THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N$^0$. 4 – 2011, ISSN 1453 – 083X

# EFFECT OF ACIDIC ENVIRONMENT ON Cu-Al$_2$O$_3$ CODEPOSITION*

**Mihaela-Daniela GAVRIL (DONOSE)**[1], **Constantin GHEORGHIEŞ**[2], **Alina-Mihaela CANTARAGIU**[1], **Denys Cristina VLADU (RADU)**[1], **Sorin DONOSE**[3]
[1]PhD students Faculty of Sciences and Environment, „Dunarea de Jos” University of Galati
[2]Faculty of Sciences and Environment, Chemistry, Physics and Environment Department, „Dunarea de Jos” University of Galati
[3]41 ”Grigore Teologul” School, Galati

## ABSTRACT

*Electrocodeposition of alumina nanoparticles with copper onto nickel substrate was prepared through the potentiostatic method. The codeposited films were obtained at different nanoparticle concentrations: 5, 10, 15, 20 and 25 gL$^{-1}$. The corrosion behaviour of codeposited films has been observed by introducing them in different corrosive environments: 0.5 M $H_2SO_4$, HCl and $HNO_3$ solutions. The corrosion study has been realized using the linear polarization method. The corrosion rate and polarisation resistance values were obtained from the Tafel curves. The highest concentration of alumina nanoparticles had increased the corrosion resistance of Cu-$Al_2O_3$ codeposited films. Also, in order to confirm these results, the gravimetric parameter was calculated by means of the mass loss method.*

KEYWORDS: electrocodeposition, cooper, alumina, corrosion, Tafel curves

## 1. Introduction

There are several methods and techniques for protecting the surface of metallic materials against the aggressive action of environment [1]. The alumina coatings have a protective function, being a physical barrier between the metal surface and the aggressive environment [2].

The corrosive process study is very important to prevent and control this spontaneous phenomenon. The corrosion study has been realized using the linear polarization method and performed in three different acid environments: 0.5 M $H_2SO_4$, HCl, and $HNO_3$ solutions.

The electrocodeposited films of the alumina nanoparticles with copper matrix on nickel substrate were obtained at different nanoparticle concentrations: 5, 10, 15, 20 and 25 gL$^{-1}$ by means of the chronoamperometric method.

This paper presents the synthesis of the Cu-Al$_2$O$_3$ nanocomposite films by means of the potentiostatic electrochemical method and the corrosion behaviour is evaluated through the comparative analysis of the corrosion resistance values obtained for solid samples.

Some results concerning the behaviour into corrosive environment of nickel samples coated with Cu-Al$_2$O$_3$ films are reported [1].

## 2. Materials and methods

Copper films have been electrodeposited onto nickel substrate from an electrolyte solution having the following composition: 0.8 M $CuSO_4 \times 5H_2O$, 0.55 M $H_2SO_4$, 0.003 M HCl diluted in 100 mL volume solution [3]. A three electrode system with an electrochemical cell volume of 100 ml was used to perform the experiments.

---

*Paper presented at the Symposium ***"The Impact of Nanotechnologies and Nanomaterials on Industrial Development and Quality of Life",*** Galati, May 19, 2011, organized by the Center for Nanostructures and Functional Materials (CNMF), Faculty of Metallurgy, Materials Sciences and Environment, “Dunarea de Jos” University of Galati

The counter electrode was a platinum sheet and the reference electrode was an Ag/AgCl.

The working electrode was the nickel substrate which has an electroactive area of 2.5 cm$^2$.

Before each experiment, the working electrode was mechanically polished with abrasive silicon carbide paper, degreased in acetone and alcohol, etched with 1:10 $HNO_3$:$H_2O$, rinsed with distilled water and then, dried in air.

The process will occur without magnetic stirring. The electrolyte pH was recorded by means of the Consort C931 equipment.

The temperature was controlled with a thermostat. Also, before and after codeposition the samples, weight was measured using an electronic balance (model ESJ200-4).

