Effect of current density on the properties of electrodeposited Ni-mullite composite coatings

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Abstract

In recent years there is a great demand for the development of electrodeposited Ni-composite coatings due to their improved corrosion and wear resistance. The properties of the electrodeposited coatings are dictated by the nature and amount of the distributed particles, the particle size and its distribution, the applied current density, the magnetic stirrer speed, etc. In the present study, the less explored mullite particles are chosen as the distributive phase and the effect of applied current density on the microhardness, corrosion and wear resistant properties of the coating is studied. The mullite powder is obtained by ball milling the commercial alumina and silica powders. The microhardness, corrosion resistance and wear resistance of the coatings are evaluated. The Ni-mullite composite coating electrodeposited at a current density of 3.1A/dm^2 exhibits improved corrosion resistance with a corrosion rate of 1.1cm/yr . Ni-mullite coatings showed a lower coefficient of friction (0.4) and higher wear loss when compared to plain nickel coating.

Keywords: Electrodeposition; mullite; Ni; corrosion; wear; microhardness

1. Introduction

There is a great demand for electrodeposited composite coatings for various engineering applications as electrodeposition is a relatively low-cost method compared to other coating techniques like thermal spraying or chemical vapor deposition [1]. Electrodeposited composite coatings are used in a wide range of industries, including aerospace, automotive, and electronics. They are used for improving the wear resistance of components such as gears, bearings and valves. The composite coatings are used in marine and chemical industries to impart corrosion resistance to the components [2].

Basically, electrodeposited composite coatings consists of metal matrix and non-metallic particles as distributed phases. The most common metals used as matrices in composite electrodeposition are nickel, copper, and chromium [3]. Other metals such as silver, gold, and cobalt are also employed depending on the application. The non-metallic particles, also called reinforcement materials or distributive phase, are selected based on the desired property enhancement. For example, ceramic particles like alumina, silica, zirconia, titania, ceria, etc are used to enhance hardness, wear resistance, and thermal stability of the metal matrix [4-16]. Polymer materials like polytetra fluroro ethylene (PTFE) and polyamide are used to improve the lubricity and reduce friction. Carbon based materials such as graphite and carbon nanotubes are used for enhancing the wear resistance and conductivity of the matrix and diamond particles are used to enhance the hardness and abrasion resistance of the matrix. The non-metallic particles gets co-deposited along with the metal matrix during the electroplating process. The process parameters—such as bath composition, temperature, current density, and agitation—can significantly affect the distribution and properties of the composite coating. The uniformity of particle distribution, the adherence between particles and metal, and the final mechanical and electrochemical properties depend on these factors. There is a vast literature on the electrodeposited Ni-composite coatings containing SiC, alumina, zirconia, ceria, titania, carbon

nanotubes, diamond, etc [5-15]. Ni-SiC is most widely studied coating and is being commercially exploited in automotive industry and also for coating the trochoid of the Wankel engine to improve the wear resistance [16].

Mullite is an important high temperature oxide material, chemically stable alumino-silicate ceramic with the general formula **$3Al_2O_3 \cdot 2SiO_2$. It exhibits** excellent thermal stability, low thermal expansion, and good mechanical strength at high temperatures [17]. It is most widely used in furnaces, kiln linings, and aerospace components. Its needle-like crystal morphology also enhances fracture toughness in composite materials. Due to its desirable combination of properties, mullite is widely used not only in structural and thermal insulation applications but also as a reinforcement in advanced ceramic matrix composites and coatings. In addition, the petrochemical and aluminium industries use mullite-based aggregates for applications that necessitate thermal shock resistance, chemical attack resistance, and hot-load strength. Mullite is also a desirable material for high-strength infrared transmitting windows. Protective coatings and electronic substrates are other applications of mullite [18].

There is limited literature on the electrodeposited Ni-composite coating containing mullite particles. Radomysel'skii et al. [19] have reported the development of electrodeposited Ni composite containing mullite whiskers and explored the high temperature oxidation resistance of the coating and observed improved oxidation resistance vis-à-vis plain nickel coating. The paper by Meenu et al. [20] explored the effect of the addition of mullite particles derived from sillaminite.

The present study is aimed at the synthesis of mullite powder by ball milling followed by the development of electrodeposited N-mullite composite coating. The effect of applied current density on the microhardness and corrosion resistance has been studies. Also, the wear behavior of the best coating is also studied and it is compared with plain Ni.

