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Electrochemical Behavior of in Situ TiB Reinforced Titanium Matrix Composites

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Abstract

Titanium matrix composites have received a lot of attention in automotive and aerospace due to their excellent properties. One of the main challenges in using titanium matrix composites is the effect of enhancing relative corrosion resistance. In this paper, the electrochemical polarization experimental method was used to comparatively study the electrochemical corrosion behavior of matrix pure titanium, 2.5 v.% TiB/Ti composites, and 5 v.% TiB/Ti composites in 0.1M NaOH and 0.1M H_2SO_4 solutions at room temperature. The corrosion rate of the titanium matrix composites was calculated by determining the corrosion current density from an extrapolated Tafel curve, and the composites were further analyzed by electrochemical impedance spectroscopy. The results show that the electrochemical corrosion resistance of titanium matrix composites in corrosive solution decreases with the increase of TiB reinforcing phase content, and the electrochemical corrosion resistance in 0.1M H_2SO_4 is poor, and the corroded composites have corrosion craters with pore formation on the exposed surface.

Keywords

Titanium Matrix Composites; TiB Reinforced Phase; Electrochemistry; Corrosion.

1. Introduction

Titanium matrix composites have broad application prospects in aerospace and automotive industries due to their high specific strength, high specific stiffness, abrasion and high temperature resistance as well as excellent fatigue and creep resistance[1,2]. Which in the electrochemical corrosion or even electro-oxidation conditions, such as in the marine environment or wastewater treatment environment, easy to occur electrochemical corrosion, its corrosion will cause its corrosion will cause very large economic losses, waste of natural resources and serious environmental pollution, but also greatly reduce its service life and increase the cost of use[3]. However, in recent years researchers have been focusing on their preparation process and mechanical properties, which has been neglected because titanium alloys inherently have better corrosion resistance than other commonly used metals. The corrosion resistance of titanium matrix composites is affected by a wide range of factors, including porosity[4], precipitation of impurity phases[5], composition of the matrix[6], type, size, and content of the reinforcing phases[7], high-density dislocations at the interface between the reinforcing body and the matrix[8], and products of interfacial reactions[9]. With the rapid development of industry, the application of titanium matrix composites will certainly face a more complex and demanding use of the environment, on this basis, it is necessary to explore the electrochemical corrosion performance of titanium matrix composites in acid and alkali solutions, in order to promote the rational use of them, and to develop the corresponding protective measures. However, there are fewer studies on the electrochemical corrosion behavior and properties of in situ TiB reinforced titanium matrix composites. Therefore, the study of electrochemical corrosion performance of titanium matrix composites is one of the inevitable trends in the development of titanium matrix composites applications.

Therefore, in this paper, the electrochemical behavior of titanium matrix composites in 0.1 M NaOH, 0.1 M H_2SO_4 at room temperature environment was mainly investigated by comparing the effect of different TiB reinforcing phase content on the electrochemical corrosion performance of titanium matrix composites. The mechanism affecting the corrosion behavior is explored through the morphological study, which can provide a reference for the rational application and further design of titanium matrix composites in the marine environment or wastewater treatment environment, as well as the development of corresponding protective measures.

2. Experimental Materials and Methods

TiB/Ti composites were prepared by fusion casting method and hot rolling process with commercially pure titanium as matrix material. Fine TiB_2 (3 μm) and high purity titanium powder (3 μm) were used as raw materials for the preparation of the composites[9].

