Corrosion behavior of Cr–P/nano Al$_2$O$_3$ composite coatings

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Abstract

The effect of Al$_2$O$_3$ nano-particles incorporation on corrosion resistance and micro hardness of chromium-phosphorous coatings was investigated. For this purpose, different amounts of alumina nano-particles (i.e. 0–35 g l$^{-1}$) were dispersed in the plating bath. Dynamic light scattering/Zeta potential analyzer was used to determine the dispersion or agglomeration tendency of nano-particles in the plating bath. Scanning electron microscope (SEM), equipped with an energy dispersive spectroscope (EDS) and optical microscope (OM), was used to study the morphology and the chemical compositions of the coatings. Corrosion behavior of the coatings was studied via electrochemical impedance spectrometry (EIS) and linear polarization tests in a 3.5 wt% NaCl solution at ambient temperature. Micro hardness of the coatings was also studied via a micro hardness tester. According to the results, phosphorous content of the coatings was decreased from 17.5 wt% to 11.5 wt% as the amount of alumina nano-particles increased in the plating bath. Similarly, micro crack density of the coatings was also decreased. Also, composite coatings revealed higher corrosion resistance and micro hardness. Corrosion current density was decreased from 2 $\mu$A cm$^{-2}$ to 0.2 $\mu$A cm$^{-2}$ and hardness of the coatings was increased from 600 HV to 930 HV, as the composition of the coating was converted from pure Cr–P alloy coating to Cr–P/nano Al$_2$O$_3$ composite coating.

1. Introduction

Conventional hexavalent chromium (Cr (VII)) baths are widely used to deposit Cr coatings, but there is a necessity to substitute them owing to their toxicity and recent regulations in some countries. Trivalent chromium (Cr (III)) coatings—deposited from Cr (III) plating baths—are considered desirable substitutes for hexavalent chromium (Cr (VI)) coatings [1–5]. However, since they are normally contaminated by some unwanted elements, Cr (III) coatings lack in some properties like hardness and corrosion resistance [4, 6–8]. Contamination by unwanted elements occurs as a result of organic complexing agents, which are used in Cr (III) plating baths in order to avoid undesirable effects of hydroxide compounds of Cr (III) [2, 4, 9]. Hence, diminution of impurities in the coating through reduction of organic complexing agents concentration in the plating bath is a possible way to modify the hardness and the corrosion resistance of these coatings [4, 10]. However, reduction of complexing agents concentration in the plating bath also results in a lower deposition rate [3, 4].

There have been many reports claiming that inclusion of second phase particles in a particular coating has resulted in a better corrosion and wear resistance. Corrosion resistance enhancement of metallic coatings via incorporation of non-metallic nano-particles in the metal matrix is said to be due to the modification of surface morphology and crystallinity of metal matrix and consequently fabrication of more uniform coating with less defects and also less electrical conductivity of the particles when well distributed in the coating. It is believed that incorporation of nonconductive particles in the coating decreases the cathodic surface area, shifting the polarization potential through negative region [11–14]. Alumina nano-particles are also considered as one of the mostly used nonconductive nano-particles, which result in an enhanced corrosion resistance when incorporated in a metal matrix [15]. However, there are insufficient reports about Cr (III) composite coatings.

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This work aims to study the effect of alumina nano-particles addition to Cr (III) plating bath, on morphology, chemical composition, corrosion resistance, and micro-hardness of the yielded coatings.

2. Experimental

All the materials used were analytical grade Merck chemicals. A sulfate-base Cr (III) plating bath was utilized for deposition of Cr–P and Cr–P/alumina coatings. The composition of the bath is presented in Table 1. Sulfuric acid (95–98 vol%) and potassium hydroxide were used to adjust the bath pH to 2.6. Alumina nano-particle with an average size of 50 nm were used in the composite electrodeposition baths. Particles were added to the plating bath in different amounts (0–35 g l$^{-1}$). The resulted suspensions were then exposed to ultrasonic waves for 60 min, followed with a mechanical agitation for 30 min to receive a well dispersed suspension of nano-particles in the plating baths. Plating was carried out at a fixed bath temperature of 37.5 $^\circ$C and a current density of 105 mA cm$^{-2}$.

