

Article

Mutual Impact of Four Organic Calcium Salts on the Formation and Properties of Micro-Arc Oxidation Coatings on AZ31B Magnesium Alloys

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Abstract: Calcium phosphate (Ca–P) coatings provide an effective approach in current research and the clinical application of Mg alloys by endowing them with improved corrosion resistance, biocompatibility, and even bioactivity. Ca-containing coatings were prepared on AZ31B magnesium alloys using the micro-arc oxidation (MAO) technique and a combination of ethylenediaminetetraacetic acid calcium disodium (EDTA–Ca), calcium glycerophosphate (GP–Ca), calcium gluconate (CaGlu₂), and calcium lactate (CaLac₂) as the Ca source in a near-neutral solution. The respective and mutual impacts of the four calcium salts on the formation and properties of the coatings were investigated. Experimental results indicated that GP–Ca was more decisive than EDTA–Ca, CaGlu₂, and CaLac₂ in the formation, morphology, and, therefore, the corrosion resistance of the coatings. GP–Ca alone could not effectively incorporate Ca²⁺ ions into the coatings but it could combine with EDTA–Ca, CaGlu₂, and CaLac₂ to bring a synergistic effect in improving the Ca content of the coatings. The bifunctional structure of CaGlu₂ and CaLac₂, containing hydroxyl groups and carboxylic groups with anchoring effects, enabled them to enhance the Ca content of the coatings. However, due to minor differences in functional group orientation, CaGlu₂ was a little more efficient than CaLac₂ in increasing Ca content, while CaLac₂ was a little more efficient than CaGlu₂ in improving the corrosion resistance of the coatings. Finally, the total concentration of the four calcium salts, [Ca²⁺]_T, should be controlled at a proper level; otherwise, excessively high [Ca²⁺]_T would produce localized microbumps originating from coating ablation, eventually deteriorating the corrosion resistance of the coatings.

Keywords: micro-arc oxidation; organic calcium salt; magnesium alloys; mutual impact



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1. Introduction

Magnesium alloys have been considered promising metallic implants for bone repair and bone tissue engineering because of their unique biomedical and biocompatible properties. However, there is a major limitation to be noted, namely that conventional Mg alloys degrade rapidly prior to completing their specified clinical mission, accompanied by H₂ formation and an alkaline shift in pH around the degrading surface [1–3]. Various surface modification and coating techniques have been applied to suppress the degradation of Mg alloys or even to endow them with improved cytocompatibility [1–8], osteogenesis ability [1–6], antibacterial ability [1–6], and antitumor ability [7,8]. Among these, micro-arc oxidation (MAO) has received considerable attention, since MAO coatings are generated via in situ oxidation and sintering on magnesium alloys [1,3,4,9], aluminum alloys [10–13], titanium alloys [14–18], and tantalum alloys [19], and therefore exhibit high hardness, good wear resistance, and corrosion resistance. Most importantly, the composition, structure,

and performance of MAO coatings can be appropriately tuned by adjusting electrolyte species and concentration or by varying process parameters [1,2,18–20]. Regarding the chemical components of corrosion-resistant or even bio-functional coatings on Mg alloys, Ca–P compounds provide an effective approach in research and clinical applications, not only for their physiochemical similarity with inorganic apatite, the chief mineral component of bone matrix, but also for their superb biocompatibility, osteo-conductivity, and osteo-integrativity [1–3,21,22].

Reviewing the literature on Ca–P coatings on Mg alloys via the MAO process, it is clear that the Ca content of the coatings is generally low, due to the low level of effective Ca^{2+} concentration in the MAO solution and the low stability of the solution, originating further from commonly used alkaline solution systems, the limited solubility of many calcium salts, and the precipitation of calcium phosphate and/or calcium hydroxide [1–4,23–27]. On the contrary, our research demonstrated, for the first time, the efficiency of a near-neutral pH solution [25–27]. More specifically, in near-neutral solutions, wherein ethylenediaminetetraacetic acid calcium disodium (EDTA-CaNa_2 , abbreviated as EDTA–Ca) and phytic acid ($\text{C}_6\text{H}_6(\text{PO}_4)_3\text{H}_3$, usually abbreviated as H_3Phy) were used separately as a Ca source and a coating-forming agent, the high solubility of EDTA–Ca and the strong chelating ability of H_3Phy helped inhibit the precipitation of calcium phosphate, and eventually increased the Ca content of the MAO coatings [26]. However, in our research, we also found that EDTA–Ca tended to be a corrosive agent for Mg alloys, and, therefore, significantly decreased the thickness and corrosion resistance of the MAO coatings [26]. These findings suggest that it is worth continuing to explore new electrolytes that are simultaneously effective in improving the Ca content, thickness, and corrosion resistance of Ca–P MAO coatings on Mg alloys in the near-neutral system. Moreover, it might be a better choice to adopt a combination of EDTA–Ca and other calcium salts as electrolyte components, efficient in inhibiting the corrosion of Mg alloys.

