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Preparation and Corrosion Properties of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ Composite Coating on Q235 Carbon Steel

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Abstract: The $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ composite coatings were fabricated on the surfaces of Q235 carbon steel via the sol-gel method to improve its corrosion resistance. The effects of the sintering temperature and the layer number on the corrosion performances were explored. The coating morphology, microstructure and phase composition were analyzed by scanning electron microscopy (SEM) and X-ray diffractometer (XRD). Friction wear experiment, immersion experiment, and electrochemical impedance spectroscopy techniques were used to investigate the corrosion properties of the coatings as well. The results show that the sample with the $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ coatings sintered at 850 °C are more uniform and denser and have better corrosion resistance and wear resistance than the other coatings. The R_p value of the 3 L coating sintered at 850 °C was about $114 \text{ k}\Omega\cdot\text{cm}^2$, and the average friction coefficient was about 0.36.

Keywords: sol-gel; Q235 carbon steel; composite coating; corrosion resistance; friction resistance

1. Introduction

Carbon steel is one of the most commonly used metal materials and widely used in various fields, such as industry, energy and marine. However, carbon steel is extremely vulnerable to corrosion after use in marine environments. Corrosion causes not only unavoidable loss and safety problems in production and life, but also a certain amount of pollution to the environment [1–3]. At present, the common protection methods of carbon steel mainly include coating protection [4], cathodic protection [5], hot dip galvanizing [6] and so on. Among them, the coating technique is widely respected due to its simple process, less pollution, greater practicality, no restriction on the size and shape of the substrate, and better corrosion protection effect [7].

Coatings prepared on the surface of carbon steel can effectively prevent and isolate the migration of corrosive media to the metal surface, resulting in a significant reduction in the corrosion rate of the metal [8,9]. In recent years, composite coatings synthesized from two or more oxides have attracted much attention. They have been used to improve the mechanical properties and corrosion resistance of steel [10–12]. Studies have shown that coatings such as TiO_2 , SiO_2 and $\text{TiO}_2\text{-SiO}_2$ are widely used to improve the corrosion resistance of metal substrates [13–19]. Among the many coatings, the Al_2O_3 coating is well known as a corrosion barrier and exhibits excellent wear and corrosion resistance. TiO_2 and SiO_2 are excellent coatings due to their chemical stability and good corrosion resistance [20–25]. The $\text{TiO}_2\text{-SiO}_2$ coatings deposited on 316 L stainless steel by the sol-gel method is effective as a corrosion protection agent in acidic media [26]. Forghani et al. [27] further improved the deposition of $\text{Al}_2\text{O}_3\text{-TiO}_2$ by texturing the coating. Mora et al. [28] observed significant wrinkling of the coating underneath the metal substrate in the study of the effects of silica nanoparticles on the coating. The study found that the $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ sol-gel powders have a considerable surface area, meaning that the powders are highly reactive [29]. In summary, composite coatings synthesized from a variety of oxides can



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effectively improve the performance of carbon steel. Among them, the sol-gel method is a simple and economical technique. It is easy to operate and can control the porosity, applying to a variety of substrates such as metals, glass, ceramics and plastics [30–33].

In this paper, many coatings, including the three-layer ($\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$, 3 L) composite coating, were prepared on the surfaces of Q235 carbon steel by the sol-gel method. The corrosion properties of the coatings with different sintering temperatures and layer numbers were explored by immersion test, friction wear, immersion experiment, and electrochemical impedance spectroscopy, separately. In addition, the surface morphology and the structures of the coatings were further investigated to explain the anti-corrosion mechanism of the 3 L coating. The successful preparation of coatings and the improvement of corrosion performance provide a simpler and more effective reference for the anti-corrosion route of carbon steel.

2. Experimental

2.1. Materials and Solution

The Q235 carbon steel samples with the size of $25\text{ mm} \times 25\text{ mm} \times 2\text{ mm}$ were cleaned in an ultrasonic bath with ethanol and deionized water orderly. The surfaces of the samples were ground using sandpaper from 240[#] to 1000[#] polished successively. Then, the polished surfaces of the samples were completed by acid pickling, activating treatment and water washing processes. After that, the samples were placed in a 500 °C air furnace for 1 h to relieve residual stress. The uncoated Q235 carbon steel was used as a blank sample (BS) for comparison.

2.2. Experimental Materials and Preparation of Coating

Tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) and tetraethyl orthosilicate ($(\text{C}_2\text{H}_5\text{O})_4\text{Si}$) were used as titanium oxide and silicon oxide precursors, respectively. Aluminum nitrate served as the raw material for preparing alumina. Nitric acid, ethanol and distilled water were used as the catalyst, solvent and hydrolysis agent, respectively. Sol-gel was prepared by step hydrolysis method, and the specific process is as follows: 10 mL of butyl titanate was added into 40 mL of ethanol and then continuously stirred for 1 h to form solution A. A total of 6.7 mL of ethyl silicate was dissolved in 40 mL ethanol to obtain solution B. Simultaneously, 5 mL of deionized water, 2 mL of nitric acid and 10 mL of ethanol were stirred subsequently for 30 min to achieve a hydrolysis agent, which was dropped into solution A and solution B, respectively. Again, they were separately stirred for 1 h. An amount of 0.98 g of aluminum nitrate was mixed with 20 mL of ethanol for 1 h to obtain solution C. After that, solution B and solution C were orderly added to solution A under strong stirring for 3 h to obtain a yellow transparent sol. Finally, the gels were formed after the prepared sol was aged at room temperature for 24 h. The synthesis process is shown in Figure 1. These chemical reagents were purchased from Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China).

The prepared sol-gel coating was deposited on the steel substrate by dip-coating [34–36]. The carbon steel was vertically immersed in the aged sol at a constant rate. After immersion for 5 min, the steel samples were pulled out and were covered with a uniform coating (one layer, 1 L). After that, the coated samples were dried in an oven at 120 °C for 30 min. Finally, they were sintered at 550 °C, 650 °C, 750 °C, 850 °C at a heating rate of 4 °C/min for 1 h and named 550 °C–1 L, 650 °C–1 L, 750 °C–1 L, 850 °C–1 L, respectively.

