



## **STUDIES ON NICKEL-ALUMINA ELECTROCOMPOSITE COATINGS OF OVER MILD STEEL SUBSTRATE**

**KR. Marikkannu, K. Amutha, G. Paruthimal Kalaighnan, and T. Vasudevan\***

*Department of Industrial Chemistry, Alagappa University,  
Karaikudi 630 003 INDIA*

### **ABSTRACT**

Codeposition of alumina powder in an acidic nickel-plating solution was studied, with the second phase particles suspended in the solution. In this work activated alumina was prepared by air oxidation of aluminium based on galvanic principle at room temperature. This alumina was used as the dispersoid for the development of electro-composite coatings. The effects of particle concentration, particle size, and plating conditions on microstructure and physical properties of the deposits were studied. Electrodeposited nickel and nickel-alumina were examined using potentiodynamic polarization and electrochemical impedance spectroscopy techniques to characterize the effect of alumina on the corrosion behaviour of the electrodeposited nickel matrix. X-ray diffraction confirms the crystalline structure as well as the incorporation of the alumina particles in the deposits.

**Key words:** Electrodeposits, Composite coatings, Ni-Al<sub>2</sub>O<sub>3</sub>, EIS

### **1. INTRODUCTION**

In recent years the interest in electrodeposited composite coatings has rapidly increased. This is mainly due to their expected new engineering applications [1]. Such coatings are produced by codeposition of fine inert particles side by side of the metal matrix atoms from electrolytic baths. Industrial applications of composite coatings with a nickel [2] or a cobalt [3] matrix have already been developed. The purpose of composite coating is to give various functional properties, such as wear resistance, self-lubricating, corrosion or oxidation resistance etc., to the plated surface [4]

A number of metal ceramic combinations possessed unusual properties [5]. Generally, carbides like silicon carbide, tungsten carbide are used as dispersoids where hardness and wear resistance are the major requirements. But oxides like TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc., are used where resistance to oxidation even at high temperatures is required along with hardness and wear improvement over conventional nickel deposits [6].

In this paper the properties of Ni-Al<sub>2</sub>O<sub>3</sub> composites, with special reference to their hardness and corrosion resistance are presented and discussed. In the present investigation activated alumina was prepared by air oxidation method.

## 2. EXPERIMENTAL

Activated alumina was prepared by air oxidation of aluminum based on galvanic principle at room temperature. The bath composition used to prepare activated alumina was 50gpl NaOH, 5-gpl mercuric chloride at room temperature. The aluminium panels were immersed in these solutions for 5 min and washed with water and dried. The aluminum oxide (alumina) is formed on the surface. This alumina was washed with water and acetone and dried in oven at 100°C. This alumina was used as the dispersoid for the development of electro-composite coatings.

The plating solution was an acidified nickel sulfate bath of composition  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  250 gpl,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  30gpl and  $\text{H}_3\text{BO}_3$  40gpl. The alumina particles of 20-40  $\mu\text{m}$  size prepared were nicely blended with a little of the electrolyte containing the wetting agent and transferred to the bulk in small portions to enhance complete dispersion of the particles in the suspension. The particles were kept in suspension by mechanical stirring and deposition was carried out for one hour at pH 4 and 60°C. The cathode current density was maintained at 4  $\text{A}/\text{dm}^2$ .

The volume percent of alumina was determined by the gravimetric method. The deposits were stripped from the substrate chemically in 1:1 nitric acid, the solution filtered through an ashless filter paper and the undissolved material washed until the filtrate was free from nickel. The filter paper was then incinerated first with a low flame and then upto red heat until pure alumina was obtained. The volume percent of alumina in the deposit was calculated from the weight of alumina obtained.

The effect of deposition parameters on the volume percent alumina and the hardness of the deposit were studied. The concentration of alumina in the baths was varied from 25-125 gpl for a current density range of 2 to 5  $\text{A}/\text{dm}^2$  with pH variation from 3-6 and time duration from 15-120 minutes in the case of the electrodeposition.