Among various corrosion inhibitors, it is well-known that calcium gluconate (CaGlu_2) and calcium glycerophosphate (GP–Ca) have been widely used as corrosion inhibitors for iron, mild steel, and carbon steel in different environments [28–31]. Moreover, in our more recent research about HA-containing MAO coatings on titanium alloys, it was found that, in comparison with CaGlu_2 or GP–Ca alone, their combination synergistically improved the Ca content of the coatings [32]. Additionally, calcium lactate (CaLac_2), also a typical hydroxycarboxylate just like CaGlu_2 , possesses both COO^- and $-\text{OH}$ groups, with comparable chelating ability but better aqueous solubility [33–35]. These characteristics make CaLac_2 comparable or even preferable in cases where solubility and sequestering ability need to be considered, for example when used as a sequestering agent in dairy products, an antioxidant in controlling water activity, and an organic precursor for self-healing concrete [33–36]. Hence, it is of importance to find out whether the similar characteristics possessed by CaGlu_2 and CaLac_2 will create the possibility of mutual promotion in the formation and properties of MAO coatings. To our knowledge, however, there are no studies so far that use CaLac_2 as a Ca source to prepare Ca–P MAO coatings.

Based on all the above viewpoints, in this study we aimed to ascertain whether it is preferable to use a combination of EDTA–Ca, GP–Ca, CaGlu_2 , and CaLac_2 to balance the demands of ease of formation, high Ca content, and better corrosion resistance for Ca–P MAO coatings on Mg alloys in near-neutral solutions. Furthermore, their respective and mutual influences on the formation and properties of the coatings were investigated using an L_9 (3^4) orthogonal experiment and single-factor experiments.

2. Experimental Section

2.1. MAO Preparation

The commercial magnesium alloy AZ31B (nominal composition: Mg–3.0Al–1.0Zn in wt.%), provided by Suzhou Chuan Mao Metal Materials Co., LTD, Suzhou, China, was machined into cuboid samples with a dimension of 10 mm × 10 mm × 6 mm. Before being subjected to MAO treatment, the sample was mechanically ground successively with SiC

papers from 80 to 3000 grits, cleaned with tap and distilled water, and finally dried in an air stream.

Based on our previous studies [25–27], a near-neutral solution composed of 6.0 g/L NH_4HF_2 , 15.0 g/L H_3PO_4 , 12.0 g/L H_{12}Phy , and 360 g/L $\text{C}_6\text{H}_{12}\text{N}_4$ was used as the base solution, in which GP–Ca alone or a combination of four organic calcium salts was dissolved. The four organic calcium salts were EDTA–Ca, GP–Ca, CaLac₂, and CaGlu₂. Their chemical structures are shown in Figure 1. An orthogonal experimental design L9 (3^4), shown in Table 1, was used to ascertain the effect of EDTA–Ca, GP–Ca, CaLac₂, and CaGlu₂ concentrations on the formation and properties of the Ca–P coatings. Correspondingly, nine MAO samples, fabricated according to the orthogonal array, were designated as Nos. 1–9. All MAO treatments were conducted under a constant current density mode with a positive pulse. A homemade MAO5D power supply (Chengdu Tongchuang New Material Surface Engineering and Technology Center, Chengdu, China) was used. The sample for MAO treatment and a stainless-steel barrel containing the MAO solution were connected separately to the anode and the cathode. The electrical parameters were a current density of 60 mA/cm², a duty cycle of 35%, a pulse frequency of 2000 Hz and a treatment time of 3.5 min. The solution pH was tested using a PHS-3C pH meter (Shanghai Yoke Instrument Co., Ltd., Shanghai, China). The solution conductivity was measured at room temperature using a DDS-307 microprocessor conductivity meter (Jiangxi Gan Instrument Technology Co., Ltd., Nanchang, China).

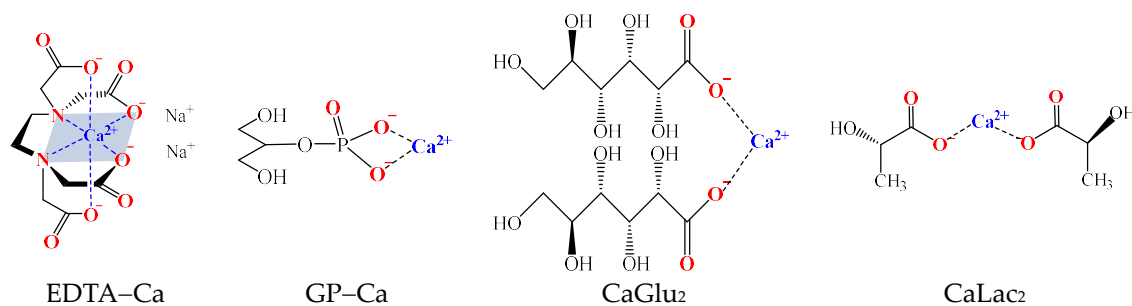


Figure 1. Molecular structures of the four organic calcium salts.