For coating two layers (2 L), the coated samples were kept at room temperature for 20 min after the first immersion for 5 min. Likewise, the carbon steel with a uniform coating was vertically immersed in the sol at a constant rate. After immersion for 5 min, the steel samples were pulled out and were covered with the second uniform coating (two layers, 2 L). After that, the coated samples were dried in an oven at 120 °C for 30 min. Finally, they were sintered at 550 °C, 650 °C, 750 °C, 850 °C at a heating rate of 4 °C/min for 1 h and named 550 °C–2 L, 650 °C–2 L, 750 °C–2 L, 850 °C–2 L, respectively.

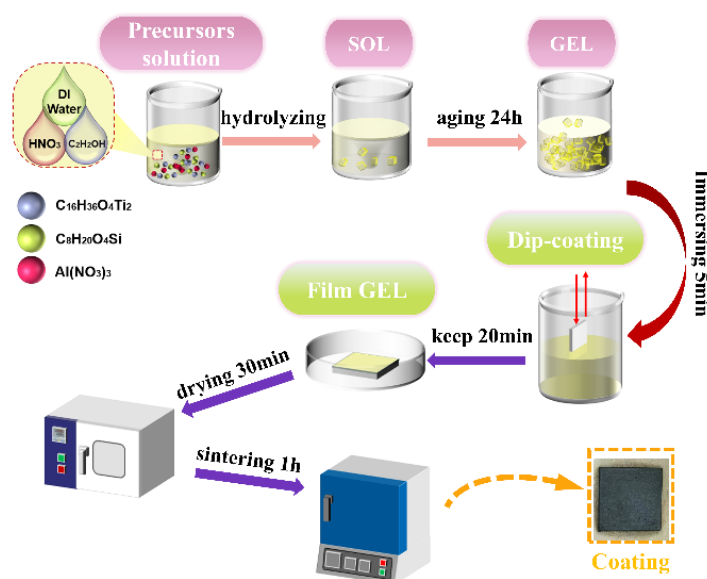


Figure 1. Preparation of the $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ coatings.

For coating three layers (3 L), the coated samples were kept at room temperature for 20 min after the second immersion for 5 min. Again, the carbon steel with two layers coating was vertically immersed in the sol at a constant rate. After immersion for 5 min, the steel samples were pulled out and were covered with the third uniform coating (three layers, 3 L). After that, the coated samples were dried in an oven at 120 °C for 30 min. Finally, they were sintered at 550 °C, 650 °C, 750 °C, 850 °C at a heating rate of 4 °C/min for 1 h and named 550 °C–3 L, 650 °C–3 L, 750 °C–3 L, 850 °C–3 L, respectively.

2.3. Coating Characterization

The surface morphology of the coatings was analyzed using a scanning electron microscope (Hitachi S-4800, Tokyo, Japan). To prevent charging, the surfaces of the samples were sprayed with gold. The surface phase composition of the coatings was investigated by an X-ray diffractometer (Rapid II, Rigaku, Japan) set at a current of 35 mA and a voltage of 40 kV (diffraction angle ranging from 20° to 80° in a step of 0.02°). The results of XRD were analyzed using MDI jade 6.5[®] software.

The wear resistances of the coating and the BS were operated by a UTM-2 friction and wear tester. Under the condition of dry sliding friction at room temperature, the experimental frequency was 2 Hz, and the load was 15 N. The unidirectional stroke was 5 mm, and the friction time was 15 min. The friction partner was a YG8 carbide steel ball with a diameter of 5.0 mm, and the dry friction wear test was conducted without lubrication.

2.4. Electrochemical Experiments

The electrochemical experiments were performed using an electrochemical workstation (CS350H, CorrTest[®] Instrument Co., Ltd., Wuhan, China). A three-electrode electrochemical cell was explored in 3.5 (wt.) % NaCl solution throughout. The samples with 1 cm² working area were utilized as the working electrode (WE). A platinum plate was used as counter electrode (CE). A saturated calomel electrode (SCE, +0.2412V vs. NHE) was used and allowed for measurement or control of the working electrode potential relative to SCE. The polarization curves were scanned at a rate of 1 mV/s and over a range of ±0.25 V relative to the open-circuit potential.

The electrochemical impedance spectroscopies were operated with sinusoidal perturbation amplitude of 10 mV and frequencies from 0.01 to 10,000 Hz. Two different equivalent circuits were used to illustrate the electrochemical values. The EIS results were analyzed using ZSimpWin3.22[®] software. All electrochemical tests were carried out using an auto-

mated laboratory unit (model PGSTAT302N,) and Nova 1.11 software. And the results were compared with the corrosion behavior of the coated and BS. To investigate the protective effect of the coatings, the optimally coated sample was immersed in 3.5% NaCl solution for 24 h, 48 h, 168 h and 336 h. Each electrochemical experiment was repeated three times to ensure reproducibility. All cell components used in the electrochemical measurement were made of glass or PTEF.

3. Results and Discussions

3.1. Surface Morphology

It is well known that surface morphology is an important parameter influencing the corrosion of metals. The SEM micrographs in Figure 2 exhibited the surface characteristics of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ 3 L coatings sintered at 550 °C, 650 °C, 750 °C and 850 °C with different magnifications. It is clear from Figure 2a,c,e that there was no apparent crack on the surface of the composite coatings when the sintering temperatures were 550 °C, 650 °C and 750 °C. However, there were some cracks on the surface of the coating sintered at 850 °C (Figure 2g). The morphology with high magnification in Figure 2b shows that the coating sintered at 550 °C was inhomogeneous and was mainly constituted of fluffy filamentous microstructures. When the sintering temperature increased to 650 °C, the filamentous microstructures accumulated gradually and generated swellings (Figure 2d). When the sintering temperature was further increased to 750 °C, the coating layer was composed of intertwining vine-shaped microstructures. In addition, many holes appeared on the coating (Figure 2e). Compared with the coating samples sintered at 550 °C, 650 °C and 750 °C, the coating sintered at 850 °C presented compact columnar structures separated by grooves (Figure 2h). The phenomena of the coating morphologies varying at different sintering temperatures is possibly attributed to the rise of the coating components [15]. The surface morphology of the coating at different sintering temperatures in Figure 2a–h also reveal that the coating surface gradually became denser and the porosity decreased with the increase of sintering temperature.

