Synthetic Effects of Frequency and Duty Ratio on Growth Characteristics, Energy Consumption and Corrosion Properties of Microarc Oxidized Coating Formed on Ti6Al4V

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Abstract

The synthetic effects of frequency and duty ratio on growth characteristics and corrosion properties of coating on Ti6Al4V fabricated by microarc oxidation are investigated comprehensively. Under the condition of uniform cumulating time of positive impulse width, the essence of altering frequency and duty ratio to determine the formation of coating is to vary the duration and interval time of positive pulse. The growth of coating is mainly controlled by duration time of positive pulse and hardly correlated to the interval time of positive pulse, while both duration and interval time of positive pulse have few influences on the morphology and phase structures of coating. The dynamic current is related to positive impulse width and the ratio of positive pulse on-time to pulse off-time. Regardless of uniform duration or interval time of positive pulse, the energy dissipation presents a descending tendency. The relationship between energy consumption and anticorrosion performance is contradictory, and obtaining excellent corrosion resistance is bound to sacrifice lots of energy. The duty ratio and frequency can be designed purposefully to realize the optimal process.

Keywords Microarc oxidation · Titanium alloy · Frequency · Duty ratio

1 Introduction

Recently, a novel method called microarc oxidation (MAO), also named plasma electrolyte oxidation, has been applied to modify the surfaces of valve metals and its alloys with excellent mechanical properties, anticorrosion capabilities, biocompatibility and catalytic activities [1–7].

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The MAO device employs the direct or alternate current pulse in constant high voltage or current mode to give rise to the electrical breakdown at the interface between substrate and solution, and in which the discharge phenomena have been explained by current mechanism and electron avalanche mechanism [8]. It is a complicated process involving a series of physical and chemical reactions. In addition, vast depletion of electric energy occurs during the MAO process [9]. The traits of coating produced by MAO are determined by the intrinsic characteristics of the valve metal substrate, the electrical parameters of the power supply and the compositions of electrolyte.

Valve metals and its alloys have been widely applied in the fields of aerospace, automobile and biomedical industry as assembly units because of high strength-to-weight ratio, corrosion resistance and biocompatibility [10–13]. Titanium and its alloys are one of the most commonly used valve metals in microarc oxidation process. The properties of the MAO coating on the surface of titanium and its alloys mainly rely on the constituents of electrolyte and electrical parameters. By virtue of doping specific nanoparticles and soluble chemical reagents into the electrolyte during the microarc oxidation process, the

peculiarities of surface of titanium are transformed to obtain superior antifriction ability [14], corrosion resistance [15], bioactivity [16, 17], photocatalysis [18], high emissivity [19] and antibacterial characteristics [20, 21]. On the other hand, the properties of coating on titanium and its alloys are strikingly influenced by the electrical parameters, such as voltage, current, frequency and duty ratio [22–26].

The discharging and quenching time, the formation of discharge channel and transmission of ions are significantly influenced by the output waveform of power source. Therefore, the electrical parameters play a key role in the microstructure and properties of coating. The processing time, voltage, current, frequency, duty ratio and the number of positive and negative pulses decide the output waveform in the potentiostatic or galvanostatic regime for bipolar pulse waveform [27–29]. The effect of frequency or duty ratio on the characteristics of coating during the MAO process has been reported by a host of literature [30–34]. According to these studies, with increasing frequency or decreasing duty ratio, the roughness and thickness of coating decreased gradually and the properties of coating varied proportionally with frequency and duty ratio. The influences of other electrical parameters on the morphology and properties of coating have also been evaluated [24, 35].

The mechanism of frequency and duty ratio on the properties of coating has been put forward through the energy of single positive pulse (ESPP) based on Eq. (1) and the energy is determined by pulse voltage, pulse current and duration time, and can be expressed as follows:

$$E = \int_0^{t_a} U_a I_a dt, \quad (1)$$

where E , U_a , I_a and t_a represent the ESPP, voltage, current and duration time of single positive pulse (DTSP), respectively. The published literature assumed that the value of current of single positive pulse was almost invariant during the discharge process in potentiostatic mode, and the forming process of coating mainly occurred during the duration time of positive pulse [19, 26, 36, 37]. However, the value of I_a cannot be constant according to the study of dynamic current of single positive pulse [38]. As a matter of fact, during the process of single positive pulse, the value of I_a increased sharply less than 5 ms and then decreased quickly to a stable state. Whereas it is important to note that the dynamic current of single positive pulse increases with the width of positive pulse, the qualitative regularity of ESPP still can be determined by virtue of Eq. (1). Therefore, it is not necessary to think about the hypothesis of constant current of single positive pulse in potentiostatic mode. Despite the fact that the current of positive pulse is variable, this theory still can be

