Preparation and characterization of phosphate-nickel-titanium composite coatings obtained by sol–gel process for corrosion protection

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Abstract

New phosphorus–titanium–nickel composites were deposited on steel substrate by using sol gel spin coating technique for application as anticorrosion coatings. Along with the synthesis, the effects of annealing temperature and various number of coating layers on anticorrosion properties were looked into. The corrosion behavior of deposited and annealed coatings was evaluated by salt spray testing in a neutral mist (ASTM B117-85 NSS) of 5% NaCl at 35 °C for 300 h. Titanium tetra-isopropoxide, tri-methyl phosphate and Nickel (II) nitrate hexahydrate were used as precursors. To characterize the coatings and powder various techniques were used: Thermogravimetric Analysis coupled to Differential Scanning Calorimetry, Fourier Transform Infrared Spectroscopy, X-Ray Diffraction, Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) analysis, Elemental Analysis ICP and X-ray photoelectron spectroscopy (XPS). The microstructure and elemental identification were done by SEM with EDX and XPS analysis. XPS analysis confirmed that Ti, Ni, P, and O elements are present in the surface. The functional groups were identified by FTIR analysis. Finally, steel plates coated with $\text{TiO}_2\text{--NiO--P}_2\text{O}_5$ composite displayed satisfactory anticorrosion properties under simulated seawater environment. The results of the study revealed that the annealing temperature at 450 °C and after six layers had a great impact on the anticorrosion properties of $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ composite.

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Graphic abstract

Keywords Sol–Gel coating · X-ray photoelectron spectroscopy · Fourier transform infrared spectroscopy · Scanning electron microscopy · Anticorrosion

1 Introduction

In the progress of advanced technologies, thin oxide films are getting more and more important for various applications (e.g., semiconductors, separation, catalysis and chemical protection) [1–5]. A strong industrial interest is focused on the improvement of coatings for anticorrosion protection. In this concordance, phosphate composite materials are expanding strongly owing to their chemical characteristics and their interesting physicochemical properties. Phosphorus composite [6, 7] have received great interest recently [8–10] for their interesting complexing properties [11] and have found applications as corrosion inhibiting agents, dispersants, deposit resistance coating, [12] flame retardants, [13] adhesion promoters for paints, [14] super lubricity coatings, [15] (super) hydrophobic photostable coatings for stone. Good adherence to the substrate with the presence of high humidity or water (wet adhesion) is the main feature of any anticorrosion coating.

Sol–gel process are techniques used for the deposition of coatings on metals. It offers a wide range of applications and it is unharmed for the environment [16, 17]. Sol–gel technology leads to many application procedures adaptable to industry in addition to the economy of scale it provides [18].

Considerable work has been done to make various sol–gel based protective coatings [19].

The sol–gel method involves spin-coating, dip-coating, spray coating of the oxide sol on a substrate. It offers high homogeneity and purity levels that may lead to obtaining a coating presenting a good adhesion to a metallic surface. Sol–gel coating were investigated for the protection of steel surfaces. Steel and stainless steel are typical substrates for corrosion studies [20, 21] and amply used in different industrial fields because of their corrosion and mechanical properties. However, they are still vulnerable in the presence of halide ions. Numerous studies have been devoted to the corrosion resistance behavior of sol–gel coatings or thin films deposited onto steel substrate [22, 23]. Among various surface treatment techniques, Ni–P matrix nanocomposite coatings have been the subject of particular attention due to their uniform thickness, their high hardness and their excellent corrosion resistance [24, 25]. Nanoparticles, such as SiO_2 , P_2O_5 , Al_2O_3 , TiO_2 , etc. are Metal oxide coatings possessing very good chemical stability and can assured real protection to metal substrate. TiO_2 has excellent chemical stability and can provide effective protection to metal substrate. TiO_2 has excellent chemical stability, heat resistance and low electron conductivity, making it an excellent anti-corrosion material [26–28]. But pure TiO_2 film is mostly used in

catalyst chemistry. The present study aims at the synthesis of a new $\text{NiO-P}_2\text{O}_5\text{-TiO}_2$ composite as an anticorrosion coating for steel in order to keep it in good condition and extend its life.