3.2. X-ray Diffraction Analysis

The crystalline phases of the coating on the carbon steel surfaces were examined by XRD. Figure 3 shows the XRD patterns of the coatings at sintering temperatures of 550 °C, 650 °C, 750 °C and 850 °C. It is clear from Figure 3 that the diffraction peaks of the coatings sintered at 850 °C, 750 °C and 650 °C are similar, and many kinds of oxides are detected. For instance, there are four kinds of titanium oxides, two kinds of silica and three kinds of alumina present in the coating sintered at 750 °C. The peaks located at (2θ) 24.23° and 39.29° were assigned to the (101) and (200) planes of TiO_2 (JCPDS No. 70-2556), respectively. The peaks situated at 35.53° and 53.54° were due to (101) and (211) planes of rutile TiO_2 (JCPDS No. 76-0325), separately. Additionally, the peaks positioned at 37.18° (111), 43.20° (200), 62.74° (220) and 75.24° (311) were attributed to TiO (JCPDS No. 77-2170), while the peaks stood at 23.83° (110), 33.055° (211), 40.23° (210), 61.31° (310) and 62.43° ($\bar{1}\bar{2}1$) belonged to Ti_2O_3 (PDF 85-0868). The peaks sited at 25.58° (110), 35.16° (121), 52.57° (220) and 57.51° (123) were stemmed from Al_2O_3 (PDF 74-1081). The peaks of Al_2O_3 (PDF 70-3321) were detected as well and located at 36.17° (104) and 54.17° (024). The peaks of SiO_2 (PDF 18-1170) were observed at 24.24° (311), 30.14° ($\bar{5}12$), 32.20° ($\bar{4}08$), 40.90° (711), 53.40° (427), 57.56° (822), 61.03° (824), 62.35° ($\bar{4}016$) and 63.35° (137). The peaks of SiO_2 (PDF 86-2333) were also present at 30.78° (110), 40.58° (101), 46.44° (111), 49.63° (210), 61.46° (211) and 78.70° (301). In addition, two composites were present as well. The peaks observed at 35.39° and 42.49° were assigned to the crystal planes of ($\bar{3}13$) and ($\bar{3}14$) of $\text{Al}_2(\text{SiO}_4)\text{O}$ (PDF 89-0889), respectively. Similarly, the peaks situated at 62.79°, 72.86° and 76.70° were attributed to the composite of Al_2TiO_5 (PDF 73-1630). The peaks observed at 71.00°, 71.92° and 74.00° should be assigned to tail peaks of the peak at 72.86° of Al_2TiO_5 (PDF 73-1630). According to the peak positions in the three top curves of Figure 3, the main components are the same in the coatings sintered at 850 °C, 750 °C and 650 °C.