Copper Tablets with an exposed area of 4 cm$^2$ were used as cathode, whereas, a dimensionally stable anode (DSA) electrode (Ti/IrO$_2$) was used as anode. Copper samples were polished with SiC papers (up to # 1500), degreased in an alkaline solution [19], and finally were activated in a 10% sulfuric acid solution.

Dynamic light scattering/Zeta potential analyzer (model: Zetasizer Nano ZSP) was used to determine the dispersion or agglomeration tendency of nano-particles in the plating bath. A scanning electron microscope (SEM, model: CAMSCAN MV2300), equipped with an energy dispersive spectroscopy (EDS, model: Rontec), was used to study the morphology and the chemical compositions of the coatings. Prior to thickness measurements, samples were cut vertically to disclose the cross sections of the coatings, mounted, and polished with diamond paste. Optical microscope (OM, model: Olympus BH2-UMA) and microstructure image process software were used for thickness measurements. Corrosion behavior of the coatings was evaluated via electrochemical impedance spectroscopy (EIS) and linear polarization tests. Both corrosion tests were carried out using a potentiostat/galvanostat EG&G setup (model: 273 A) in 3.5 wt% NaCl solution. Prior to corrosion tests, samples were immersed in the corrosive solution for 10 min. All of the corrosion experiments were performed in a three electrode corrosion cell composed of a platinum plate, a calomel electrode, and the sample as auxiliary, reference, and working electrodes, respectively. Linear polarization tests were executed via sweeping the sample potential within the potential range of $\pm$600 mV versus open circuit potential (OCP). The potential sweep rate was 1 mV s$^{-1}$. EIS tests were carried out by applying a sinusoidal voltage wave with an amplitude of 5 mV (rms) at OCP. The voltage frequency was varied in the range of 0.01 Hz–100 kHz and the respective impedances were recorded. Z-view software was utilized for analyzing, plotting equivalent circuit, and fitting of EIS data. Hardness of the coatings was measured using a Vickers micro-hardness setup (model: AMSLERD-6700) with an applied load of 100 g within 10 s.

3. Results and discussion

Dispersion and volume fraction of nano-particles in composite coatings are very effective parameters on coating properties such as corrosion resistance [20–22]. These parameters are dependent on particles concentration and dispersion in plating bath [23, 24]. Ceramic particles are polarized in aqueous solutions and their surfaces are charged [25]. This charge is called zeta potential [26, 27]. The absolute value of zeta potential is representative of nanoparticles dispersion and stability in aqueous solutions. When zeta potential of the whole particles is high enough, whether positive or negative (±20 mV), they will repulse each other. In consequence, there is no tendency for particles agglomeration in existence of high zeta potential and a well dispersed suspension can be achieved [27].

| Bath components | Roll in the bath | Concentration | Plating conditions |
|-----------------|------------------|---------------|--------------------|
| Cr$_2$(SO$_4$)$_3$.6H$_2$O | Source of Cr (III) ion | 0.15 M | Anode: Ti/IrO$_2$ |
|                  |                   |               | Cathode: copper Tablets |
| CH$_3$(COOH)$_2$ | Complexing agent  | 0.45 M | Temperature: 37 $^\circ$C |
| Na$_3$PO$_4$.9H$_2$O | Complexing agent  | 0.525 M | Current density: 105 mA cm$^{-2}$ |
| Na$_2$SO$_4$ | Conductivity salt | 0.56 M | Stirring rate: 400 rpm |
| H$_3$BO$_3$ | Buffering agent  | 0.9 M | pH = 2.6 |
| SDS | Surfactant | 0.2 g l$^{-1}$ | Plating duration: 1 h. |

Table 1. Composition of plating bath and plating conditions.
The amount of zeta potential of alumina nano-particles in Cr(III) plating bath was measured, which appeared to be —23 mV. Thereupon, alumina nano-particles are thoroughly dispersed in plating bath and they have no tendency for agglomeration.

3.1. The effect of nano-particles concentration on chemical composition and morphology of Cr–P coatings

Concentration of Nano-particles in a plating bath is a very impressive factor on their volume fraction in a composite coating. This effect is represented in figure 1 for alumina nano-particles in Cr–P plating bath in this work. Regarding to figure 1, volume fraction of alumina nano-particles in Cr–P coatings changes in two distinctly different manners as the concentration of nano-particles in the plating bath is increased;

(I) Volume fraction of nano-particles in the coating has raised as the concentration of nano-particles in the plating bath is increased (up to 4.3 vol%)

(II) Increasing of nano-particles concentration in the plating bath (more than 24 g l\(^{-1}\)) has not made a definite change in the amount of nano-particles incorporation in the coating. Beyond this point, volume fraction of nano-particles in the coating is in its saturation state (4.3 vol%).

