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Effect of Voltage on Morphology and Corrosion Behaviour of MAO Ceramic Coatings on Titanium Matrix Composite

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Abstract

Titanium matrix composites have excellent properties and have received a lot of attention in the automotive and aerospace sectors. In this paper, micro-arc oxidised (MAO) TiO_2 films were prepared from titanium matrix composite using an electrolyte with sodium silicate as the main salt. The effects of different applied voltages on the surface morphology, microstructure, phase composition and corrosion resistance of the ceramic coatings were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD) and electrochemical workstations. The results show that after MAO treatment, the coating exhibits a microporous structure, which is mainly composed of Ti phase, anatase and rutile TiO_2 phases. All coating surfaces showed good performance without obvious cracks, and as the voltage increased, the micropores on the coatings became larger and the rutile TiO_2 phase in the coatings increased. The MAO coatings formed at 400 V were the thickest, had a denser surface morphology, the lowest corrosion current density, and the highest corrosion resistance. In summary, the best overall performance of the prepared membrane layer was achieved when the MAO voltage was 400 V.

Keywords

Titanium Matrix Composite; Micro-arc Oxidation; Oxidation Voltage; Corrosion Resistance.

1. Introduction

Titanium (Ti) and its alloys have many excellent properties, including low density, high specific strength, excellent biocompatibility, and relatively low Young's modulus [1]. These excellent properties make titanium and its alloys ideal materials for applications in fields including medical devices, marine, aerospace, etc., and have great potential for future practical applications [2]. However, the relatively poor surface hardness, wear and corrosion resistance, and biological activity of titanium and its alloys greatly limit their use in practice. In recent years, researchers have been focusing on the study of the preparation process and mechanical properties of titanium matrix composites, while neglecting the waste of resources, environmental pollution and economic losses caused by corrosion of the materials under the conditions of use [3].

Among the various treatments, surface treatment has received more attention due to its numerous methods and good performance. Titanium alloys are available in a variety of surface treatments, some of the traditional surface treatments include Micro Arc Oxidation (MAO), Physical and Chemical Vapour Deposition, Magnetron Sputtering, Sol-gel, etc [4]. In the field of material surface treatment, the traditional surface treatment technology has certain limitations, the formation of the coating and the substrate bonding force is not good, it is difficult to achieve the desired anti-corrosion effect.

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And micro-arc oxidation (MAO) technology, as an advanced development of anodic oxidation technology, occupies an important position in material surface modification technology by virtue of its significant unique advantages [5]. MAO is a high-pressure plasma electrolytic oxidation process widely used for surface treatment of titanium, magnesium and aluminium, Micro-arc oxidation technology can grow a layer of rough and porous ceramic oxide coating in-situ on the surface of the substrate, forming an oxide coating with excellent performance, strong bonding between the coating and the substrate, which can be tightly adhered to the substrate surface and can increase the service life of the alloy [6]. The MAO process is favoured as a surface treatment method because of the relative ease and convenience of the equipment used and the simplicity of the operating method. The MAO process has already reached industrial production level and has a very promising application prospect. With the continuous progress of technology and cost reduction, the application of micro-arc oxidation technology is very promising and will be further expanded to more emerging areas. For example, in the field of marine engineering, metal parts of marine equipment can be treated to enhance their resistance to seawater corrosion and the adhesion of marine organisms [7].

In the micro-arc oxidation reaction process, the first step is to select a suitable metal material as the substrate. This is based on the different materials and application requirements, the next step is to choose the right electrolyte composition. For example, in aqueous electrolyte solutions of silicates and phosphates, the electrolyte plays a crucial role. It not only provides ions involved in the oxidation reaction, but also plays a cooling and insulating role in the micro-arc discharge process, which has a key influence on the smooth progress of the micro-arc oxidation reaction and the reaction results [8].

Substrate material and electrolyte are prepared, then the micro-arc oxidation operation is performed. The cleaned substrate material is first put into the electrolyte, in which the metal material is used as anode to connect to the positive pole of the power supply, and the stainless steel plate is used as cathode to connect to the negative pole of the power supply, and then a high voltage is applied. Under the action of high voltage, micro-arc discharges occur on the surface of the material, forming tiny sparks [9].These sparks increase the local temperature of the material surface, which in turn promotes the oxidation reaction. As the oxidation reaction continues to progress, a ceramic film gradually forms on the surface of the material. During the micro-arc oxidation process, the ceramic film grows and repairs itself. The micro-arc discharge will result in the repair of pores and cracks in the oxide film, as well as a denser and more uniform film layer [10]. However, due to differences in process parameters and differences in electrolyte components, the thickness of the resulting coating can be inconsistent. It is worth noting that the intensity of arc discharge and plasma radiation during the micro-arc oxidation reaction changes with the micro-arc oxidation process, which also affects the formation of ceramic film and the quality of the coating to a certain extent [11].