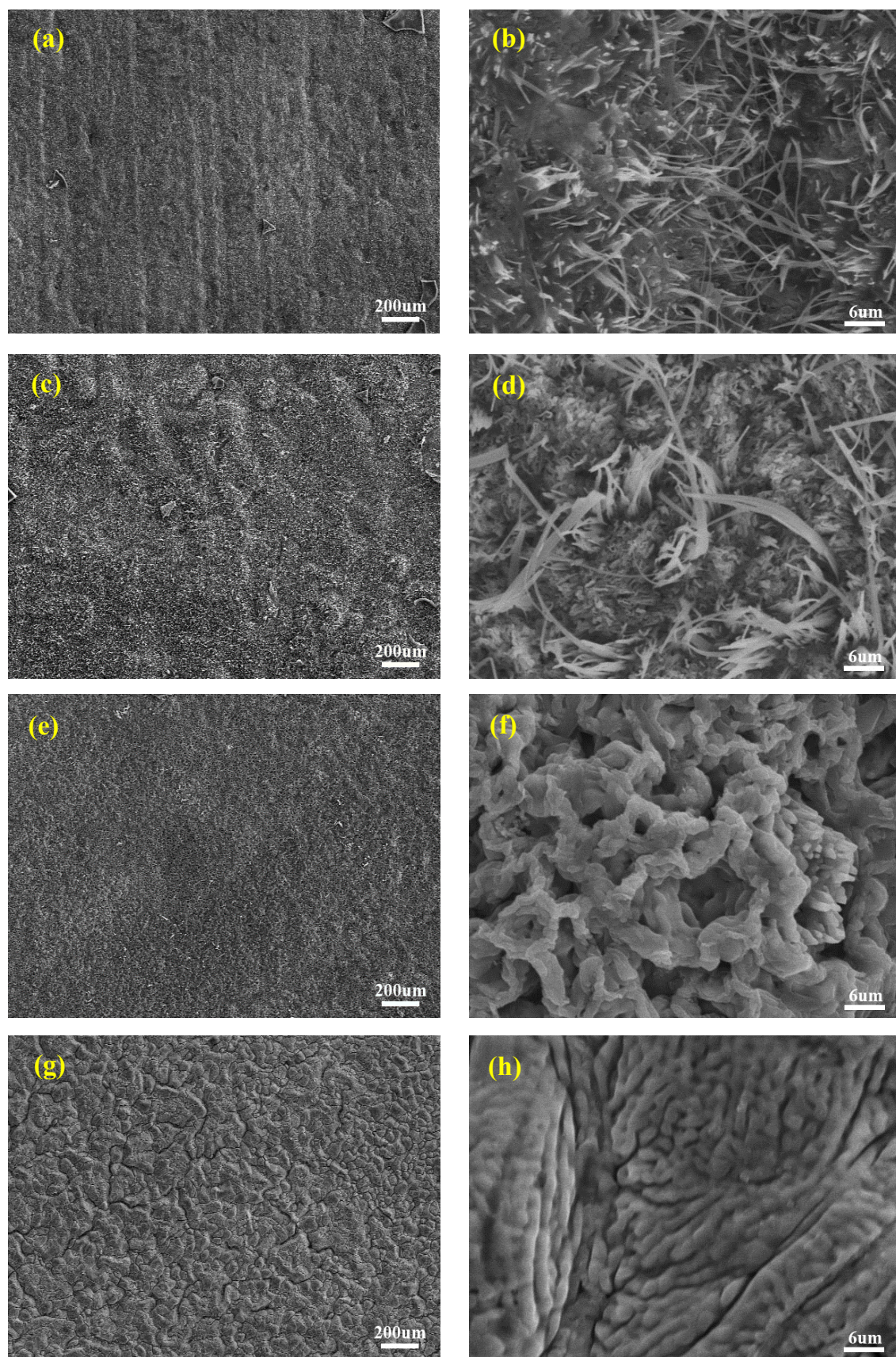


Figure 2. Surface and the corresponding high-magnification SEM micrographs of the $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-3 L}$ coatings sintered at (a,b) 550 °C, (c,d) 650 °C, (e,f) 750 °C and (g,h) 850 °C.

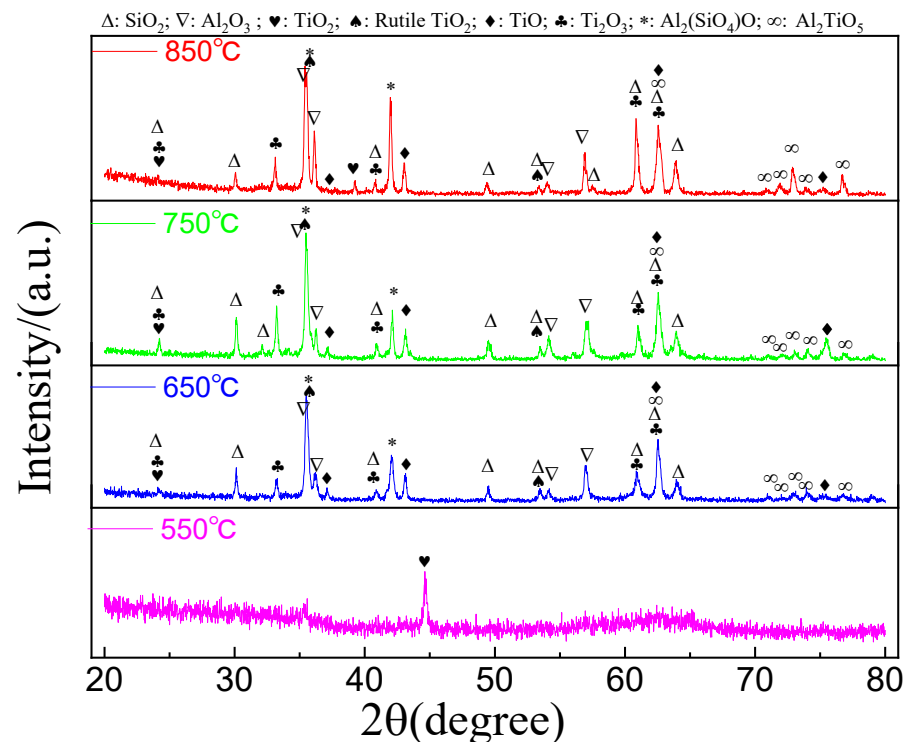


Figure 3. XRD patterns of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ coatings sintered at 550 °C, 650 °C, 750 °C and 850 °C.

Nevertheless, the relative intensities of the peaks of the components are different, which indicates the relative amounts of the crystal phases in every coating are different. It is obvious from Figure 3 that the relative amounts of TiO and Ti_2O_3 in the coatings sintered at 750 °C and 650 °C are higher than that in the coating sintered at 850 °C. Furthermore, the amounts of Al_2O_3 , $\text{Al}_2(\text{SiO}_4)\text{O}$ and Al_2TiO_5 in the coating sintered at 850 °C are higher than that in the coatings sintered at 750 °C and 650 °C. However, the coating sintered at 550 °C presents amorphous phases together with the crystal phase of TiO_2 (PDF 35-0088) located at 44.67° (511).

3.3. Electrochemical Corrosion Behavior

3.3.1. Linear Polarization

Figure 4 depicts the potentiodynamic polarization curves (A~G) of the BS and the composite coatings with different layers and sintered at various temperatures. The self-corrosion potentials (E_{corr}) together with the corrosion current density (i_{corr}) and the approximate polarization resistance (R_p) obtained by Tafel curve fitting are summarized in Table 1. It can be clearly observed from Figure 4 and Table 1 that the self-corrosion potentials of the coatings were more positive than that of the BS, while the corrosion current densities of the coatings were smaller than that of the BS. For instance, the R_p value of the 3 L coating sintered at 850 °C was about $114 \text{ k}\Omega\cdot\text{cm}^2$, which was 110 times that of the BS at the same test conditions. It can be seen from Figure 4 and Table 1 that the corrosion performances were affected by the number and the sintering temperatures of coating layers. For the coatings, the highest E_{corr} (-0.68 V) and R_p ($1449 \Omega\cdot\text{cm}^2$) were attributed to the 1 L coating sintered at 550 °C. In addition, both E_{corr} and i_{corr} decreased while the polarization resistance increased with the number of coating layer and sintering temperature, respectively. The increase in the number of coating layers prevented the corrosion process from extending down to the surface of the substrate and thus improved the corrosion resistance [15].