2 Experimental procedure

2.1 Materials

Titanium, phosphorus and nickel oxide sols were prepared using titanium tetra-isopropoxide $[\text{Ti}(\text{OC}_3\text{H}_7)_4]$, TTIP 97%, tri methyl phosphate $[(\text{CH}_3\text{O})_3\text{P}(\text{O})\text{TMP}]$, Nickel(II) nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ as precursor, isopropanol as solvent and acetic acid (CH_3COOH), were purchased from Sigma-Aldrich (Merck). All reagents and alkoxide precursors were used as received, without further purification.

2.2 Preparation of precursor solution

$57.5\text{TiO}_2\text{-}12.5\text{NiO-}30\text{P}_2\text{O}_5$ thin films were prepared by using a sol-gel process combined with the spin-coating method. TTIP $[\text{Ti}(\text{O-}i\text{-C}_3\text{H}_7)_4]$, Nickel(II) nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and TMP $[(\text{CH}_3\text{O})_3\text{P}(\text{O})]$ were used as precursors for TiO_2 , NiO and P_2O_5 , respectively. TTIP, Nickel (II) nitrate hexahydrate and TMP were dissolved in isopropyl alcohol (2-Propanol) separately to form three pre-solutions.

For TiO_2 , TTIP (7.18 ml) was hydrolyzed in isopropyl alcohol (14 ml) by adding a few drops of concentrated acetic acid (CH_3COOH) and stirred continuously for 30 min.

NiO precursor solution was prepared by dissolving 1.4 g $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ Nickel Hexa hydrate in 5 ml of isopropanol as a solvent. The solution was stirred (1 h) to completely dissolve the nickel salt to obtain a homogeneous solution.

For phosphorus P_2O_5 precursor: dissolution of 3 ml of trimethyl phosphate in 6 ml of 2-propanol and added 1 ml of distilled water. The solution was stirred for 1 h to hydrolyse the phosphate.

The three pre-solutions were mixed and stirred for 3 h to obtain the sol of $\text{TiO}_2\text{-NiO-P}_2\text{O}_5$.

2.3 Preparation of thin film

The obtained sol was deposited on steel substrates by spin-coating. To form thin films, some drop (50 μL) of solutions was added to galvanized steel plates using a bar coater by a micropipette.

Before the coating process, the substrates were carefully cleaned by acetone, ethanol and distilled water. These substrates were spin coated at 3000 rpm for 30 s. After natural drying in air flow, samples were heated in an oven at 120 °C for 10 min. Such an operation was repeated for

one, two, four and six times to form monolayer and multilayers. The samples (substrates) were then heat-treated at 450 °C for 2 h to enable oxide conversion and to remove the solvent and residual organics.

In order to gather more information about the thin layers deposited on steel, we conducted the sol prepared in the deposition phase to gelation for a period of 24 h. The gel thus obtained was transformed into powder (xerogel) after treatment in an oven at 120 °C for 24 h. The xerogel thus obtained was calcined in a muffle furnace at 450 °C for 2 h in the same manner that was used for processing the coated. The final product obtained is a black powder designed $57.5\text{TiO}_2\text{-}12.5\text{NiO-}30\text{P}_2\text{O}_5$ (in mol %). The latter was characterized by ICP-AES, X-ray diffraction (XRD), infrared and Raman spectroscopy and thermal DSC/TG analysis.

2.4 Characterization

ICP-AES (iCAP 7400 Thermo Scientific) were used for the quantification of the elements in the sample (P, Ti and Ni).

XRD spectra were collected to check the amorphous state and to detect any crystalline phase in samples by using a Philips X'Pert PRO MPD (Multi Purpose Diffractometer) X-ray diffractometer using Cu ($\lambda = 1.5418 \text{ \AA}$) with the scanning rate of 0.5°/min for 2θ ranging from 20° to 90°.

Infrared Spectroscopy (FTIR) analyses were performed in ATR mode using a Perkin Elmer Spectrum 1000 recorded from 400 to 4000 cm^{-1} range in the transmission mode.