The coatings preparation was carried out potentiostatically with a potentiostat/galvanostat VoltaLab10 interfaced with VoltaMaster4 software for data acquisition and analysis. After deposition, the samples were rinsed with bidistilled water to remove loosely adherent nanoparticles.

The composite coatings consisting of $Al_2O_3$ nanoparticles in a copper matrix have been electrocodeposited onto nickel substrate during 30 min. as deposition time at 50°C and pH of 1.7 [4]. Five different $Al_2O_3$ particle concentrations were used to obtain the composite films (5 , 10, 15, 20 and 25 gL$^{-1}$). The process starts at 450 rpm as stirring rate.

The corrosion behaviour was carried out with a VoltaLab10 potentiostat. Potentiodynamic polarisation curves of the codeposited films were measured from -1000 mV toward the anodic direction of 1000 mV with a scan rate of 50 mV/s. The corrosion behaviour of codeposited films has been observed by introducing them in different corrosive environments: 0.5 M $H_2SO_4$, HCl and $HNO_3$ solutions. The exposure corrosion time is 60 s.

The linear polarisation (Tafel curves) was used as method to study the corrosion behaviour. From the anodic and cathodic polarization potentiodynamic curves were obtained the main electrochemical parameters of the corrosion process: corrosion potential $E_{corr}$, corrosion current density $i_{corr}$, polarization resistance $R_p$ and corrosion rate $V_{corr}$.

The corrosion rate is automatically calculated by specialized computer software using the Randles-Sevcik equation (1). Before and after each experiment, the weight of samples was measured by means of analytical balance. The mass losses (difference between the final and initial weight) are calculated by means of the gravimetric method and showed in Table 1. Also, the penetration index was calculated.

## 3. Results and discussion

The corrosion rates (Table 1) determination was achieved by means of the “mass loss method” [5] in static regime at room temperature and it is calculated based on the equation (1):

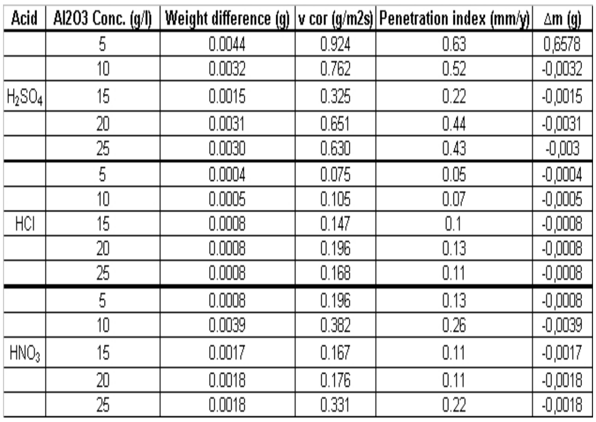
$$V_{corr} = \frac{\Delta m}{S \cdot t} \qquad (1)$$

where: $V_{corr}$ = gravimetric index [g/m$^2$s$^1$]; $\Delta m$ = weight loss (before and after the corrosion test) by corrosion [g]; $S$ = corroded surface area [m$^2$]; $t$ = corrosion time [s]. The average depth of the composite corrosive destruction is calculated using the formula (2):

$$p = \frac{V_{corr}}{\rho} \cdot 8.76 \qquad (2)$$

where: $p$ = penetration index [mm/y]; $V_{corr}$ = gravimetric index [g/m$^2$s]; $\rho$ = composite film density [g/cm$^3$]. The results are presented in Table 1.