The microscopic morphology, thickness and performance of the coating after treatment with micro-arc oxidation technology are affected by a number of factors, mainly including electrolyte composition, voltage, duty cycle, frequency and time [12]. The most commonly used electrolytes for titanium and its alloys in micro-arc oxide coatings are phosphates, silicates and aluminates. Most of the studies on MAO coatings of titanium matrix composites have been focused on their corrosion resistance and morphological characteristics, and there are few reports in the literature on the effect of voltage on the morphological characteristics and corrosion resistance of MAO coatings of titanium matrix composites [13]. Metal matrix composites are more demanding in terms of the electrical parameters required for surface micro-arc oxidation due to the presence of non-conductor reinforcing phases. Therefore, the feasibility of preparing micro-arc oxidation coatings on the surface of titanium matrix composites still needs to be thoroughly investigated. The presence of reinforcing phases changes the electrical parameter requirements, so it is of great practical significance to continue to explore suitable electrical parameters on the basis of titanium alloy micro-arc oxidation and try to prepare micro-arc oxidised coatings with excellent comprehensive performance on the surface of titanium matrix composites.

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Voltage plays a decisive role in the micro-arc oxidation process and is a key research focus. At lower voltages, the discharge energy is insufficient, coating growth is retarded, and the film layer is thin and underperforms; With the voltage gradually increasing, the coating growth rate gradually becomes faster, the film layer becomes thicker, and the hardness and corrosion resistance, etc. are usually enhanced, and at the same time, it is conducive to the transformation of the substable anatase to the stable rutile. However, when the voltage is too high, the pore size of the film micropores will become larger, the surface roughness will increase, the corrosion resistance may decrease, and even defects such as cracks may appear [14]. Therefore, when micro-arc oxidation is carried out on different metals, the voltage needs to be precisely matched in order to prepare a film layer with excellent performance.

Based on the above background, this chapter prepares the micro-arc oxidation film layer on the surface of titanium matrix composites by the micro-arc oxidation process, and analyses the micro-morphology and physical phase composition of the micro-arc oxidation film layer with sodium silicate electrolyte as the main salt to investigate the morphology and corrosion performance of the micro-arc oxidation coatings formed under different applied voltages.

2. Material and methods

2.1 Sample Preparation

The TiB/Ti composite (TMC) specimens were cut into Φ14 mm × 2 mm discs using a wire-cutting machine, and the surface of the samples was polished with 400 #, 800 #, 1500 #, and 2000 # SiC sandpaper, and then ultrasonically cleaned for 10 minutes with alcohol and deionised water, respectively, and then dried and set aside. TMCs were prepared in silicate ($NaSiO_3$ + KF + NaOH) electrolyte keeping the same parameters to prepare different MAO film layers with the dosage of 8, 1.5, and 2 g/L of the three electrolytes, respectively. Subsequently, micro-arc oxidation treatment was carried out with the sample as the anode and the stainless steel plate as the cathode, with a duty cycle of 20%, a frequency of 500 HZ, and a time of 10 min, to study the corrosion resistance of MAO-modified titanium matrix composite under constant pressure conditions. The nomenclature of the MAO film layers formed at different applied voltages is shown in Table 1, and the voltages were set to 250 V, 300 V, 350 V, 400 V, and 450 V in that order.

Table 1. Nomenclature of MAO coated specimens formed at different voltages

voltage(V)	Name
250V	V1
300V	V2
350V	V3
400V	V4
450V	V5

2.2 Characterization

The phases on the surface of the samples were analysed using a diffractometer (called XRD, D8 ADVANCE) with a scanning angle 2θ ranging from 20 ~ 80° and a scanning speed of 6°/min. The coated sections were sprayed with gold using a coating machine (Q150TES, Quorum) for subsequent observation. The surface and cross-sectional morphology of the samples were observed by scanning electron microscopy (called SEM, Quanta FEG 450). The corrosion resistance of the MAO-treated surface oxide layer was tested using an electrochemical workstation (CHI660E).