utilized to explain the impacts of frequency and duty ratio on the properties of coating qualitatively. In addition to the microscopic perspective of single positive pulse, the MAO process also can be evaluated in macroscopic aspect. The MAO process consumes large amounts of electricity, while the energy consumption has not been considered in the process of fabricating the excellent coating by vast researches. The electrical work of the process can be characterized by the overall voltage and current; this method is put forward to represent the energy dissipation in present work. On the other hand, the cumulating time of positive pulse has not been taken into consideration in all of the reported literature related to the duty ratio. The influence of duty ratio on the properties of coating merely has been investigated with uniform frequency and treatment time. In reality, the growth of coating dominantly takes place during the active course of positive pulse in the whole process except for the soft sparking mode; both ESPP and cumulating time of positive pulse corporately determine the formation of coating. However, varying the duty ratio with uniform processing time cannot guarantee the same cumulating time of positive pulse. As far as we know, the cumulating time of positive pulse is an important point that all of articles have not considered.

In this work, the integrated impacts of frequency and duty ratio on the growth, energy consumption and corrosion properties of coating on Ti6Al4V alloy during the MAO process are investigated. The values of frequency and duty ratio are designed with matching the processing time to keep the cumulating time of positive pulse constant. By virtue of analyzing the morphology, thickness, roughness, phase structures, transient current and voltage curves, energy consumption and electrochemical characterization, the nature of regularity of frequency and duty ratio can be comprehended. Furthermore, the roles of DTSP and interval time between two adjacent single positive pulses (ITSPs) are disclosed. Meanwhile, preparing the coating with superior property through MAO treatment could be more efficient and economic by setting proper electrical parameters, which is meaningful for industrial production on a large scale.

2 Experiments

2.1 Specimen Preparation

Ti6Al4V alloy used as substrate was processed by wire-cut electrical discharge machine with a dimension of 50 mm × 50 mm × 3 mm. Firstly, the samples were ground with 150#, 360#, 800# and 1500# Al₂O₃ waterproof abrasive paper. Then, the samples were cleaned with acetone, ethanol and pure water in an ultrasonic washer for

5 min, respectively. Finally, all the samples were dried in oven under 40 °C.

2.2 Microarc Oxidation Process

The oxidized coatings were fabricated on the surface of Ti6Al4V alloy sample with a bipolar pulse MAO system. The sample was used as the anode, while a stainless steel container was applied as the cathode. The stirring and cooling system were conducted to maintain the homogeneity of electrolyte and processing temperature below 40 °C during the process. An aqueous solution composed of 10 g/L NaAlO₂, 10 g/L (NaPO₃)₆, 6 g/L EDTA-2Na·2H₂O and 6 g/L Ca(CH₃COO)₂·H₂O was used as the electrolyte.

DTSP is a decisive variable for ESPP in potentiostatic mode. Besides, the cumulating time of positive pulse is also required to maintain constant. Changing the frequency or duty ratio is essentially equal to alter the DTSP and ITSP. Therefore, we design the electrical parameters of frequency and duty ratio to ensure the uniform DTSP with different ITSPs and the uniform ITSP with different DTSPs. The frequency, duty ratio and processing time are altered simultaneously to ensure the uniform cumulating time of positive pulse. Furthermore, the temporal values of current and voltage of the circuit loop are recorded automatically by MAO equipment. The consumption of electric energy can be represented by electric work and can be calculated as follows:

$$E_c = \int_0^t UI dt, \quad (2)$$

where E_c , t , U and I represent the consumption of electric energy, processing time, temporal voltage and current, respectively.

Fig. 1 Schematic diagram of the output waveform of MAO device

The schematic diagram of the output waveform of MAO device in potentiostatic mode is depicted in Fig. 1. U_a , T_a , t_a^{on} and t_a^{off} represent the anodic voltage and period, DTSP and ITSP, respectively. Identically, U_c , T_c , t_c^{on} and t_c^{off} represent the cathodic voltage and period, duration time of single negative pulse and interval time between two negative pulses, respectively. It should be pointed out that U_a and t_a^{on} are equal to the U_a and t_a in Eq. (1). The mathematical relationships between frequency $f_{a/c}$, duty ratio $D_{a/c}$, $t_{a/c}^{\text{on}}$ and $t_{a/c}^{\text{off}}$ are expressed by following equations:

$$f_a = f_c = 1/T_a = 1/T_c, \quad (3)$$

$$T_a = T_c = t_a^{\text{on}} + t_a^{\text{off}} = t_c^{\text{on}} + t_c^{\text{off}}, \quad (4)$$