2. Experimental Procedure

2.1. Mullite powder synthesis and characterization

Mullite powder was synthesized by mechanical alloying, which is a very high-energy ball milling process. 27.2 g alumina (Loba Chemie) and 10.7 g cabosil (Cabot Sanmar Ltd) powders were mixed with ethanol and ball milled for three hours at 350 rpm using a planetary ball mill (Fritsch Pulveristte 6 Classic). The mullite powders were characterized using a Field Emission Scanning Electron Microscope (FESEM) system integrated with Energy Dispersive X-ray Analysis (EDAX) facility (Supra 40VP model, Carl Zeiss with a Gemini column) to understand their surface morphology and to estimate their individual size. Particle size analysis was used to find the extent of agglomeration of the particles. In the present study Master sizer 2000 (Malvern, UK) particle size analyzer, which works on the principle of the laser light scattering method was employed. The X-ray Diffraction (XRD) pattern of the powder was recorded using a Bruker-Advance-D8 X-ray diffractometer with Cu Kα as the radiation source and Ni as the filter. The average crystallite size was obtained by the line-broadening method. The average crystallite size values were estimated using Scherrer formula:

$$D = \frac{0.9\lambda}{\left(B^2 - b^2\right)^{1/2} Cos\theta}$$

where D is the crystallite size, λ is the wavelength of the radiation, θ is the Bragg's angle and B and b are the FWHMs observed for the sample and standard, respectively.

2.2. Preparation and characterization of nickel-mullite composite coatings

Composite coatings were prepared by cathodic electrodeposition in which the object to be electroplated was taken as the cathode (brass) and an electrode of the same material (Ni) to be coated was taken as the anode and both cathode and anode were of the same size. The electrolyte used was a nickel sulphamate bath into which the prepared particles were dispersed. Brass substrates were used and the electrodeposition was done using a

DC power supply.

A 200 mL Ni-sulfamate bath containing 20 g of mullite powder (100 g/L) was taken in a glass beaker and stirred for 16 hours before electrodeposition [7]. Electrodeposition was carried out at 0.75 A/dm^2 for 6 h, 1.54 A/dm^2 for 3 h, 3.1 A/dm^2 for 1.5 h and 4.65 A/dm^2 for 52 min, on a magnetic stirrer (400 rpm). The pH was maintained at 4 and the electrodeposition was carried out on brass plates and mild steel substrates, respectively, for microhardness and corrosion studies.

Cross-sectional metallography specimens were prepared by sandwiching the electrodeposited brass coupons with a copper backup in a Bakelite matrix. After mechanical grinding using emery sheets of different grades (100, 240, 320, 400, 600, 800, 1000 and 1200 μm), the samples were polished with Al_2O_3 slurry down to 0.05 μm. The optical micrographs of the cross sections of Ni-mullite composite were recorded using a vertical metallurgical microscope. Microhardness indentations were made into cross sections to avoid the effect of the substrate. The microhardness measurements were performed on ten different locations on the cross-section of each coating (Micromet 2103, Buehler) using a Knoop indenter at 50 gf load.

In this study, a pin-on–disc tribometer with a track radii varying between 5-40 mm, a load of 0.5-2 kg and a speed between 10-600 rpm was used. In this method of wear measurements, a pin with the coating to be analyzed was kept stationary and fixed to a lever arm while a disc rotates at a fixed speed. In order to study the wear performance of the composite coatings, a brass pin with a hemispherical head of about 6 mm radius was used. The hemispherical region was coated with Ni and the composite coating at 3.1 A/dm^2. All wear tests were conducted at a wear track radius of 30 mm at 200 rpm at a slide speed of 0.628 m/s .The disc used was hardened EN 31 steel with a Vickers hardness of 750 HV. An LVDT transducer was used to measure the total height loss of the pin and disc. More details of the wear test are already provided in literature [7,11]. The optical micrographs of the disc after wear test was also recorded.

The corrosion behavior of Ni and Ni-composite coatings on mild steel coupons **was** studied using CHI 604 2D electrochemical workstation [11]. The test was carried out in deaerated 3.5 wt% (0.6 M) NaCl solution (200 ±2 mL) using a conventional **three-electrode** cell equipped with the coated mild steel coupon with an active area of 1cm^2 as the working electrode. A platinum foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The reference electrode was connected to a Luggin capillary and its tip was placed very close to the surface of the working electrode to minimize the IR drop. The coupon was immersed in NaCl solution for an hour in order to establish the open circuit potential (E_{OCP}). The Electrochemical Impedance Spectroscopy (EIS) studies were carried out in the frequency range of 100 kHz - 10 mHz. The amplitude of the applied alternating potential was 10 mV on the E_{OCP}. The impedance data was displayed as Nyquist and it is a plot of real (Z′) vs. imaginary impedance (Z″). After EIS measurements, the system was allowed to attain open circuit potential and then the upper and lower potential limits of linear sweep voltammetry were set at ±200 mV with respect to the E_{OCP}. The sweep rate was 1 mV/s. The Tafel plots obtained were represented as potential vs. log i plot**.** Omitting the contribution of particles for the weight loss, the corrosion rates (CR) were calculated from corrosion current by using Faraday's law [Standard Practice for calculation of corrosion rates and related information from Electrochemical measurements, American National Standards, ANSI/ASTM G 102-89 (Reapproved 1994)]:

$$CR = K\left(\frac{i_{corr}}{\rho}\right)EW$$

Where CR is given in mm/yr, K=3.27 × 10^{-3} mm g/μA cm yr, ρ= density in g/cm^3 (density of nickel is 8.9 g/cm^3) and EW (Equivalent weight of Ni) = 29.36.

