

Effects of NaAlO_2 concentrations on structure and characterization of micro-arc oxidation coatings formed on biomedical NiTi alloy

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The MAO coating was prepared on biomedical alloy by micro-arc oxidation (MAO) in sodium aluminate (NaAlO_2) solution using pulsed bipolar power supply. It was found that the coating consists of O, Al, Ti and Ni, and Ni concentration in the coating surface is much lower than that of Ni in the NiTi substrate. The concentration of sodium aluminate (NaAlO_2) solution has an influence on the surface morphologies, surface roughness, corrosion resistance and bonding strength. XRD analysis reviewed that MAO coating formed in solution of 0.05 M sodium aluminate (NaAlO_2) is amorphous, the coating was composed of crystalline $\gamma\text{-Al}_2\text{O}_3$ when the sodium aluminate (NaAlO_2) concentration is from 0.075 M to 0.15 M. The intensity of $\gamma\text{-Al}_2\text{O}_3$ peaks increased with increasing the concentrations of NaAlO_2 . The corrosion resistance and bonding strength of the MAO coatings increased with the increasing NaAlO_2 concentration. Especially, the bonding strength of MAO coating to NiTi substrate was up to 28.0 MPa when NaAlO_2 concentration is up to 0.15 M.

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1. Introduction

NiTi shape memory alloys (SMA) are interesting candidates for a wide range of biomedical applications such as bone fracture fixation plates and nails, vascular, non-vascular stenting and so on.¹⁾ However, despite their unique and attractive shape memory effect, super-elasticity and high damping capacity, they are still controversial materials because of toxic, allergic and potentially carcinogenic effects that might be caused by Ni release into the human body.²⁾ It is well known that the release of metal ions is dependent upon either corrosion of the material or leaching of the ions from the metal surface, a process that has been shown to be related to the concentration of ions on the metal surface. Therefore, in order to reduce the amount of Ni on the surface layer and further improve the corrosion resistance of the NiTi alloys, many surface modification techniques have been employed in previous literature, including thermal oxidation, anodic oxidation, sol-gel, electropolishing, plasma immersion ion implantation and laser surface treatment, etc.^{3),4)}

Micro-arc oxidation (MAO), also commonly called “plasma electrolytic oxidation (PEO)” and “micro-plasma oxidation (MPO)” in modern scientific literature, has attracted more and more attentions to prepare oxide ceramic coatings on the surface of valve metals, such as Ti, Al, Mg and their alloys.⁵⁾⁻⁸⁾ Recently, Al_2O_3 coatings have been successfully prepared on biomedical NiTi alloy by MAO, and the Al_2O_3 coatings exhibit good corrosion resistance.⁹⁾⁻¹²⁾ MAO is a room-temperature electrochemical process and suitable for the formation of uniform coatings on the substrates with complex geometries. Thus, the MAO is promising technique for preparing coating on NiTi alloy. It is well known that the MAO technique is a multifactor-controlled pro-

cess, such as electrolyte composition and concentration, types of electrical source and electrical parameters, etc.¹³⁾ For MAO of Ti, Al, Mg and their alloys, the electrolyte composition and concentration play a key role for the structure and characterization of the MAO coatings and have been studied frequently by researchers. However, due to near history of MAO coatings on NiTi alloy, no paper has been reported on effects of electrolyte concentration on structure and characterization of micro-arc oxidation coatings formed on NiTi alloy.

In this study, this paper is focused on the effects of NaAlO_2 concentrations on the structure and characterization of micro-arc oxidation coatings formed on biomedical NiTi alloy. The breakdown voltage, microstructure and composition of the coatings formed by MAO in different NaAlO_2 concentrations were studied and the corrosion resistance behavior and bonding strength of the MAO coatings was also evaluated.