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3. Results and Discussion

3.1 Surface Morphology of MAO Coatings

Figure 1 shows the surface morphology of MAO coatings at different voltages. From the SEM image, it can be seen that the surface of the coating is rough and uneven, with a large number of 'crater' type holes distributed, showing a typical porous structure [15]. As the voltage increases, the pore size of the micropores increases and the number decreases significantly. V1 micropores were the smallest in diameter and had pitted surfaces, some of which were not yet open, while V5 coated micropores showed a large amount of molten oxide around them and had the largest micropores in diameter and the smallest number of micropores. It is shown that the morphology of the micropores on the surface of the ceramic coating changes with increasing voltage, the diameter becomes larger and the number decreases.

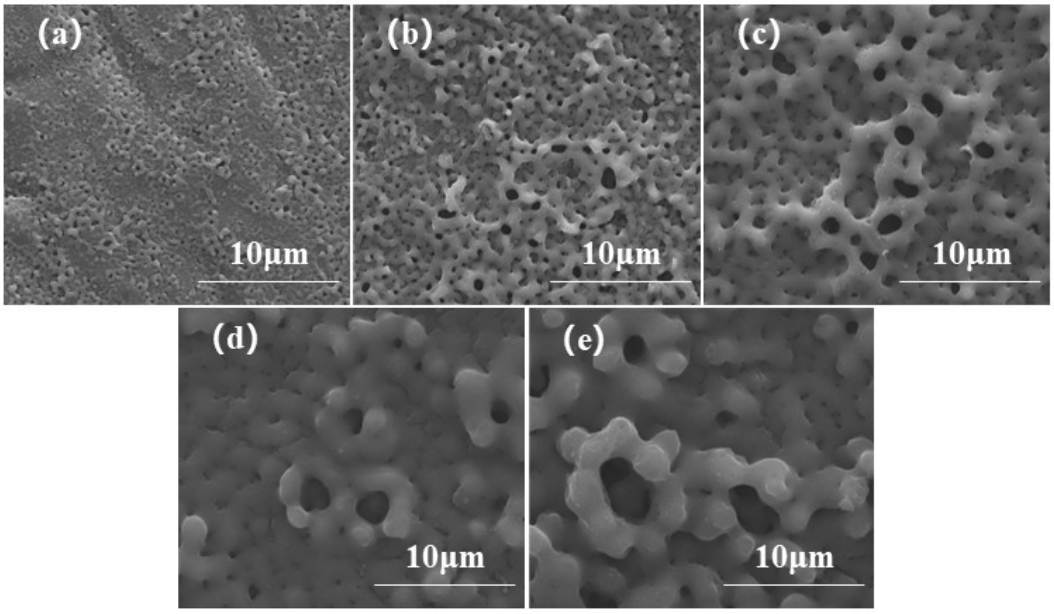

Figure 1. Surface morphology of MAO coatings at different voltages: (a)V1, (b)V2, (c)V3, (d)V4, (e)V5

3.2 Phase Composition Analysis of Oxide Layer

Figure 2 shows the phase composition of the titanium matrix composite MAO coated samples at different voltages. It can be seen that Ti, rutile TiO_2 and anatase TiO_2 phases are present in the coating, but the difference in quantity is not significant. As the voltage increases, the rutile phase increases while the anatase phase in the coating decreases. This is due to the fact that as the voltage increases, the surface reaction of the coating intensifies, leading to an increase in temperature, and Anatase-TiO_2 transforms into the Rutile-TiO_2 phase under high voltage and high temperature conditions. As a result, part of the anatase phase is transformed into the rutile phase [16].

3.3 Cross-sectional Morphological Analysis of the Oxide Layer

Figure 3 shows the cross-sectional morphology of MAO coatings under different voltage conditions. From the cross-section SEM, it can be seen that the MAO coatings prepared under the voltage parameters of V1, V2, V3, and V4 are more tightly bonded to the substrate, and have better coating bonding strength. And the film thickness increases from 4.43 μm to 9.33 μm with increasing voltage. Yet there are small cracks between the V5 coating and the substrate, and the growth of the coating becomes slow, probably too high voltage makes the internal defects of the coating increase [17]. All the results show that the thickness of the MAO coating can be changed by varying the applied voltage and whether the coating thickness affects the corrosion resistance of the material needs to be further examined in different specimens.

