

Ceramic coatings by sol-gel method for corrosion protection of mild steel

S.K. Tiwari* and Raghuvir Singh

*Corrosion & Surface Engineering Division, CSIR-National Metallurgical Laboratory,
Jamshedpur-831007, Jharkhand.*

Abstract

Mild steel finds extensive applications in automobile, household appliances, heavy construction and business machines due to its mechanical properties and machinability at low cost. However, it is prone to corrosion that leads to industrial accidents and loss of material resources. Sol-gel derived ceramic coatings have been deposited on mild steel (MS) with a prior conversion coating for its corrosion protection. The prior conversion coating led to the formation of well adherent coatings of Al_2O_3 , ZrO_2 and TiO_2 . The Scanning Electron Microscope (SEM), X-ray diffractometer (XRD) and FT-IR was used to study the morphology, phases formed and nature of bonding in the coating. The electrochemical corrosion behavior of the coated MS was evaluated in 3.5 wt.% NaCl solution. The coatings show barrier type protection of MS up to about 1 V_{SCE} . The Al_2O_3 and ZrO_2 coatings were observed unaffected during prolong immersion in 3.5 wt.% NaCl solution. The physicochemical and electrochemical properties have been correlated and discussed.

Introduction

Mild steel is extensively used structural material in several engineering applications due to its good machinability, high thermal conductivity and superior mechanical strength at low price. However, it is prone to wear and corrosion which reduces its service life. Ceramic coatings in recent years have been increasingly adopted for hot and wet corrosion protection of several engineering components [1-5]. The coatings have been tried out using various methods including thermal spray, PVD, CVD, plasma, laser surface coating etc. However, these coatings have certain limitations such as huge equipment cost, low coating adherence, large porosity, requirement of controlled environment (such as vacuum), and line of site etc. Ceramic coatings produced by sol-gel route have been extensively used for prevention of corrosion/wear in case of stainless steel and other metals that form naturally passive film on their surface [6]. Very limited work has been done to develop ceramic coatings on active substrate such as mild steel for corrosion and wear protection of this widely used material [7-12]. Such active substrate gets oxidized during sol-gel coating resulting into poor bonding between substrate and the coating. Efforts have been made to modify the active steel surface through chemical route before sol-gel ceramic coating [7-9]. However, the modified surface through chemical route contains high porosity and the sol-gel coating on such modified porous surface resulted into less corrosion resistant coating. The present paper describes the corrosion behavior of sol-gel Al_2O_3 , ZrO_2 and

Keywords: Mild steel, Corrosion protection, Ceramic coating, Sol-gel, Surface modification

- Corresponding & Presenting Author: E-mail: tkshashi@gmail.com;

TiO₂ coatings on surface modified mild steel in 3.5 wt.% NaCl. The surface of mild steel was modified by introducing phosphate layer using conventional phosphating method, electroless Ni-P layer and a composite layer through sol-gel route. The results of electrochemical behaviour of sol-gel coatings on modified surfaces were compared with bare mild steel.

Experimental procedure

Coupons of 30 mm×20 mm×2 mm size were cut from mild steel (MS) sheet of nominal composition (in wt.%) C-0.06, Si-0.04, Mn-1.46, S-0.01, P-0.02, and Fe-balance. The coupons were polished successively on emery paper from 120 to 500 grit. The coupons were cleaned with soap solution followed by degreasing with acetone and finally cleaned with ethanol.

The surface of mild steel was modified by introducing a conversion coating. For the purpose the cleaned coupons were dip-coated in aluminum oxy-hydroxide sol. The aluminum oxy-hydroxide sol was prepared by addition of aqueous NH₃ drop wise to the aluminum nitrate hexahydrate. The resultant precipitate was filtered and redispersed in distilled water. The dip-coated coupons were dried in ambient atmosphere and finally heated at 500 °C for 1 hour. The furnace cooled plates were again cleaned with ethanol and used for further sol-gel coating. The conversion coated MS plates will be referred as CcMS in the text. The MS surface was also modified by fabricating electroless Ni-P and phosphate layer prior to sol gel coating as reported in literature [13, 14].

