Electrodeposition of Ni-Al$_2$O$_3$ nano composite coating and evaluation of wear characteristics

C R Raghavendra$^1$, S Basavarajappa$^2$, Irappa Sogalad$^3$

$^1$Department of Mechanical Engineering, Government Engineering College, Haveri, Karnataka, India
$^2$Registrar , IIITDWD, IT park, Hubballi, Karnataka, India
$^3$University BDT College of Engineering, Davanagere, Karnataka, India

* Corresponding author: raghavendra.crekl@gmail.com

Abstract. Electrodeposition is one of the most technologically feasible and economically superior technique for producing metallic coating. The advancement in the application of nano particles has grabbed the attention in all fields of engineering. In this present study an attempt has been made on the nano particle composite coating on aluminium substrate by electrodeposition process. The aluminium surface requires a specific pre-treatment for better adherence of coating. In light of this a thin zinc layer is coated on the aluminium substrate by electroless process. This layer offers protection against oxidation thus prevents the formation of a native oxide layer. In this work Ni-Al$_2$O$_3$ composite coating were successfully coated by varying the process parameters such as bath temperature, current density and particle loading. The experimentation was performed using central composite design based 20 trials of experiments. The effect of process parameters on surface morphology and wear behavior was studied. The results shown a better wear resistance of Ni-Al$_2$O$_3$ composite electrodeposited coating compared to Ni coating. The particle loading and interaction effect of current density with temperature has greater significant effect on wear rate followed by the bath temperature. The decrease in wear rate was observed with the increased current density and temperature.

Keywords: Ni-Al$_2$O$_3$ nano-composite coating, electrodeposition, Aluminium, wear behavior, and surface morphology.

1. Introduction
A composite coating is highly advanced method in material science as it produces new material at room temperature and appropriately it is referred to cold fusion. There are different methods of producing composite materials with a metallic matrix. The purpose of the composite coating is to give a various functional properties, such as wear resistance, self-lubrication, corrosion or oxidation resistance to the plated surface[1,2]. The base metal to be plated is, usually made the cathode of the electrolytic cell which
is termed as substrate, where as the anode is either made of coating metal or an insert material of good electrical conductivity with graphite [3]. Coatings provides a way of extending the limit of use of materials at the upper end of their performance capabilities, by allowing the mechanical properties of the substrate material to be maintained, while protecting them against wear and corrosion [4]. In addition a metal matrix is used to hold the particles together and facilitate good adhesion to the metal surface being coated [5]. The introduction of nanoparticles in a metal matrix has found to be super strong in Tribological strength[2,6,7]. The metal matrix composite coatings composed of Ni-Al2O3 are frequently used to solve the problems of reduced life under severe abrasive conditions, which are the main cause of the growing interest in the electrochemical co-deposition[8–12]. It seems in the literature not much papers have concentrated on the industrial application of nano Al2O3 thin coating. In this paper we report our approach on composite coatings. We have prepared Ni-nano Al2O3 composite coatings on Aluminium substrate by electrodeposition process and made an attempt to study the influence of coating parameters on wear.

2. Experimentation
2.1 Surface preparation of Aluminium Substrate
Surface preparation plays a major role in adhesive strength of coating on aluminium substrate. The substrate is taken as per ASTM G99 standard for wear. In order to improve the adhesion of Ni deposits to Al substrate, before electroplating, the Al substrate was polished in a dust-free area and it is removed from the area of sectioning, mounting and rough grinding. The substrate is then cleaned ultrasonically. Making the substrate plating ready is very important and it was done in stages. The first stage was the mechanical polishing to make sure the surface to be plated is smooth and has very good surface finish. This is done on a double disc grinder. For this purpose polishing specimen with different SiC grits (220, 320, 400, 600, 800, 1000 and 1200) were used at 350 rpm to get a fine surface roughness.

Then the substrate is degreased for 1-5 min, eroded in NaOH solution at room temperature for 1-0.5 min, then polished in a polishing solution for 1-2 min, finally immersed in a zinc bath containing 10-20 g/L of ZnO, 80-100 g/L of NaOH and 10-20 g/L FeCl3, at room temperature twice. After the first immersing for 0.5-1.0 min, the Al substrate was immersed in the HNO3 solution to remove the zinc layer, then it was immersed in a zinc bath secondly for 0.5 min to form a uniform and fine zinc layer. After each steps mentioned above, the Al plate was rinsed with deionized water. Then the specimen was immersed in the electrolyte bath[13].