2. Experimental procedure

Rectangular samples of commercially available NiTi alloy (50.8 at.% Ni) with dimensions of 15 mm × 15 mm × 2 mm were successively polished with SiC sandpaper down to 800#, and then ultrasonically cleaned in acetone and distilled water, respectively. The micro-arc oxidation process was conducted on a 20 kW homemade pulsed bipolar electrical source and all the samples were treated in constant voltage 400 V for 30 min. The NiTi alloy samples were used as the anode, while the wall of the stainless steel container as the cathode. An aqueous electrolyte was prepared from an aqueous solution of NaAlO_2 (concentration, $C = 0.05\text{--}0.15$ M). During the experiment process, the electrolyte solution was stirred and cooled below 35°C. Coated samples were flushed with water after the treatment and dried in air at room temperature.

The surface morphologies of the coated samples were

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observed by a scanning electron microscopy (SEM, Hitachi, Ltd. S-4800). The element concentration on the surface of the coated samples was measured by an energy dispersive X-ray spectrometer (EDS, Oxford Model 7537). The phase composition of the coated samples was analyzed by thin-film X-ray diffraction (TF-XRD, Rigaku Co. D/max-2500) using a Cu K α radiation generated as 40 kV and 300 mA with a glancing angle of 1°. The chemical state of Al in the coating formed in C = 0.05 M was investigated with an X-ray photoelectron spectroscopy (XPS, PHI 5700). Surface roughness (Ra) was measured using a JB-4C surface roughmeter (Guangzhou, China).

The corrosion behavior of the coated and uncoated samples in 0.9% NaCl solution at room temperature was evaluated by potentiodynamic polarization test by CHI604 electrochemical analyzer (Shanghai, China). The electrochemical measurement was conducted using a conventional three electrodes electrochemical cell with a saturated calomel electrode (SCE) as the reference, a Pt foil as the auxiliary electrode, and the samples with the area of 1 cm² as the working electrode. The polarization scan continued in the anodic direction with a potential scan rate of 0.167 mV/s.

Bonding strengths of MAO coating to NiTi substrate were measured by a modified ASTM C-633 method. Both sides of substrates (on one side of which the coating were formed by microarc oxidation) were attached to cylindrical stainless steel jigs 10 mm in diameter and 15 mm in length by using the epoxy. The prepared samples were placed in an Instron-5569 testing machine and tensile was loaded until failure occurred.

3. Results and discussion

3.1 Effects of solution concentrations on breakdown voltage

In order to observe the breakdown voltage, the working voltage keeps a constant rise rate of 300 V/min in 0.05–0.15 M NaAlO₂ aqueous solutions at the initial of the MAO process. Breakdown voltage values were obtained using the appearance of the visible sparks as criterion for identifying the breakdown voltage. **Figure 1** shows the variation of breakdown voltage with the concentration of NaAlO₂. It can be seen that the breakdown voltage decreases linearly from 224 V to 165 V with increasing the concentrations of NaAlO₂. The breakdown voltage values decrease with increasing the concentrations of the electrolyte, which is consistent with Refs.¹⁴⁾

Figure 2 shows the variation of conductivity with the concentration of NaAlO₂. It can be seen that the electrolyte conductivity

increases linearly with increasing the concentrations of NaAlO₂. It is well-known that the resistivity of the electrolyte is proportional to the reciprocal of the electrolyte conductivity, and the conductivity of the electrolyte is proportional to the concentration of the electrolyte. Therefore, the resistance of the electrolyte is decreased with the increasing concentrations of NaAlO₂, accompanied by a decrease of voltage consumed on the electrolyte and a corresponding increase of voltage loaded on the anode, which may be one of the reasons for the decrease of breakdown voltage (see Fig. 1).