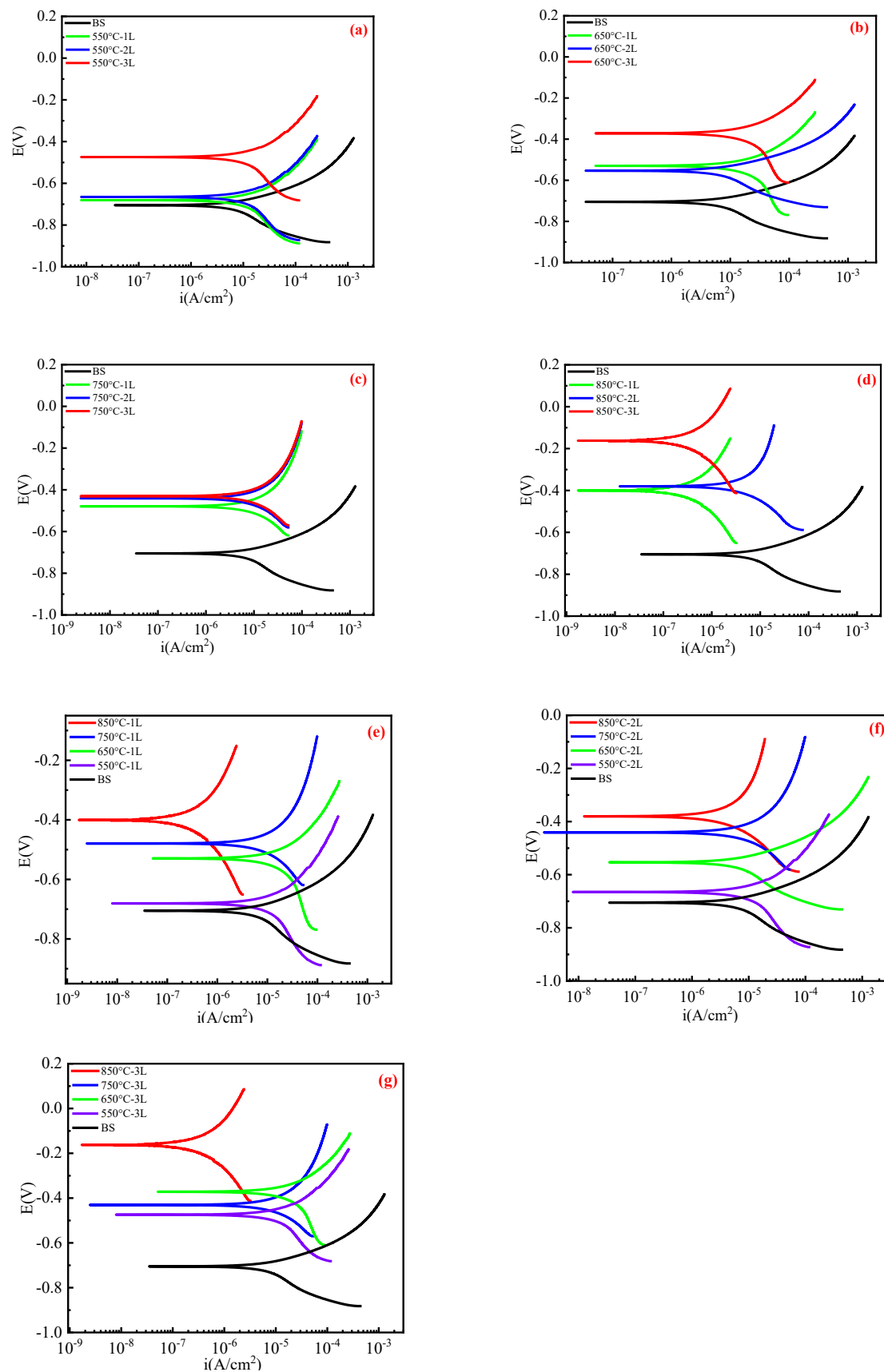


Figure 4. Potentiodynamic polarization curves of Q235 carbon steel and the composite coatings with different layers sintered at various temperatures. (a) 550 °C, (b) 650 °C, (c) 750 °C, (d) 850 °C, (e) 1 L, (f) 2 L and (g) 3 L.

Table 1. Polarization fitting data of the composite coatings in 3.5 (wt) % NaCl solution.

Samples		E _{corr} (V)	I _{corr} (A/cm ²)	R _p (Ω·cm ²)
BS		−0.71	7.7×10^{-8}	1028
550 °C	1 L	−0.68	6.3×10^{-8}	1449
	2 L	−0.67	6.2×10^{-8}	2004
	3 L	−0.47	3.9×10^{-8}	2380
650 °C	1 L	−0.53	5.1×10^{-8}	1362
	2 L	−0.55	5.2×10^{-8}	3352
	3 L	−0.37	3.5×10^{-8}	3358
750 °C	1 L	−0.48	2.5×10^{-9}	1889
	2 L	−0.44	5.6×10^{-8}	7043
	3 L	−0.43	2.4×10^{-9}	8399
850 °C	1 L	−0.40	6.9×10^{-9}	8277
	2 L	−0.34	1.7×10^{-9}	21,213
	3 L	−0.16	1.3×10^{-9}	114,000

Moreover, it can be seen from Table 1 that the 3 L coatings sintered at 550 °C, 650 °C, 750 °C and 850 °C have the lowest corrosion current density and the highest R_p. The corrosion current densities are 3.9×10^{-8} A/cm², 3.5×10^{-8} A/cm², 2.4×10^{-9} A/cm² and 1.3×10^{-9} A/cm², respectively. The corrosion current density is a significant parameter to characterize the corrosion resistance of the samples in salt solution and which is obtained from potentiodynamic polarization curves. In addition, Figure 4e–g displays that the corrosion potential of the coating increased from −0.68 V to −0.16 V with the increase in sintering temperature, indicating better protection from coatings sintered at 850 °C.

It is known that the positive shift in E_{corr} suggests a decrease in the corrosion tendency, and I_{corr} is proportional to the corrosion rate [37]. Lower I_{corr} indicates higher corrosion resistance [38]. The positive shift of E_{corr} and the decrease in I_{corr} indicated that the composite coating is efficient in protecting the Q235 carbon steel substrate from corrosion, and the protection property of the composite coating sintered at 850 °C was better than other temperatures, which was in agreement with the results of the polarization resistance.