Potentiodynamic Polarization and Impedance Studies were made using an EG & G potentiostat. The electrolyte used was 3.5 % NaCl. The specimens were masked with lacquer so that only 1 $\text{cm}^2$  area was exposed to the electrolyte. A Saturated Calomel Electrode was used as the reference electrode. The corrosion potential and corrosion current were obtained from polarization curves using the Tafel extrapolation method. Specimens were examined using a Scanning Electron Microscopy (SEM). X-ray diffraction measurement were carried out examine the crystallinity of Ni and incorporation of alumina particles using X'Pert Software.

## 3. RESULTS AND DISCUSSION

The effect of alumina concentration in the bath on its volume percent in the deposit was determined in electroplating process. The codeposition of alumina depends also on the effective collision of the particles at the cathode and hence one may expect the volume percent of alumina in the deposit to increase with the increase in concentration of alumina in the bath. Figure 1 shows this effect at a constant current density of 4  $\text{A}/\text{dm}^2$ . As the concentration of alumina increases, its volume % in the deposit also increases upto 7.5% corresponding to 100 gpl of the bath load. But beyond that there is a slight decrease in volume % and this may be due to the lateral interactive destabilizing forces between the adsorbed  $\text{Al}_2\text{O}_3$  particles at very high concentrations.

The effect of pH on the rate of deposit is shown in Figure 2. It is found that as the pH is increased, the plating rate increases and reaches a steady value around pH 5-6. This indicates that higher concentration of  $\text{H}^+$  ions result in a competitive reduction reaction to metal

reduction. At pH 5 not only the deposition rate is high, but also we could get a bright and adherent deposit as well.

Figure 3 shows the effect of temperature on the volume percent inclusion of alumina and the rate of deposition. The temperature increase results in the increase in the volume percent of alumina in the deposit. When the temperature is increased from 50°C to 65°C, the rate of deposition increases due to the faster thermally aided transport of  $\text{Ni}^{2+}$  ions to the electrode surface besides forced the hydrodynamic flow that is ensured through stirring at constant speed. However at 70°C, we find a small decrease in the plating rate and this could be due to the desorption forces in the initial stages of that become prominent at higher temperatures resulting in the reduced surface concentration of  $\text{Ni}^{2+}$  ions.

### 3.1 Physical Characteristics Of The Electrodeposits

#### 3.1.1 Hardness

Figure 4 shows the effect of pH on the volume percent inclusion of alumina and their corresponding hardness. During hardness measurements, a small portion of the material undergoes plastic deformation under load. In the case of pure nickel this deformation takes place due to the relatively easy movements of dislocations and the resultant flow of the metal and hence a low hardness value is obtained. The hardness is found to increase with the increase of the alumina particles in the nickel matrix [7, 8]. The presence of fine particles in uniform dispersion obstructs the easy movement of dislocations and resists the plastic flow.

#### 3.2 Corrosion Resistance

The potentiodynamic polarization results of pure nickel and nickel-alumina are presented in Table 1 and in Figure 5. It is noted that the composites are found to be less corrosion resistant than pure nickel and as the alumina content increases in the deposit, its corrosion resistance is decreased. Such a behavior is already been reported in the literature [9]. It is explained that the initial corrosion starts around the particles i.e., the metal particle boundary as the anodic region. Since the number of particles in the bulk of the coating is enormous, a continuous distribution of the corrosion current occurs on the anodic area. The inclusions may act as favorable sites for crevice corrosion and acceleration. The fine particles may become dislodged during dissolution exposing more area to corrosion, and is confirmed by the corrosion potential showing a positive shift.

For most of the cases the Nyquist plots are semicircle indicating the activation control of the corrosion reaction as shown in Figure 6 (a-d). The  $R_t$  values (Table 2) reflect the trend of the polarization studies i.e., poor corrosion resistance of the composites compared to pure nickel. The  $C_{dl}$  values calculated also confirm the less corrosion resistance of the composites suggesting increased charge in the interface due to more active dissolution of the composites in the sodium chloride medium.

#### 3.3 Structural Investigations

The pure nickel deposits as well as the nickel composites developed were subjected to XRD studies to ascertain the incorporation of composite particles in the nickel matrix. The result for pure nickel is presented in Figure 7a. The XRD results for  $\text{Ni-Al}_2\text{O}_3$  composites are represented in Figure 7b. The results confirm that alumina of gibbsite form with the crystal structure monoclinic and lattice parameters  $a=8.62$ ,  $b=5.06$ ,  $c=9.70$  is incorporated into nickel matrix.