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3.4 Electrochemical Corrosion Properties of MAO Coatings

Figure 4 shows the polarisation curves of MAO coatings at different voltages. The polarisation curves of different coated samples were analysed using Tafel extrapolation, which gives the corrosion potentials and corrosion current densities of different coated specimens, as shown in Table 2. The corrosion current densities of the MAO membrane samples at the five voltages were1.815*10-7, 6.843*10-8, 5.306*10-10, 2.333*10-10, 5.789*10-10μA/cm^2. The corrosion resistance of a material is generally evaluated more specifically by the Icorr value. The smaller the Icorr, the lower the corrosion rate of the material, and the relatively good corrosion resistance of the specimen at high pressure [18]. As can be seen from the data in the table, the V4 coated samples have the lowest corrosion current density, proving that the V4 coating has the best corrosion resistance.

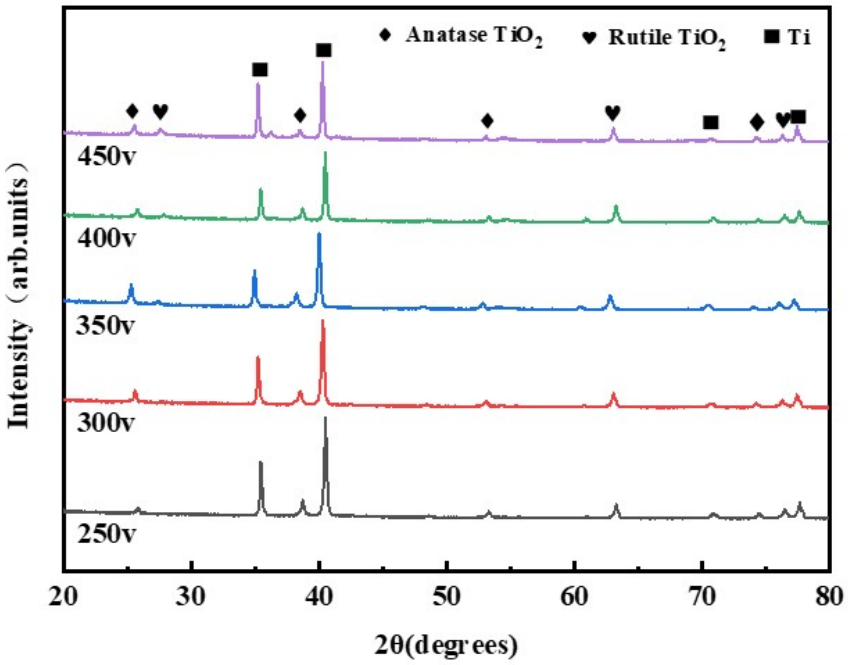

Figure 2. XRD patterns of MAO coatings at different voltages: (a)V1, (b)V2, (c)V3, (d)V4, (e)V5