$$D_{a/c} = t_{a/c}^{\text{on}} / (t_{a/c}^{\text{on}} + t_{a/c}^{\text{off}}), \quad (5)$$

$$t_{a/c}^{\text{on}} = D_{a/c} / T_{a/c}; \quad (6)$$

on the basis of the above parameters, the cumulating time of positive pulse can be expressed as follows:

$$T_{ac} = f_a \cdot t_{pr} \cdot t_a^{\text{on}} = f_a \cdot t_{pr} \cdot D_a / T_a = D_a \cdot t_{pr}, \quad (7)$$

where T_{ac} and t_{pr} represent the cumulating time of positive pulse and processing time, respectively.

Based on the above equivalent relationships, experiments are divided into two groups to study the synthetic effects of frequency and duty ratio on the growth characteristics of coating on Ti6Al4V prepared by MAO, and the electrical parameters of two groups are shown in Table 1. Both groups are implemented under +500 V positive potential and −60 V negative potential with the uniform cumulating time of positive pulse. In group A, in order to verify the effects of ITSP on the coating, the duty ratio of positive pulse and frequency increase proportionally along with decreasing processing time, which ensures the constant DTSP and a decline in ITSP. In group B, altering the duty ratio of positive pulse and frequency synchronously is designed to guarantee the constant ITSP and a decrease in DTSP. Thus, the effect of DTSP on the coating is evaluated. In brief, the electrical parameters are designed to understand the role of DTSP and ITSP on the growth, energy consumption and corrosion properties of coating during the MAO process. Thus, the essences of the effects of frequency and duty ratio are disclosed.

2.3 Characterization of MAO Coating

Surface and cross-sectional morphology and microstructure of coating were characterized by a scanning electronic microscope (SEM, HITACHI S-4800), and the thickness of coating was obtained by using an eddy current thickness tester (TIME2510). The surface roughness of samples was studied by a roughness meter (HOMMEL-ETAMIC

Table 1 Electrical parameters of bipolar pulse power supply for two groups

Group	Label	Duty ratio (%)	Frequency (Hz)	Processing time (min)
A	A1	10	300	10
	A2	20	600	5
	A3	30	900	3.3
	A4	40	1200	2.5
B	B1	42	500	2.5
	B2	30	600	3.5
	B3	18	700	5.8
	B4	7	800	15

T1000). The phase structures of coating were determined by a X-ray diffractometer (XRD, Rigaku ULTIMA IV) with Cu $K\alpha_1$ radiation ($\lambda = 0.15405$ nm) at 30 kV and 40 mA, and the diffraction data were collected during the range from 20° to 80° with a scanning rate of $5^\circ/\text{min}$. In addition, the values of dynamic current and voltage of circuit loop during the MAO process were recorded automatically by MAO device. Potentiodynamic polarization (PDP) test and electrochemical impedance spectroscopy (EIS) test were carried out using a CHI660E electrochemical system in 3.5 wt% NaCl solution at 25°C . A three-electrode system was used with a saturated calomel electrode (SCE) as a reference electrode, the sample with 1 cm^2 exposed to solution as working electrode and a platinum sheet as counter electrode. Prior to test, the sample was immersed in the NaCl solution for 3600 s to reach a quasi-steady state and attain the open-circuit potential (E_{ocp}). The EIS measurement was taken at E_{ocp} with a sinusoidal voltage perturbation of 5 mV in the frequency range of 0.01 Hz to 100 kHz. The polarization resistance (R_p) was determined by linear potentiodynamic sweep in the range of ± 10 mV versus E_{ocp} with sweep rate of 0.5 mV/s. The potentiodynamic polarization was performed from -500 to $+900$ mV with respect to E_{ocp} at a scan rate of 1 mV/s to obtain the anodic and cathodic Tafel slopes (β_a and β_c). The corrosion current density (i_{corr}) was calculated by the Stern–Geary equation [39]:

$$i_{\text{corr}} = \frac{\beta_a \cdot \beta_c}{2.303 \cdot R_p \cdot (\beta_a + \beta_c)}. \quad (8)$$