3.2 Effects of solution concentrations on the surface structure and composition of coating

Figure 3 shows the surface morphologies of the MAO coatings formed on NiTi alloy by MAO in different NaAlO₂ concentrations. It is obviously seen that the different concentrations make pronounced changes in the surface morphologies of the coatings and some of them completely differ from the typical MAO porous structure. For the coating formed in C = 0.05 M, there are many conch-like humps with some crackles on the surface layer; while for C = 0.075 M, there mainly exist white network inclusions that form the discontinuous circular matrix with a few discharging channel pores; when the concentration increases to 0.1 M, white inclusions become fewer and smaller but discharging channel pores get more in comparison with C = 0.075 M; At last, when the concentration is up to 0.15 M, the white inclusions disappear, leaving a large number of crater-like discharging channel pores over the surface layer.

The effect of electrolytic concentrations on the surface roughness of the coatings is shown in **Fig. 4**. As can be seen from Fig. 4, the increasing NaAlO₂ concentration from 0.05 M to 0.1 M leads to a corresponding decrease of the surface roughness of the coating, while the surface roughness is sharply increased when the concentration is up to 0.15 M. Derived from Fig. 3, the size of inclusions is decreased with increasing concentration of NaAlO₂ from 0.05 to 0.1 M, which results in the decrease of surface roughness. However, the sharp increase of the surface roughness of the coating formed in C = 0.15 M should be owing to the essential change of surface morphology of the coating.

Table 1 gives the element concentration of the coatings formed in different NaAlO₂ concentrations. All the coatings mainly contain O, Al, Ti and Ni, though a little Na is found in some coatings (not listed in Table 1). The content of Al in the coating increases with increasing the concentrations of NaAlO₂,

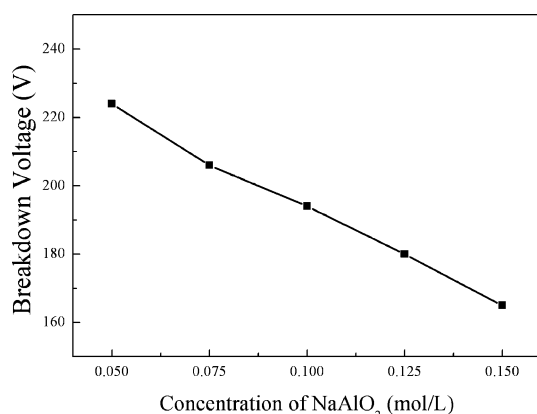


Fig. 1. Variation of breakdown voltage with the concentration of NaAlO₂.

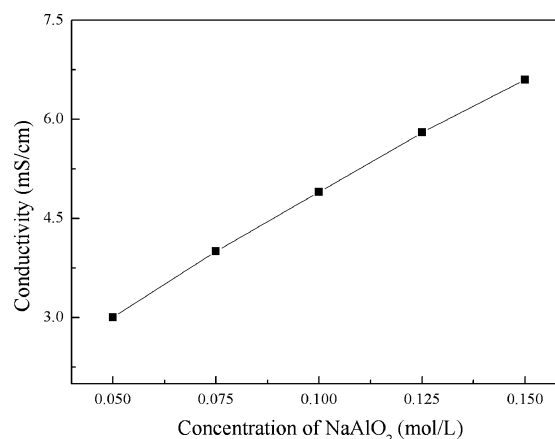


Fig. 2. Variation of conductivity with the concentration of NaAlO₂.

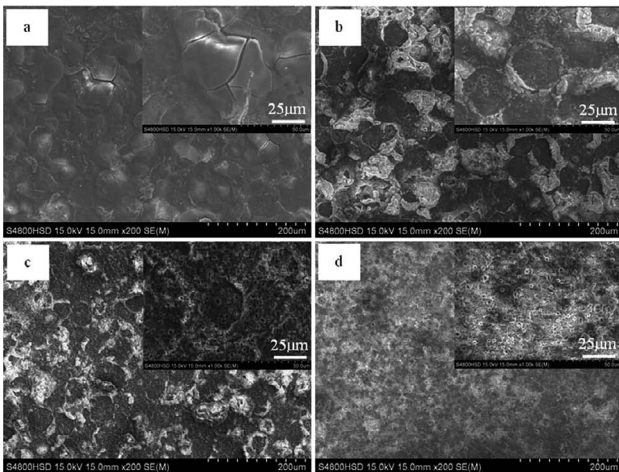


Fig. 3. Surface morphologies of the coatings formed by MAO in different NaAlO₂ concentrations: (a) C = 0.05 M; (b) C = 0.075 M; (c) C = 0.1 M; (d) C = 0.15 M. The inset pictures on the right of (a), (b), (c) and (d) are high magnification of (a), (b), (c) and (d), respectively.