The Al₂O₃, TiO₂ and ZrO₂ sols were prepared by hydrolysis of aluminum isopropoxide, titanium isobutoxide and zirconium (IV) n-propoxide respectively using HNO₃ as catalyst. The surface modified MS plates were dip-coated in the respective sol and withdrawn at a constant rate of 30 mm/min. The coated plates were dried in ambient atmosphere for 30 min. The process of dip-coating and drying was repeated 5 times in order to increase the thickness of the coating. The dip-coated MS plates were then subjected to heat treatment at 500 °C for 1 hour and then furnace cooled. The surface morphology and phases formed on MS plates were studied by SEM (JEOL, 840A, Japan) and XRD (Seifert, PTS 3003) using Cu-K_α radiation, respectively. Powder samples of sol-gel Al₂O₃ and ZrO₂ were analyzed in KBr pellets by recording FT-IR spectra using a NICOLET-7500 spectrometer in the wave number ranging from 400 to 4000 cm⁻¹.

The electrochemical behavior of sol-gel coating was studied in 3.5 wt% NaCl solution at room temperature (25 °C). A conventional three electrode cell, consisting of saturated calomel (SCE), graphite and coated MS as reference, auxiliary and working electrode respectively, was used to study the electrochemical behavior. 1.0 cm² area of the coated surface was exposed to the electrolyte and remaining was covered with Araldite. After OCP stabilization, the AC (alternating-current) impedance measurements were made at open circuit potential with 10 mV amplitude of the sinusoidal voltage signal at applied frequencies in the range of 10⁵ to 10⁻² Hz using ten points per decade. The polarization curves were recorded by sweeping the potential from -100 mV to ≥1.0 V (with respect to OCP) in the noble direction at a constant scan rate of 0.5 mV/s. All electrochemical experiments were carried out using computer controlled Potentiostat/Galvanostat/ZRA (PC4/750, Gamry Instruments, USA). The impedance and Tafel parameters were extracted by curve fitting procedure available in the software.

Results

(i) Potentiodynamic polarization

(a): Effect of surface pretreatment

The effect of surface modification prior to Al₂O₃ sol-gel coating on the corrosion protection of MS was studied by recording potentiodynamic polarization curves in 3.5 wt.% NaCl solution. The electrochemical parameters, calculated from the curves, by Tafel extrapolation method are shown in Table-1. The sol-gel Al₂O₃ coating on pre-phosphated MS (MS/Phos/Al₂O₃) shifts corrosion potential (E_{corr}) in noble direction by 88 mV and the corrosion current density (i_{corr}) is reduced by about 2 orders of magnitude. However, the nature of polarization curve is more or less identical to bare MS which shows linear increase of current with potential.

Table-1: Electrochemical parameters calculated from potentiodynamic polarization curves on bare MS and sol-gel Al₂O₃ coatings on MS with different surface pretreatment

Electrodes	E_{corr} (mV _{SCE})	i_{corr} (A cm ⁻²)	E (V _{SCE}) at $i = 0.1 \mu\text{A cm}^{-2}$
Bare MS	-633	1.2×10^{-4}	NA (Active corrosion)
MS/Phos/Al ₂ O ₃	-521	6.2×10^{-6}	NA (Active corrosion)
MS/ENi-P/Al ₂ O ₃	-42	2.6×10^{-10}	0.2 (barrier protection)
MS/Cc/ Al ₂ O ₃ (CcMS/ Al ₂ O ₃)	+212	2.9×10^{-10}	1.08 (barrier protection)

The Al₂O₃ coating on electroless Ni-P coated MS (MS/ENi/Al₂O₃) reduces i_{corr} by 6 orders of magnitude and shifts E_{corr} further in noble side. However, the barrier protection ceases at about 0.2 V_{SCE} and the current increases linearly thereafter. On the other hand, the sol-gel coating on conversion coated MS (CcMS) shows barrier type of protection up to more than 1 V_{SCE}. The E_{corr} of the substrate shifts by 845 mV in noble side and i_{corr} is reduced by 6 orders of magnitude on CcMS/Al₂O₃ which shows the formation of a compact and adherent sol-gel Al₂O₃ coating on conversion coated MS. Thus, conversion coating on MS was chosen as the only surface treatment prior to sol-gel coating for further study.