3 Results and Discussion

3.1 Surface and Cross-sectional Morphology of MAO Coating

The surface and cross-sectional morphologies of MAO coating of two groups are similar (see the supplementary Fig. S1 and Fig. S2). Therefore, Fig. 2 just presents the representative morphology of coating prepared under A1

conditions in Table 1. It is found that the morphology of the coating is consistent with the reported literature [19, 35], and the coating is coarse and craterlike and possesses some cracks and microscale porosities distributed dispersedly on the surface. The cross section of the coating is porous and uneven as shown in Fig. 2b, and it displays a typical structure of a tight thin inner layer and a loose thick outer layer of MAO coating. There are no obvious crevices at the interface between the substrate and coating, indicating the coating is bonded with the substrate well. Besides, a lot of small holes exist in the outer layer of coating. During the MAO process, the discharge occurs at the weak area of the coating accompanying with electron avalanche [8], leading to the ultrahigh temperature and pressure nearby the discharge area. Thus, the substances around the sparks are melted, and the molten substances are ejected out from the discharge channels and leave a volcano-like topography and holes to form in the coating. The coating is composed of molten substrates and electrolyte through a series of complicated physical and chemical reactions. During the ITSP and period of negative pulse, the molten substances solidify rapidly due to the remarkable temperature discrepancy between the electrolyte and discharge arc. Consequently, cracks generate owing to the thermal stress release of the coating in the process of rapid solidification. Based on the similar morphology of coating, it can be deduced that the DTSP and ITSP have few effects on the morphology of coating under the condition of uniform cumulating time of positive pulse in our designed electric parameters and electrolyte. Namely, it means that the ESPP which is pivotal in the growth of coating hardly influences the topography of coating. In other words, the morphology of the MAO coating is independent of the duty ratio and frequency under the condition of united cumulating time of positive pulse.

3.2 Thickness of MAO Coating

The thickness of coating is a crucial target in the growth of coating during the MAO process. Although the cross-

Fig. 2 Cross-sectional **a** and surface morphologies **b** of Al MAO coating prepared with 10% (duty ratio), 300 Hz (frequency) and 10 min (treatment time)

sectional morphology of coating is alike, the thickness of coating displays a significant difference. Figure 3 depicts the thickness of coating for two groups. The thicknesses of the coating in group A are almost changeless in Fig. 3a, indicating that variance of the ITSP has few impacts on the thickness of coating under the condition of same DTSP. Hence, the effects of ITSP on the growth of coating are negligible. When the ITSP is constant, the thickness of coating decreases gradually with diminishing DTSP in Fig. 3b, which is in agreement with the results in the literature [30, 31]. The ESPP is mainly determined by DTSP in constant potential mode, and the ESPP affects the formation of coating during the MAO process. Obviously, the smaller ESPP triggers the thinner coating. Thus, by means of conjugating with the foregoing results in Fig. 3, it can be denoted that the DTSP and ITSP have remarkably different impacts on the growth of coating, the formation of coating shows a positive correlation with the DTSP and ESPP, while it is hardly linked to the ITSP.

On account of the above standpoints, the phenomena of the thickness of coating changing with the frequency and duty ratio can be explained. In the related reported literature [30–34], the thickness of coating reduces with

increasing the frequency and it should be pointed out that the cumulating time of positive pulse is same and independent of altering the frequency with uniform duty ratio and processing time in the literature. The augmentation of frequency leads to the concurrent decrease in DTSP and ITSP. However, the growth of coating is hardly correlated to the ITSP according to the results in Fig. 3a. Therefore, the decrease in thickness of coating is primarily determined by the function of decrease in DTSP. Therein, decreasing DTSP is equal to the decline in ESPP, and the essence of altering the frequency is to vary the ESPP to influence the growth of coating. On the other hand, the thickness of coating increases with the duty ratio of positive pulse. The increment of the duty ratio of positive pulse results in increasing the DTSP and lessening the ITSP. As mentioned above, the growth of coating is hardly linked to the ITSP. Hence, the increase in thickness of coating is principally decided by the increase in DTSP. Additionally, the cumulating time of positive pulse becomes large with increasing duty ratio and uniform frequency and processing time. Therefore, the increase in thickness is ascribed to both the DTSP and the cumulating time of positive pulse. In fact, according to the energy theory of

Fig. 3 Thicknesses of MAO coating of two groups: **a** different ITSPs with uniform DTSP; **b** different DTSPs with uniform ITSP

single positive pulse, the nature of changing the duty ratio is to alter the ESPP to determine the growth of coating. In brief, the growth of coating is mainly controlled by the DTSP and independent of the ITSP. The nature of changing the frequency and duty ratio is to alter the DTSP and ESPP to determine the formation of coating.

3.3 Roughness of MAO Coating

The melt and solidification of substances occur repeatedly at the interface between the formed coating and electrolyte, leaving a coarse topography with hollow cavities and protuberant elevations. The roughness related to the morphology of coating is distinctly changeable in different MAO processing stages and generally increases with the processing time. Therefore, the roughness of coating is an important factor to represent the peculiarity of coating.

