ni– CNT coatings

The composite covering (Ni+CNT) and unadulterated Ni covered Aluminum substrate were analyzed for surface morphology and microstructure utilizing a filtering electron microscope. The diffraction point was changed in the vicinity of 40 and 70°.A small-scale hardness analyzer was utilized for measuring hardness by performing Vickers spaces at a stacking power of 45 g and holding time of 20 seconds. The last esteem cited for the hardness of the covering was normal of 5 estimations. The wear tests were performed on a stick on-circle tribometer at room temperature with no grease. An alumina ball (breadth, 5 mm) was utilized as the counter body. The wear tests were performed utilizing heap of 7 N and speed of 150 rev min 21 for the equivalent interims of 4 min. After each 5 min, a worn example was cleaned in an ultrasonic cleaner with CH3)2CO for 2 min, and the weight reduction esteem was recorded. The ideal test parameters, for example, load and plate transformation every moment, utilized as a part of wear testing were acquired after numerous investigations. These ideal test parameters brought about obvious weight reduction after 5 min time interim of testing. The position of example on the tribometer was kept up after each weight reduction perusing with the end goal that wears proceeds on the same worn track amid proceeded with wear testing

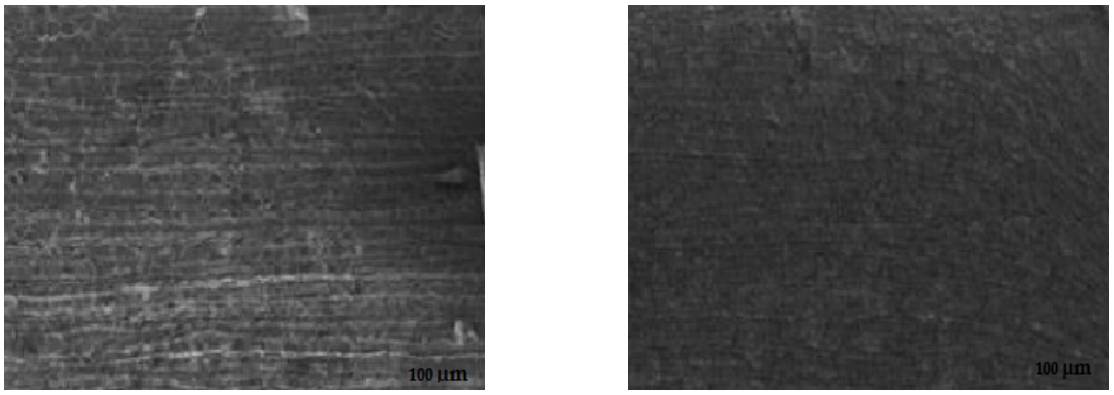
RESULTS AND DISCUSSION

Coating Morphology

To find an uncoated zone on the covered steel thing being checked, or use an uncoated base like that bearing the covering to be measured. Base metal surface must be set up in an indistinguishable way from the covered steel thing. Place a standard shim of the required thickness on the uncoated base. Modify the standard gage to demonstrate the known thickness of the shim, following the producer's guidelines. With the standard gage balanced and utilizing a similar base area, measure the thickness of a moment shim including a known thickness of 5 mil of the shim utilized for change. The standard gage must show the known thickness of the second shim inside ± 0.2 mil. Measure the paint film thickness in chose areas. Record the test areas and film thickness. Check the precision of the standard gage intermittently amid utilize. Different Coatings (Galvanizing, Fusion Bonded Epoxy, and so on.). Utilize standard gages or approximating gages for measuring the thickness of coatings other than dry paint film. When utilizing standard gages, alter each gage as expressed in Sections. Take after the gage producer's directions when taking readings from the dial or scale. Record the readings on the suitable. The cross-sectional images of pure Ni and Ni–CNT composite coatings deposited using the same PED parameters are presented in Fig.-5.

Despite the fact that the electrodeposition parameters were the same, the thickness of unadulterated Ni coatings (17 µm) was seen to be very nearly two times the thickness of Ni– CNT composite coatings (6.7 µm). It appears that the support of the CNTs in the nickel network disallows the ordinary columnar development of the gem (opposite to the substrate surface). The ensuing irregular nucleation of nickel on the CNTs and development in off-ordinary bearing outcomes in the reduction in the viable development rate typical way (and consequently less covering thickness in given electrodeposition time). This is additionally clarified in the accompanying areas. Regular SEM pictures from the surface of the unadulterated nickel covering are exhibited in Fig.-6a. The nickel covering shows the smoothest and most