(b) Influence of Ceramics

In order to study the influence of different ceramics on the corrosion protection of mild steel, sol-gel Al₂O₃, ZrO₂ and TiO₂ coatings were obtained on CcMS by dip-coating method. The process of dip-coating and drying was repeated 5 times and finally heated at 500 °C. The potentiodynamic polarization behavior of sol-gel Al₂O₃, ZrO₂ and TiO₂ coatings on CcMS is shown in Figure 1. The polarization curve on bare MS is also included in the figure for the sake of comparison. The sol-gel ceramic coatings show barrier type protection to the substrate up to more than 1.0 V_{SCE}. The smallest corrosion current density of 2.94×10^{-10} A cm⁻² was noted on MS/Al₂O₃ followed by CcMS/ZrO₂ (6.4×10^{-9} A cm⁻²) and CcMS/TiO₂ (21.8×10^{-9}). The E_{corr} also follows similar order. This indicates the formation of dense and adherent coatings on mild steel surface with a prior conversion coating.

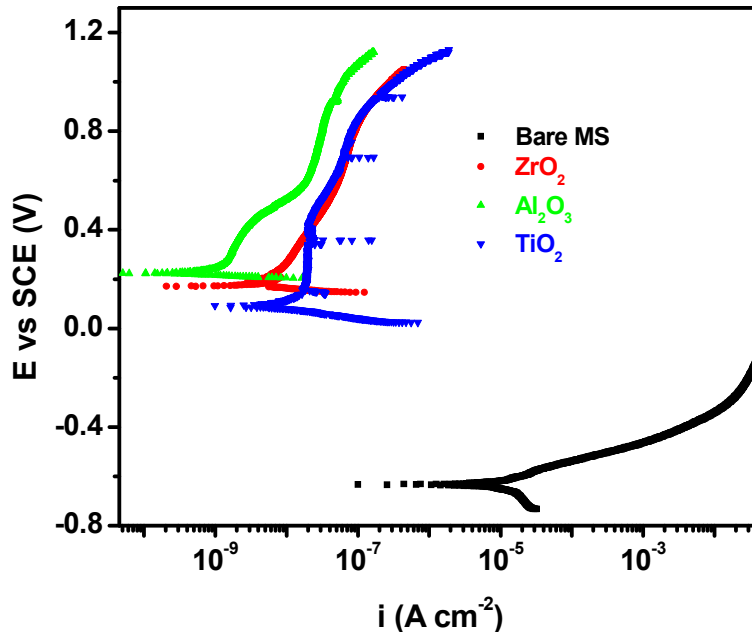


Fig.1 Effect of different ceramic coatings on potentiodynamic polarization of mild steel in 3.5 wt.% NaCl

(ii) *Electrochemical Impedance Spectroscopy*

The stability under long term exposure of the coating was evaluated by measuring the impedance of the coating in 3.5 wt.% NaCl at different time intervals. The results of impedance measurements on Al₂O₃, ZrO₂ and TiO₂ coated CcMS are shown in Figs.2-4. Impedance plot on bare MS has also been added (Fig.4) for comparison. The global