$$Ti+TiB_2 \rightarrow 2TiB. \quad (1)$$

Electrochemical testing is the most widely used technique for corrosion studies in the laboratory and in real structures. In this experiment, a GAMRY Interface 1000 electrochemical workstation was used to measure the kinetic potential polarization curves of titanium matrix composites. The size of the sample is 10 mm x 10 mm x 2 mm. Before the test, use 200~1500# sandpaper to sand the sample step by step to remove the oxidized layer, and make sure the test surface is flat and smooth. The wires were then adhered to the back of the specimen using conductive adhesive, and epoxy resin was used to wrap the sample around the perimeter, exposing only the bottom surface with an area of 1 cm^2. A three-electrode system, consisting of a working electrode (sample), a reference electrode (saturated calomel electrode) and an auxiliary electrode (metal platinum sheet), was used for this test, which was tested in 0.1 M NaOH, 0.1 M H_2SO_4 baths in a room temperature environment. At the beginning of the test, no current is loaded, and when the open circuit potential changes with time not more than 10mV/3min, it can be determined that the system has been in a stable state, and maintain this state for 1.8ks to obtain the self-corrosion potential (Ecorr) of the alloy. Dynamic potential polarization curves were measured at a constant temperature of 27°C. Scanning speed: 1mV/s, scanning range: -0.5~2V.

3. Experimental Results and Discussion

3.1 Electrochemical Behavior in 0.1 M NaOH

3.1.1 Kinetic Potential Polarization

Figure 1 shows the test curves (Tafel curves) of the kinetic potential polarization of the matrix, 2.5 v.% TiB/Ti composite, and 5 v.% TiB/Ti composite in 0.1 M NaOH at room temperature. The kinetic potential polarization process in a typical Tafel curve includes a cathodic polarization zone, an anodic polarization zone, an activation transition zone, a passivation zone, and an over-passivation zone; however, the Tafel curves of matrix pure titanium and titanium matrix composites consisted of cathodic polarization, anodic polarization, and passivation zones, and had no obvious activation transition zone or over-passivation zone. This indicates that the passivation films of the matrix pure titanium and the composites can be formed rapidly and are difficult to dissolve, and that the materials have similar cathodic polarization branches, showing the reduction kinetics of dissolved oxygen, and the materials are mainly subjected to the erosion of OH^-[10]. The shapes of the kinetic potential polarization curves of the materials are basically similar, indicating that their kinetic potential polarization behaviors are similar, and the incorporation of TiB reinforcing phase did not significantly change the polarization behaviors of the composites, whereas the positions of the polarization curves on the axes change with the content of TiB reinforcing phase. In the linear phase of the anodic and cathodic curves, the Tafel extrapolation method was used to fit the kinetic potential polarization curves, and the intersection point of the cathodic polarization tangent and the anodic polarization tangent was usually taken as as the corrosion potential (Ecorr) and corrosion current (Icorr), and the corrosion current density (Icorr) and the self-corrosion potential (Ecorr) of the oxide layer of the surface of the composite material after the fitting were shown in Table 1. Ecorr is the thermodynamic corrosion trend, icorr is the kinetic corrosion trend, and the corrosion current density is usually used as an important parameter for evaluating the kinetics of corrosion reaction. The correlation study of self-corrosion potential shows that the larger the absolute value of corrosion potential and the larger the corrosion current density, the faster the corrosion rate and the worse the corrosion resistance[11].