The corrosion protection efficiency of Ni-mullite coatings was calculated using the Tafel extrapolation method by comparing the corrosion current density (i_{corr})

of Ni-mullite coating with that of the Ni metal coating. The protection efficiency was evaluated from the Tafel plot using the equation:

$$P = \frac{I'corr - Icorr}{I'corr} x\ 100$$

where I'corr and Icorr are the corrosion current densities in the absence and presence of particles. The protection efficiency of Ni-composite coatings was also calculated according to the following equation:

$$P = 1 - \left(\frac{R^{o}p}{Rp}\right) x \quad 100$$

Where $R^{o}p$ is polarization resistance in absence of oxide particles (i.e plain nickel) and Rp is polarization resistance in the presence of oxide particles i.e composite coating.

3. Results and discussions

The surface morphology and the particle size of the incorporated particles play an important role in the properties of composite coatings. The FESEM images (Fig.1) of mullite particles showed agglomerates of differently sized particles. The smaller particles were found to be silica particles and the bigger ones were alumina. Bigger particles were in the size range of 0.5-1µm and the smaller particles were in the size range of 10-20 nm. Figure 2 shows the powder XRD pattern of mullite powder. It shows a mixture of α-alumina and silica particles.

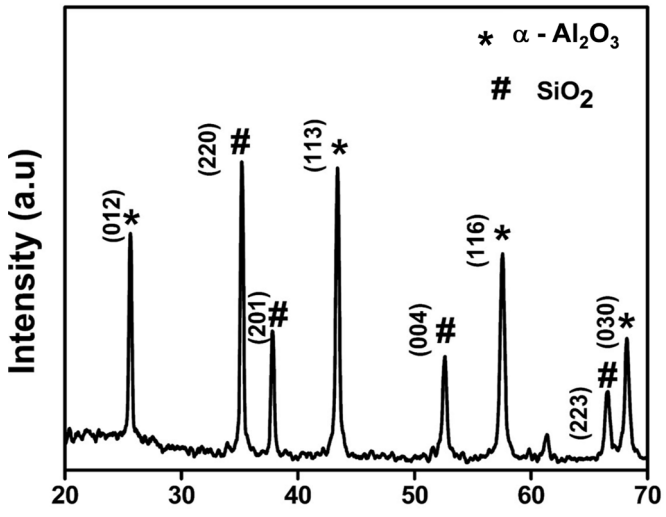
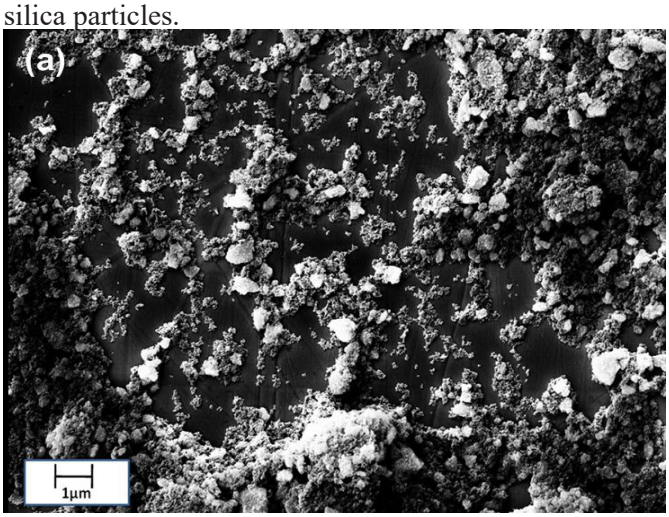


Fig.2. XRD pattern of mullite powder.