The amount of codeposition of the inert particles depends on their effective collisions at the cathodic surface and therefore should increase with the increase the alumina concentration in the suspension. As indicated in Figure 1, the volume percent of alumina in the deposit increases linearly upto 100 gpl in the bath, but there after there is no significant variation in the amount of codeposition probably indicating the saturation limit for the number of effective collisions at the electrode surface. SEM photographs in Figure 8a and Figure 8b indicate the pure nickel as distinct from the composite obtained from solution containing 100 gpl load. Guglielmi's[10] mechanism based on successive adsorption steps for the codeposition of abrasive particles in a metal matrix can hold good for this deposition process also.

#### 4. CONCLUSION

Electrodeposited nickel-alumina composites can be produced from a conventional electrodeposits using nickel-plating bath. The bath load of alumina was varied and the composition of the composites estimated for alumina contents in the deposit. The micro hardness of the composite showed significant improvement as a result of restriction to the movement of dislocation in the metal matrix. The corrosion resistance studies by polarization and impedance measurement in sodium chloride medium showed a declining trend due to increased heterogeneity and porosities in the deposits. The XRD and SEM studies confirm the incorporation of alumina particles in nickel matrix.

#### REFERENCES

1. Apurbba Kr. Sharma and R.Krishnamurthy, J.European Ceramic Society, 22 (2002) 2849.
2. N.S.U.Neckarsulm, Br. Pat., 1,200,410 (July 1970).
3. Gang Wu, Ning Li, Derui Zhou and Kurachi Mitsuo, Surface and Coating Technology, 176 (2004) 157.
4. C.S Ramesh and S.K. Seshadri, Wear 255 (2003) 893.
5. Tontlani, et al., Rev. Coatings and Corr. (1976).
6. P.K.Sinha, et al., Plating 55 (1973) 56.
7. M.Verelst, J.P.Bonino, M.Brieu and A.Rousset, Meter. Sci.Eng. A191 (1995) 165.
8. M.Verelst, J.P.Bonino, and A.Rousset, Meter. Sci.Eng. A135 (1991) 51.
9. Malathy Pushpavanam, K.Balakrishnan and L.R.Sharma, 10 th International congress on metallic corrosion, Vol.II, Sessions 5 to 9 (1987) 13434.
10. N.Guglielmi, J. Electrochem. Soc., 119 (1972) 1009.

## TABLES

Table 1: Evaluation of corrosion resistance in 3.5 % NaCl solution by potentiodynamic polarization studies

Ni an Ni-Al <sub>2</sub> O <sub>3</sub> deposits	-E <sub>corr</sub> (mV) Vs SCE	i <sub>corr</sub> (A/cm <sup>2</sup> ) x 10 <sup>-4</sup>
Ni	695	2.00
Ni-Al <sub>2</sub> O <sub>3</sub> (4.2%)	662	4.10
Ni-Al <sub>2</sub> O <sub>3</sub> (5.3%)	588	3.16
Ni-Al <sub>2</sub> O <sub>3</sub> (6.7%)	527	4.47
Ni-Al <sub>2</sub> O <sub>3</sub> (7.5%)	603	6.31
Ni-Al <sub>2</sub> O <sub>3</sub> (7.2%)	626	7.10

Table 2: Evaluation of corrosion resistance in 3.5 % NaCl solution by impedance studies

Ni an Ni-Al <sub>2</sub> O <sub>3</sub> deposits	R <sub>t</sub> (ohm cm <sup>2</sup> )	C <sub>dl</sub> (μF/cm <sup>2</sup> )
Ni	359	4.44
Ni-Al <sub>2</sub> O <sub>3</sub> (5.3%)	310	7.53
Ni-Al <sub>2</sub> O <sub>3</sub> (7.5%)	226	11.69
Ni-Al <sub>2</sub> O <sub>3</sub> (7.2%)	124	17.11