Thermal behavior is conducted using Thermogravimetric Analysis (TG) coupled to Differential Scanning Calorimetry (DSC): the thermogravimetric analysis (under Argon) of the synthesized samples was performed using a NETZSCH STA 449F1. The samples were heated from 40 to 1000 °C at 10 °C/min.

X-ray photoelectron spectroscopy (XPS) measurements were performed with an X-ray spectrometer ESCALAB 250 from Thermo Electron with Al K α X-ray radiation (1486.6 eV) X-ray photoelectron.

Scanning Electron Microscopy (SEM) and Energy X-ray Dispersive Spectroscopy (EDXS) analyses were performed with an environmental scanning electronic microscope Quanta 200 coupled with an Oxford INCA analyzer to check out the morphology and microstructure.

Profilometer optic was used to examine the topography surface and the roughness of coated steel substrates samples. The value considered in this work was the roughness mean (R_a) that corresponds with the measurement between the peaks and depressions travelled by the active tip of the device. This value was calculated from at least three individual measurements at different sites on the surface.

Water Contact Angle (WCA) measurements were performed at ambient temperature on Contact Angle System

OCA-Data Physics using the water sessile drop method on the composite coated steel substrate.

2.5 Anticorrosive properties

The steel plates were coated with the composite using a bar coater (120 mm Braive Instruments) to achieve 3–7 μm thick films.

The anticorrosive behavior of the composite $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ was evaluated following the accelerated salt spray test (ASTM B117-85 NSS). The steel plates were placed inside a chamber at 35 °C, and an aqueous sodium chloride solution NaCl 5% (with a concentration by mass of 50 g L⁻¹) was continuously sprayed by means of compressed air for a specified period to evaluate the resistance to corrosion.

3 Results and discussion

3.1 Inductively coupled plasma atomic emission spectrometry ICP-AES

Table 1 shows the theoretical and experimental molar ratios of the different elements constituting the powder sample of the composition $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$. The results show that the theoretical and experimental values are in good agreement.

Table 1 The theoretical and experimental molar ratios

	Ti/P	Ti/Ni	P/Ni
Theoretical	0.958	4.6	4.8
Experimental	1.01	4.52	4.44

3.2 Thermal properties of $\text{TiO}_2\text{--NiO--P}_2\text{O}_5$ powder

The TG-DSC curves for the powder sample having a composition of $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ are shown in Fig. 1 it can be seen that there are three weight loss regions in the TG curve. According to the curve-a (in green) the total weight loss is equal to 35.95%. The first weight loss 3.8% is between 25 and 250 °C, this loss characterized by the broad and low endothermic peak located at 100 °C is related to the removal of absorbed water. The second weight loss (22.15%) in the temperature range of 250–400 °C is due to the evaporation and the decomposition of the organic materials and the exothermic peak at 205 °C corroborates this phenomenon [29]. The third loss of 10% occurs at almost 700 °C and can be attributed to the starting of all the remaining organic matter.

3.3 X-ray diffraction

Figure 2 shows the X-ray diffraction spectra of $\text{TiO}_2\text{--P}_2\text{O}_5\text{--NiO}$ composite powder and coated in steel surface formed two, four and six layers before and after annealing at 450 °C.

From Fig. 2a, it appears on examination of the X-ray powder diffraction spectrum that the structure obtained before and after the annealing is amorphous because we don't observe any diffraction peaks on the recorded diffractograms of our synthesized composite sample. A broad peak appearing around 2θ of 45° indicates that the samples are amorphous.

The crystalline peaks observed in Fig. 2b, c for coated steels result from the iron (Fe) substrate. We have the appearance of peaks of iron oxides of low intensity at 120 °C (Fig. 2b), the intensity of the peaks decreases considerably and the peaks at 20° disappear after 4 layers. The

Fig. 1 TG/DSC curves of powder sample having a composition of $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$

Fig. 2 XRD spectra of $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ composite powder and coated in steel surface formed two, four and six layers before and after annealing at 450°C

occurrence of low-intensity iron oxide peaks is due to the reaction of the substrate with organic compounds remaining on the surface that have not yet been removed as indicated by thermal analysis and oxygen excess. We can conclude that the samples are all amorphous after 450°C heat treatment (Fig. 2c) because we do not detect any sign of crystallization due to titanium or nickel or phosphorus.