With respect to the above discussion, the effect of nano-particles concentration in plating bath on their incorporation in the coating is initiating the Langmuir isotherm adsorption phenomenon [12, 20].

Due to silicon dioxide co-deposition method, transportation of particles towards cathode is exerted through diffusion mechanism [20]. According to Fick’s low, diffusion rate is a function of concentration gradient. Thus, with increased concentration of nano-particles in the plating bath a greater concentration gradient is formed, which consequently results in an increased amount of particles incorporation in the coating. Although, for particles concentrations more than 24 g l\(^{-1}\) their incorporation in the coating (figure 1) has experienced no change, this theory cannot be perfect. Each of ceramic particles are enclosed with ions (especially metallic ions) when they are added to an electrolyte. This phenomenon results in the formation of ionic clouds around the particles [20]. Once a particular particle is in contact with the cathode, the respective ionic cloud around the particle is reduced, and thus the particle is strongly attached to the cathode [12]. With increased amount of nano-particles in the bath, the probability of ionic cloud formation around the particles is decreased (since there are not enough ions for all the particles). Hence, the possibility of strong attachment of particles to the cathode is decreased and fewer particles are incorporated in the coating. On the other hand, the viscosity of the bath is increased when a higher concentration of particles is added to the bath [20]. A higher viscosity will result in the less mobility of particles and so incorporation of particles will be eliminated.

The effect of nano-particles concentration in the bath on phosphorous content of the coatings is illustrated in figure 2. With increased amount of nano-particles concentration in the bath, phosphorous content of the coatings has decreased from 17 wt% to 11.5 wt%. Since alumina nano-particles are not electrically conductive, their attendance in the coating would decline the effective surface of the coating and so current density will increase in metallic positions of the cathode [25]. Any increase in current density will increase the potential of hydrogen reduction and so fewer hydrogen atoms will be absorbed to the cathode surface [28]. Regarding to equation (1), fewer absorption of hydrogen atoms to the cathode surface will lessen the rate of phosphorous

![Figure 1. The effect of alumina nano-particles concentration on their attendance in Cr–P coatings.](image-url)
formation on the cathode surface. On the other hand, equation (1) can only be accomplished on the cathode surface. Reduction of effective surface on the cathode by attendance of alumina nano-particles on the surface also reduces the suitable positions for occurrence of equation (1); and hence the phosphorus content of the coating is reduced.

\[
4\text{H}_2\text{PO}_4^- + \text{H}_{\text{ads}} = 3\text{P} + 3\text{OH}^- + 2\text{H}_2\text{O} + \text{H}_2\text{PO}_5^-, 
\]

(1)

Surficial SEM images of different Cr–P/alumina coatings are presented in figures 3 and 4. According to these figures, incorporation of alumina nano-particles in the coatings has decreased the crack density of the coatings. It can also be concluded that the more incorporation of alumina nano-particles in the coating has resulted in the less crack density of the respective coating. Regarding to Cr–P phase diagram [29], phosphorous has a minor solubility in chromium at room temperature. Thereupon, any attendance of phosphorus atoms in chromium atoms lattice will result in the increased internal stresses. Incorporation of nano-particles in Cr–P coatings has reduced the phosphorus content of the coatings. Less phosphorous content causes a less internal stress and consequently a reduced amount of crack density in the coating [17, 30–32]. In the other hand, incorporation of alumina nano-particles in the coating gives rise to the less reduction of hydrogen ions on the cathode, as previously was discussed. This phenomenon results in the less increment of the bath pH around the cathode; and accordingly a fewer amounts of chromium hydroxide is formed; which consequently results in the less crack density at the coating surface [4].