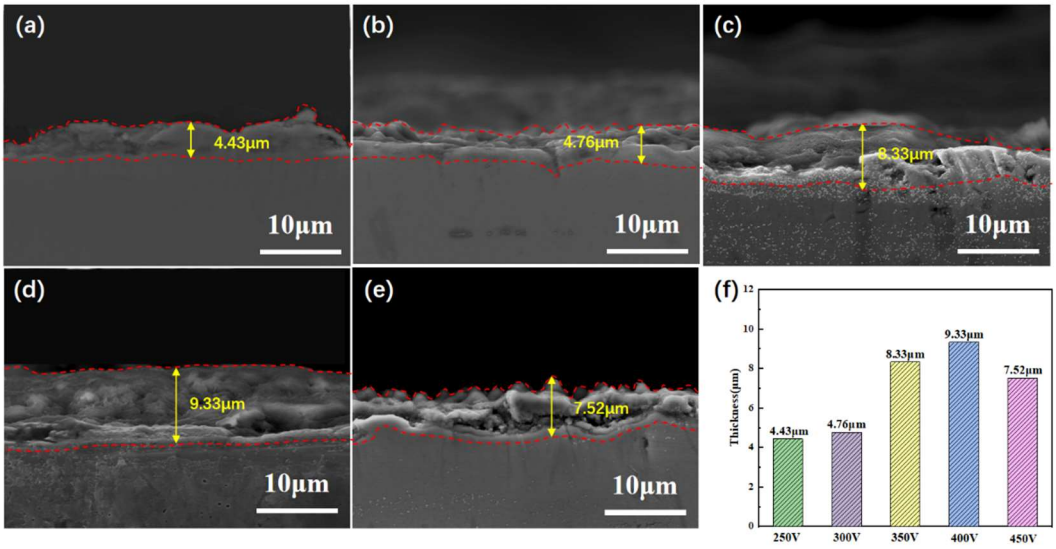

Figure 3. Cross-sectional morphology and thickness of MAO film at different voltages: (a)V1, (b)V2, (c)V3, (d)V4, (e)V5, (f) Oxide film thickness

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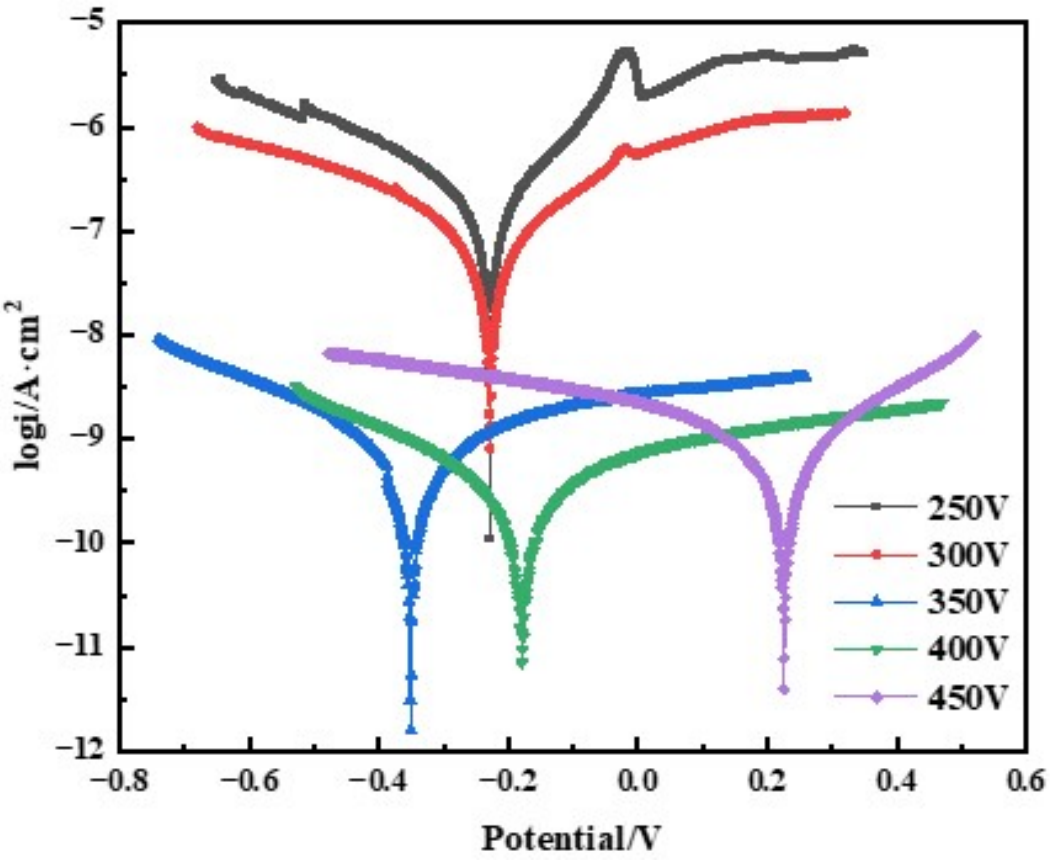

Figure 4. Polarization curves of MAO coatings at different voltages

Table 2. Self-corrosion potentials and self-corrosion currents of MAO coatings at different voltages

Sample	Icorr (A/cm^2)	Ecorr (V)
V1	$1.815*10^{-7}$	-0.2257
V2	$6.843*10^{-8}$	-0.2282
V3	$5.306*10^{-10}$	-0.3516
V4	$2.333*10^{-10}$	-0.1801
V5	$5.789*10^{-10}$	+0.2234