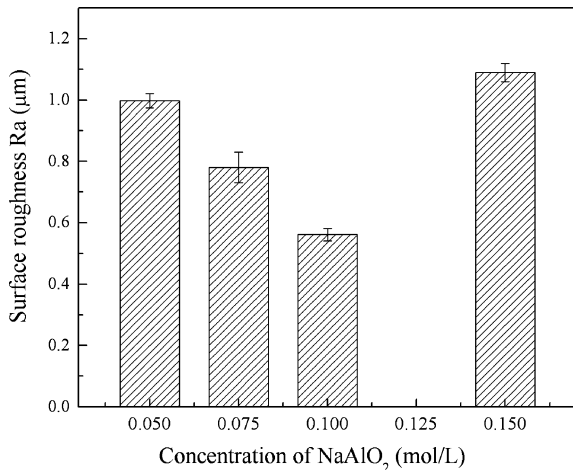


Fig. 4. Surface roughness of MAO coatings formed in different NaAlO₂ concentrations.

Table 1. Element Concentration of MAO Coatings Formed in Different NaAlO₂ Concentrations

NaAlO ₂ concentration (mol/L)	Element concentration of coatings (at.%)			
	Ni	Ti	Al	O
0.05	0.74	1.14	23.38	74.74
0.075	1.97	2.25	27.39	67.68
0.1	2.19	2.64	29.85	65.31
0.15	2.53	2.20	30.53	64.74

while the O decreases markedly. At the same time, the Ni in the surface layer slightly increases from 0.74% to 2.53%, but all of them is greatly lower than that of NiTi substrate. It is well known that Ni is allergenic and toxic when its concentration in the human body exceeds a certain level.¹⁵⁾ Consequently, it should be advantageous to suppress the release of Ni ion and improve the biocompatibility through MAO treatment on NiTi alloy.

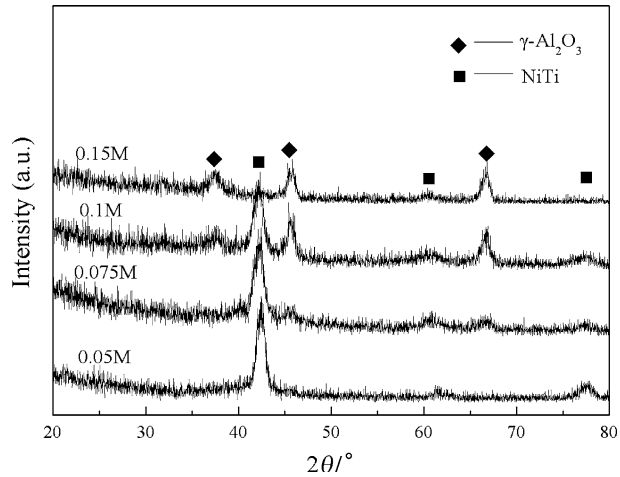


Fig. 5. TF-XRD patterns of the MAO coatings formed on NiTi alloy in different NaAlO₂ concentrations.

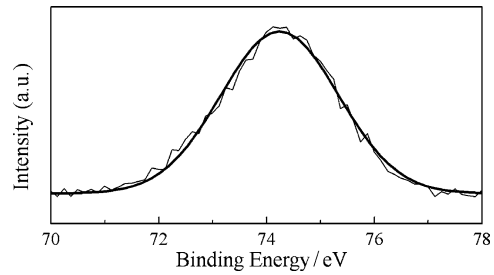


Fig. 6. XPS 2p spectra of Al for the coating formed in C = 0.05 M.