***Table 1.*** *The Cu-$Al_2O_3$ electrocodeposition behaviour in various acid environments by means of the gravimetric method*



| Acid | Al2O3 Conc. (g/l) | Weight difference (g) | v cor (g/m2s) | Penetration index (mm/y) | Δm (g) |
|---|---|---|---|---|---|
| | 5 | 0.0044 | 0.924 | 0.63 | 0,6578 |
| | 10 | 0.0032 | 0.762 | 0.52 | -0,0032 |
| $H_2SO_4$ | 15 | 0.0015 | 0.325 | 0.22 | -0,0015 |
| | 20 | 0.0031 | 0.651 | 0.44 | -0,0031 |
| | 25 | 0.0030 | 0.630 | 0.43 | -0,003 |
| | 5 | 0.0004 | 0.075 | 0.05 | -0,0004 |
| | 10 | 0.0005 | 0.105 | 0.07 | -0,0005 |
| HCl | 15 | 0.0008 | 0.147 | 0.1 | -0,0008 |
| | 20 | 0.0008 | 0.196 | 0.13 | -0,0008 |
| | 25 | 0.0008 | 0.168 | 0.11 | -0,0008 |
| | 5 | 0.0008 | 0.196 | 0.13 | -0,0008 |
| | 10 | 0.0039 | 0.382 | 0.26 | -0,0039 |
| $HNO_3$ | 15 | 0.0017 | 0.167 | 0.11 | -0,0017 |
| | 20 | 0.0018 | 0.176 | 0.11 | -0,0018 |
| | 25 | 0.0018 | 0.331 | 0.22 | -0,0018 |

The results from Table 1 are indicated that the less aggressive environment is the HCl against the nanocomposite Cu-$Al_2O_3$ (5 gL$^{-1}$).

On the other hand, the codeposited films are highly corroded in the $H_2SO_4$ solution.

Fig. 1 shows the influence of the alumina nanoparticle concentrations on the composites corrosion rate measured during the polarisation studies. These data show that the Cu-$Al_2O_3$ codeposition has a real protection effect.

The $Al_2O_3$ nanoparticle concentrations increasing lead to the significant decrease of the corrosion rate in each acid environment. 15 gL$^{-1}$ $Al_2O_3$ nanoparticles present the higher corrosion rate in $HNO_3$ and the nanocomposites with 5, respectively 25gL$^{-1}$ are more resistant to corrosion.

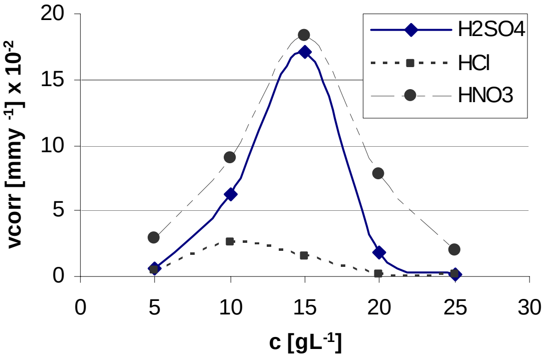


***Fig. 1***. *The corrosion rate variation with the $Al_2O_3$ nanoparticle concentrations.*

In this case, the corrosion rate values are automatically calculated by the VoltaMaster4 software [6] based on the equation (3):

$$V_{corr} = \frac{0.051 \cdot i_{corr}}{\rho \cdot A} \quad (3)$$

and according to the Stearn-Geary equation (4) [6,7]:

$$R_p = \left[\frac{1}{2.303 \cdot i_{corr}}\right] \cdot \left[\frac{\beta_a \cdot \beta_c}{\beta_a + \beta_c}\right] \quad (4)$$

where: $V_{corr}$ = corrosion rate [mm/y]; $i_{corr}$ = corrosion current density [A/dm$^2$]; $A$ = composite molecular weight [g/mol]; $\rho$ = composite film density [g/cm$^3$]; $R_p$ = polarisation resistance [Ωcm$^2$]; $\beta_a$ = anodic Tafel slope [mV]; $\beta_c$ = cathodic Tafel slope [mV].

The most aggressive environments are the 0.5M $H_2SO_4$ and $HNO_3$ solutions for which are recorded the highest corrosion values. Namely, the composites Cu-$Al_2O_3$ with 15 gL$^{-1}$ nanoparticle concentrations are exposed to a very aggressive corrosion into acid environment. In the presence of 0.5 M HCl solution, almost all samples have a good behaviour by surface passivation process.