The results of roughness of coating for two groups are diagrammed in Fig. 4. The roughness of coating in Fig. 4a fluctuates around 2.3 μm with a narrow range. Under the condition of the uniform DTSP and cumulating time of positive pulse, changing the ITSP hardly affects the roughness of coating, which means that all the coatings in group A are mostly in the same growth stage. However, keeping the ITSP invariable and altering the DTSP significantly influences the roughness of coating and the roughness of coating decreases with the DTSP in Fig. 4b. The results disclose that the roughness of coating is controlled by the DTSP but independent of the ITSP, which is in agreement with the results of thickness. These results also can be explained by energy theory of single positive pulse. The intensity of discharge recedes along with decreasing the ESPP. Thus, the intensity of physical and chemical reactions becomes subdued, and it weakens the process of melt and solidification, resulting in a smoother surface. Both the variation of frequency and duty ratio essentially affects the DTSP and ESPP, and the roughness of coating principally depends on ESPP. Therefore,

although increasing the frequency causes the synchronous diminution of DTSP and ITSP, the ITSP has no relationship with the roughness of coating. Hence, the roughness of coating decreases with the increase in frequency due to the diminution of the DTSP [32]. While the augmentation of duty ratio induces the increase in DTSP and reduction in ITSP, the roughness of coating increases with the increase in duty ratio [33]. Based on the analysis from the perspective of energy, altering the frequency and duty ratio is bound to alter the ESPP and higher ESPP leads to a much rougher surface. In brief, the results of roughness are consistent with that of thickness and the DTSP plays a key role in determining the growth of coating.

3.4 XRD of MAO Coating

The phase structures of coating for two groups are alike (see the supplementary Fig. S3), regardless of the different electrical parameters. The XRD patterns of group A are shown in Fig. 5 and display the typical amorphous in MAO coating [16]. All the coatings possess the same phases, and the main crystal phases are aluminum phosphate (AlPO_4) and alumina (Al_2O_3), which are the representative phases in the phosphate and aluminate electrolyte [26]. They may be generated through the following reactions (9) and (10).

Besides, the peak of substrate is strongest and highlighted; this may account for the porous surface. In spite of the thick coating, the X-ray penetrates the coating into the substrate by means of porosities that go deep into inner layer according to the cross-sectional morphology in Fig. 2b. On the other hand, there is an obvious bread-shaped profile from 20° to 40° , disclosing that the coating contains abundant amorphous substances. The disappearance of calcium element could exist in the amorphous

Fig. 4 Roughness of MAO coating of two groups: **a** different ITSPs with uniform DTSP; **b** different DTSPs with uniform ITSPs

Fig. 5 XRD patterns of MAO coatings of group A with decreasing ITSP and uniform DTSP

phases. The DTSP and ITSP mainly control the intensity and rate of reactions during the MAO process. Therefore, altering the electrical parameters merely influences the growth rate of the coating and the formation mechanism of the coating is independent of the frequency and duty ratio. Consequently, the phase structures of coating remain uncontrolled with the variance of DTSP and ITSP in the same electrolyte.

3.5 Transient Current and Voltage

In general, the whole MAO process is a dynamic course, the transient current decreases with processing time in constant potential mode, while the transient voltage increases with processing time in constant current mode. The trend of current and voltage presents strikingly different stages involved in the growth of coating during the process.

Fig. 6 Transient voltage curves of group B during MAO process with decreasing DTSP and uniform ITSP

The curves of temporal voltage for two groups are almost identical (see the supplementary Fig. S4); hence, Fig. 6 just depicts the typical temporal voltage of group B during the process. The curves of temporal voltage are almost entirely overlapping, signifying that the transient voltage is independent of the frequency and duty ratio under the constant potential mode. The curves of temporal voltage reveal four obvious stages as shown in the inset in Fig. 6, which is in accordance with the results in the literature [41]. Firstly, the voltage increases to about 220 V sharply and linearly and this corresponds to the anodic oxidation of substrate. Then linear incremental rate reduces slightly due to the increase in resistance of formed anodizing coating. When the voltage reaches 450 V, the trend of voltage becomes slow rapidly due to the breakdown of the anodic coating. Finally, the voltage fluctuates at the vicinity of 500 V with a very small amplitude.