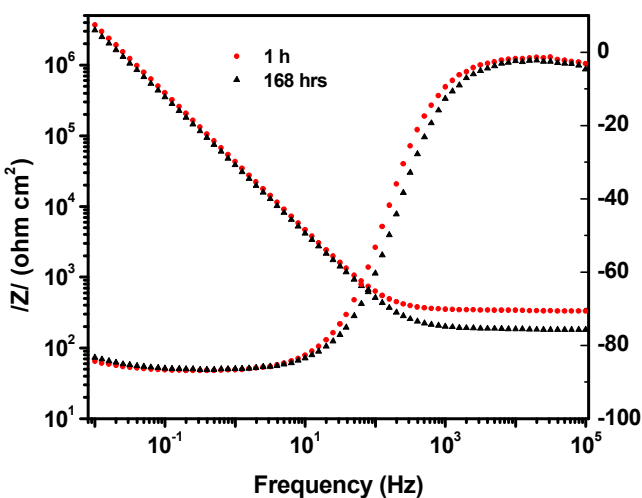


Fig.2 Bode plot on CcMS/Al₂O₃ in 3.5 wt.% NaCl

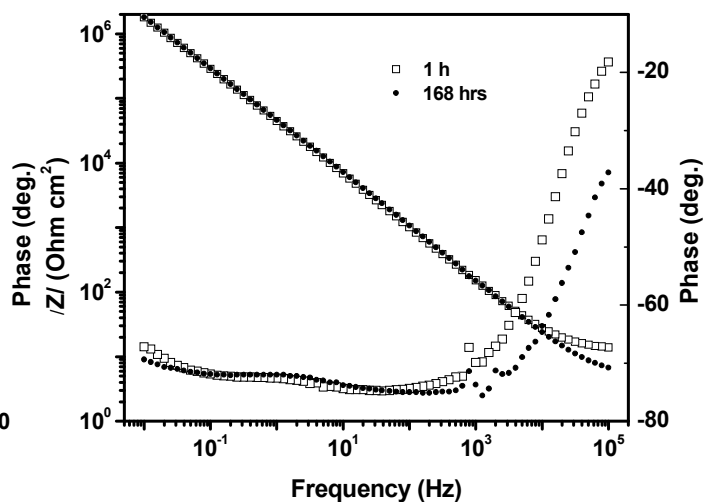


Fig.3 Bode plot on CcMS/ZrO₂ in 3.5 wt.% NaCl

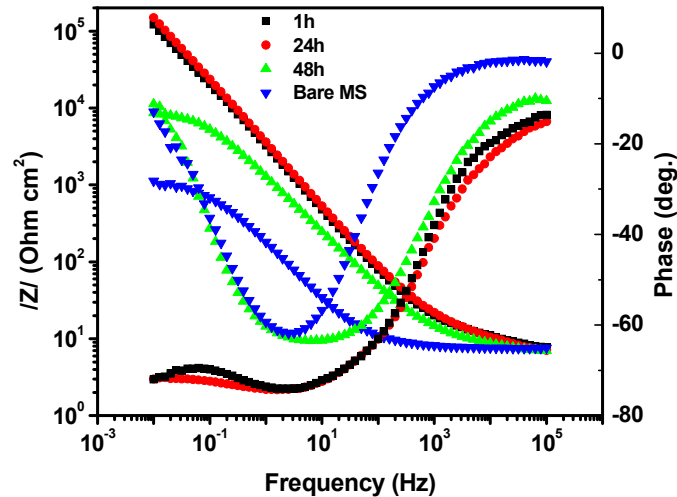


Fig. 4 Bode plot on CcMS/TiO₂ in 3.5 wt.% NaCl

Impedance of MS is increased by more than 3 orders of magnitude with the application of sol-gel coatings. The increased impedance of the coating shows better corrosion protection of the substrate. The sol-gel coatings display capacitive behavior with a large phase angle ($\geq 75^\circ$) between the low and middle frequency regions, which can be correlated with the insulation property and compactness of the coating [9, 15]. It is clearly seen from the figures 2-4 that the sol-gel Al₂O₃ and ZrO₂ coated CcMS do not show any appreciable change in impedance behavior during continuous immersion for 7 days of present study. This indicates the defect-free and stable nature of Al₂O₃ and ZrO₂ coatings prepared in the present study. However, TiO₂ shows ~ 1 order of magnitude reduction in global impedance after 48 hours of immersion which is in between the impedance of bare MS and CcMS/TiO₂. This shows the penetration of electrolyte to the substrate through the coating.

The above results can be explained by considering the equivalent circuit $R_s(R_{ct}Q_{dl})$ and $R_s(R_{def}Q_{coat}(R_{ox}Q_{ox}))$ for bare MS and sol-gel coatings, respectively. In the equivalent circuit shown above, R_s is the solution resistance, R_{ct} and Q_{dl} are the resistance and pseudo capacitance associated with the double layer formed at the substrate-electrolyte interface, R_{def} is the resistance of the sol-gel coating with defects (pores/cracks) while Q_{coat} models the intact layer, R_{ox} and Q_{ox} are the resistance and pseudo capacitance of the inner oxide layer. Here a constant phase element (CPE) is generally used to represent capacitance because it is hardly capacitance in the real electrochemical process. The CPE is defined by the admittance Y and power index number n , given by $Y = Y_o(j\omega)^n$; where ω is angular frequency. If $n = 0$ it stands for resistance, while $n = 1$ represents the capacitive behavior of the interface. These results are in fair agreement with the polarization studies. Further, the reduction in global impedance of TiO₂ coating after 48 hours of continuous immersion indicates the presence of defects/pores in the coating that facilitates the diffusion of electrolytes to the substrate during longer immersion time and results corrosion resistance to decrease. Under such situation, a mesh describing the substrate (Q_{dl} and R_{ct}) is added, to the circuit given for sol-gel coating, in series with Q_{ox} as reported by Zheludkevich, Andreatta and coworkers [16, 17]. Based on the modified circuit, the charge transfer process takes place on the substrate, which is covered with sol-gel TiO₂ coating having defects/pores. This occurs by the penetration of electrolyte through the defects/pores that reaches to the substrate resulting into corrosion of the substrate during continuous immersion.