The effect of $Al_2O_3$ nanoparticle concentrations on the composite layer thickness was studied. The layer thickness was calculated using the formula (5):

$$d = \frac{\Delta m}{S \cdot \rho} \cdot 10^4 \quad (5)$$

where: $d$ = thickness [µm]; $\Delta m$ = weight difference [g]; $S$ = surface area [cm$^2$]; $\rho$ = composite density [g/cm$^3$].

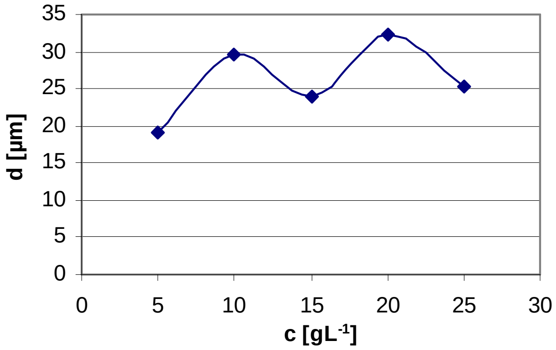


***Fig. 2.*** *The layer thickness variation with the $Al_2O_3$ nanoparticle concentrations.*

The layer thickness shows a non-linear increased tendency when increasing the $Al_2O_3$ nanoparticle concentrations due to the stirring effect on the electrolyte solutions. The degree of alumina nanoparticles included in copper matrix increases when increasing the nanoparticle concentrations. Thereby, the thickness has varied with concentration and the high values of thickness correspond to 10 and 20 gL$^{-1}$ nanoparticles in electrolyte.

The composites were carefully cleaned and rinsed with bidistilled water before their immersion in the electrochemical cell with acid solution. Each measurement started after 60 s to access an equilibrium potential between composite films and acid solution, because of electronic interactions at the interface [7, 8, 9]. The point of intersection between the anodic and cathodic reactions establishes the corrosion potential ($E_{corr}$) of the composites and indicates the magnitude of the corrosion current ($i_{corr}$). The corrosion process at Cu-$Al_2O_3$ composite films surface was studied by means of the linear polarisation method [6].

Fig. 3-5 present the electrochemical behaviour of Cu-$Al_2O_3$ composite films tested in three acid environments. Fig. 3 shows the polarization curves in case of Cu-$Al_2O_3$ composite films immersed in 0.5M $H_2SO_4$ solution. The $E_{corr}$ potential was shifted to high negative values when increasing nanoparticle concentrations.

The Cu-$Al_2O_3$ composite with 25 gL$^{-1}$ has the most negative $E_{corr}$ value potential, thus confirming the highest corrosion rate value. This fact can be due to the poor inclusion ability of alumina nanoparticles into a metallic matrix when the concentration is higher. More corrosion resistant could be Cu-$Al_2O_3$ composite film with 5 gL$^{-1}$ nanoparticle concentrations. All cathodic branches are linearly shaped (no surfaces passivated) and the composite surfaces are more susceptible in the $H_2SO_4$ electrochemical solution.

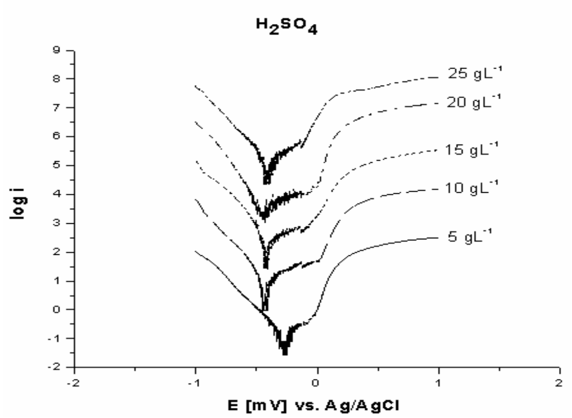


***Fig. 3.*** *Tafel polarisation curves of Cu-$Al_2O_3$ composite films in 0.5 M $H_2SO_4$ environment.*

Fig. 4 shows the polarization curves in case of Cu-$Al_2O_3$ composite films immersed in 0.5 M HCl solution. The $E_{corr}$ potential was shifted to less negative values (compared to the first corrosion test) when increasing nanoparticle concentrations [6].