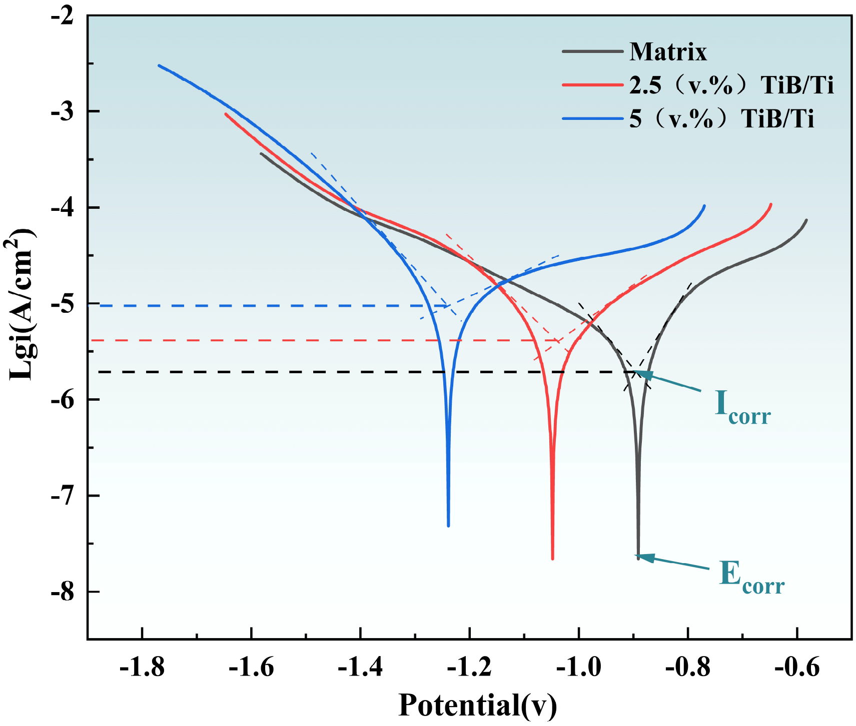

Figure 1. Kinetic potential polarization curves of matrix, 2.5 v.% TiB/Ti, and 5 v.% TiB/Ti composites

The electrochemical parameters of the matrix pure titanium and composite in 0.1 MNaOH can be seen in Table 1. Open-circuit potential refers to the potential of the working electrode compared to the reference electrode in the case of an open (broken) circuit; the more positive the open-circuit potential, the smaller the corrosion tendency. The open-circuit potentials of matrix pure titanium, 2.5% TiB/Ti, and 5% TiB/Ti were finally stabilized to -1.108 V, -1.168 V, and -1.270 V, respectively. 5% TiB/Ti exhibited the most negative potentials, probably due to the fact that the most defects on the surface were generated during the electrochemical corrosion process, which made it easy for the corrosive elements to penetrate the passivation film and to further corrode with the substrate material, to The corrosion ability of the composite material is reduced. The self-corrosion potentials of matrix pure titanium, 2.5 v.% TiB/Ti composites, and 5 v.% TiB/Ti composites were -0.897V, -1.051V, and -1.238V, respectively, and the composites showed a decrease in corrosion potentials compared to matrix pure titanium. In addition to this, the corrosion currents of the matrix pure titanium, 2.5 v.% TiB/Ti composites, 5 v.% TiB/Ti composites were 2.319x10-1 μv.cm^{-2},4.925x10-1 μv.cm^{-2},1.301 μv.cm^{-2}, respectively. The corrosion of the 5 v.% TiB/Ti composites was accelerated by nearly 6 times compared with that of the pure titanium substrate, and the corrosion rate was the fastest. The above studies show that matrix pure titanium has the best electrical corrosion resistance, corrosion current density increases with the increase of TiB reinforced phase content, the corrosion rate accelerates, the worse the corrosion resistance. Because the TiB reinforced phase joins, refines the grain, increases the composite material grain boundary and phase boundary, at the same time TiB reinforced phase is non-conducting body, hinders the formation of the material itself complete passivation film, makes the TiB reinforced titanium matrix composites corrosion resistance is reduced[12].The higher the content of TiB reinforced phase, leads to the more serious interfacial defects of the composite material, the surface of the material accelerates the corrosion process.

Table 1. Electrochemical parameters of matrix pure titanium, 2.5 v.% TiB/Ti, 5 v.% TiB/Ti in 0.1 M NaOH

0.1M NaOH	EOCP(V)	Ecorr(V)	Icorr(μv.cm^{-2})
Matrix	-1.108	-0.891	2.319x10-1
2.5%TiB/Ti	-1.168	-1.051	4.925x10-1
5%TiB/Ti	-1.270	-1.238	1.301