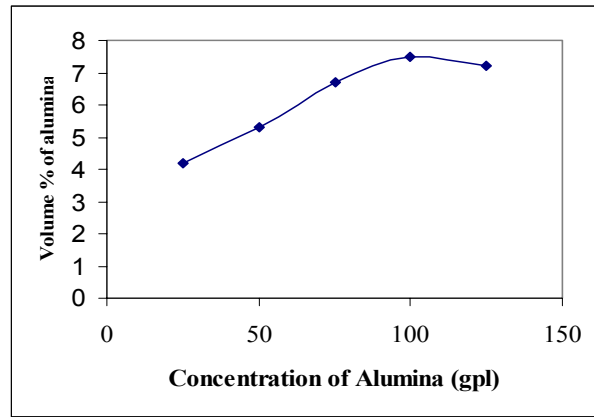
**FIGURES**

Figure 1: Effect of alumina concentration in the bath on the volume percent of Ni-Alumina composites

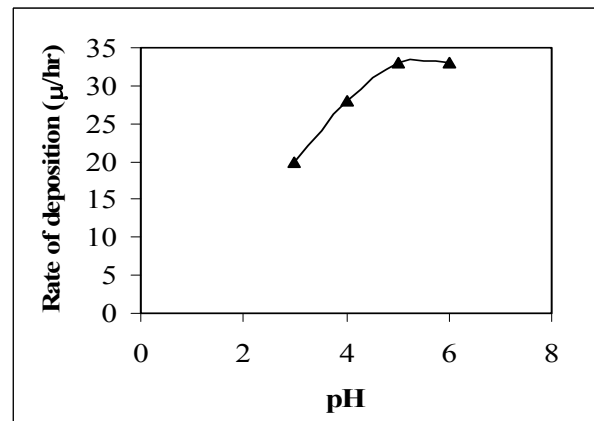


Figure 2: Effect of pH on the rate of deposition

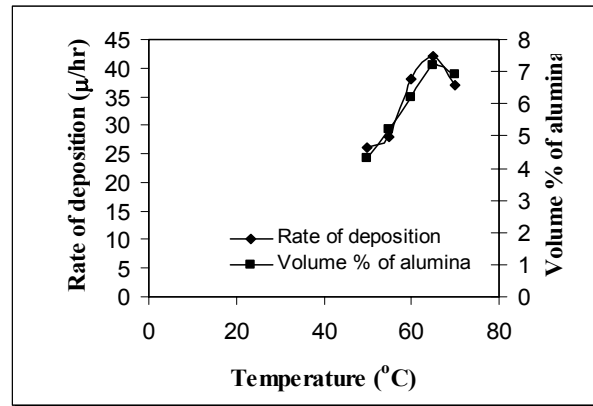


Figure 3: Effect of temperature on the volume percent of alumina and rate of deposition