The Cu-$Al_2O_3$ composite with 15 $gL^{-1}$ has the most negative $E_{corr}$ value potential, thus confirming the highest corrosion rate value. This fact can be due to the poor inclusion ability of alumina nanoparticles into a metallic matrix when the concentration increases. More corrosion resistant could be the Cu-$Al_2O_3$ composite film with 5 $gL^{-1}$ nanoparticle concentrations due to the surface passivation process. However, all sample surfaces, are not stable in this solution due to the non-linear shape of the cathodic and anodic branches.

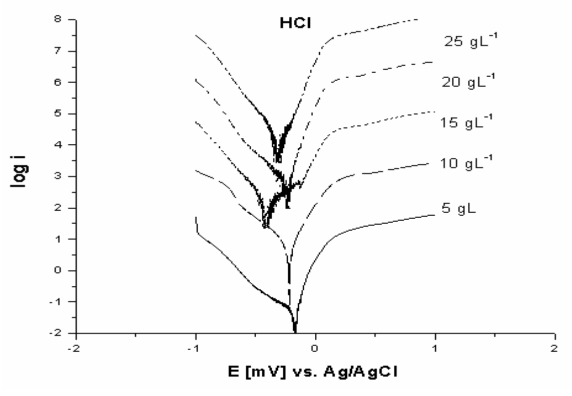


***Fig. 4.*** *Tafel polarisation curves of Cu-$Al_2O_3$ composite films in 0.5 M HCl environment.*

Fig. 5 shows the polarization curves in case of Cu-$Al_2O_3$ composite films immersed in 0.5 M $HNO_3$ solution. The $E_{corr}$ potential was shifted to most negative values.

The Cu-$Al_2O_3$ composite with 25 $gL^{-1}$ has the most negative $E_{corr}$ value potential, thus confirming the highest corrosion rate value. The cathodic branch appears linearly shape for 25 $gL^{-1}$ nanoparticle concentrations, so there is no passivity reaction [6].

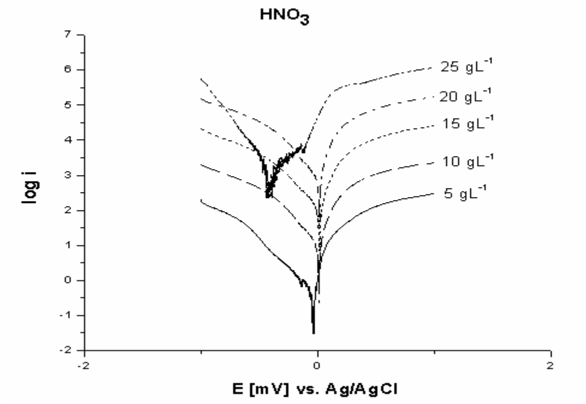


***Fig. 5.*** *Tafel polarisation curves of Cu-$Al_2O_3$ composite films in 0.5 M $HNO_3$ environment.*

However, for the other concentration, the cathodic branches are non-linear due to the oxide layer formation. The most corrosion resistant could be the Cu-$Al_2O_3$ composite film with 5, 10, 15 and 20 $gL^{-1}$ nanoparticle concentrations due to the surface passivation process ($E_{corr}$ is shifted to zero value). The decreasing of nanoparticle concentrations in the electrolyte increases the electrochemical passivation from cathodic and anodic polarisation curves. This behaviour can be explained on the basis of the inert action of this environment against samples.