In addition to the amount of nano-particles in the coating, state of dispersion and similarly size of the incorporated particles are also impressive factors in coating properties [22, 24, 33]. X-ray maps are usually employed to survey the particles dispersion on a coatings surface. X-ray map of aluminum (blue spots) for the Cr–P coating containing 4.3 wt% alumina is illustrated in figure 5. Regarding to this figure, alumina particles are favorably dispersed in the coating. Surficial SEM images of the Cr–P coating containing 4.3 wt% alumina is presented in figure 6. Dominant black spots are clear in figure 6. EDS analysis of the area indicated with a circle in figure 6 has been carried out to distinguish the chemical composition of the black spots. The result of the EDS analysis is presented in figure 7. As it can be seen, the alumina content of the determined area is 6.6 wt%, and hence the black spots must be alumina nano-particles. According to figures 5 and 6 it can be concluded that alumina particles are thoroughly dispersed in the coating and are smaller than 100 nm.

3.2. The effect of alumina nano-particles concentration on deposition rate of Cr–P coatings

Relevancy of deposition rate of Cr–P coatings to the concentration of alumina nano-particles in the plating bath is illustrated in figure 8. Deposition rate of Cr–P coatings has increased from 7.8 \( \mu \text{m} \text{h}^{-1} \), when there are no particles in the bath, to 10.5 \( \mu \text{m} \text{h}^{-1} \), at particles concentration of 24 g l\(^{-1}\). Reduction of hydrogen ions causes a respective increase of the bath pH around the cathode. pH increment results in the formation of chromium hydroxide molecules around the cathode (via polymerization reaction) and as a consequence the activity of chromium ions is decreased [4, 9, 34, 35]. Due to silicon dioxide co-deposition method, nano-particles are surrounded with metallic ions when they are in the bath. Hence, transportation of nano-particles towards the cathode increases the concentration of chromium ions and accordingly the deposition rate is increased (figure 9). On the other hand, as it was discussed before, since ceramic particles are not electrical conductive,
they result in the reduction of the effective surface area when they attend in the cathode. A decreased surface area redounds to a decrease in the hydrogen ion reduction rate, which consequently enhances the deposition rate \[25, 28\]. Addition of nano-particles to the plating bath also shifts up the potential of metal ion reduction in the direction of positive potentials axis, which consequently improves the deposition rate. There are similar work reports claiming that incorporation of nano-particles to a plating bath has improved the deposition rate \[11, 13, 16, 20, 25, 35\].

Further increase of nano-particles concentration results in the reduction of metallic ions activity, enhancement of bath viscosity, and reduction of electrolyte conductivity. On the other hand, presence of nano-particles reduces the current density in charge-transfer-controlled and complex-controlled areas \[20\], and thus, deposition rate is reduced. Finally, it can be concluded that an increase of alumina nano-particles concentration in the plating bath upon an optimum concentration (24 g l\(^{-1}\)) will decrease the deposition rate.

3.3. Corrosion resistance

3.3.1. Electrochemical impedance tests

Nyquist curves of Cr–P coatings containing different amounts of alumina nano-particles are presented in figure 10. Accordingly, the Nyquist curves are mostly like imperfect semicircles, which are distributed through horizontal axes. Essence of imperfect semicircles can be due to the existence of two time constants at the electrochemical system or a quasi-capacitive behavior in coating/electrolyte interface. It is necessary to plot bode and bode-phase diagrams to better study the electrochemical system. Any time constant in an
Figure 4. SEM images of (a) and (b) Cr-13.4% P/1.6% Al₂O₃ and (c) and (d) Cr-11.5% P/4.3% Al₂O₃ coatings morphology.

Figure 5. (a) SEM image surface morphology of a Cr–P coating containing alumina particles and (b) x-ray map of aluminum element (blue spots) on a Cr–P background.
The electrochemical system shows up like a step in bode diagrams [30]. On the other hand, phase angle in a bode-phase diagram tends to approach $-90^\circ$ (but never equals $90^\circ$) when there is a quasi-capacity in an electrochemical system [36]. Bode and bode-phase diagrams for different coatings are presented in figures 11 and 12. Thus, with regards to the above discussions and bode and bode-phase diagrams, it can be concluded that there is a quasi-capacity in the studied electrochemical system. A quasi-capacity in electrolyte/coating interface is usually ascribed to the existence of any inhomogeneity in the interface, such as micro-cracks, porosity, roughness or any change in chemical composition [36–38].