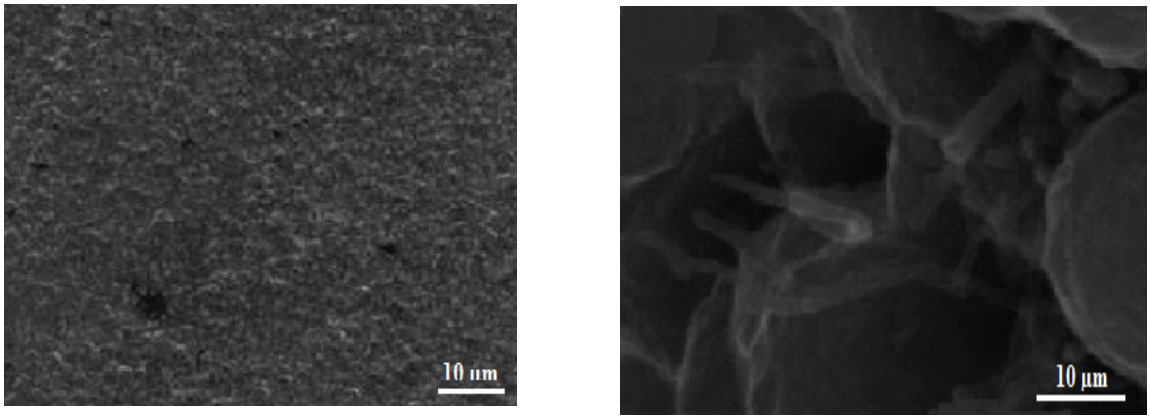
reduced microstructure. The surface structure of the unadulterated nickel covering is comprised of consistent pyramidal precious stones with uniform grain measure.



(a) Pure Ni coating (b) Ni–CNT composite coating

Fig.-5: SEM images of cross section of pulse electrodeposited coating

High momentary current thickness amid PED upgrades the nucleation rate, which prompts the development of better grains. Figure-6b indicates SEM pictures of the Ni– CNT composite covering. While a portion of the territories indicates individual CNTs, the microstructure essentially comprises of systems of CNTs. Such CNT systems speak to better-improved dispersion contrasted with packaged CNTs frequently found in the composites. These micrographs demonstrate that the CNTs were stacked (co-saved) in the coatings with sensibly uniform appropriation. Endeavors are in progress to measure the weight part of CNTs in the composite coatings by dissolving the coatings took after by filtration.



(a) Pure Ni coating (b) CNT reinforced Ni composite coating

Fig.-6: SEM images of pulsed electrodeposited composite coatings

Micro Hardness

The microhardness of fabricated electrodeposited unadulterated Ni and Ni– CNT composite coatings utilizing a similar heartbeat parameters is displayed in Fig.-6. The normal microhardness of unadulterated nickel coatings was 302 ±15 HV. The hardness expanded to 567±15 HV on account of Ni– CNT composite coatings stored with nitric corrosive pretreatment of CNTs. This striking increment in microhardness of Ni– CNT composite coatings can be come about because of a mix of orowan reinforcing and Hall-Petch fortifying.[22] On account of Ni– CNT composites, the orowan fortifying is relied upon to include bowing of

the skimming disengagement between invulnerable CNTs and bypassing them, deserting separation circles. The refinement of nickel crystallite estimate because of CNT support (as examined prior) is likewise anticipated that would build the hardness inferable from Hall- Petch reinforcing.

Wear resistance of composite coating

This testing strategy depicts a research center methodology for deciding the wear of materials amid sliding utilizing a stick on-plate device as per the ASTM standard. Materials are tried in sets under ostensibly non-rough conditions. The primary territories of exploratory consideration in utilizing this kind of mechanical assembly to measure wear are portrayed. The coefficient of grinding may additionally be resolved. The specification of the machine is shown in Table-3.

Table-3: Wear testing machine specification

S. No.	Description	Specification
1	Pin Size	Min-3mm ,Max-10 mm
2	Disc Size	160 mm Dia
3	Disc Rotation	100 to 1500 RPM
4	Normal load	0-100 N
5	Frictional Force	0-100 N
6	Wear	0-3MM

The wear weight reduction information for unadulterated Ni and Ni– CNT composite coatings are exhibited in Fig. 6. With the investigated wear testing parameters in this examination, the unadulterated nickel coatings show practically straight wear misfortune with time.