3.3.2. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is an important electrochemical technique to provide key information about the polarization resistance of coatings. The resistance of the composite coatings was evaluated using EIS as well. Figure 5 shows that the Nyquist diagrams of EIS for 1 L, 2 L and 3 L coating samples sintered at different temperatures in 3.5% NaCl aqueous solution. The partial views of the impedance diagram were enlarged as the insets of Figure 5b–d. All impedance diagrams show the semicircle diameters of the capacitance arc of the composite coatings are much greater than that of the BS. And the larger diameter of the semicircle corresponds to a larger corrosion resistance [39]. As a result, it indicates that the coatings effectively improved the corrosion resistance of the Q235 carbon steel. Moreover, it can be observed that variation of the number of layers and sintering temperature changed the shape and the radius of the capacitance arc. The radii of the capacitance arc of the coatings enlarged with increasing sintering temperature. Moreover, the composite coatings sintered at 850 °C exhibit the greatest arc radius.

Figure 5a depicts the electrochemical impedance spectra of the coatings sintered at 550 °C. Obviously, two capacitive reactance arcs appeared in the EIS impedance spectra of the 1 L and 2 L coatings. The first (in the high-frequency range) characterizes the geometric capacitance of the porous oxide layer and the electrolyte resistance in the pores. The second arc is located in the low-frequency ranges, which can be attributed to the capacitance of the double electric layer at the interfacial boundary of the dense oxide layer with the substrate and to the charge transfer resistance [40].

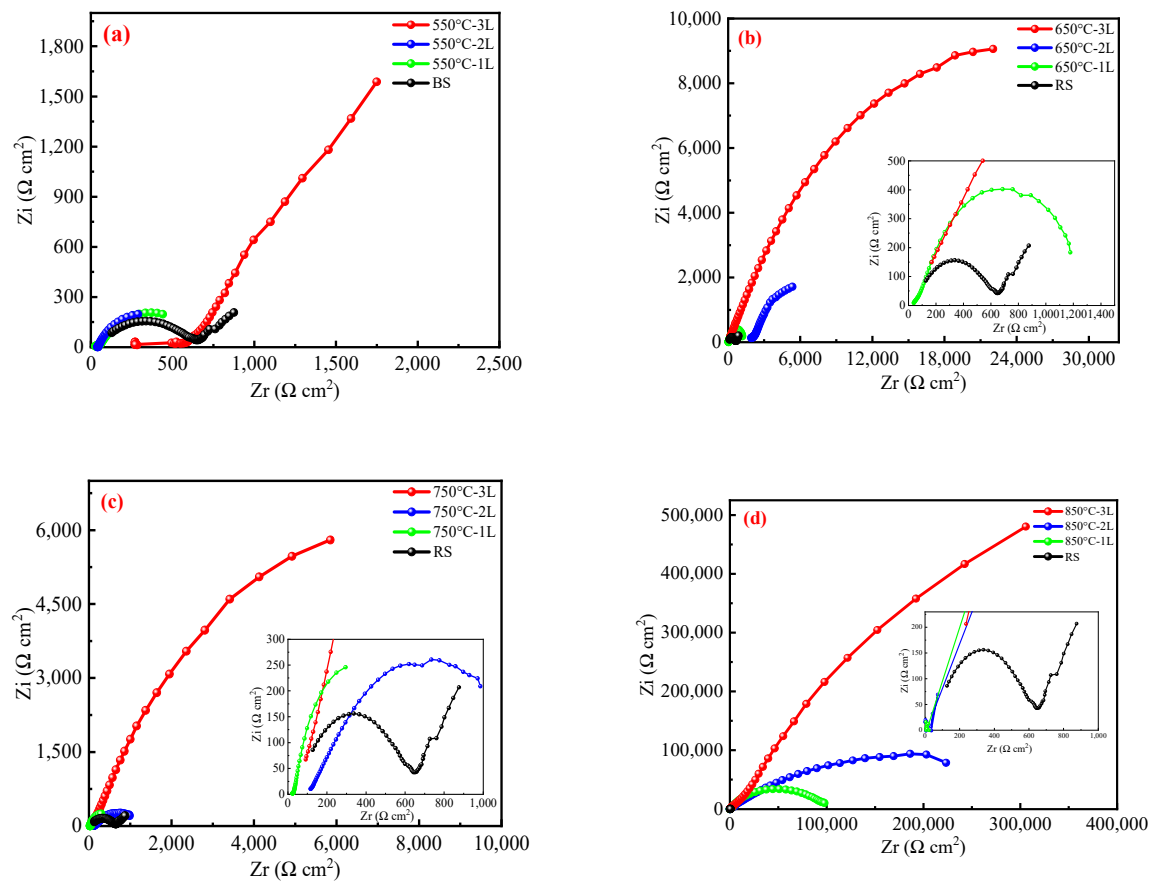


Figure 5. Electrochemical impedance spectra of the 1 L, 2 L and 3 L $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ coatings sintered at different temperatures. (a) 550 °C, (b) 650 °C, (c) 750 °C and (d) 850 °C.

The EIS impedance spectra consist of two time constants, corresponding to the high frequency characteristics and the low frequency characteristics of the protective coatings, which indicated that the corrosion behaviors were controlled by the charge transfer process [41]. It can be observed in Table 2 that the resistance (R_t) of the coating increased with the number of layers.

Table 2. The values of the equivalent circuit elements coinciding with the impedance spectra of composite coatings of 1 L, 2 L and 3 L at different temperatures compared to the BS.