3.3 Effects of solution concentrations on phase structure of MAO coating

The TF-XRD patterns of MAO coatings formed on NiTi alloy in different NaAlO₂ concentrations is shown in Fig. 5. For the coating formed in C = 0.05 M, no Bragg peaks can be detected with resolution of the XRD apparatus used except peaks of NiTi substrate, which indicates that the coating is basically amorphous. However, for the coating formed in C = 0.075 M, there are two obvious diffraction peaks observed at $2\theta = 45.9^\circ$ and $2\theta = 66.8^\circ$ representing the (400) and (440) peaks of γ -Al₂O₃, respectively. For higher NaAlO₂ concentration (i.e., C = 0.1 M and C = 0.15 M), the (311) peak of γ -Al₂O₃ at 37.3° is also detected. In addition, the intensity of Al₂O₃ peaks is increased with increasing the concentrations of NaAlO₂. Meanwhile, the intensity of NiTi substrate peaks decreases, especially in C = 0.15 M the peaks of NiTi almost disappear, indicating that the coatings become thicker and compacter. In terms of the result of EDS, there is much Al element in the coating formed in C = 0.05 M, but no crystallized Al oxides or compounds are detected by TF-XRD. In order to identify the chemical state of Al in the presence of MAO coating, the XPS of the coating for Al2p is studied, as shown in Fig. 6. Only one peak at 74.2 eV is detected on the coating, which is characteristic for Al³⁺, present in Al₂O₃.¹⁶⁾ Therefore, the MAO coating formed in C = 0.05 M also mainly consists of Al₂O₃, but it is in the form of amorphous state. The results imply that it is beneficial to enhance the crystallinity of Al₂O₃ through increasing the concentrations of NaAlO₂.

The state of aluminates ions in the NaAlO₂ solution is very complicated, which is mainly related to solution concentration,

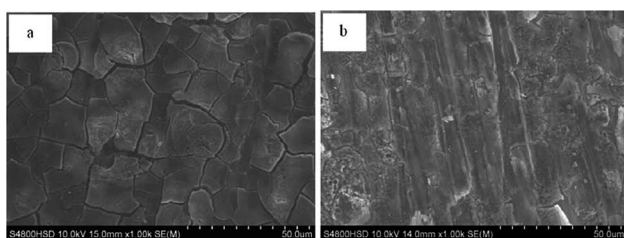
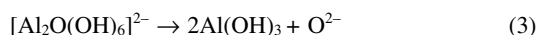


Fig. 7. Surface morphologies of the oxide film formed in (a) $C = 0.075$ M and (b) $C = 0.15$ M at the initial stage of the MAO process.

preparation process and existing time. According to Refs.,¹⁷⁾ aluminates ions exist in the form of $[\text{Al}(\text{OH})_4]^- (\text{H}_2\text{O})_x$ under the low NaAlO₂ concentration ($C < 0.1$ M), and $\text{Al}(\text{OH})^-$ under the moderate concentration ($C = 0.1$ M), while it will dehydrate and form $[\text{Al}_2\text{O}(\text{OH})_6]^{2-}$ or more complicated poly-aluminates ions under the high concentration ($C > 0.1$ M). At the initial stage of the MAO process, a large number of aluminates ions are congregated on the anode surface due to the effect of the electric field. Apart from the electrochemical process, chemical precipitation of aluminum hydroxide can occur on the anode surface according to the following reactions:



The formation of the oxide film on valve metals at the initial stage of MAO process is the prerequisite for MAO to be able to proceed. Compared with valve metals, such as Ti, Mg and Al, NiTi alloy is difficult to form the oxide film with dense layer through the conventional anodic oxidation due to its high nickel content on the surface layer.⁴⁾ The results of EDS demonstrate that the oxide films formed in $C = 0.05$ – 0.15 M at the initial stage of the MAO process contain almost only Al and O (not shown here). In terms of Eq. (1)–(3) and the results of EDS analysis, the surface of NiTi alloy can form the oxide film through chemical precipitation of aluminum hydroxide at the initial of MAO process, which is consistent with Refs.^{18),19)} However, considering the charge number and size of the aluminates ions, the reaction-progressing ability of the equations may be ranked in ascending order as: Eq.1 < Eq.2 < Eq.3. Therefore, the different quality of the oxide films can be formed on NiTi alloy in different NaAlO₂ concentrations, as shown in Fig. 7. However, according to the results of XRD and XPS, the Al₂O₃ can not be crystallized in $C = 0.05$ M, which may be mainly due to the lower valid voltage. With increasing the concentrations of NaAlO₂, the valid voltage increases, accompanied by the increase of single spark temperature, which is beneficial to enhance the crystallinity of Al₂O₃. Therefore, the crystallized Al₂O₃ coatings are formed in $C > 0.05$ M and the crystallinity is enhanced with increasing concentration of NaAlO₂.

3.4 Effects of solution concentration on corrosion resistance of MAO coatings

The different NaAlO₂ concentrations have an influence on the surface morphology, element and phase composition of the coatings, and therefore, it is bound to influence the corrosion resistance of the coatings. Figure 8 shows the potentiodynamic polarization curves of the MAO coatings formed in different NaAlO₂ concentrations. The corrosion potential (E_{corr}) and corrosion cur-

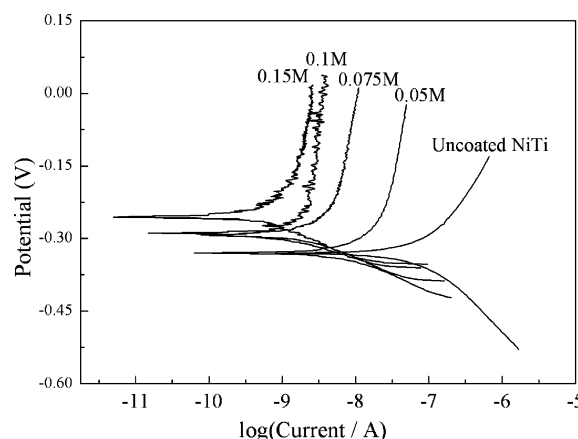


Fig. 8. Potentiodynamic polarization curves of the uncoated and coated samples in 0.9% NaCl solution.

Table 2. The Results of Potentiodynamic Corrosion Test in 0.9% NaCl Solution

NaAlO ₂ Concentration (mol/L)	E_{corr} (V)	i_{corr} (A/cm ²)
NiTi	−0.331	1.10×10^{-7}
0.05	−0.330	1.10×10^{-8}
0.075	−0.292	3.24×10^{-9}
0.1	−0.289	1.74×10^{-9}
0.15	−0.256	5.01×10^{-10}

rent density (i_{corr}) extracted from the polarization curves are shown in Table 2. The results show that the MAO coated NiTi alloy samples possess much higher corrosion potential and lower corrosion current than that of uncoated NiTi alloy, indicating that the coated samples have a better corrosion resistance in comparison with uncoated NiTi alloy. The corrosion potential of the coatings increases from −0.330 to −0.256 V when the NaAlO₂ concentration is varied from 0.05 to 0.15 M, while the corrosion current density reduces from 1.10×10^{-8} to 5.01×10^{-10} , indicating that the corrosion resistance of the coatings is increased with the increase of NaAlO₂ concentration within the range studied in this work. And the best one, formed in $C = 0.15$ M, is two orders of magnitude higher than that of uncoated NiTi alloy.

The breakdown voltage decreases linearly from 224 V to 165 V with increasing the concentrations of NaAlO₂. In this study, the MAO coating was prepared at constant voltage treatment for 30 min, so the thickness of MAO coating increase with increasing concentration of solution. It can be concluded that thicker MAO coating can improve the corrosion resistance of coated NiTi alloy than thin coating.