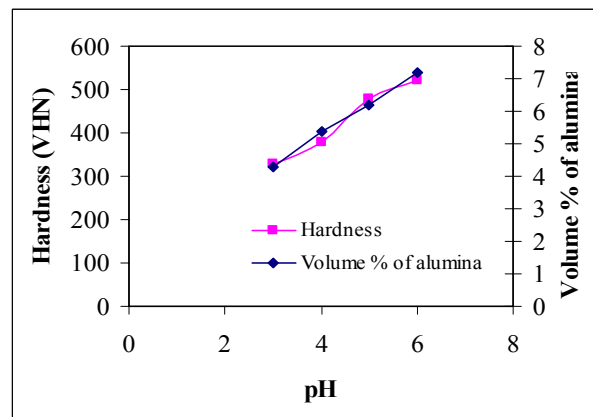


Figure 4: Effect of pH on the hardness and volume % of alumina in the deposit

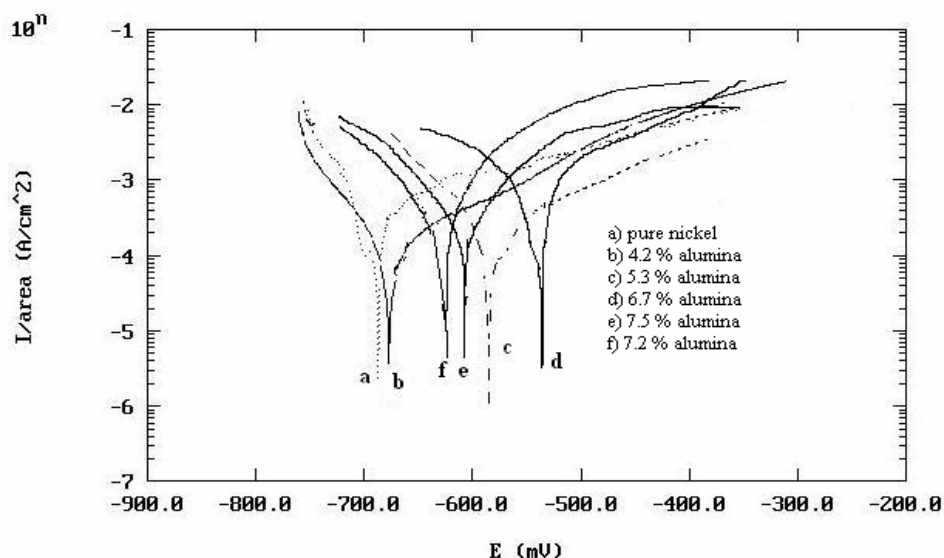


Figure 5: Potentiodynamic polarization curves of pure nickel and various volume % of alumina particles using 3.5% NaCl at 32°C

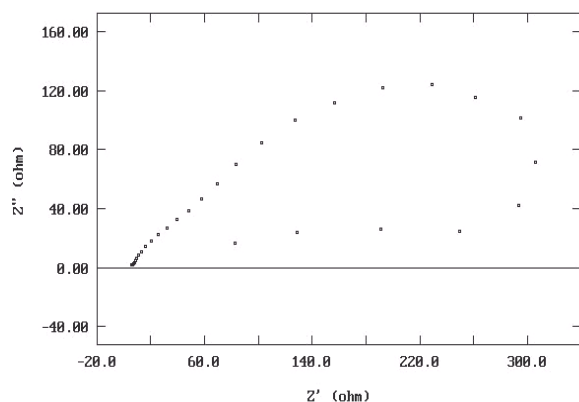


Figure6a: Electrochemical impedance behaviour of pure Ni using 3.5 % NaCl Medium

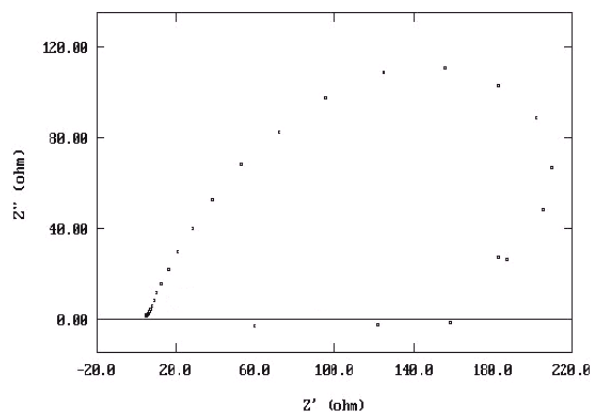


Figure6b: Electrochemical impedance behaviour of Ni-Al<sub>2</sub>O<sub>3</sub> (5.3%) using 3.5 % NaCl Medium

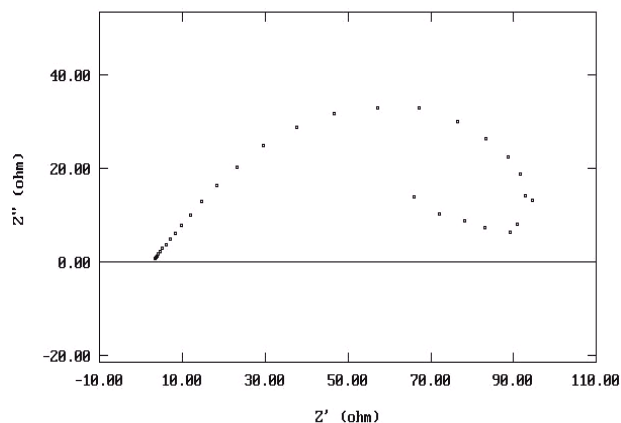


Figure6c: Electrochemical impedance behaviour of Ni-Al<sub>2</sub>O<sub>3</sub> (7.5 %) using 3.5 % NaCl Medium