2.2 Electrodeposition of Ni-Al2O3 coating
Nickel electrodeposition was performed as per standard Watts bath solution with the following composition: nickel sulphate (NiSO4 .6H2O) 240 g.L-1; nickel chloride (NiCl2 .6H2O) 45 g.L-1 and boric acid (H3BO3) 30g.L-1[13–21]. In the present work Ni of purity 99.98% is taken as anode and substrate Al is taken as cathode. We worked at for three different parameters temperature, current density, % of particle loading in Five different levels of 30-50°C, 1-2A dm-2, 0-8gms/lit respectively. During the process of coating a constant speed of 250rpm is maintained and pH values is held between 3-4 by adjusting NaOH. The distributions and contents of Al2O3 in the coating were examined using scanning electron microscopy.

2.3 Central composite Design (CCD)
Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes. Central composite design (CCD) method is build by adding centre points and axial points to a two level full factorial design. Factorial part of CCD is a two level factorial design (2k), where 2 is the number of levels and k is the number of factors. The experiments were designed according to CCD method. In Experimental model, each variable was studied at two different factorial levels (-1,+1), two axial points (-1.68179,+1.68179), and a centre point (0) which is the midpoint of each factor range. In this study, CCD consists of 2k + 2k + m runs, where k is the number of factors, 2k is the number of the factorial points at the corners of the cube, 2k is the number of the axial
points on the axis of each design factor at a distance of ±α (α= 2 k/4 = 1.682 for k = 3) from the center of the cube and m is the number of the centre points at the centre of the cube. The total number of experiments in the present study is 8 + 6 + 6 = 20. The five variables as per CCD for three coating parameters are given in the table1.

**Table 1. Experimental range of the variables studied using CCD**

| Factors                   | Symbols coded | Encoded values of coded levels |
|---------------------------|---------------|--------------------------------|
|                           |               | -1.682 | -1 | 0 | 1 | 1.682 |
| Bath temp( ºC)            | X₁            | 30     | 34 | 40 | 46 | 50    |
| Current density(A/dm²)    | X₂            | 1      | 1.2 | 1.5 | 1.8 | 2     |
| Particle loading (gm)     | X₃            | 0      | 1.6 | 4 | 6.3 | 8     |

Wear test were conducted on the coating surfaces by dry sliding wear test rig. The load, speed, distance and the temperature are kept constant for 20N, 1.2m/s, 1000m and 30°C respectively for all the 20 specimen which were drawn from central composite design for 3 parameters and 5 levels. The wear rate is calculated by the amount of weight lost in the friction. Then the individual and interaction effect of coating parameters on the wear is calculated by ANOVA.

3. Results and Discussion

3.1 Morphology study

The fig 1 shows morphology of coating at different coating conditions. Fig1(a) shows uniform distribution and presence Al₂O₃ particles in the coating. fig 1(b) shows the composite coating at 2A/dm², 40°C and 6.3 g/l. Further increase in current density has lead to agglomeration of particles, see in fig 1(c). Agglomerated coating leads to clusters which fails the coating characteristics.
Figure 1. Scanning electron micrograph of the surface of a Ni-Al₂O₃ composite coating by electrodeposition (100KX) (a) uniform particle distribution of nano Al₂O₃ (b) composite coating at 2A/dm² and 40°C (c) Agglomeration of Al₂O₃ for 1.5A/dm².

3.2 Effect of process parameters on wear rate.

Fig 2 shows the effect of temperature on the wear, as it is seen the wear rate keep increasing as temperature increases till 40°C as the movement of particles from the anode is more hence deposition rate will be more. After 40°C the wear rate almost becomes stable as the higher KE of particles affects the coating. The wear rate increases with the increase in temperature due to increase in KE of particle movement. As the current density is increased the amount of particles liberating from anode increases resulting in better coating and wear rate. Beyond the current density of 1.5A/dm², wear rate increases due to higher particle concentration leading to agglomeration and hence weak coating. The better wear rate is obtained at the current density at 1.5A/dm². The wear resistance keeps increasing as particle concentration is increased from 0g/l to 8g/l. It signifies the presence of Al₂O₃ particles increases the wear resistance.