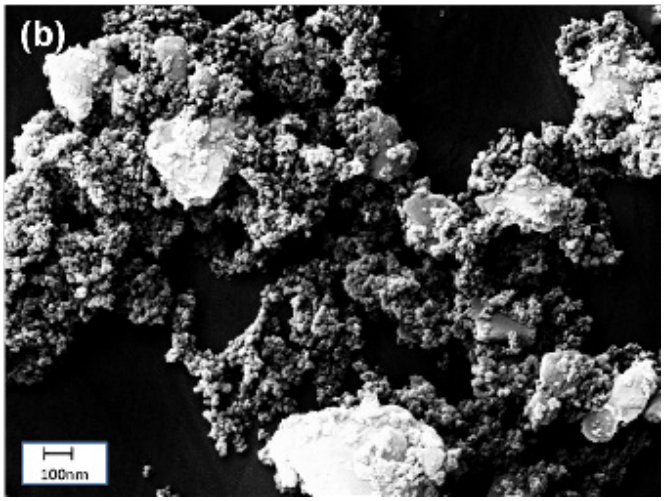


Fig. 1. FESEM of of mullite powders at different magnificatiotns

The characteristic peaks of α-Al_2O_3 and SiO_2 were observed and the average crystallite size of the mullite particles was calculated to be 42.095 nm as calculated by the Scherrer formula with the crystallite size of α-Al_2O_3 being 46 nm and that of SiO_2 as 32.8 nm. The average agglomerated particle size was found to be 3.9 µm from particle size analysis. The bimodal distribution shows the presence of two different sizes of particles (Fig.3). The broad peak covering 1-100 µm size corresponds to alumina particles and a sharp peak below 1 micron corresponds to cabosil silica which is having very high surface area and smaller size.

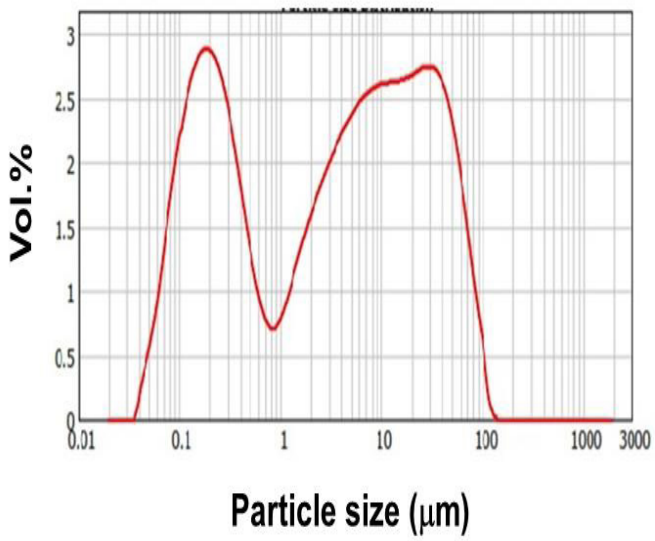


Fig.3. Particle size distribution of mullite particles.

Figure 4 shows the cross-sectional micrographs of Ni-mullite composite coatings electrodeposited at various current densities. From Fig.4, it is evident that at lower current densities, more of particle incorporation occurs. The incorporated particles seen in the optical microscope images may correspond to alumina particles. However, due to the fine nature of the silica particles, they may not be visible in the optical microscope images. The incorporated particles are responsible for increasing the microhardness of the coatings. Further, at higher current denisties, bigger agglomerates are observed in the coatings.