3.4 FT-IR spectra analysis

Figure 3 shows the FTIR spectra of a powder sample having a composition of $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ and heat treated at 450°C for 2 h in air atmosphere.

The absorption spectrum of powder before heat treatment represents a set of absorption bands. The first band

at 3236 cm^{-1} can be attributed to the vibrations of the OH and C–H groups [30] [31]. This disappears under the effect of the heat treatment at 450°C . Between 1500 and 3000 cm^{-1} , the spectrum indicates the presence of a band that is attributed to the deformation of the OH group of water, with peaks corresponding to the vibrations of the COO^- group [32]. The frequency band between 751 and 783 cm^{-1} can be associated with the symmetric stretching vibration $\nu_s(\text{P--O--P})$, the band around 841 cm^{-1} and around 900 cm^{-1} is associated with the asymmetric stretching vibration $\nu_{as}(\text{P--O--P})$ of metaphosphate chains. The peak at towards 1026 cm^{-1} can be attributed to symmetric stretching vibrations $\nu_s(\text{PO}_3)^{2-}$, the band around 1186 cm^{-1} can be associated with symmetric stretching vibrations $\nu_s(\text{PO}_2)^-$, the peak around 1264 cm^{-1} is attributed to asymmetric

Fig. 3 FTIR spectra of powder sample having a composition of $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ and heat treated at 450°C for 2 h in air atmosphere

stretching vibrations $(\text{PO}_2)^-$ or $(\text{P}=\text{O})$ and the band around 590 cm^{-1} is attributed the deformation vibration $\delta(\text{P-O-P})$ in $(\text{PO}_4)^{3-}$. The heat treatment at 450°C causes the disappearance of the bands in the region of $700\text{--}900\text{ cm}^{-1}$ and exhibit only one band near the 979 cm^{-1} corresponding to the elongation vibration of the anion $(\text{PO}_4)^{3-}$ characteristic of Orthophosphates groups. The band at 551 cm^{-1} after heat treated at 450°C is attributed to Ti-O vibrations [33]. The band around 412 cm^{-1} can be assigned to the vibration of the Ni-O bond [34]. The high frequency bands 1397 , 1535 , 1995 and 2358 cm^{-1} are due to the fact that the powders have a physical tendency to absorb water and carbonates. The presence of the band at 2358 cm^{-1} is due to the adsorption of atmospheric CO_2 after the decomposition of P-O-C and/or Ti-O-C from the R groups in the starting products. A small shift of the $\nu_{\text{as}}(\text{P-O-P})$ band to higher energy is observed, as is a general broadening of the spectral features. This is due to the presence of titanium and nickel, which form short chains compared to the phosphorus.

3.5 XPS measurement analysis

The surface composition and the chemical states of the component element of $\text{TiO}_2\text{--NiO--P}_2\text{O}_5$ composites coated in steel substrates were investigated via XPS, as shown in Fig. 4.

Results of surface chemical composition analysis of coated samples from six layers and heat treated at 450°C are compiled in Table 2. In addition to the expected oxides, the coated surfaces were found to be contaminated with 15.48% carbon. Analysis of the binding energies showed the elements (C, Ti, P, Ni, O and Fe assigned to $\text{C}1\text{s}$, $\text{Ti}2\text{p}$, $\text{P}2\text{p}$, $\text{Ni}2\text{p}$, $\text{O}1\text{s}$, and $\text{Fe}2\text{p}$, respectively) which were found in the samples, and enabled assessment of the content and forms of these elements.

The trace amounts of carbon may be caused by the incomplete roasting of organic compounds (Including precursor of TMP, TTIP and so on) or the indefinite hydrocarbons of the XPS instrument themselves.

The carbon line ($\text{C}1\text{s}$) has three main peaks Fig. 4a. The dominant peak at the energy $E_b = 284.4\text{ eV}$ corresponds to graphite. The peak observed at $E_b = 286.0\text{ eV}$ known as single bonded carbon C-C , and it is generally related to contaminants. The peak observed at higher energy ($E_b = 288.9\text{ eV}$), and this corresponds to carbon double-bonded to oxygen C=O .

