

Influence of Surface Post-Processing on Crystal Refinement and Characteristics of Hopeite Coating by Phosphating

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Abstract: Hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) conversion coating was prepared on pure titanium using mild phosphate chemical conversion technology. In this investigation the effect of post-processing after phosphating was focused on coating microstructure, chemical composition, adherence and corrosion resistance. Different sequential order of drying and rinsing of the coated samples were carried out. The results demonstrated that the priority shift of rinsing or drying did not change the hopeite phase of the conversion coating, but played a significant role in the crystal size and coating microstructure. Compared with the traditional preparation of the coating, a more compact and uniform coating with finer crystals grains (3–5 μm) was obtained by the unconventional post-treatment of drying before rinsing, along with a higher bonding strength and corrosion resistance.

Keywords: phosphating; conversion coating; post-processing; bonding strength; corrosion resistance



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1. Introduction

The coating technology of phosphate chemical conversion, also known as phosphating, has been widely used as one of the effective surface modification methods to be applied on various of metals for improvement of surface corrosion protection, wear resistance, adhesion of face painting and functional properties, etc. [1–4]. Currently, phosphating coatings are preferred in both industrial and biomedical fields due to their adherent nature and rapid coating formation besides being economical and easy operation [5–8]. More importantly, the specific porous structure in micro or nano scale of the converted coatings can respond to cell adhesion and migration by providing directional guiding, which is known as “contact guidance” [9]. Therefore, it is important to develop appropriate coating microstructures and characteristics for various applications.

Generally, in laboratory studies, a typical phosphate chemical conversion procedure contains mainly three modules (pre-processing, phosphating and post-processing), which can be carried out through eight operating sequences, as illustrated in the flow chart of Figure 1. Besides the phosphating operation, which plays a prominent role in coating formation, researchers prefer to pay more attention to the pre-processing rather than post-processing. After all, a clean and active surface of the metal substrate is predictably requisite. A variety of methods such as sand or shot blasting and alkaline or acid cleaning have been used to get an ideal substrate surface [10–13]. In contrast, less attention has been given to the post-processing after phosphating [14]. Even though only two steps are involved in a typical post-processing period of chemical conversion, it should be supposed that each step contributes to the final coating formation and performances. Moreover, it is recognized that rinsing and drying followed by phosphating is indispensable for removing any soluble salts, foreign ions, acid residue, and non-adherent particles on the surface which would otherwise cause coating heterogeneity and reduce adherence, as well as promote blistering of subsequent paintings [15].

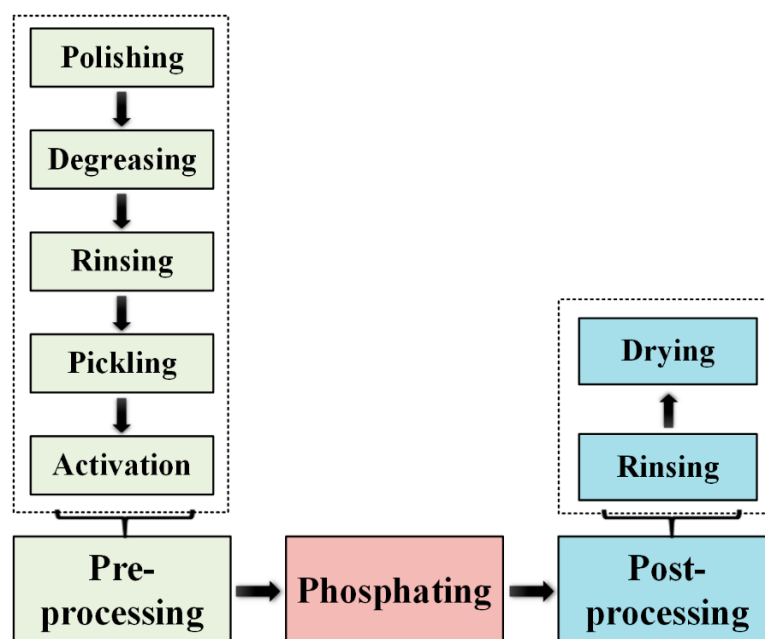


Figure 1. Flow chart depicting the processing procedures involved in the fabrication of phosphate chemical conversion coating on metal substrates.