3.1.2 Electrochemical Impedance Spectroscopy

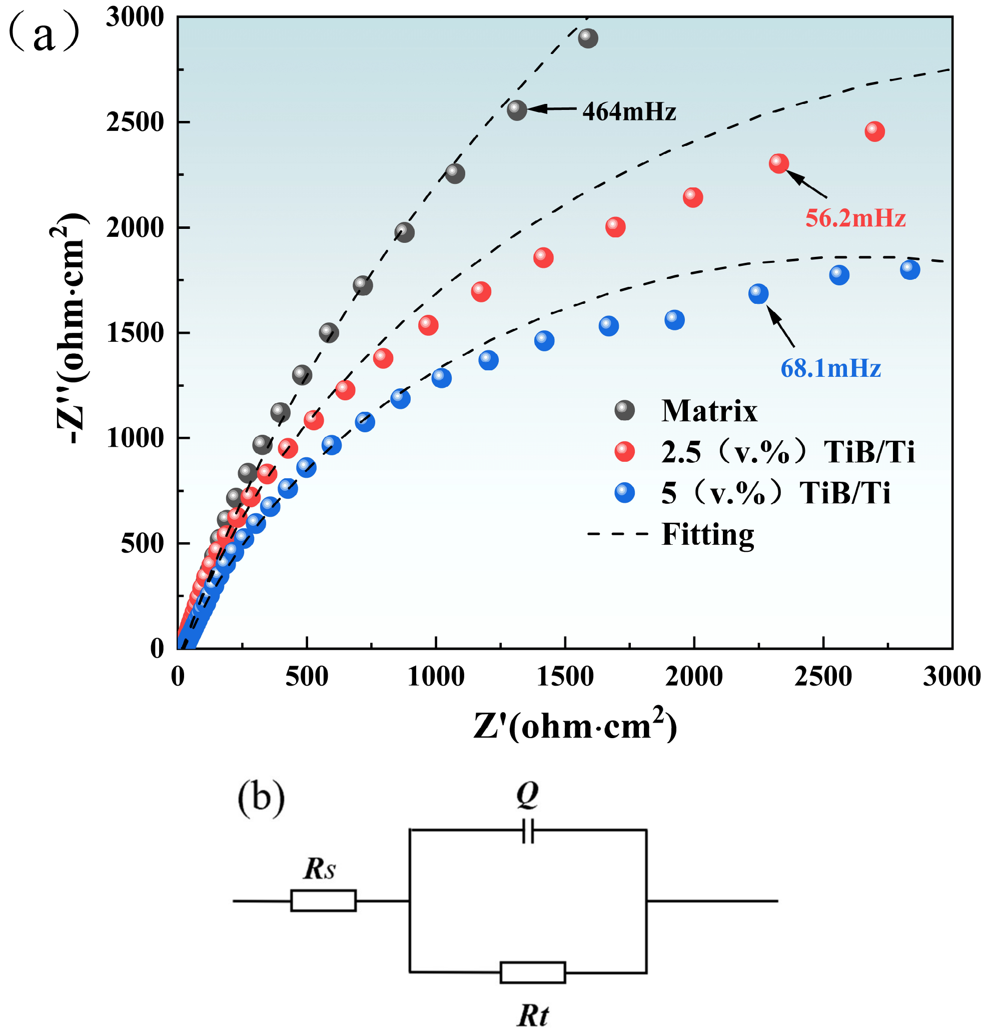

Figure 2. Nyquist curves and equivalent circuit diagrams of the matrix, 2.5 v.% TiB/Ti composite, and 5 v.% TiB/Ti composite in 0.1 M NaOH solution

In order to further confirm the polarization results, the EIS was fitted by ZsimpWin software according to the equivalent circuit model shown in Figure 2(b).The fitted electrochemical impedance spectroscopy measurement curves are shown in Figure 2(a),which mainly investigates the passivation behavior of the electrode surface as well as the charge transfer mechanism at the electrode-solution interface. Due to the large time constant, the entire capacitive resistance arc could not be measured, thus all the samples showed the typical semicircular arc characteristics of titanium matrix composites and some deviations of the Nyquist plots from the ideal values could be due to the frequency dispersion, the inhibitor adsorption, and the degree of inhomogeneity of the Ti surface. Among them, the capacitive arc resistance of matrix pure titanium is the largest, and the capacitive arc resistance is the smallest when the TiB content is 5%, and the capacitive arc resistance tends to decrease with the increase of TiB content. It is well known that the arc diameter of the capacitive resisting arc reflects the polarization resistance, and in general, the larger the polarization resistance, the stronger the hindering effect on the electric charge, and the better the corrosion resistance[13]. Therefore, the corrosion resistance of TiB/Ti composites is lower than that of the matrix pure titanium as shown by electrochemical experiments in 0.1 M NaOH at room temperature, and the electrochemical corrosion resistance decreases with the increase of TiB content.