Figure 4b is the $\text{Ti}2\text{p}$ region spectra, which shows the presence of the main composition of two symmetrical, the binding energies of 458.8 and 465.8 eV belong to $\text{Ti}2\text{p}3/2$ and $\text{Ti}2\text{p}1/2$, respectively, corresponding to Ti^{4+} , indicating that the chemical valence of Ti is $+4$ valence [35–37].

In Fig. 4c, we found one single peak at 133.91 eV , indicating the presence of elemental P in the pentavalent oxidation state ($\text{P}2\text{p}$). The high-resolution XPS spectrum

Fig. 4 XPS high resolution spectra of C, Ti, P, O and Ni

Table 2 Chemical composition analysis of coated samples form six layers heat treated at 450 °C

Name	C1s	Ti2p	Ni2p	P2p	O1s	Fe2p
Peak BE	284.82	458.71	855.97	133.23	530	710.3
Atomic %	15.48	16.66	2.82	6.99	57.07	0.99

of O1s from Fig. 4d can be seen. Obviously, the O1s region can be deconvoluted into two peaks at 530.0 and 532.3 eV, indicating the co-existence of two distinguishable chemical states of oxygen on this surface. The peak at 530.0 eV is ascribed to the lattice oxygen [38] and the peak around 532.3 eV can be assigned to the surface hydroxyl groups of the oxides, and the corresponding values indicate that O is – 2 valence [39].

The spectrum of the Ni2p region is shown in Fig. 4e. The main peaks are located at binding energies E_b (Ni2p3/2) at 856.85 eV and E_b (Ni 2p1/2) at 873.2 eV, indicating the existence of NiO, and that the nickel exists in the form of + 2 valence [39].

3.6 Surface morphology SEM

The thermal annealing is done only after obtaining the last layer. The samples obtained were observed by scanning electron microscopy in order to study their surface aspects. Figure 5 shows the surface view and the energy dispersive X-ray EDX of coated steel formed two and six layers after heat treatment at 450 °C. The micrograph (Fig. 5a, c) show homogeneous surfaces of coated steel form two and six layers treated at 450 °C respectively, which increase proportionally with increase of the number of layers. In (Fig. 5 b and d) we show the energy dispersive X-ray of coated steel form two and six layers treated at

Fig. 5 Surface view and the energy dispersive X-ray EDX of coated steel formed two and six layers after heat treatment at 450 °C (**a** and **b** for two layers) (**c** and **d** for six layers)

450 °C respectively. The chemical constituents present in the sample according to EDX analysis are Ti, Ni, P, O, C and Fe. The presence of C and Fe is from the steel substrate. Decreasing the peak intensity relative to iron content with increasing number of layers confirms the formation of a continuous film that protects the steel. We note that as the number of layers increases, the intensity of the peak relative to the iron content decreases considerably and that the peaks representing the elements of titanium, nickel and phosphorus increase, this is consistent with the increase in the thicknesses of the deposits related to the number of deposited layers.

The thickness of two and six layers coatings deposited on steel substrate and cured at 120 °C with and without annealing at 450 °C was measured by studying the sample on the side (observations in transverse section in Fig. 6) by SEM analysis (Table 3).

Homogenous coatings 3.68 μm thick were obtained from two layers cured at 120 °C without annealing. When using a heating the thickness was smaller, 3.34 μm , indicating that denser coatings are obtained in these conditions because of elimination of the solvents; consequently, a more cross-linked 'network' structure is formed. For six layers coatings thickness of 9.36 or 7.23 μm are obtained,

Fig. 6 Thickness observations in transverse section

Table 3 The thickness of two and six layers coatings deposited on steel substrate

Samples	2 layers		6 layers	
	120 °C	450 °C	120 °C	450 °C
Thickness (μm)	3.68	3.34	9.36	7.23

depending on whether the annealing procedure was used or not.