In this work, we focused on the investigation of the post-processing stage followed by phosphating, and a different sequential order of rinsing and drying was carried out to prepare a hopeite conversion coating on pure titanium. The effect of operation of post-processing on the coating microstructure and phase compositions were analyzed. The bonding strength between the coating and substrate was evaluated via scratching, along with the corrosion characteristics by electrochemical measurements.

2. Materials and Methods

The pre-processing was carried out in the routine way [16,17]. Briefly, pure titanium disks ($\varnothing 10 \times 2$ mm) were selected as coating substrates subjected to polishing with SiC emery papers to #1000-grit, degreasing in sodium hydroxide solution and rinsing in deionised water and alcohol, successively. After pickling in hydrofluoric acid solution for 15 s and surface activation in colloidal titanium phosphate for 30 s, the disks were immersed into a phosphating bath containing 25 g/L ZnO, 5 g/L $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 2 g/L NaClO_3 , 15 mL/L phosphoric acid and 30 mL/L nitric acid for 10 min at room temperature. In addition, 5 g/L pure iron powders were added into the bath for accelerating coating formation [18]. The pH value of the bath was adjusted to 2.75 using phosphoric acid and sodium hydroxide. After that, one group of the coated disks were post-treated as usual, i.e., firstly rinsed with deionised water for several times, and then dried at 30–40 °C for 3 h. The other group of disks were post-treated by the same way but in reverse order, and allowed to air dry finally. According the post-processing sequence, the two groups of samples were named as R-D (rinsing first and drying followed) and D-R (drying first and rinsing followed), respectively.

The microstructure and chemical composition of the coatings were analyzed by scanning electron microscope (SEM, Hitachi SU-70, Tokyo, Japan) equipped with an energy dispersive spectrometer (EDS). The coating phase was detected by X-ray diffractometer (XRD, Rigaku D/max-rc, Tokyo, Japan). The coating adherence was tested by an acoustic emission scratch tester (WS-2005, CAS, Lanzhou, China). A normal force of 0–100 N was applied on the coating surface with a loading rate of 100 N/min. The electrochemical corrosion resistance of the coatings was investigated by measuring the corrosion potential versus immersion time, potentiodynamic polarization behavior and electrochemical

impedance spectroscopy (EIS) in 3.5% NaCl solution using an electrochemical workstation (CHI660e, CH Instruments Ins., Shanghai, China) with a classical three-electrode cell.

3. Results and discussion

Figure 2 shows the surface morphologies and cross-sectional images of the coatings prepared by different post-processing sequences. Surprisingly the coating morphology and crystal size were significantly influenced only by the change in priority of rinsing and drying. In detail, the conventional R-D coating presented a loose structure comprised of plate-like crystals with length of 20–40 μm (Figure 2a). It could be observed that after 10 min of phosphating immersion, the R-D coating was uniform but incomplete while the titanium substrate was partially exposed (Figure 2b). Observed from the cross-section of the R-D sample, crystal blocks distributed discretely on the surface of titanium substrate and the coating presented an uneven thickness of about 8–10 μm (Figure 2c). The D-R one, in contrast, exhibited a more compact and complete microstructure with a significant grain refinement (Figure 2d). The crystals were still plate-like but shortened to 3–5 μm length. In addition, amounts of amorphous particles filled in the crystal gaps leading to a high surface coverage of the substrate (Figure 2e). The coating cross-sectional image illustrated that the D-R coating was thinner and much more uniform in thickness (about 6 μm) than that of the R-D one, which was due to the refined grains and dense structure (Figure 2f).

The forming of film by phosphate chemical conversion can be recognized as an artificially controlled corrosion process [19,20]. The coating crystals are undergoing acid attack throughout the entire growth period. It is known that a dynamic balance of dissolution and crystallization existed at the last period of phosphating coating formation, until removing of reactive ions at the interface of coating and solution [21]. The traditional rinsing procedure after phosphating is to remove the residual bath on the coating surface including the effective reactive ions. In other words, the balance of the coating formation is terminated at this stage. Therefore, the reactive time of coating growth can be deemed as only 10 min in this investigation. However, for the D-R sample small amounts of phosphating solution were retained in the interspace of the coating without rinsing in time, resulting in continued reactions between the formed crystals and soluble salt ions. The actual reaction time of the D-R coating was probably far greater than 10 min. Therefore, the reorganization of the coating crystals was more sufficient to get a more integrated and finer microstructure, as shown in Figure 2d,e. On the other hand, the unreacted ions of soluble salts possibly precipitated as an amorphous state due to aqueous evaporation during the drying process, as illustrated by the little particles in the inset of Figure 2e. It is conceivable that the adherence of these amorphous particles was strong enough to remain unperturbed by the rinsing process after drying.