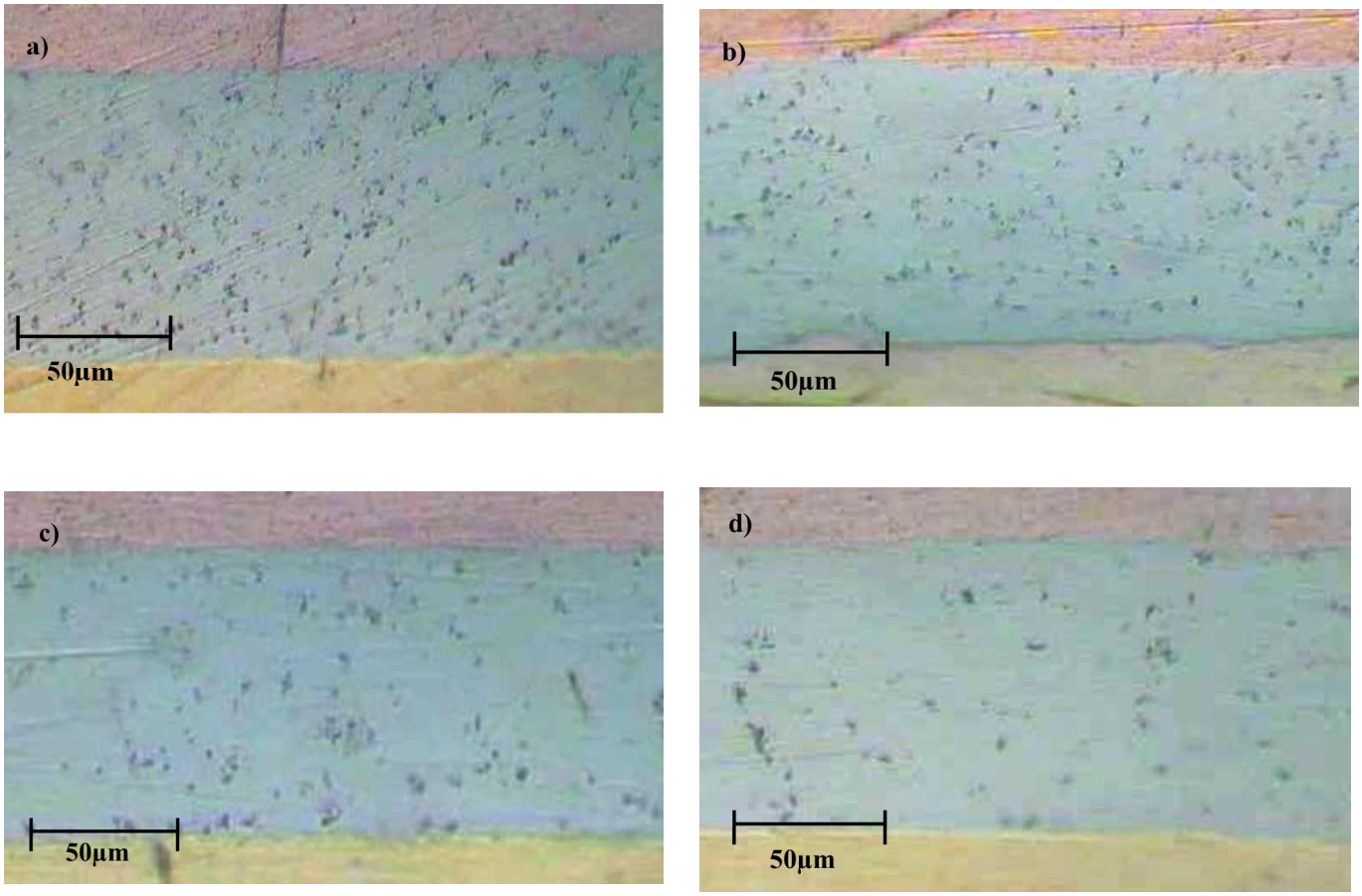


Fig.4. Optical micrographs of the Ni-mullite coating crosssection electrodeposited at various current densities (a) 0.75A/dm^2,(b) 1.54A/dm^2(c) 3.1 A/dm^2 and (d) 4.65A/dm^2

Figure 5 shows the plot of microhardness vs. current density for the Ni-mullite coating electrodeposited at various current densities. The observed microhardness is greater than that reported in the literature (400 HK at 50_{gf}). This is attributed to the lower current density used for the electrocomposite coating development in this study. The lower current density during the electrodeposition of Ni-based composite coatings generally improves the incorporation of particles due to the following reasons: (i) Lower hydrogen evolution during lower current density reduces the turbulence and there by ensures the proper adhesion of the particles and prevents the dislodgement of the particles; (ii) With lower current density, the rate of metal ion reduction slows down, allowing more time for the suspended particles in the electrolyte to reach and adhere to the cathode surface before being encapsulated by the growing nickel layer. This enhances particle entrapment; (iii) At lower current densities, the reduced electric field strength and deposition rate minimize disruption, helping maintain particle stability at the interface, (iv) Better uniformity and less agglomeration: Lower current densities promote more uniform metal deposition, which reduces the likelihood of localized roughness or defects that can either block particle incorporation or cause clustering. This results in a more homogeneous distribution of particles within the nickel matrix, and (v) Operating at lower current densities keeps the system closer to electrochemical equilibrium, which helps maintain consistent ion concentrations near the cathode. This avoids concentration gradients that could interfere with both metal deposition and particle capture. Lower current density is preferred as it provides a more controlled and less turbulent deposition environment, enhancing the likelihood that reinforcement particles are successfully embedded in the nickel matrix and distributed uniformly throughout the coating.

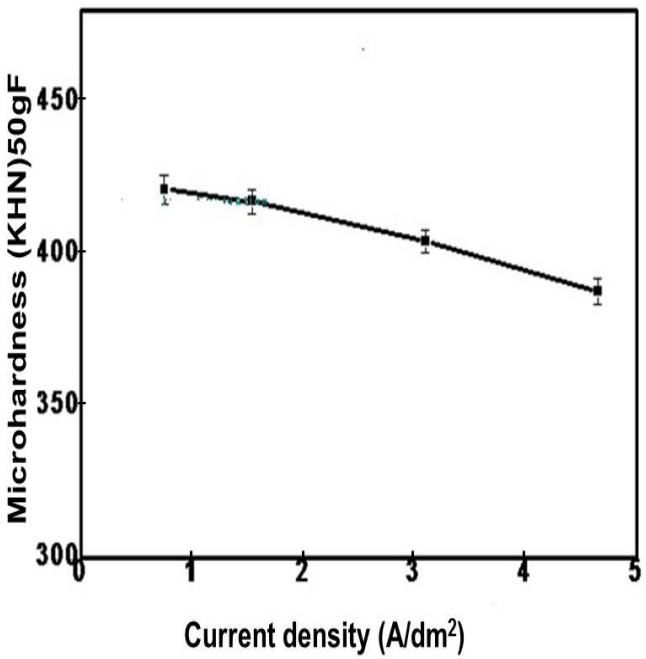


Fig.5. Microhardness vs. current density plots of Ni-mullite coatings.