3.5 Effects of solution concentrations on the bonding strength.

The bonding strength of MAO coating to NiTi substrate were measured by a modified ASTM C-633. Figure 9 shows the bonding strength MAO coating formed in different NaAlO₂ concentration to NiTi substrate. It can be seen that the bonding strength increase with increasing NaAlO₂ concentration. The bonding strength of coating to NiTi substrate is only 6.0 MPa when the NaAlO₂ concentration is 0.05 mol/L. However, the

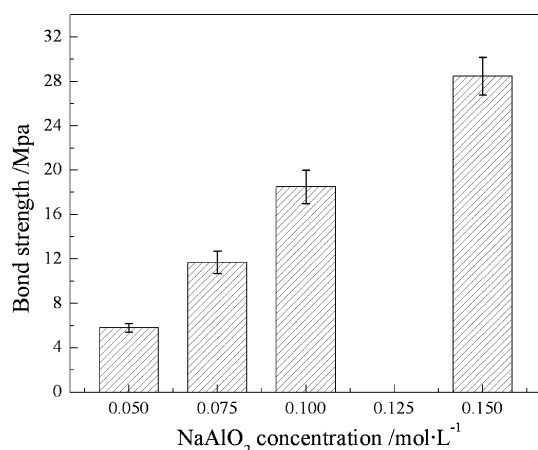


Fig. 9. Bonding strength of MAO coatings formed in different NaAlO₂ concentrations.

NaAlO₂ concentration increase to 0.15 M, the bonding strength of coating to NiTi substrate was improve remarkably, from 6 MPa increasing to 28.0 MPa. It can be seen from Fig. 2 that the coating has many conch-like humps with some crackles on the surface layer when the NaAlO₂ concentration is 0.05 M. The conch-like humps with some crackles on the surface layer remarkably reduced the bonding strength of coating to NiTi substrate. Although coating formed in solution of 0.075 M and 0.10 M has not crackles in the surface, because the white network inclusions exist in the surface of coating, the bonding strength of coating to NiTi substrate also is lower. The NaAlO₂ concentration is up to 0.15 mol/L, the coating formed on NiTi substrate exhibit typical MAO coating, not crackles and white network inclusions found. So the bonding strength of coating to NiTi substrate was up to 28.0 MPa, which indicates that coating appears to be well bonded with the NiTi substrate.

4. Conclusions

The MAO coating was prepared on biomedical MAO alloy by micro-arc oxidation (MAO) in sodium aluminate (NaAlO₂) solution using pulsed bipolar power supply. It was found that NaAlO₂ concentrations have an influence on structure and characterization of micro-arc oxidation coatings formed on biomedical NiTi alloy. The below conclusion can be concluded:

(1) The Al₂O₃ coatings were successfully formed on biomedical NiTi alloy by MAO in the electrolytes of different NaAlO₂ concentrations. The surface morphologies of MAO coating depend on the concentration of NaAlO₂ solution.

(2) The breakdown voltage values decrease linearly with increasing the NaAlO₂ concentrations. Increasing the concentration of NaAlO₂, the coating can change from amorphous Al₂O₃

to crystallized Al₂O₃.

(3) The corrosion resistance of the coatings is increased with the increase of NaAlO₂ concentration. And the best one, formed in C = 0.15 M, is two orders of magnitude higher than that of uncoated NiTi alloy.

(4) The bonding strength of coating increases with increasing NaAlO₂ concentration. Especially, the bonding strength of MAO coating to NiTi substrate was up to 28.0 MPa when NaAlO₂ concentration is 0.15 M.

(5) The 0.15 M NaAlO₂ solution is the best to prepare the MAO coating with good corrosion resistance and highly bonding strength to the NiTi substrate compared to 0.05 M, 0.075 M and 0.10 M NaAlO₂ solution.

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