Figure 3A represents the EDS results of different regions in the surface of D-S sample. Besides of the matrix element of Ti, little white particles adhered on the coating surface consisted of elements of O, P, Fe and Zn, which were the main components of the phosphating bath (Figure 3a). This result confirmed the suggestion of precipitation of soluble salts. The bulk crystals were composed of O, P, and Zn elements, which were the components of zinc phosphate (Figure 3b). As illustrated in the XRD patterns (Figure 3B), the main diffraction peaks detected in both R-D and D-R samples were indexed to hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, JCPDF #37-0465), tending to grow along (020), (220) and (241) planes. This indicated that sequential order of rinsing and drying had no influence on the coating phase. However, by comparison the peak intensity of D-R sample was lower than that of R-D, probably attributable to the coating refinement observed by D-R sample.

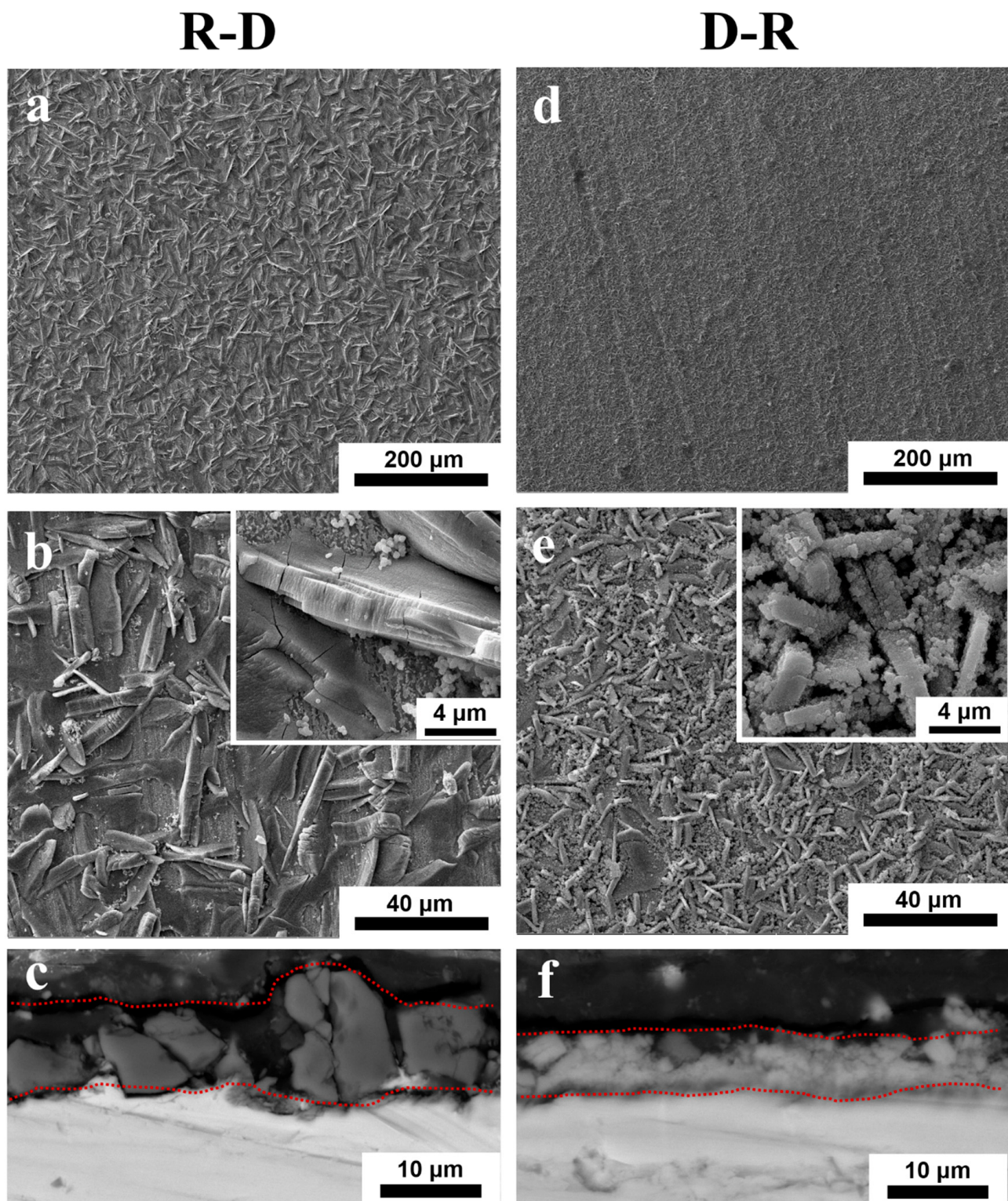