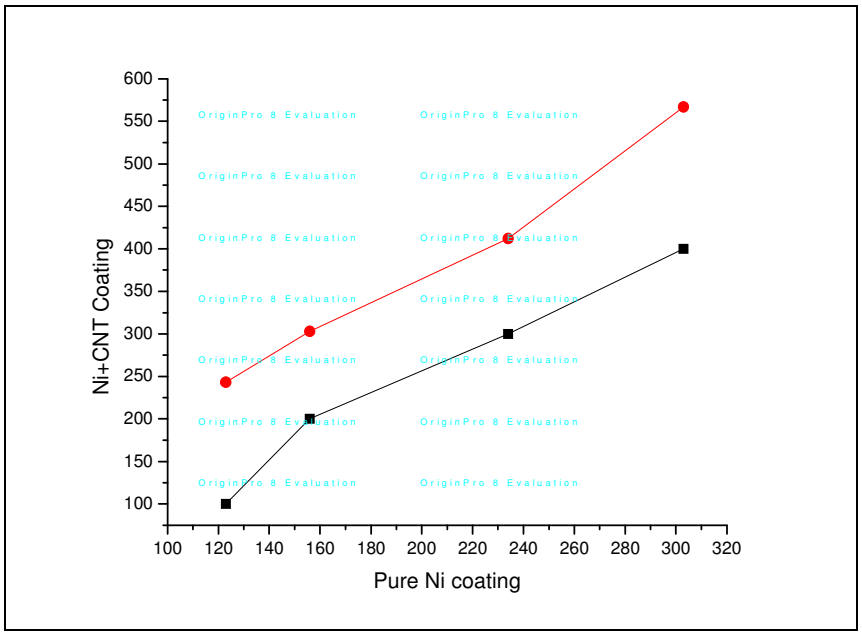
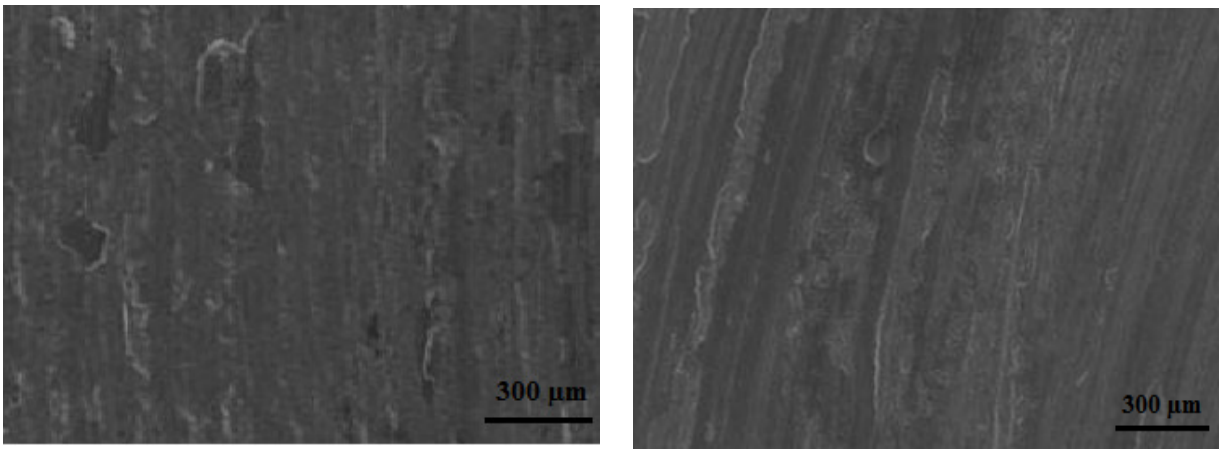


Fig.-7: Variation in weight loss with time for pure Ni and Ni– CNT composite coatings

The Ni– CNT composite coatings show a critical change in the wear protection contrasted with unadulterated nickel coatings as demonstrated by the fundamentally lesser weight reduction. The aggregate weight reduction in the unadulterated nickel covering is just about three times that in the Ni– CNT composite covering. It appears that better wear protection of Ni– CNT composite coatings contrasted with unadulterated Ni covering is an immediate result of the expansion in surface hardness of the coatings. The SEM pictures from the wear tracks of unadulterated Ni and Ni– CNT composite coatings are introduced in Fig.-7a. The ragged surface from unadulterated nickel demonstrates numerous ceaseless and wide

depressions and in addition serious plastic misshapening. The developments of wide furrows and in addition plastic distortions are characteristic of extreme wear circumstance, prompting poor wears protection of unadulterated nickel coatings. The morphologies of wear tracks from Ni– CNT composite coatings appear in Fig.-7b. The well-used surfaces of composite coatings indicate irregular scratches related to essentially lesser weight reduction. The CNTs scattered in the nickel grid appears to disallow the plastic distortion amid wear. Attributable to the nonappearance of serious plastic twisting, the wear protection of Ni– CNT composite coatings is essentially superior to that of unadulterated nickel coatings. The uniform scattering of CNTs into nickel grid prompts huge expanded in microhardness and in addition wear protection of Ni–CNT composite coatings.



(a) pure Ni coating (b)) Ni–CNT composite coating

Fig.-7: worn surface morphology under dry sliding condition under same pulse parameters

CONCLUSION

Unadulterated nickel and Ni– CNT composite coatings were effectively created on Al6061 utilizing beat electrodeposition process utilizing a Watts shower. In light of the trial, the accompanying conclusions were drawn.

- For a similar electrodeposition parameters the thickness of unadulterated Ni coatings acquired was 17 µm and for Ni– CNT composite coatings the thickness got was 6.7 µm.
- It appears that the fortification of the CNTs in the nickel lattice disallow the ordinary columnar development of the gem (opposite to the substrate surface).
- The fortification of CNTs in the composite covering restricted the columnar development of the nickel grains bringing about irregular/feeble surface and littler covering thickness in the composite coatings. The CNT reinforcement further refined the crystallite size in the composite coatings.
- The Ni–CNT composite coatings exhibited significantly improved microhardness (567±15 HV) compared to pure nickel coatings (302 ±15 HV) primarily due to a combination of Hall–Petch and Orowan strengthening mechanisms.
- The ballon-disc wear testing data indicated that the reinforcement of CNTs significantly improved the wear resistance of the composite coating compared to pure nickel coatings.

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