Impedance of a constant phase element (CPE) is calculated by equation (2).

$$Z_{\text{CPE}} = 1/Y_0(j\omega)^n,$$

(2)

Where, $\omega$ is angular frequency (rad/s), $Y_0$ is the CPE constant ($s^n$/ohm) and $n$ is the CPE power, which can be describes as $n = \alpha(\pi/2)$ ($\alpha$ is the phase angle constant in radians) [39]. $Y_0$ parameter is directly dependent on the active surface of coating. Value of $n$ is representative of the amount of deviance of electrolyte/coating interface from an ideal capacity [18].

The equivalent circuit used to study the electrochemical parameters of the coatings is presented in figure 13. In this figure, $R_s$ is representative of the resistance of solution between the working electrode (coating surface) and the reference electrode; $R_p$ is representative of the sample resistance to corrosion (and exactly equals the diameter of the semicircles in Nyquist plots); and CPE is representative of quasi-capacitive behavior (non-ideal capacity). Electrochemical parameters extrapolated from fitting the theoretical impedance curves (regarding to equivalent circuit) on the experimental impedance curves (using Z-View software) are summarized in table 2.

With regard to table 2, it can be concluded that existence and increase of alumina nano-particles in the coatings result in an increased polarization resistance and a decreased amount of $Y_0$ parameter. A decreased amount of $Y_0$ parameter is caused by a decreased area of coating surface taking part in the corrosion reaction.
Referring to the SEM images (figures 3 and 4), the decrease in the corrosion-active surface of the coatings must be a result of the decrease in micro-cracks density on Cr–P coatings. On the other hand, existence of the nonconductive alumina nano-particles in composite coatings also decreases the active surface of the samples. Hence, the corrosion-active surface ($Y_0$) is decreased.

As nano-particles increase in the coatings, $n$ (the CPE power) is also increased. The increase of CPE power (the increase of phase angle maxima in figure 12) is due to any decrease in surficial inhomogeneity (porosity, micro-cracks, roughness). As it was discussed before, composite coatings have a lower micro-crack density and so the increase of CPE power must be a result of this phenomenon.

![Figure 7. EDS spectra of (a) pure Cr–P and (b) composite coating.](image)

![Figure 8. The effect of alumina nano-particles concentration in the plating bath on the deposition rate of Cr–P coatings.](image)
In accordance to the discussion above (the enhancement of polarization resistance and decrease of corrosion-active area), it can be deduced that the incorporation of alumina nano-particles in Cr–P coatings results in an increased corrosion resistance of coatings in 3.5 wt% NaCl media.

3.3.2. Linear polarization tests
EIS tests results showed that presence and increase of the phosphorous element in chromium coatings have a destructive effect on the corrosion resistance of the coatings. However, EIS tests normally examine corrosion behavior of samples only at OCP. Therefore, polarization tests were also performed to study the corrosion behavior of the coatings, even at potentials higher than OCP. Polarization diagrams of the Cr–P and composite coatings in 3.5 wt% NaCl media are presented in figure 14. The respective electrochemical parameters extrapolated from polarization diagrams are presented in table 3. Corrosion current density ($i_{corr}$) and corrosion potential ($E_{corr}$) are extracted from cross point of the tangent lines drawn on cathodic and anodic branches of polarization diagram. According to the table 3, existence of nano-particles in the coatings has decreased the amount of current density from 2 μA cm$^{-2}$ (for Cr–P) to 0.2 μA cm$^{-2}$ (where the highest amount of nano-particles is incorporated in the coating). With regards to SEM images shown in figures 3 and 4, the increases in current density with the presence of nano-particles in the coatings must be due to the decreased density of micro-cracks on composite coatings surfaces. On the other hand, inclusion of non-conductive ceramic nano-

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**Figure 9.** A sketch of the effect of nano-particles on the concentration of metallic ions around the cathode. (a) No nano-particles are present and (b) nano-particles are present in the plating bath.

**Figure 10.** Nyquist plots of Cr–P coatings containing different amounts of alumina nano-particles in a 3.5 wt% NaCl solution.
Figure 11. Bode plots of Cr–P coatings containing different amount of alumina nano-particles in a 3.5 wt% NaCl solution.

Figure 12. Bode-phase plots of Cr–P coatings containing different amounts of alumina nano-particles in 3.5 wt% NaCl solution.

Figure 13. Equivalent electrical circuit of Cr–P coatings containing alumina nano-particles.