Figure 2. SEM micrographs of the surface of (a) R-D and (d) D-R samples. (b,e) are their corresponding images at high magnification. (c,f) are their corresponding cross-sectional images.

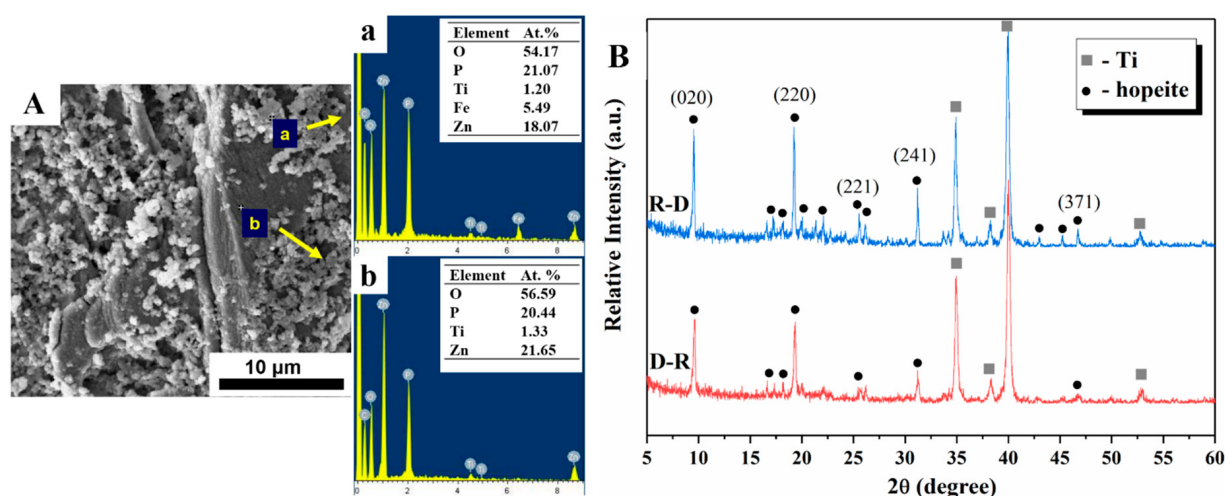


Figure 3. (A) EDS results of different regions in the surface of D-S sample, (B) XRD patterns of the coatings prepared by different post-processing.

Figure 4 depicts the acoustic emission signal curves of the coatings. From the position of the first mutation in the curves, i.e., the critical load L_c , meaning the maximum load until coating damage or peeling occurred during scratching, the D-R sample represented a larger value of L_c (nearly 70 N) than the R-D sample (about 65 N). It indicated that drying first was conducive to the enhancement of bonding strength to a certain degree. This could be largely ascribed to the coating refinement, or probably due to the amounts of amorphous particles which improved the adherence between the hopeite crystals.