Table 1 summarizes the corrosion potential, corrosion rates and Tafel plots for Ni-mullite composite coatings electrodeposited at different current densities. All the coatings show same order of corrosion resistance. However, the coating electrodeposited at 3.1 A/dm^2 shows lower icorr. The corrosion current density (μA/cm^2) is derived from Tafel plot (Fig.6). It reflects the rate of the electrochemical reactions occurring on the metal surface, specifically it indicates how fast metal atoms are oxidized and dissolve into the corroding medium. A lower corrosion current indicates improved corrosion resistance because it directly corresponds to a slower rate of metal dissolution, meaning the material is corroding more slowly.

Table 1: Corrosion potential, corrosion rates and Tafel slopes calculated from potentiodynamic polarization curves for Ni-mullite composite coatings.

Current density *A/dm²*	100gpl				
	Ecorr (V)	Icorr (μA/ cm²)	βa (V/dec)	βc (V/dec)	Rp Ω/cm²
1.54	-0.245	0.20	0.11	0.138	130686
3.1	-0.242	0.11	0.19	0.105	269248
4.65	-0.315	0.51	0.202	0.124	65361

Further, interestingly, the polarization resistance of the Ni-mullite coating electrodeposited at 3.1 A/dm^2 is double that of Ni-mullite coating electrodeposited at 1.54 A/dm^2. Polarization resistance is a measure of how much a material resists the flow of electric current during the electrochemical reaction associated with corrosion. It's typically measured using electrochemical techniques like linear polarization resistance (LPR). The value is derived from the slope of the potential vs. current plot near the open circuit potential. A higher polarization resistance in an electrodeposited coating typically means that the coating offers better protection against corrosion, making it more effective as a barrier to environmental degradation. Table-2 summarizes the corrosion protection efficiency of the coatings derived from the Tafel plot and from polarization resistance. There was a good correlation in the efficiency values derived from both the methods.

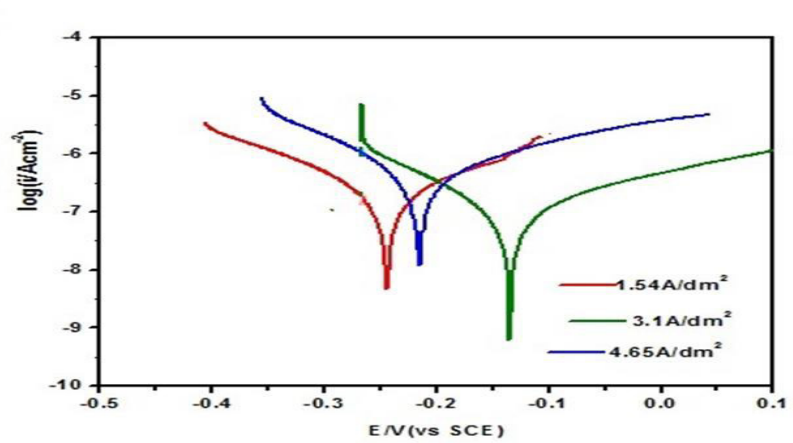


Fig. 6. Tafel plots of Ni-mullite composite coatings electrodeposited at different current densities.

Table 2. Comparison of protection efficiency obtained from Tafel plot to that obtained from the polarization resistance for 100gpl Ni-Mullite composite coating.

Current Density (A/dm²)	P% obtained from Tafel	P% obtained from Rp
1.54	96	94
3.1	98	97
4.65	91	87

The observed Tafel plots substantiate the results of Nyquist plots. The Ni-mullite composite coating electrodeposited at 3.1 A/dm^2 showed a larger semicircle compared to the coatings obtained at 1.54 and 4.65 A/dm^2 (Fig.7). In the case of Nickel-mullite coating, the corrosion resistance was found to be better in the case of 3.1A/dm^2 with a corrosion rate of 1.1 cm/yr.