3.1.3 Microscopic Morphology

After electrochemical corrosion of titanium matrix composites in 0.1M NaOH solution, the surface microscopic morphology of the specimen is shown in Figure 3, Figure 3 (a) can be seen, NaOH solution on the matrix of pure titanium has a slight erosion, the surface is only visible in the slight corrosion, corrosion of the surface of the existence of trace corrosion pits as well as shallow pores, the surface passivation film is more intact, and better prevented from being further corroded. In comparison, as shown in Figure 3(b)(c), the surface of 2.5 v.% TiB/Ti and 5 v.% TiB/Ti composites is eroded by NaOH solution to a certain extent, resulting in the existence of certain corrosion pits and pores on the surface of the material, in which the damage to the passivation film on the surface of 5 v.% TiB/Ti composites is more obvious, and there are larger corrosion pits and pores on the surface. Corrosive elements can enter through the surface passivation film defects, and further contact with the substrate material, corrosion reaction, corrosion rate accelerated, the material corrosion performance is reduced. It was shown that in room temperature 0.1 M NaOH electrochemical solution, the surface corrosion of the material intensified with increasing TiB content, the corrosion rate accelerated and the corrosion performance decreased.

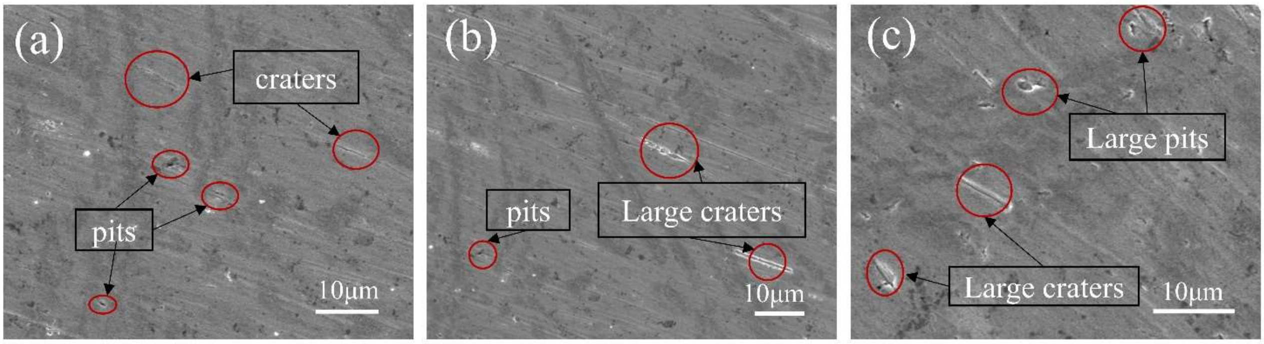

Figure 3. SEM images of electrochemical corrosion surfaces in 0.1M NaOH: (a) substrate pure titanium (b) 2.5 v.% TiB/Ti (c) 5 v.% TiB/Ti

3.2 Electrochemical Behavior in 0.1 M H_2SO_4

3.2.1 Kinetic Potential Polarization

The kinetic potential polarization curves of the matrix, 2.5 v.% TiB/Ti, and 5 v.% TiB/Ti in 0.1 M H_2SO_4 at room temperature are shown in Figure 4. The similar shapes of the kinetic potential polarization curves of the titanium matrix composite materials indicate that their kinetic potential polarization behaviors are similar, and the incorporation of TiB reinforcing phase did not significantly change the polarization behaviors of the titanium matrix composites, whereas the position of the polarization curves on the axes changed with the change of TiB content. The anodic portion of the polarization curve for matrix pure titanium shows a region of small amplitude oscillations beyond which the current density increases indicating the onset of pitting, however for composites the current density increases even at low overpotentials indicating that titanium matrix composites are more prone to pitting than matrix pure titanium[14]. Compared to the polarization behavior in 0.1M NaOH, the material shows more active dissolution in 0.1MH2SO4, which is due to the fact that the corrosion in 0.1M H_2SO_4 is induced by H^+ and SO_4^{2-}, which makes the material more severely eroded.