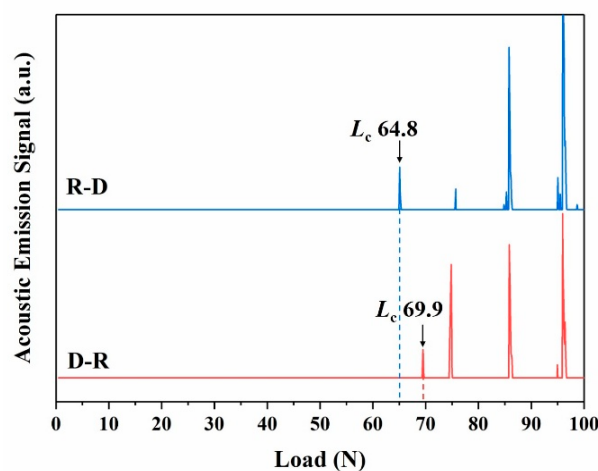


Figure 4. Acoustic emission signal curves of the coatings.

Figure 5a,b compares the variation of corrosion potential (E/V_{SCE}) as a function of time for the different coated samples. It can be seen from Figure 5a that the potential E value of R-D increased rapidly from -0.230 V to about -0.215 V in the initial few seconds, and then gradually increased to nobler potentials reaching a steady value of nearly -0.140 V after 1400 s of immersion. This might result from the oxidation that occurred on the exposed surface of Ti substrate. In contrast, the variation of E with time for D-R sample was slight from -0.158 V to -0.147 V and reached a steady state within less immersion time of 1200 s (Figure 5b). It indicated that the D-R sample owed a better corrosion and chemical stability.

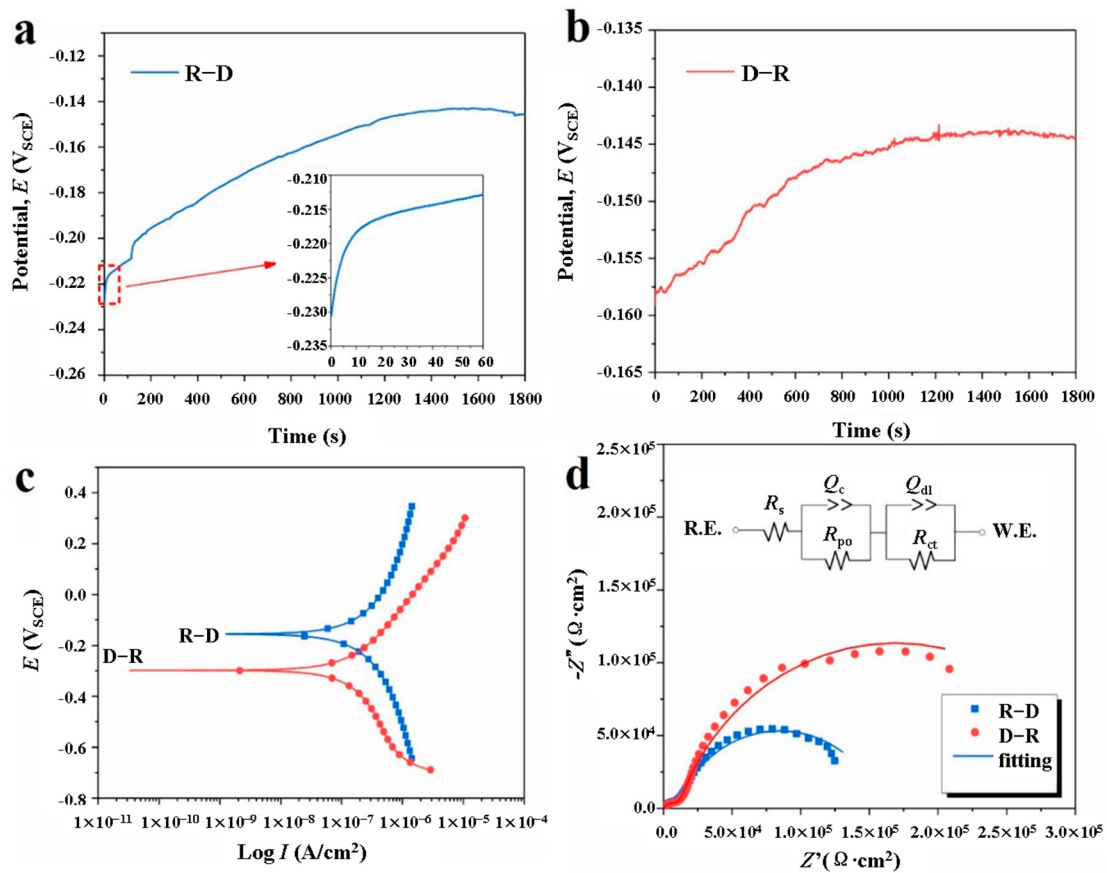


Figure 5. Variation of corrosion potential versus time (0–1800 s) for (a) R-D and (b) D-R samples. (c) potentiodynamic polarization curves and (d) Nyquist plots of EIS spectra of the different coatings. The inset is the equivalent electrical circuit model.