Figure 2. shows the effect of temperature, current density and particle loading on wear.
3.3 Analysis of Variance

Analysis of variance (ANOVA) is a statistical technique used to check the adequacy of the developed empirical relationships. This technique is used to identify the significance of the factors and their interactions. In this, confidence was considered to be 95%. The effect of three parameters and their interaction effects were found by analysis of variance table for the wear rate shown in the table 2. ANOVA is carried on in order to find the optimization values of coating parameters on wear rate.

The value of probability >F is less than 0.05 for the empirical relationships which indicates that empirical relationships are significant, the model is adequate. The coefficient of determination R^2 of the model is 94.22%, this clearly indicates that 94.22% of the data is in compatibility with the predicted by model. The R^2 value always varies between 0 and 1. The predicted determination coefficient is 71.56%, it is in the reasonable agreement with adjusted determination coefficient value 89.02%. From the ANOVA table it indicates that the contribution of particle loading on wear rate is more followed by interaction effect of temperature and current density.

Table 2. ANOVA for Wear rate.

| Source | DOF | Sum of squares | Mean square | F | P | % contribution |
|--------|-----|----------------|-------------|---|---|----------------|
| Model  | 9   | 4.57212        | 0.50801     | 18.12 |   | 6.4            |
| T      | 1   | 0.29287        | 0.29163     | 10.40 | 0.009 | 36.15          |
| C      | 1   | 0.46034        | 0.28453     | 10.15 | 0.010 | 10.088         |
| P      | 1   | 0.60416        | 0.00234     | 0.08 | 0.778 | 13.21          |
| T*T    | 1   | 0.04057        | 0.01173     | 0.42 | 0.532 | 0.88           |
| C*C    | 1   | 1.76337        | 1.69971     | 60.62 | 0.000 | 38.56          |
| P*P    | 1   | 0.04220        | 0.01173     | 5.1 | 0.248 | 9.22           |
| T*C    | 1   | 0.58179        | 0.58179     | 20.75 | 0.001 | 12.724         |
| T*P    | 1   | 0.24874        | 0.24874     | 8.87 | 0.014 | 5.44           |
| C*P    | 1   | 0.53810        | 0.53810     | 19.19 | 0.001 | 11.76          |
| Residual error | 10  | 0.28039 | 0.02804 | | | 6.13 |
| Lack of fit | 5   | 0.15431 | 0.03086 | 1.22 | 0.415 | |
| Pure error | 5   | 0.12608 | 0.02522 | | | |

R-Sq = 94.22%  R-Sq(pred) = 71.56%  R-Sq(adj) = 89.02%

4. Conclusion

In summary, Ni-Al2O3 composite coating with better wear resistance were prepared by conventional DC electrodeposition process. The presence of Al2O3 nano particles has increased wear resistance. The effect of coating parameters at different levels certainly effects the coating and wear rate. the following observations were from the optimization of coating parameters i) The particle concentration has major influence followed by the interaction effect of temperature and current density ii) Wear rate is good at the temperature 40°C and 1.5A/dm² iii) Higher the values of current density and temperature leads to agglomeration of particles on the coating resulting in weak coating.

References:
[1] M.R. Vaezi, S.K. Sadrnezhda, L. Nikzad, Electrodeposition of Ni – SiC nano-composite coatings and evaluation of wear and corrosion resistance and electroplating characteristics, 315 (2008) 176–182. doi:10.1016/j.colsurfa.2007.07.027.
[2] M. Srivastava, V.K.W. Grips, A. Jain, K.S. Rajam, Influence of SiC particle size on the structure.
and tribological properties of Ni – Co composites, 202 (2007) 310–318. doi:10.1016/j.surfcoat.2007.05.078.

[3] B.G. Mellor, Surface coatings for protection against wear, Woodhead Publishing Limited, 2006. doi:10.1533/9781845691561.

[4] D. Thiemig, A. Bund, J.B. Talbot, Electrochimica Acta Influence of hydrodynamics and pulse plating parameters on the electrocodeposition of nickel – alumina nanocomposite films, 54 (2009) 2491–2498. doi:10.1016/j.electacta.2008.04.004.

[5] Q. Feng, T. Li, H. Yue, K. Qi, F. Bai, J. Jin, Preparation and characterization of nickel nano-Al 2 O 3 composite coatings by sediment co-deposition, 254 (2008) 2262–2268. doi:10.1016/j.j.apsusc.2007.09.014.