Electrochemical impedance spectroscopy (EIS) is an effective method to analyse the impedance of MAO coatings. The EIS curves of MAO coatings prepared under different voltage parameter conditions and their fitted curves are given in Figure 5. With other conditions fixed, we can derive the size of the capacitive arc diameter in the high frequency region: V4>V3>V5>V2>V1. Combined with the partially enlarged inset in the upper left corner, this shows that the capacitive arc diameter is largest at 400V for different voltages. It is shown that the coatings prepared at 400 V have maximum polarization resistance and best corrosion resistance. This finding suggests that the MAO film layer can be more effective in preventing substrate corrosion at this voltage. This two-layer structure of the micro-arc oxide layer significantly enhances the impedance of the MAO samples, thereby improving the corrosion resistance of the TMC [19]. The combined results indicate that the results of the EIS analysis are consistent with the polarization curve results presented in the previous section.

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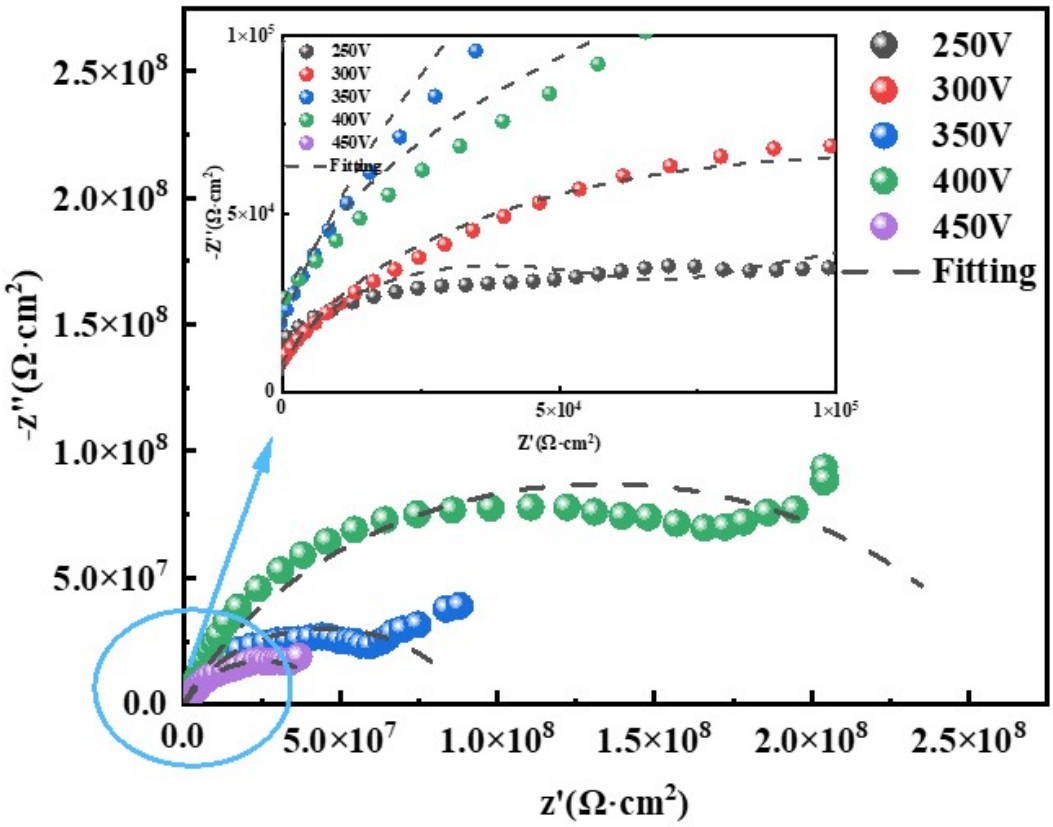

Figure 5. Nyquist curves at different voltages

4. Conclusion

Voltage significantly affects the structure and properties of MAO coatings for titanium matrix composite. Higher voltages result in larger microporous diameters and fewer micropores compared to lower voltages. With increasing voltage, the strong reaction induced by the strong discharge leads to a thickening of the MAO coating, while the thickness initially increases and then decreases. XRD results show that the physical phase of the porous structure is mainly composed of Ti and TiO2 phases (anatase and rutile). At a voltage of 400 V, the coatings obtained showed excellent adhesion, thicker film layers, and no visible defects or cracks. In addition, it exhibits the lowest corrosion current density, indicating optimum corrosion resistance. All the results show that the best overall performance of the film layer is obtained at a voltage of 400 V.

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