3.7 Profilometer optic

A profilometer with a diamond stylus was used to determine the surface roughness. The roughness profiles of thin films formed monolayer and six layers are depicted in Fig. 7. The surface roughness of samples coated by one and six layers before and after annealing at 450 °C whose Ra values of monolayer at 120 °C (a1), monolayer at 450 °C (a2), six layers at 120 °C (b1) and six layers at 450 °C (b2) are 1.089, 0.52, 3.6 and 1.22 μm, respectively are summarized in Table 4. The number of layers and annealing procedure are considered to explain the results. A coating formed by monolayer exhibits much less roughness (1.089 and 0.52 μm) before and after heat treatment while the formed by six layers showed a greater roughness, (3.6 and 1.22 μm). The increase the numbers of layers provokes

Table 4 Roughness of the coated substrate

samples	1 layer		6 layers	
	120 °C	450 °C	120 °C	450 °C
Ra (μm)	1.089	0.52	3.6	1.22

the increase of thickness and roughness of coatings coming from a porous structure. Considering the effect of the annealing, less roughness was obtained for annealing, likely related to a more uniform evaporation of solvents during the heating, this leading to a denser and rigid structure.

3.8 Surface properties of the coated and uncoated substrates

Surface properties of the films made from the composite $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ were examined in terms of water contact angle (WCA) measurements. The results were compared to that of uncoated substrate (a). The coating surface of the composite $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ (b), which is adhering to the steel plate is more hydrophilic (WCA = 33°) as compared to the uncoated surface (WCA = 61°), (Fig. 8). In general, contact angles of heated coatings are greater than those obtained without a heat treatment associated with the difference in roughness.

Fig. 7 3D images of the $\text{TiO}_2\text{--NiO--P}_2\text{O}_5$ composite film coated on steel

Fig. 8 Water contact angle obtained on: **a** uncoated substrate and **b** coated substrate by the composite $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$

3.9 Anticorrosion studies of $\text{TiO}_2\text{--NiO--P}_2\text{O}_5$ coated steel

The anticorrosive behavior of the $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ composite was estimated following the salt spray test in aqueous sodium chloride solution (with a concentration by mass of 50 g L^{-1}) (Fig. 9). The results of the corrosion tests show bare surfaces were full of corrosion within 1 h only whereas the adherence of the composite onto the metal surface prevented the spread of corrosion (Fig. 9). The coated surface formed six layers of $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ composite annealed at 450°C , was without porosity, even after 300 h.

The Scanning Electron Microscopy analysis was used to examine the state of the coated and uncoated

surfaces. Figure 10 shows the surface SEM images of uncoated and coated substrate from six layers treated at 450°C after salt spray test. As can be seen in Fig. 10a, b, corrosion cracks were observed on the surface of uncoated steel substrate after salt spray tests. As for the coated substrate, no obvious corrosion was identified in either Fig. 10c or d, their microstructures are very similar to those before salt spray tests. EDX results of the corrosion products, as illustrated in the Fig. 11, indicate that the products were composed of metals (Fe, C, O), Na and Cl. The results of this spectrum suggest the presence of Chloride (and Sodium) in uncoated substrate surfaces.

Fig. 9 Visual appearance of coating samples after different exposure times in salt spray chamber: (1–5) Steel plates coated with $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ composite; (6) uncoated steel plate as reference sample

Fig. 10 Surface SEM images of uncoated and coated substrate (**a** and **b**: uncoated before and after salt spray), (**c** and **d**: coated before and after salt spray)

4 Conclusion

We have prepared $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ composite thin films on the steel substrate by the sol-gel using spin coating method followed by a post heat treatment process. It is indicated that these films can improve the corrosion resistance of the substrate in a 5% NaCl in salt spray.

The influences of coating compositions and multilayers numbers were examined. The coated surface forming six layers of $57.5\text{TiO}_2\text{--}12.5\text{NiO--}30\text{P}_2\text{O}_5$ composite annealed at 450°C remained undamaged for 300 h in salt spray testing (ASTM B117-85 NSS) of 5% NaCl at 35°C , indicated that the films having a composition of the above findings suggest that $\text{TiO}_2\text{--NiO--P}_2\text{O}_5$ can improve the corrosion resistance behavior of the steel substrate.

Fig. 11 EDX spectrum of uncoated substrate after salt spray

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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