Samples	$R_s (\Omega \cdot \text{cm}^2)$	n1	$R_c (\Omega \cdot \text{cm}^2)$	n2	$R_t (\Omega \cdot \text{cm}^2)$
RS	42.25				589.9
550-1 L	14.92	0.4	44.51	0.7	784.8
550-2 L	39.86	0.8	72.68	0.8	599.2
550-3 L	56.88	0.7	341.8	0.8	6023
650-1 L	32.75	0.6	85.49	0.8	1257
650-2 L	17.94	0.6	686.4	0.7	5398
650-3 L	31.17	0.5	3868	0.7	4684
750-1 L	22.82	0.6	106.9	0.8	916.7
750-2 L	10.42	0.5	426.1	0.5	1178
750-3 L	56.15	1	4005	0.7	41,510
850-1 L	24.59	0.7	5505	0.9	97,840
850-2 L	25.63	1	13,360	0.6	360,300
850-3 L	28.28	0.7	15,580	0.9	1,874,000

There is only one time constant on the EIS impedance spectra of the 3 L coating. The 3 L coating acted as a shielding layer to effectively isolate the direct contact between the corrosive medium and the substrate and thus protected the substrate from corrosion. It can also be observed from Figure 5b–d that the impedance spectrum radii of the capacitance arc of the 3 L coatings are higher than those of the other coatings sintered at the same temperature. The number of layers has a great influence on the corrosion resistance of the substrate.

Figure 5d shows that the Nyquist diagram of the coatings sintered at 850 °C has a larger circular diameter, which indicates that the coating effectively inhibits the invasion of corrosive ions to a certain extent and thus the coating protects the substrate from corrosion. Finally, it can be concluded that the Nyquist diagrams obtained by EIS test are largely consistent with the linear polarization results.

There are two appropriate equivalent circuits that were consistent with the results of the coating impedance test and that were used for the EIS data model of the coated samples and BS in Figure 6. Figure 6a is the equivalent circuits for the uncoated sample (BS); R_s , R_c and Q_1 are the solution resistance, the polarization resistance and a constant phase element (Q_1), respectively, whereas the equivalent circuit (Figure 6b) was utilized to measure the corrosion resistance of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ coated samples, which consists of the solution resistance (R_s), the series resistance (R_c), the coating charge-transfer resistance (R_t) and the capacitance (Q_2). Usually, the phase angle element Q is used instead of the capacitor C to obtain a higher fitting result. Table 2 displays the results of all samples obtained from ZSimpWin3.3[®] software. The fluctuation of R_s is small in Table 2; it indicates that the test system is in a relatively stable state. The R_c and R_t values gradually increased with the growth of the number of layers, indicating that the corrosion rate of 3 L coatings is lower than other layers. Where n is between 0–1 that means the behavior of the constant element is resistance–capacitance behavior. The 3 L composite coating sintered at 850 °C displayed the largest R_t value among all the coatings (Table 2), and the R_t is about 3×10^3 times that of the uncoated coating. It can be concluded that this is the best corrosion resistance verified by these electrochemical tests in this study.

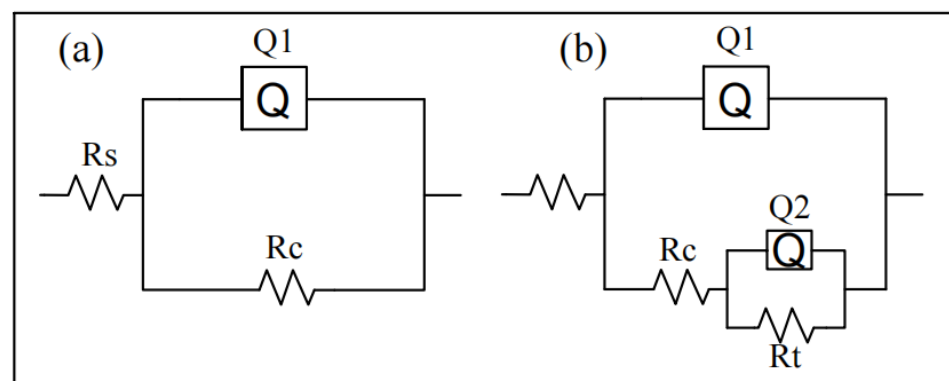


Figure 6. Equivalent electrical circuits for impedance data: BS and 1 L, 2 L and 3 L composite coatings sintered at different temperatures. (a) the equivalent circuits for uncoated sample BS, (b) the equivalent circuit for coated samples.

3.4. Friction Resistance Analysis

Figure 7 shows the change of friction coefficient of different coatings and BS with time. It can be seen from Figure 7 that the friction coefficient fluctuates during the first 200 s and then achieves dynamic balance afterwards. In addition, the friction coefficient of the coatings were less than that of the BS. The average friction coefficient of the BS is about 0.64, while the average friction coefficient of 550 °C–3 L, 650 °C–3 L, 750 °C–3 L and 850 °C–3 L coatings were approximately 0.41, 0.39, 0.37 and 0.36, respectively. It can also be seen from Figure 7 that the friction coefficient decreased with the increase in temperature. During

the friction process, when the steel ball slid on the coating surface, the contact between the friction pairs was stable. The steel ball barely jumped, and the friction coefficient fluctuated stably. When sliding on the BS surface, the steel ball jumped obviously, and the friction coefficient fluctuated greatly.

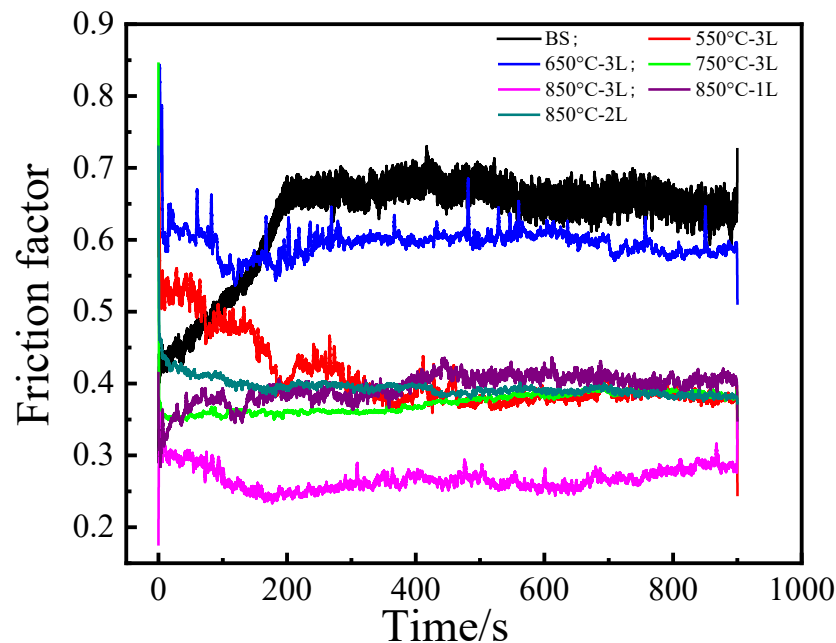


Figure 7. Friction coefficient curves of 3 L composite coating sintered at different temperatures and BS.