Figure 7 shows the dynamic current of two groups during the oxidation process, and the curves during the initial 70 s are shown as insets separately for detailed information. All the curves display similar variation tendency in potentiostatic mode, and two significant peaks of dynamic current appear in initial 60 s, which are different from single peak in the literature [42]. The dynamic current increases fast in initial several seconds because of the linear increase in voltage in stage I in Fig. 6. The anodic oxidative coating is formed with the rapid increase in linear voltage, triggering the fast increment of the resistance. On the other hand, considerable amounts of tiny bubbles form at the interface between the solution and anode during the anodic oxidation stage, causing the rapid increase in resistance. Therefore, the rising rate of voltage is inferior to that of resistance. Thus, the dynamic current falls down from the first peak. The applied voltage continues to elevate in stage II in Fig. 6, when the voltage reaches the critical threshold, the interface between the oxidative coating and solution is disrupted, and some tiny arcs start to occur at the weak areas due to the dielectric breakdown caused by the ultrahigh electric field, the leakage of current triggers the ultrafast reduction of resistance, the increasing rate of voltage exceeds that of the resistance, leading to the current increase again to achieve the second peak. After treating for 40 s, the temporal voltage stabilizes at 500 V, while the growth of coating still carries on with the microarc oxidation. Hence, the dynamic current decreases gradually on account of the incremental resistance of coating.

The value of peak dynamic current changes with the frequency and duty ratio. The dynamic current increases with the decrease in the ITSP and constant DTSP in Fig. 7a. According to the previous results of thickness and roughness, the ITSP hardly influences the growth of coating and the increase in dynamic current may account

Fig. 7 Transient current curves of two groups during MAO process: **a** different ITSPs with uniform DTSP; **b** different DTSPs with uniform ITSP

for the rising ratio of DTSP to ITSP. Larger ratio provides relatively less time for the molten substance to solidify; when the next positive pulse comes, the molten substance is too late for solidification to be broken down by the plasma discharge easily, which promotes the more intense discharge reactions and leads to higher dynamic current. The dynamic current rises with increasing DTSP and invariable ITSP in Fig. 7b. The increase in DTSP triggers the higher ESPP which is conducive to enhance the plasma discharge, inducing the larger dynamic current. Furthermore, the dynamic current is also strengthened by the incremental ratio of DTSP to ITSP. In conclusion, the dynamic current is correlated to the DTSP and the ratio of DTSP to ITSP; the larger DTSP and ratio of DTSP to ITSP cause the higher dynamic current.

3.6 Consumption of Electric Energy

Based on the temporal current and voltage curve, the consumption of electric energy during the MAO process is calculated by Eq. (2), and the calculated results are listed in Table 2. The energy dissipation almost agrees with the

specific energy consumption of MAO process in the literature [9]. The consumption of electric energy declines with the decrease in ITSP and uniform DTSP in group A and also diminishes with the decrease in DTSP and uniform ITSP in group B. Namely, under the condition of uniform cumulating time of positive pulse, regardless of uniform DTSP or ITSP with lessening complementary variable in one period for positive pulse, the consumption of electric energy always displays a descending tendency.

From the perspective of energy conservation and emission reduction, incorporating the consumption of electric energy with the growth of coating is meaningful. As a matter of fact, the MAO equipment possesses high power consumption and a lot of electric energy is consumed during the oxidation [9, 40]. According to the results in group A of Table 2 and Fig. 3a, it can be found that under the condition of larger duty ratio and frequency with uniform cumulative time of positive pulse, expending the minimum consumption of electric energy can obtain the coating with similar thickness and the treatment time declines from 10 to 2.5 min, disclosing that larger duty ratio and frequency induce the higher energy-efficient and time-saving process, whereas, under the condition of the uniform ITSP, both the energy dissipation and thickness of coating decline with the DTSP illustrated in group B of Table 2 and Fig. 3b. The thickness of coating falls down 33%, while the consumption of electric energy is reduced by 65% from 58.88×10^4 to 20.23×10^4 J, which is two times higher than the reduction rate of thickness. To some extent, it elucidates the process becomes more efficient with the decrease in DTSP and uniform ITSP. However, large duty ratio and frequency are obviously more favorable for efficient process compared with small duty ratio incorporated with high frequency. Therefore, applying the larger DTSP with smaller ITSP to carry out the MAO process is worthy of promotion. These results corroborate that implementing the process with proper electrical

Table 2 Consumption of electric energy of two groups during MAO process

Group	Label	Depletion of energy ($\times 10^4$ J)	SD (%)
A	A1	50.51	2.22
	A2	49.22	2.06
	A3	44.97	1.64
	A4	41.85	1.50
B	B1	58.88	2.89
	B2	49.01	3.08
	B3	40.32	1.60
	B4	20.23	0.88

parameters effectively improves the utilization of electric energy and decreases the processing time. Hence, there are crucial guiding significances for preparing large quantities of specimens during the microarc oxidation process.