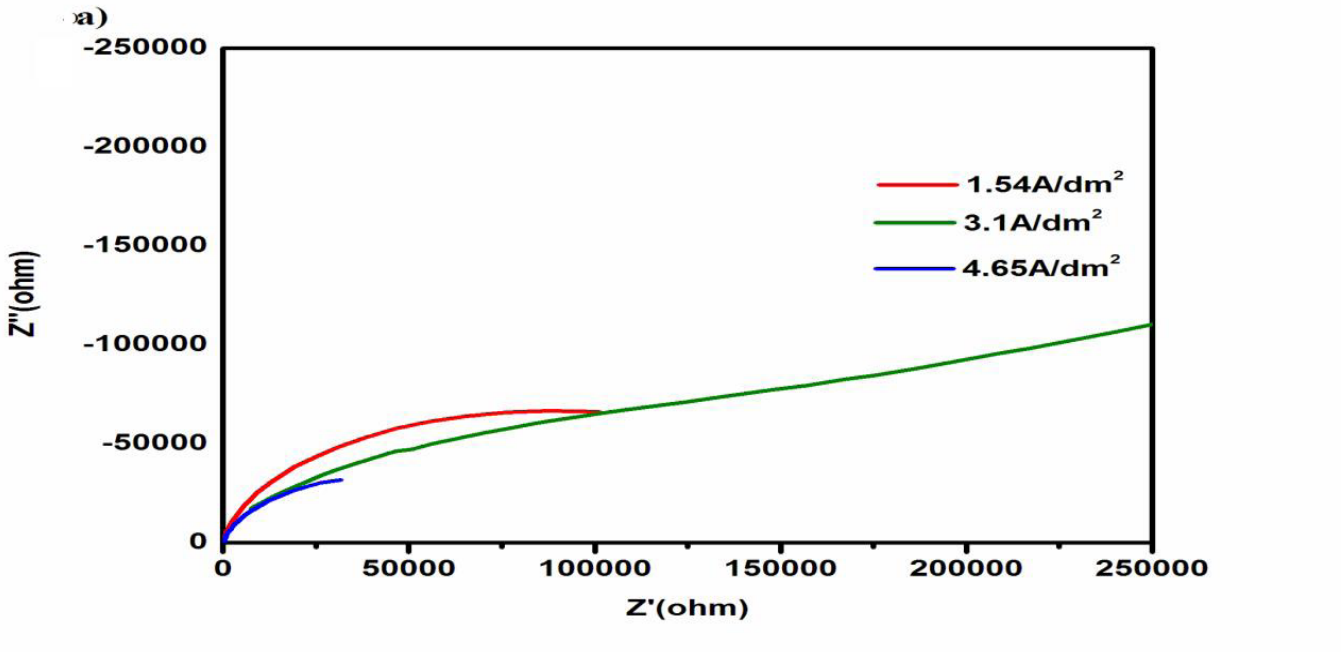


Fig. 7. Nyquist plots of Ni-mullite coatings.

Interestingly, the Ni-mullite coating exhibited higher wear loss compared to plain Ni coating (Fig.8) despite exhibiting a lower coefficient of friction (0.4) compared to plain Ni (0.75). Initially, the wear loss is constant for Ni-mullite coating and the coefficient of friction was constant at 0.45. As the wear loss increases, the coefficient of friction decreases. It is interesting to note that mullite, as a material, doesn't inherently possess lubricating properties. However, when used as an additive in lubricating materials or in composite materials, it can improve the overall tribological performance (friction and wear behavior). Mullite can enhance lubrication by reducing the friction coefficient [21].

The increased wear loss despite possessing a lower friction coefficient may be attributed to the formation of a transfer film that reduces friction in the beginning. The film will become unstable and it flakes off and further increasing the wear loss. Figure 9 shows the optical micrographs of the wear track on the discs after wear. Clearly, mullite particles are seen on the wear track of the Ni-mullite coating tested wear disk (Fig. 9(b)).