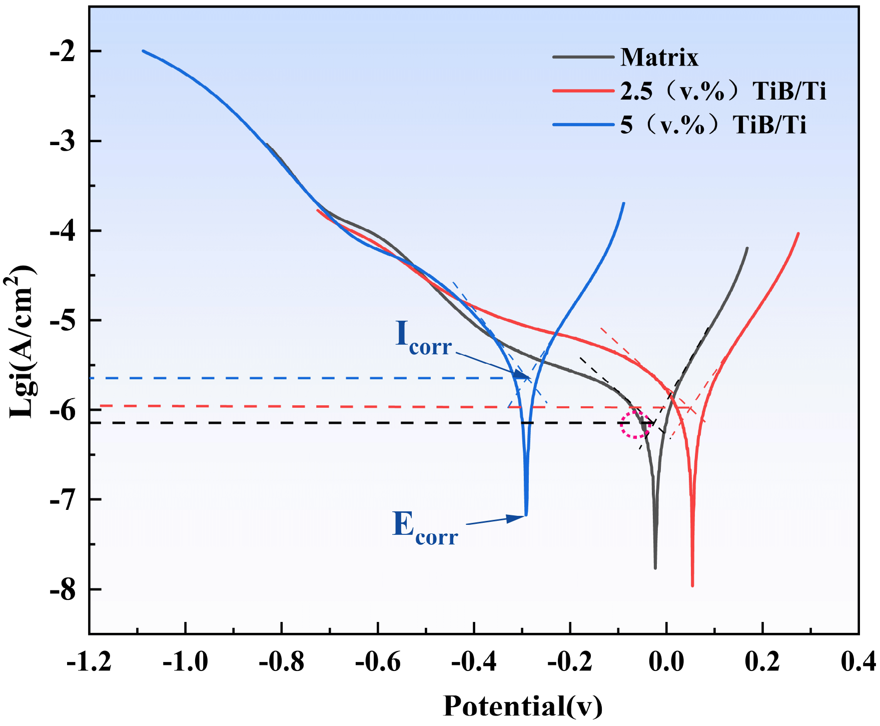

Figure 4. Kinetic potential polarization curves of matrix, 2.5 v.% TiB/Ti, and 5 v.% TiB/Ti composites

At the linear stage of the anodic and cathodic curves, Tafel extrapolation was used to fit the kinetic potential polarization curves, and the fitted surface corrosion current densities (icorr) and self-corrosion potentials (Ecorr) of the composites are shown in Table 3. As can be seen in Table 3, the substrate pure titanium, 2.5% TiB/Ti, and 5% TiB/Ti open-circuit potentials were eventually stabilized at -0.226V, -0.332V, and -0.389V, respectively. Among them, 5% TiB/Ti exhibits the most negative potentials, probably due to the fact that the most defects are generated on the surface during the electrochemical corrosion process, which makes it easy for the corrosive elements to penetrate the passivation film and have further corrosion reactions with the matrix material, reducing the corrosion capacity of the composites. The self-corrosion potentials of matrix pure titanium 2.5 v.% TiB/Ti composites, 5 v.% TiB/Ti composites were classified as -0.023V, 0.054V, -0.291V, as can be seen from the corrosion current densities in Table 3. The corrosion currents of matrix pure titanium, 2.5 v.% TiB/Ti and 5 v.% TiB/Ti were 3.334x10-1 $\mu v.cm^{-2}$, 1.085 $\mu v.cm^{-2}$, and 2.365 $\mu v.cm^{-2}$, respectively, in which the corrosion of 5 v.% TiB/Ti composites was accelerated by nearly 7 times compared with that of matrix pure titanium with the fastest corrosion rate. The above studies show that the matrix pure titanium has the best electrical corrosion resistance, the corrosion current density increases with the increase of TiB reinforced phase content, the corrosion rate is accelerated and the corrosion resistance is worse.