3.7 Electrochemical corrosion studies

The PDP curves of coating are depicted in Fig. 8. The E_{corr} , i_{corr} , β_a , β_c and R_p are listed in Table 3. It is found that both the E_{corr} and R_p increase first and then decrease with diminishing ITSP and uniform DTSP under the same cumulating time of positive pulse in group A, while the corresponding i_{corr} displays an opposite trend. It discloses that the A2 coating possesses the optimal corrosion resistance. As for the A1 and A2 coatings, the similar thickness is obtained with different processing times; thus, the growth rate of A2 coating is higher than that of A1 coating, and it can be deduced that smaller cavities exist in A1 coating, while holes with relatively larger size appear in A2 coating. There are larger surface areas exposed to the NaCl solution in A1 coating compared with A2. Therefore, the A2 coating displays better corrosion resistance. With respect to the A3 and A4 coatings, the processing time is much shorter for the same thickness, the fast growth of coating leads to amounts of defects leaving in the coating, inducing the degradation of corrosion resistance. The anticorrosion property of coating shows a 'Λ' trend with decreasing ITSP and uniform DTSP. On the contrary, the E_{corr} and R_p decrease initially and increase afterward in group B; meanwhile, the i_{corr} presents similar contrary tendency. Obviously, the B3 coating exhibits the worst anticorrosion property. In the case of B1, B2 and B3 coatings, although the processing time becomes enlarged, the thickness of coating decreases with the DTSP and the corrosion resistance is impaired mainly due to the thinner layer. Regarding the B3 and B4 coatings, the processing time is also extended in B4 condition, the thickness of B4

coating is smaller than that of B3 coating; namely, the growth rate of B4 coating is reduced. It can be speculated that the B4 coating is more compact; thereby, the corrosion performance is enhanced. Hence, the corrosion resistance of coating presents a 'V' tendency with decreasing DTSP and uniform ITSP.

EIS measurements are taken to get further information concerning the effects of frequency and duty ratio on corrosion resistance and to confirm the results obtained by PDP tests. Figure 9 shows the experimental and simulated Nyquist and Bode plots of samples for two groups. In order to further understand the corrosion behavior of all the samples, the equivalent circuit model is applied and diagrammed in Fig. 10. The R_s is the solution resistance, the R_{ct} and C_{dl} associate with the charge transfer process at the interface between substrate and coating, and R_1 and CPE_1 represent the porous layer. n_1 and n_2 are indices of the CPE_1 and C_{dl} , respectively. The fitting parameters of the equivalent circuit are listed in Table 4.

It can be seen that the radius of the impedance arc exhibits in the following order $A2 > A1 > A3 > A4$ in Fig. 9a, which is in accordance with the PDP test for group A. The total impedance modular follows the preceding order on the whole in Fig. 9b, while the higher $|Z|$ of A3 and A4 coating appears in the high-frequency range which is consistent with the larger phase angle in Fig. 9c, indicating that they possess better corrosion resistance at high frequency than A1 and A2 coating. In addition, A1 and A2 coatings display a higher and wider profile in Fig. 9c, disclosing the great anticorrosion performance. The disappeared peak of A4 coating at the range of 10^{-1} to 10^1 Hz is suggestive of worse corrosion resistance than A3 coating. In addition, the R_{ct} in Table 4 for group A follows the order $A2 > A1 > A3 > A4$. Therefore, the corrosion resistance also presents a 'Λ' trend according to the EIS plots, and the EIS results conform the PDP of group A well. As for group B, the radius of impedance arc in Fig. 9d

Fig. 8 Potentiodynamic polarization curves of the MAO coating: **a** different ITSPs with uniform DTSP; **b** different DTSPs with uniform ITSP

Table 3 Polarization parameters of coating

Group	Label	E_{corr} (V vs. SCE)	i_{corr} (A/cm ²)	β_a (V/dec)	β_c (V/dec)	R_p (Ω cm ²)
A	A1	− 0.13	1.45E−8	0.2053	0.1771	2.85E6
	A2	− 0.08	4.58E−9	0.2421	0.1572	9.04E6
	A3	− 0.19	3.40E−8	0.2781	0.1897	1.44E6
	A4	− 0.35	1.03E−7	0.2920	0.1444	4.09E5
B	B1	− 0.11	2.61E−8	0.2046	0.1449	1.41E6
	B2	− 0.15	1.70E−7	0.1192	0.1500	1.70E5
	B3	− 0.18	3.47E−6	0.1063	0.1014	6.49E3
	B4	− 0.14	1.34E−6	0.2032	0.1975	3.24E4