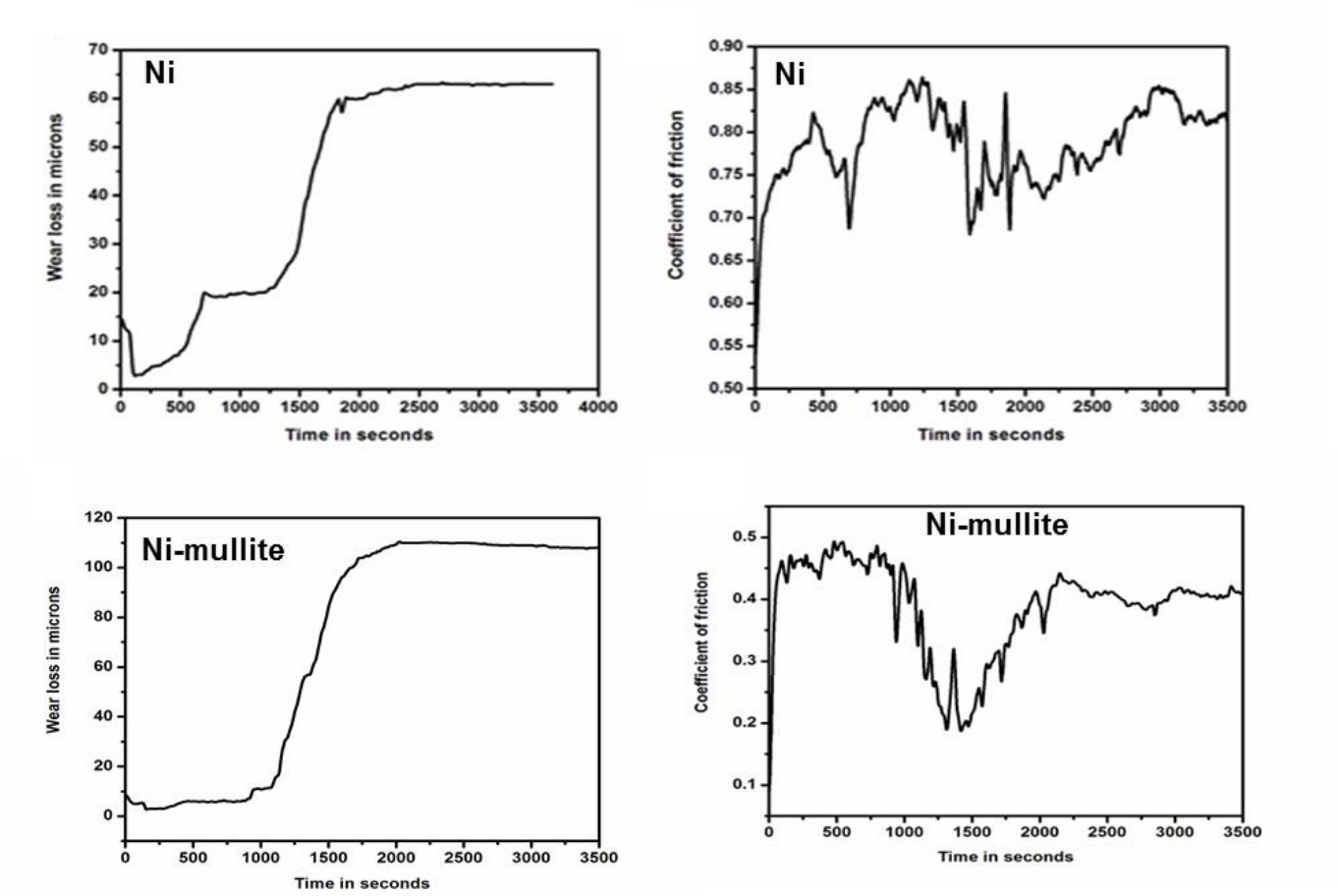


Fig.8. Wear test results of Ni and Ni-mullite coatings.

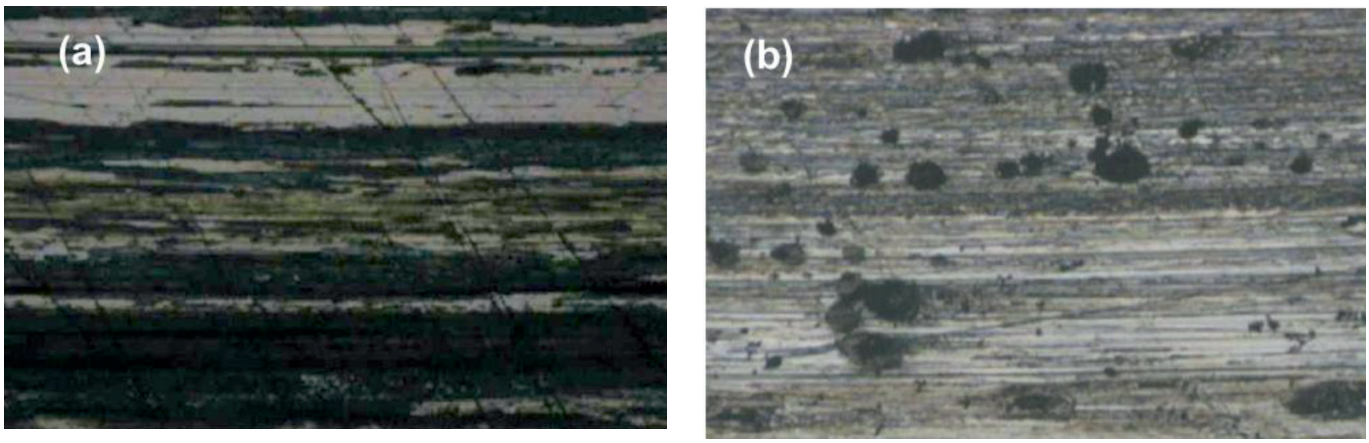


Fig. 9. Optical micrographs of the wear track on the disc after wear test with (a) Ni and (b) Ni-mullite composite coated brass pin.

Conclusions

Electrodeposited Ni-mullite composite coatings were developed using ball milled mullite powder and nickel sulphamate bath. The effect of current density on microhardness and in turn on corrosion resistance of the coatings were studied. The coating electrodeposited at lowest current density (1.54A/dm^2) exhibited higher microhardness (430 HK) and higher number of mullite particles were incorporated. Interestingly, the coating electrodeposited at 3.1 A/dm^2 exhibited better corrosion resistance as evident from the Tafel and Nyquist plots. The coating also demonstrated lower coefficient of friction (0.4) and higher wear loss. Thus Ni-mullite coatings are promising for applications that require higher microhardness and corrosion resistance.

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