Table 2. Electrochemical parameters of matrix pure titanium, 2.5 v.% TiB/Ti, 5 v.% TiB/Ti in 0.1 M H_2SO_4

0.1M H2SO4	EOCP(V)	Ecorr(V)	Icor(μv.cm^{-2})
Matrix	-0.226	-0.023	3.334x10^{-1}
2.5%TiB/Ti	-0.332	0.054	1.085
5%TiB/Ti	-0.389	-0.291	2.365

3.2.2 Kinetic Potential Polarization

In order to further confirm the polarization results, according to the equivalent circuit model shown in Figure 5(b), where Rs is the solution resistance, Rt is the equivalent polarization resistance corresponding to the capacitive arc, and Q is the constant-phase-angle element corresponding to the capacitive arc,the EIS was fitted by the ZsimpWin software, and the fitted electrochemical impedance spectroscopy measurement curves are shown in Figure 5(a). Due to the large time constant, it was not possible to measure the entire capacitive resistance arc, thus all samples showed the typical semicircular arc characteristic of titanium matrix composites, with the largest capacitive resistance arc in matrix pure titanium. The capacitive arc resistance is minimized when the TiB content is 5%, and tends to decrease with the increase of TiB content. Therefore, the electrochemical corrosion resistance of TiB/Ti composites is lower than that of the matrix pure titanium and decreases with the increase of TiB content.

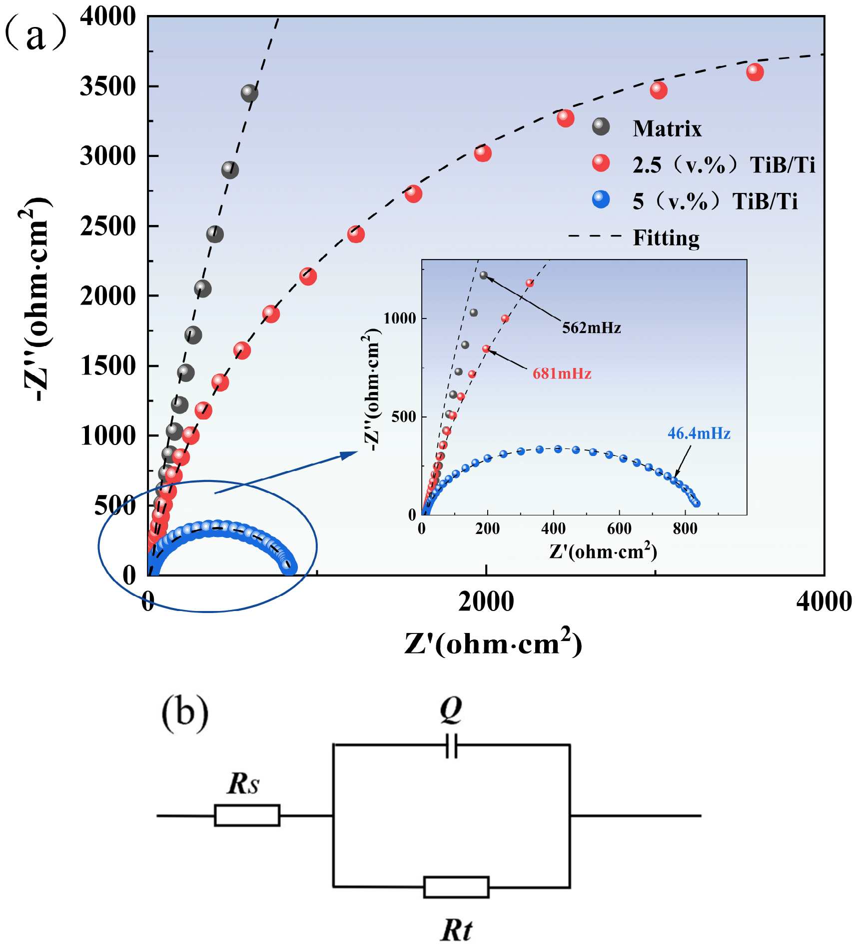

Figure 5. Nyquist curves and equivalent circuit diagrams of the matrix, 2.5 v.% TiB/Ti composite, and 5 v.% TiB/Ti composite in 0.1 M H_2SO_4 solution