Fig. 9 Experimental and fitting Nyquist and Bode plots of the MAO coating: **a** Nyquist plot for group A; **b** Bode spectra—impedance for group A; **c** Bode spectra—phase angle for group A; **d** Nyquist plot for group B; **e** Bode spectra—impedance for group B; **f** Bode spectra—phase angle for group B **Fig. 10** Electrical equivalent circuit model for MAO coating

shows the order $B1 > B2 > B4 > B3$; similarly, the total impedance modular is also in agreement with this order in Fig. 9e. With respect to B1, B2 and B3 coatings, the phase angle of B1 coating exhibits the highest and widest outline, indicating the best corrosion performance. The profile of phase angle for B2 coating wraps that of B3 coating, which is well consistent with the foregoing order. While the phase

angle of B3 is completely lower than that of B4 coating, validating that B4 coating is more superior than B3 coating. In the case of B2 and B4 coatings, despite the relatively wide phase angle of B4 coating, two obvious high peak of phase angle is presented by B2 coating. In addition, both the $|Z|$ and radius of impedance arc for B2 coating are larger and this may account for the better performance for B2 coating. Besides, it can be observed from Table 4 that for group B, R_{ct} still complies with the order $B1 > B2 > B4 > B3$. Consequently, the corrosion resistance for group B shows a ‘V’ tendency, which is well in accordance with the PDP in Fig. 8b.

Taking the growth rate, energy consumption and corrosion resistance into comprehensive consideration, in group A, the growth rate of the coating increases with decreasing ITSP and uniform DTSP, while the energy dissipation is reduced, whereas the corrosion resistance presents a ‘A’ trend. These results indicate that the growth

Table 4 Fitting parameters of EIS plots of all the samples in 3.5 wt% NaCl solution

Group	Label	R_s (Ω cm ²)	CPE_1 (F cm ⁻²)	n_1	R_1 (Ω cm ²)	C_{dl} (F cm ⁻²)	n_2	R_{ct} (Ω cm ²)
A	A1	93	8.59E-7	0.70	1.46E6	2.13E-6	0.70	2.25E6
	A2	98	1.85E-7	0.74	1.26E6	2.61E-7	0.46	5.11E7
	A3	78	2.15E-8	0.81	1.02E5	6.60E-7	0.67	2.22E6
	A4	54	5.21E-8	0.73	8.00E4	4.13E-6	0.32	1.78E6
B	B1	75	4.03E-7	0.77	1.13E3	8.89E-7	0.64	5.11E6
	B2	49	4.07E-6	0.67	1.42E4	1.51E-5	0.68	8.36E4
	B3	31	8.38E-6	0.65	1.72E3	3.75E-5	0.70	1.31E4
	B4	56	4.86E-6	0.65	489	1.13E-5	0.52	5.94E4

rate is too fast to weaken the anticorrosion performance and trigger more defective layer despite the effective utilization of electric energy during the process. It is found that the energy dissipation is in contradiction with the anticorrosion performance. On the contrary, under the condition of uniform ITSP, to some extent, accelerating the growth of coating with decreasing the DTSP is beneficial for corrosion resistance in the case of group B, which is attributed to the large thickness. However, the energy consumption is still high. In brief, the relationship between energy dissipation and corrosion resistance is contradictory, while the duty ratio and frequency can be designed to obtain better anticorrosion performance. Besides, the corrosion resistance is linked to the defects in the coating and the preceding conclusion can be promoted to other properties, such as photocatalysis, antifriction, bioactivity and high emissivity, if the microdefects hardly influence these property, thus, the energy-saving process is worthy of popularizing with proper electrical parameters. Otherwise, setting the electrical parameters are necessary to balance the microstructure and energy consumption, which is meaningful for MAO process in large scale.

4 Conclusions

By virtue of designing frequency and duty ratio with uniform cumulating time of positive pulse, the synthetic effects of frequency and duty ratio on the growth characteristics, energy consumption and corrosion properties of coating produced on Ti6Al4V by MAO process have been evaluated and the following conclusions can be drawn:

- Both DTSP and ITSP determined by frequency and duty ratio hardly have influences on the morphology and phase structures of coating.
- The DTSP is a decisive factor in the growth of coating during MAO process, while the ITSP is hardly correlated to the formation of coating. Altering frequency and duty ratio is to change the above factors substantially.
- The transient current relies on the intensity of reaction and is correlated to the DTSP and the ratio of DTSP to ITSP. Regardless of uniform DTSP or ITSP with changing complementary variable in one period, the consumption of electric energy presents a descending tendency.
- The relationship between energy dissipation and corrosion resistance is contradictory, and the duty ratio and frequency can be designed purposefully to obtain better anticorrosion performance.

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