## 4. Conclusions

From the obtained results of the polarization measurement method (Tafel curves) of the Cu-$Al_2O_3$ composite films exposed to various acid environments it may be concluded that:

- Nanocomposite thin films which consist of $Al_2O_3$ nanoparticles in a copper metal matrix were deposited on a nickel substrate and synthesized using the electrocodeposition method.
- The corrosion process and electrochemical parameters depend on some factors: electrolyte type, exposure time, pH value, chemical composition of working electrode, applied scanning potential, nanoparticle concentrations and particles size.
- The increasing of $Al_2O_3$ nanoparticle concentrations led to the increasing corrosion resistance.

- The highest corrosive rate corresponds to $H_2SO_4$ atmospheres (for 25 $gL^{-1}$ $Al_2O_3$).
- The 0.5 M $HNO_3$ solution is the least corrosive environment because this environment can limit the corrosion process by hydrogen ions evolution inhibition.
- The presence of $Al_2O_3$ nanoparticles led to quickly passivation into the 0.5 M HCl environment.
- The thickness layer increases non-linearly with the nanoparticle concentrations. The largest thickness corresponds to 20 $gL^{-1}$ $Al_2O_3$.
- The destructive action shown in these experiments could be determined by the chemical reactions occurred as a result of electric currents passing through the liquid environment.

## Acknowledgments

The work of Mihaela-Daniela Gavril (Donose) was supported by Project SOP HRD - TOP ACADEMIC 76822.

## References

**[1]. A. Vicenzo and P.L. Cavallotti** - *Copper electrodeposition from a pH 3 sulfate electrolyte*, J. Appl. Electroch., 32: 743–753, 2002.

**[2]. M. Palaniappa, M. Jayalakshmi, P. M. Prasad, K. Balasubramanian** - *Chronopotentiometric studies on the passivation of industrial copper anode at varying current densities and electrolyte concentrations*, Int. J. Electrochem. Sci., 3, 452–461, 2008.

**[3]. D. Grujicic and B. Pesic -** *Electrodeposition of copper: the nucleation mechanisms,* Electrochimica Acta, 47, 2901-2912, 2002.

**[4]. Z. Anđić, M. Korać, M. Tasić, Ž. Kamberović, K. Raić,** *Synthesis and Sintering of Cu-$Al_2O_3$ Nanocomposite Powders Produced by a Thermochemical Route*, Metalurgija Journal of Metallurgy, 13(1), 71-81, 2007.

**[5]. D. Popovici, E. Trimbitasu, O. Pantea, D. Bombos, L. Antonescu** - *Determinarea eficientei inhibitorului de coroziune Aticamina OTM 2*, Buletinul Universităţii Petrol-Gaze din Ploieşti, LIV, Seria Tehnică, 4, 189-196, 2002.

**[6]. A. M. Cantaragiu, G. Carac, C. Gheorghies -** *Electrochemical study of AISI 316L Stainless Steel in different nanoparticle suspensions*, J. Optoel. Adv. Mater., 12(20), 12, 2391-2399, 2010, ISSN: 1454-4164.

**[7]. W. Stephen Tait -** *Ph.D. An introduction to electrochemical corrosion testing for practicing engineers and scientists*, Pair O Docs Pubns, ISBN 9780966020700, 1994.

**[8]. H. Davy** - *On some chemical agencies of electricity (Bakerian Lecture of 1807)*, Phil. Trans. Roy. Soc. (London), 97, 56, 1807.

**[9]. K. Babic-Samardzija, K. F. Khaled and N. Hackerman** - *heterocyclic amines and derivatives as corrosion inhibitors for iron in perchloric acid*, Anti-Corrosion Methods and Materials 52(1), 11-21, 2005.

**[10]. VoltaMaster 4** - *Application Help Handbook*; www.radiometer-analytical.com/voltalab/en_ocp.asp.

**[11]. M. Stoica, G. Cârâc, C. Apetrei, A.M. Cantaragiu -** *Electrochemical study of stainless steel surfaces in biodegradable biocides,* J. Optoel. Adv. Mater., 12(35), 4, 919-922, 2010.