Figure 7 depicts that the friction coefficient decreases with the increase in the number of layers. For the 850 °C–1 L, 850 °C–2 L and 850 °C–3 L coatings, the average friction coefficients were about 0.40, 0.39 and 0.36, separately. From the point of view of the coefficient of friction, the smaller the coefficient of friction, the better the surface friction. Therefore, the friction performances of the coatings are better than that of the BS, and the 850 °C–3 L coating has the best friction performance.

3.5. Immersion Experiment

In order to test the anti-corrosion effect of the composite coating on Q235 steel, the sample of 3 L coatings sintered at 850 °C were completely immersed in 3.5% NaCl solution for 0 h, 24 h, 48 h, 168 h and 336 h. Figure 8 shows the AC impedance spectra of the coatings after being immersed for different times. It can be seen from Figure 8 that the coating resistance decreases slightly with the prolongation of the immersion time. After being immersed for 336 h, the impedance radius of the coating became slightly larger, and the performance of the coating shielding corrosion medium was enhanced. The possible reason is a slight adsorption of H₂O into the coatings therefore forming chemical bonding and chemical adsorption, blocking the micropores and permeation channels. Due to the permeation route of water, oxygen and other corrosive ions through the nanopolymer particles is extended, increasing the resistance of the medium to further diffuse into the coating. Usually, the size of the capacitive reactance arc radius reflects the size of the charge transfer resistance in the electrochemical corrosion process. The larger the capacitive arc radius with the larger the charge transfer resistance, the better the corrosion resistance of the material [42]. From Figure 8, the radius of the impedance spectrum before and after soaking has not changed obviously, indicating that the coating surface after immersion still has good corrosion resistance.

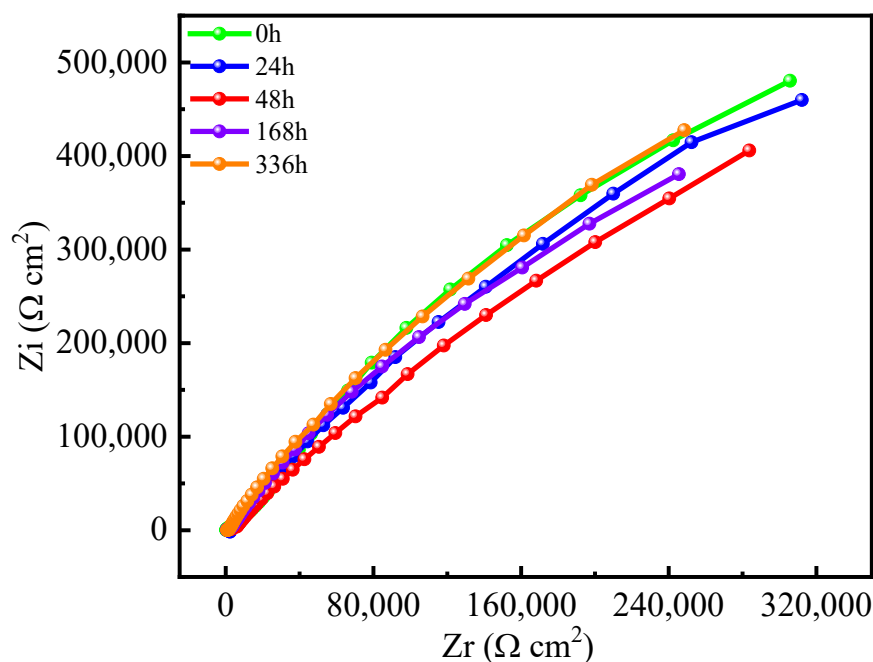


Figure 8. Electrochemical impedance spectra of 850 °C-3 L-TiO₂-SiO₂-Al₂O₃ coating soaked and unsoaked in 3.5%NaCl.

4. Conclusions

The study obtained the optimum parameters for the preparation of TiO₂-SiO₂-Al₂O₃ coatings on carbon steel by studying the effect of different sintering temperatures and number of layers on the composite coatings. And the surface morphology, corrosion resistance and friction properties of the TiO₂-SiO₂-Al₂O₃ composite coatings were investigated.

The SEM shows that the sintering temperature influenced the microstructural changes on the surface of the composite coating. With the increase of the sintering temperature, the coating surface gradually became denser, and the porosity decreased.

The XRD analysis of the coating fully verified that the coating sintered at 550 °C presents amorphous phases, while the main components are the same in the coatings sintered at 850 °C, 750 °C and 650 °C.

The corrosion resistance tests show that the increase in the number of coating layers also improves the corrosion resistance. The potentiodynamic electrochemical polarization tests indicated that all coatings had an apparent improvement in corrosion resistance as compared to the BS. The immersion experiments confirmed that the coating still had excellent corrosion resistance when immersed in 3.5% NaCl solution for 336 h. The coating successfully acted as a physical and electrochemical protective barrier to prevent the corrosion of the steel substrate. The 3 L TiO₂-SiO₂-Al₂O₃ composite coating at 850 °C greatly enhanced the polarization resistance to be 114 kΩ·cm², much bigger than naked Q235 carbon steel.

Under dry friction conditions, the 3 L TiO₂-SiO₂-Al₂O₃ composite coating at 850 °C had the smallest friction coefficient. It was 0.36, and lower than the substrate under the same conditions. The coating can effectively act as friction resistance.

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