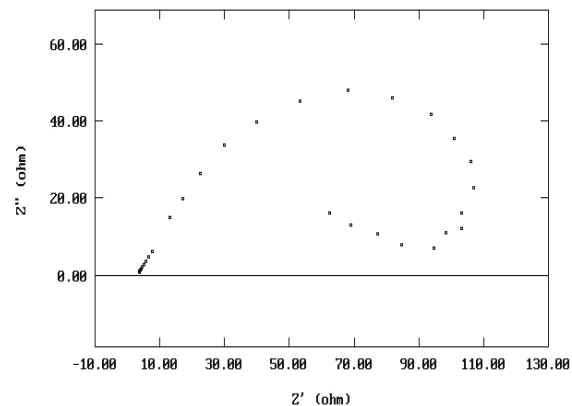


Figure6d: Electrochemical impedance behaviour of Ni-Al<sub>2</sub>O<sub>3</sub> (7.2 %) using 3.5 % NaCl Medium



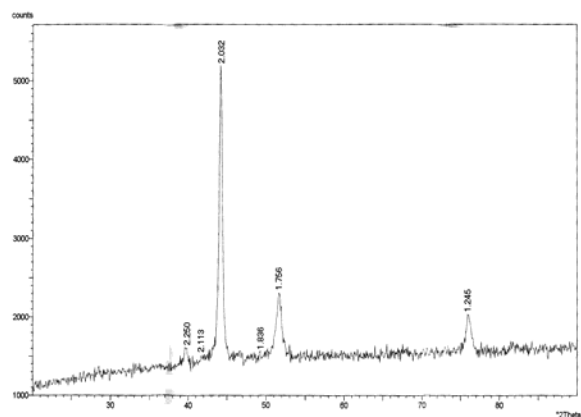


Figure 7a: X-ray diffraction patterns of pure nickel deposit

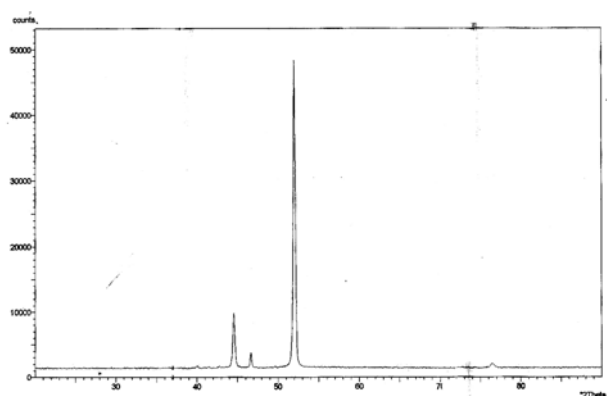


Figure 7b: X-ray diffraction patterns of nickel-alumina composite deposit

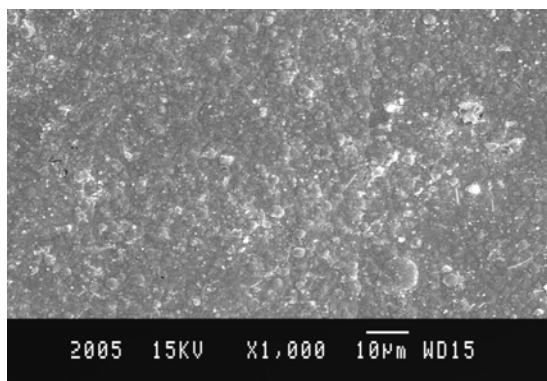


Figure 8a: SEM photographs showing the microstructure of pure nickel deposit

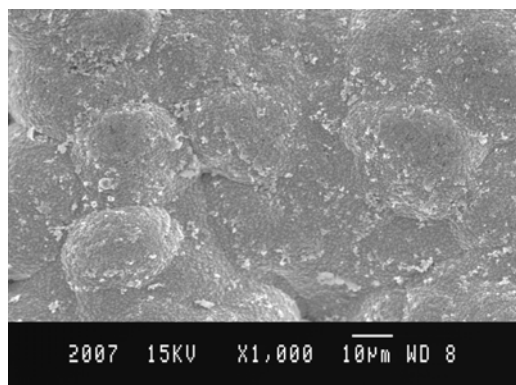


Figure 8b: SEM photograph showing the microstructure of nickel-alumina composite obtained from a bath containing 100 gpl alumina deposits