(iii) Morphology of the coatings

The surface morphology of conversion coating, sol-gel Al_2O_3 , ZrO_2 and TiO_2 coating is shown in Figure 5.

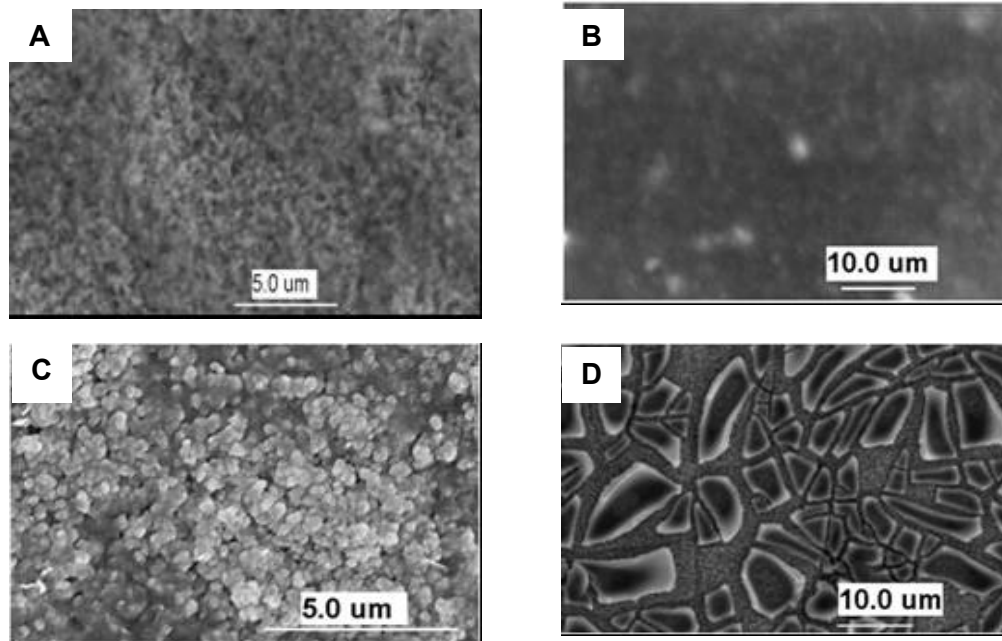


Fig.5 Surface morphology of the coatings on MS: A: CcMS; B: CcMS/ Al_2O_3 ; C: CcMS/ ZrO_2 ; D: CcMS/ TiO_2

The morphology of the CcMS is dense vermicular which covers the entire surface uniformly. The sol-gel Al_2O_3 coated CcMS surface appears smooth with featureless morphology and free from any defect. The sol-gel ZrO_2 coating is free from cracks containing agglomerated circular particles. However TiO_2 contains numerous cracks on the surface having dry cracked mud like appearance on the surface.

Physical characterization

The X-ray diffraction on CcMS shows the formation of composite oxide of iron and aluminum mainly consisting of $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The gel powders of Al_2O_3 , ZrO_2 and TiO_2 , obtained by drying the respective sols at 60°C for 72 hours, heated at 500°C for 1 h show the formation of $\gamma\text{-Al}_2\text{O}_3$ along with boehmite, t- ZrO_2 and anatase, respectively. The formation of $\gamma\text{-Al}_2\text{O}_3$ and t- ZrO_2 is also seen in FT-IR analysis.

Discussion

It has been reported that traditional phosphating of MS substrate produces needle shaped particles with an average grain size of 10 – 30 μm [14]. The subsequent sol-gel coating on pre-phosphated MS though produces better mechanical bonding between the sol-gel coating and the phosphate layer but at the same time it produces porosity in the coating. Thus, in spite of adherent ceramic coating, the aggressive ions from the electrolyte (Cl^-) approaches the substrate through these micro-pores during the corrosion studies and the current increases linearly with potential as in the case of bare steel. The sol-gel Al_2O_3 coating on pre-electroless Ni-P coated MS shows highest corrosion protection in terms of corrosion current density but the barrier current ceases at $\sim 0.1 V_{\text{SCE}}$ and the current increases in identical manner to bare electroless Ni-P coating. This indicates the failure of the sol-gel coating. The failure of sol-gel Al_2O_3 coating on electroless Ni-P may be attributed to the formation of oxides at Ni-P and sol-gel coating interface. Formation of oxides has also been observed by Luo et al. [18] on $\text{Al}_2\text{O}_3/\text{Ni-P}$ during studies on oxidation resistance of the coating. On the other hand, the conversion coating on MS produces $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ on the surface having dense vermicular structure. Such structure of the conversion coating helps in improving the bonding of the coating with the substrate resulting in the formation of defect-free adherent sol-gel coating. Further, the composite oxides of iron and aluminum protects the mild steel surface from oxidation during the heat treatment of the coating at 500 $^\circ\text{C}$. The lower corrosion protection of TiO_2 coating and its further degradation with time during longer exposure is due to multiple cracks in the coating through which the electrolyte penetrates to substrate resulting into degradation of the protection property of the ceramic. On the other hand no such cracks are seen on Al_2O_3 and ZrO_2 coatings which provide quite stable protection to the substrate.