Table 2. Electrochemical parameters resulted from the fitting of theoretical and experimental impedance plots.

| coating/parameter | R_c (R_p) (Ω cm²) | Y_0 (Ω⁻¹ cm² s⁰) | n   |
|-------------------|-------------------|------------------|-----|
| Cr-17% P          | 2390              | 13.432E-5        | 0.8219 |
| Cr-15.2% P/0.8% Al₂O₃ | 21 098            | 11.839E-5        | 0.877 84 |
| Cr-13.4% P/1.6% Al₂O₃ | 22 954            | 11.097E-5        | 0.877 56 |
| Cr-13.0% P/3.7% Al₂O₃ | 24 159            | 10.811E-5        | 0.878 68 |
| Cr-11.5% P/4.3% Al₂O₃ | 28 046            | 10.592E-5        | 0.887 81 |
Equation (3) was utilized to calculate the porosity percentage of the coatings.

\[
\text{Porosity(P)}\% = (R_{p,s}/R_{\text{P,c}}) \times 10^{-\frac{(\Delta E_{\text{corr}})}{b_a}},
\]

Where, \(R_{p,s}\) is the polarization resistance of the substrate (\(\Omega \text{cm}^2\)), \(R_{\text{P,c}}\) is the polarization resistance of the coating (\(\Omega \text{cm}^2\)), \(\Delta E_{\text{corr}}\) is the difference between corrosion potentials of the substrate and the coating (mV), and \(b_a\) is the anodic slope of the substrate (mV/dec) [11, 34, 40]. Porosity percentages of different coatings, calculated through equation (3), are presented in Figure 15. With attendance of alumina nano-particles in the coating, particles on coatings surface (proportionately to the amount of incorporation) decreases the metallic surface in contact with the corrosive area. Hence, the corrosion resistance of the composite coatings is increased [18].

| Coating/parameter | \(E_{\text{corr}}\) (mV versus SCE) | \(I_{\text{corr}}\) (\(\mu\text{A cm}^{-2}\)) | \(b_a\) (mV dec\(^{-1}\)) |
|-------------------|-------------------------------------|-----------------|-----------------|
| Cr-17% P          | 294                                 | 2               | 43              |
| Cr-15.2% P/0.8% Al\(_2\)O\(_3\) | 320                               | 0.9             | 35              |
| Cr-13.4% P/1.6% Al\(_2\)O\(_3\) | 320                               | 0.45            | 36              |
| Cr-13.0% P/3.7% Al\(_2\)O\(_3\) | 320                               | 0.4             | 40              |
| Cr-11.5% P/4.3% Al\(_2\)O\(_3\) | 280                               | 0.2             | 36              |

Figure 14. Polarization plots of Cr–P coatings containing different amounts of alumina particles in 3.5 wt% NaCl solution.

Figure 15. Porosity percentage of Cr–P coatings containing different amounts of alumina nano-particles.
porosity percentage of Cr–P coatings has decreased from 6.7% (for Cr–P) to 1.5%, where the highest amount of nano-particles are incorporated.

Presence of nano-particles on the coatings results in a decreased rate of hydrogen ion reduction [25]. A reduced rate of hydrogen ion reduction clearly results in a decreased percentage of porosities. However, there is also a possibility of nano-particles tangle in porosities, which results in a decreased percentage of porosities. Reduction of porosity percentage with the presence of nano-particles is the reason for the corrosion current reduction. There are many reports presenting the same results as this work [11, 17, 21, 33].

EIS results showed that incorporation of the nano-particles decreases the admittance of the coatings which, (referring to figure 15), this phenomenon could be due to a decrease in porosity percentage.

4. Conclusion

Composite Cr–P coatings containing alumina nano-particles were plated via electroplating process.

- With the addition of the Al2O3 nano-particles to plating bath, incorporation of nano-particles in Cr–P coatings increased to the highest amount of 4.3 wt%.
- With the existence and increase of nano-particles in the coatings, microcracks densities on the coatings were decreased.
- The corrosion resistance of Cr–P coatings increased with the presence of nano-particles in composite coatings. Accordingly, the corrosion current density also decreased from 2 A cm−2 μ to 0.2 A cm−2 μ.
- With the presence of nano-particles, the porosity percentage of Cr–P composite coatings decreased from 6.7% to 1.5%.

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