3.2.3 Microscopic Morphology

After electrochemical corrosion of titanium matrix composites in 0.1M H_2SO_4 solution at room temperature, the surface microscopic morphology of the specimen is shown in Fig ure 6, Fig ure 6(a) shows that the H_2SO_4 solution has a more serious erosion of the matrix pure titanium, the surface is visible as a more serious corrosion, the existence of more corrosion pits as well as deeper porosities, and the surface passivation film is severely damaged compared to the corrosion in 0.1M NaOH, and the matrix is further corroded. As can be seen in Figure 6(b)(c), the surfaces of 2.5 v.% TiB/Ti and 5 v.% TiB/Ti materials are also more severely eroded by the H_2SO_4 solution, resulting in numerous and large corrosion pits and pores on the surfaces. Among them, 5 v.% TiB/Ti composites have the most serious damage to the surface passivation, corrosive elements enter through the defects of the surface passivation film, contact with the substrate increases, more corrosive reactions occur, the corrosion rate is accelerated, and the corrosion performance is reduced. It was shown that in 0.1 M H_2SO_4 electrochemical solution, with the increase of TiB content, the surface corrosion of the material was intensified, the corrosion rate was accelerated, and the corrosion performance was reduced. And compared with 0.1M NaOH, the corrosion rate of titanium matrix composites in 0.1M H2SO4 is faster, the corrosion morphology is more obvious, and the electrochemical corrosion resistance is worse.

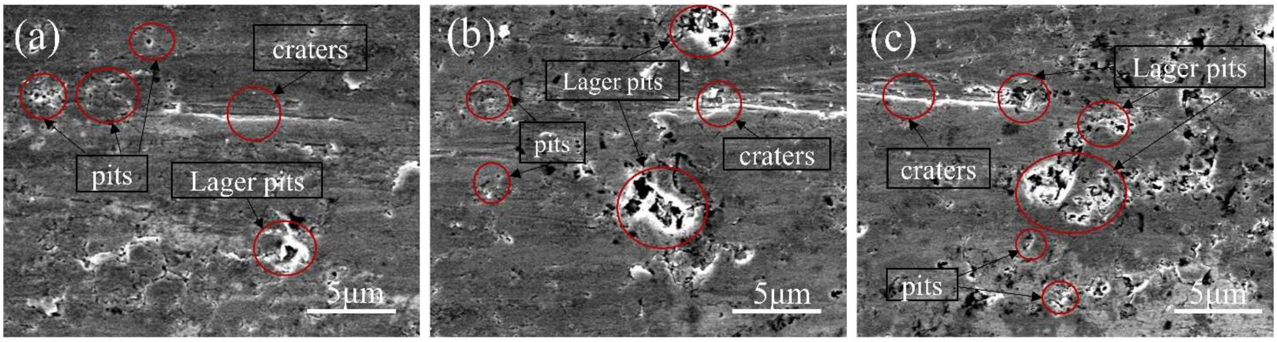

Figure 6. SEM images of electrochemical corrosion surfaces in 0.1M H_2SO_4: (a) substrate pure titanium (b) 2.5 v.% TiB/Ti (c) 5 v.% TiB/Ti

4. Conclusion

In this paper, the electrochemical corrosion method was used to comparatively study the effect of adding different contents of TiB reinforcement to titanium matrix composites on their electrochemical corrosion resistance in 0.1MNAOH and 0.1MH2SO4 solutions at room temperature. The effect on the electrochemical corrosion resistance of titanium-based materials with increasing TiB reinforcing phase content was explored. The electrochemical corrosion resistance of matrix pure titanium was higher than that of in-situ TiB-reinforced titanium matrix composites in 0.1M NAOH and 0.1M H_2SO_4, and the electrochemical corrosion resistance of titanium matrix composites decreased with the increase of TiB content.Compared with 0.1M NaOH, the titanium matrix composites corrode faster in 0.1M H_2SO_4, the corrosion morphology is more pronounced, the electrochemical corrosion resistance is worse, and the damage by hydrogen and sulfate ions is the main influencing factor.

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