Figure 5c shows the potentiodynamic polarization curves of the coated samples. The corresponding electrochemical parameters of corrosion potential (E_{corr}) and corrosion current (I_{corr}) calculated using Tafel fit are listed in Table 1. The two coatings revealed similar polarization behaviors. Compared with the parameters, the R-D sample processed a nobler E_{corr} (-0.16 V) and I_{corr} ($0.12 \mu\text{A}\cdot\text{cm}^{-2}$) than the D-R sample (-0.30 V, $0.09 \mu\text{A}\cdot\text{cm}^{-2}$). Normally a greater value of E_{corr} and less value of I_{corr} suggest a better corrosion protective behavior [22]. However, considering the thermodynamics parameter of E_{corr} showing the anti-corrosion trend, the kinetic parameter of I_{corr} could better express the corrosion resistant rate of the coating. On account of the minor difference between the I_{corr} values of the two samples, EIS tests were used to further evaluate the anti-corrosion properties. Figure 5d represents the Nyquist plots for the two coatings and an equivalent electrical circuit (EEC) model inserted was used to fit the impedance data. In the EEC model, R_s , R_{po} and R_{ct} represented the resistance of solution, pore resistance of coating and charge transfer resistance, respectively; Q referred to the constant phase element. The fitted results were also listed in Table 1. It was clear that both of the two coatings represented two time constants from the Nyquist plots. A higher R_{po} value ($3.17 \times 10^5 \Omega\cdot\text{cm}^2$) for the D-R coating than that of the R-D coating ($1.50 \times 10^5 \Omega\cdot\text{cm}^2$) indicated a greater inhibition of ions erosion through the pores in the D-R coating. The electrolyte penetration into the surface of substrate might be blocked over the more compact and finer microstructure of D-R coating. On the other hand, the adherence of amorphous particles in the coating might play a positive role in the corrosion protection. These insulated particles could block the penetration of corrosive ions to the surface of substrate without engaging in any electrochemical reactions, thereby making up for the porosity flaws of hopeite coating [23].

In this respect the post-treatment of drying before rinsing on the porous conversion coating was favorable to the enhancement of corrosion resistance.

Table 1. Electrochemical fitted parameters determined by potentiodynamic polarization curves and Nyquist plots.

Coatings	E_{corr} (V _{SCE})	I_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	R_s ($\Omega\cdot\text{cm}^2$)	R_{po} ($\Omega\cdot\text{cm}^2$)	R_{ct} ($\Omega\cdot\text{cm}^2$)
R-D	-0.16 ± 0.06	0.12 ± 0.08	4.09 ± 2.99	$1.50 \times 10^5 \pm 2.50$	$1.01 \times 10^4 \pm 2.67$
D-R	-0.30 ± 0.04	0.09 ± 0.03	2.00 ± 1.89	$3.17 \times 10^5 \pm 5.35$	$1.08 \times 10^4 \pm 3.19$

4. Conclusions

A mild phosphate chemical conversion technology has been exploited to produce a hopeite coating on pure titanium with different prioritization of post-processing between rinsing and drying at the last stage of operation. As expected, the coating phase was not affected by the change of post-processing, which remained a pure chemical phase of hopeite. However, an interesting result indicated that the priority of drying before rinsing significantly reduced the crystal size by almost an order of magnitude, as well as improved the coating microstructure. Likewise, the hopeite coating treated with drying followed rinsing post-processing presented superior properties in the measurements of bonding strength and corrosion resistance. In addition, amounts of little amorphous particles were observed adhered on the coating surface by precipitation of residual phosphating salts. They were supposed to provide an active influence on promoting coating refinement and corrosion protection. It was suggested that the sequential order of rinsing and drying post-processing has a significant influence on coating characteristics and should be paid more attention in coating fabrication.

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