[6] P. Narasimman, M. Pushpavanam, V.M. Periasamy, Applied Surface Science Synthesis, characterization and comparison of sediment electro-codeposited nickel – micro and nano SiC composites, 258 (2011) 590–598. doi:10.1016/j.apsusc.2011.08.038.

[7] M. Rostami, A. Fahami, B. Nasiri-tabrizi, R. Ebrahimi-kahrizsangi, Applied Surface Science Characterization of electrodeposited Ni – SiC – C g nanocomposite coating, Appl. Surf. Sci. 265 (2013) 369–374. doi:10.1016/j.apsusc.2012.11.014.

[8] L. Chen, L. Wang, Z. Zeng, J. Zhang, Effect of surfactant on the electrodeposition and wear resistance of Ni – Al 2 O 3 composite coatings, 434 (2006) 319–325. doi:10.1016/j.msea.2006.06.098.

[9] H. Gül, F. Kılıc, S. Aslan, A. Alp, H. Akbulut, Characteristics of electro-co-deposited Ni – Al 2 O 3 nano-particle reinforced metal matrix composite (MMC) coatings, 267 (2009) 976–990. doi:10.1016/j.wear.2008.12.022.

[10] R. Starosta, a. Zielinski, Effect of chemical composition on corrosion and wear behaviour of the composite Ni–Fe–Al2O3 coatings, J. Mater. Process. Technol. 157-158 (2004) 434–441. doi:10.1016/j.jmatprotec.2004.09.068.

[11] N.K. Shrestha, K. Sakurada, M. Masuko, T. Saji, Composite coatings of nickel and ceramic particles prepared in two steps, Surf. Coatings Technol. 140 (2001) 175–181. doi:10.1016/S0257-8972(01)01045-3.

[12] A. Sasi, M. Mondal, S. Dayal, S. Kumar, Electro deposition of Nickel-Alumina Composite Coating., 2 (2015) 3042–3048. doi:10.1016/j.matpr.2015.07.292.

[13] Y.F. Yang, Z.Q. Gong, L.Y. Deng, B.P. Luo, Y.T. Ma, Z.H. Yang, Electrodeposition of Ni-Cr alloy on aluminum substrate, J. Cent. South Univ. Technol. (English Ed. 13 (2006) 219–224. doi:10.1007/s11771-006-0134-1.

[14] S. a. Lajevardi, T. Shahrabi, Effects of pulse electrodeposition parameters on the properties of Ni-TiO2 nanocomposite coatings, Appl. Surf. Sci. 256 (2010) 6775–6781. doi:10.1016/j.apsusc.2010.04.088.

[15] B. Lv, Z. Hu, X. Wang, B. Xu, Surface & Coatings Technology Electrodeposition of nanocrystalline nickel assisted by flu exible friction from an additive-free Watts bath, 270 (2015) 123–131.

[16] P. Gyftou, E. a. Pavlatou, N. Spyrellis, Effect of pulse electrodeposition parameters on the properties of Ni/nano-SiC composites, Appl. Surf. Sci. 254 (2008) 5910–5916. doi:10.1016/j.apsusc.2008.03.151.

[17] I. Garcia, a. Conde, G. Langelaan, J. Fransaer, J.P. Celis, Improved corrosion resistance through microstructural modifications induced by codepositing SiC-particles with electrolytic nickel, Corros. Sci. 45 (2003) 1173–1189. doi:10.1016/S0010-938X(02)00220-2.

[18] R.P. Socha, P. Nowak, K. Laajalehto, J. Väyrynen, Particle-electrode surface interaction during nickel electrodeposition from suspensions containing SiC and SiO2 particles, Colloids Surfaces A Physicochem. Eng. Asp. 235 (2004) 45–55. doi:10.1016/j.colsurfa.2004.01.011.

[19] A.M. El-sherik, J. Shirokoff, U. Erb, Stress measurements in nanocrystalline Ni electrodeposits, 389 (2005) 140–143. doi:10.1016/j.jallcom.2004.08.010.
[20] S.S.E.A. Pavlatou, Pulse electrodeposition of Ni / nano-TiO$_2$ composites: effect of pulse frequency on deposits properties, (2010) 1325–1336. doi:10.1007/s10800-010-0080-3.

[21] M.E. Bahrololoom, R. Sani, The influence of pulse plating parameters on the hardness and wear resistance of nickel – alumina composite coatings, 192 (2005) 154–163. doi:10.1016/j.surfcoat.2004.09.023.