Conclusion

The conversion coating on MS provides suitable template for sol-gel coating. Prior conversion coating on MS produces well adherent and defect-free coating of Al_2O_3 and ZrO_2 . The sol-gel coating protects mild steel substrate for longer duration in the aggressive environment. The sol-gel Al_2O_3 and ZrO_2 coatings provides barrier type of protection to MS up to $\sim 1V_{\text{SCE}}$ in 3.5 wt.% NaCl and reduces corrosion current density of MS by 5-6 orders of magnitude.

Acknowledgement

Financial support to perform the present work from CSIR through a Network Project (NWP 0010) is gratefully acknowledged.

References

1. Ya-li Gao, Cun-shan Wang, M. Yao and Hong-bin Liu, *Appl. Surf. Sci.* 253 (2007) 5306.
2. C. Monticelli, A. Balbo and F. Zucchi, *Surf. Coat. Technol.*, 205 (2011) 3683.
3. J.A. Alegría-Ortega, L.M. Ocampo-Carmona, F.A. Suárez-Bustamante and J.J. Olaya-Flórez, *Wear*, 290-291 (2012) 149.
4. G. Bolelli, B. Bonferroni, G. Coletta L. Lusvarghi and F. Pitacco, *Surf. Coat. Technol.*, 205 (2011) 4211.
5. G. Wu, A. Shanaghi, Y. Zhao, X. Zhang, R. Xu, Z. Wu, G. Li and P.K. Chu, *Surf. Coat. Technol.*, 206 (2012) 4892.
6. D. Wang and G.P. Bierwagen, *Prog. Org. Coat.* 64 (2009) 127.
7. S.K. Tiwari, R.K. Sahu, A.K. Pramanick and Raghuvir Singh, *Surf. Coat. Technol.* 205 (2011) 4960.
8. S.K. Tiwari, Manju Tripathi and Raghuvir Singh, *Corros. Sci.* (2012) (In Press) <http://dx.doi.org/10.1016/j.corsci.2012.06.026>.
9. G. Ruhi, O.P. Modi, A.S.K. Sinha and I.B. Singh, *Corros. Sci.* 50 (2008) 639.
10. H. Wang and R. Akid, *Corros. Sci.* 50 (2008) 1142.
11. M.A.D. Crespo, A.G. Murillo, A.M. Torres-Huerta, C. Yáñez-Zamora and F.de. J. Carrillo-Romo, *J. Alloys Compd.* 483 (2009) 437.
12. M.A.D. Crespo, A.G. Murillo, A.M. Torres-Huerta, E. Onofre-Bustamante and C. Yáñez-Zamora, *Electrochim. Acta.* 54 (2009) 2932.
13. I. Baskaran, T.S.N. Sankara Narayanan and A. Stephen, *Mater. Chem. Phys.* 99 (2006) 117.
14. G. Li, L. Niu, J. Lian and Z. Jiang, *Surf. Coat. Technol.* 176 (2004) 215.
15. M. Metikos-Hukovic, E. Tkalcec, A. Kwokal and J. Piljac, *Surf. Coat. Technol.* 165 (2003) 40.
16. M.L. Zheludkevich, R. Serra, M.F. Montemor, I.M. Miranda Salvado and M.G.S. Ferreira, *Surf. Coat. Technol.* 200 (2006) 3084.
17. F. Andreatta, P. Aldighieri, L. Paussa, R. di Maggio, S. Rossi and L. Fedrizzi, *Electrochim. Acta* 52 (2007) 7545.
18. L. Luo, J. Yao, J. Li and J. Yu, *Ceram. International* 35 (2009) 2741.