Table 1. Orthogonal array and results of orthogonal experiment to ascertain the influences of EDTA–Ca, GP–Ca, CaLac₂, and CaGlu₂ concentrations on the Ca content and i_{corr} of the MAO coatings.

Experiment No.	Concentration of Calcium Salt (mol/L)				Ca Content (wt.%)	i_{corr} (nA/cm ²)
	EDTA–Ca	GP–Ca	CaLac ₂	CaGlu ₂		
No. 1	0.01	0.01	0.01	0.01	3.37	6.89
No. 2	0.01	0.02	0.02	0.02	6.48	27.7
No. 3	0.01	0.03	0.03	0.03	8.08	55.1
No. 4	0.02	0.01	0.02	0.03	0.19	246
No. 5	0.02	0.02	0.03	0.01	3.72	39.7
No. 6	0.02	0.03	0.01	0.02	6.02	34.5
No. 7	0.03	0.01	0.03	0.02	0.19	356
No. 8	0.03	0.02	0.01	0.03	4.45	74.0
No. 9	0.03	0.03	0.02	0.01	5.16	47.0
k_1	5.98	1.25	4.61	4.08		
	(29.90)	(203.0)	(38.46)	(31.20)		
k_2	3.31	4.88	3.94	4.23		
	(106.7)	(47.13)	(106.9)	(139.40)		
k_3	3.27	6.42	4.00	4.24		
	(159.0)	(45.53)	(150.27)	(125.03)		
Difference	2.71	5.17	0.67	0.16		
	(129.10)	(157.43)	(111.80)	(108.20)		
Rank	2	1	3	4		
	(2)	(1)	(3)	(4)		

2.2. Characterization of MAO Samples

2.2.1. Surface and Cross-Sectional Analysis

After coating with gold powder, the surface and cross-sectional morphology, chemical composition, and elemental mapping of the MAO-treated samples were observed with a SIGMA scanning electron microscope (SEM, Zeiss Sigma, Jena, Germany) attached with an energy-dispersive X-ray spectroscopy (EDS) with the original WD of 10.0 mm and HV of 15 kV. The MAO coatings were scraped from the MAO-treated samples, ground into powder with a mortar and characterized using an X-ray diffractometer (XRD, Shimadzu XRD-6100, Tokyo, Japan) using Cu K α radiation in the 2 θ range of 10–80° at a scanning speed of 4°/min. The chemical states of elements in the MAO coatings were determined using an X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo VG Scientific, Waltham, MA, USA) with an Al K α anode (λ = 1486.6 eV). All binding energy values were calibrated according to the adventitious C 1s set at 284.6 eV. The average size of the micropores on the coating surface was measured using Nano Measurer 1.2 software.

2.2.2. Electrochemical Analysis

Potentiodynamic polarization (PDP) measurements were performed using a Gamry Reference 600 electrochemical workstation (Gamry Instruments, Warminster, PA, USA). All the PDP tests were conducted at 37 ± 0.5 °C in Hank's solution, which was composed of 8 g/L NaCl, 0.4 g/L KCl, 0.14 g/L CaCl₂, 0.35 g/L NaHCO₃, 1.0 g/L C₆H₁₂O₆, 0.2 g/L MgSO₄·7H₂O, 0.1 g/L KH₂PO₄, and 0.06 g/L Na₂HPO₄·7H₂O. All the electrochemical analyses were conducted in a conventional three-electrode electrochemical cell. A sample with an exposed surface of 10 mm × 10 mm was used as the working electrode, while a saturated calomel electrode (SCE) and a platinum electrode were employed as the reference electrode and the counter electrode, respectively. After an initial delay of 300 s, a PDP test was performed from −0.25 to 0.5 V with respect to the open circuit potential (OCP) at a scanning rate of 1 mV/s. Each sample was tested five times in duplicate to ensure reproducibility. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined using the Tafel method through linear extrapolation of the active polarization zone [37,38]. The average i_{corr} of five duplications for each group was taken as the final result and the PDP curve with the nearest i_{corr} to the mean value is shown in subsequent figures. The polarization resistance R_p was calculated using the Stern–Geary equation.

$$R_p = \frac{\beta_a \times \beta_c}{2.303 i_{\text{corr}} (\beta_a + \beta_c)} \quad (1)$$

3. Results

3.1. Characteristics of MAO Samples

3.1.1. Morphology and Chemical Composition

The SEM surface morphologies of the nine samples are shown in Figure 2, while the enlarged details of the defects and the real images of the samples are shown in the top-right subfigures and the bottom-right subfigures, respectively. It was clear that MAO coatings could not be successfully prepared on samples No. 4 and No. 7 (Figure 2d,g), on which there were some randomly distributed pits. All the remaining seven samples exhibited the typically porous morphology of MAO coatings; however, on samples No. 3 and No. 8 there were some microbumps that are presented at the top-right corner of Figure 2c,h. On samples No. 5 and No. 9 (Figure 2e,i) the microcracks were obvious and the micropores were smaller than those on the others.

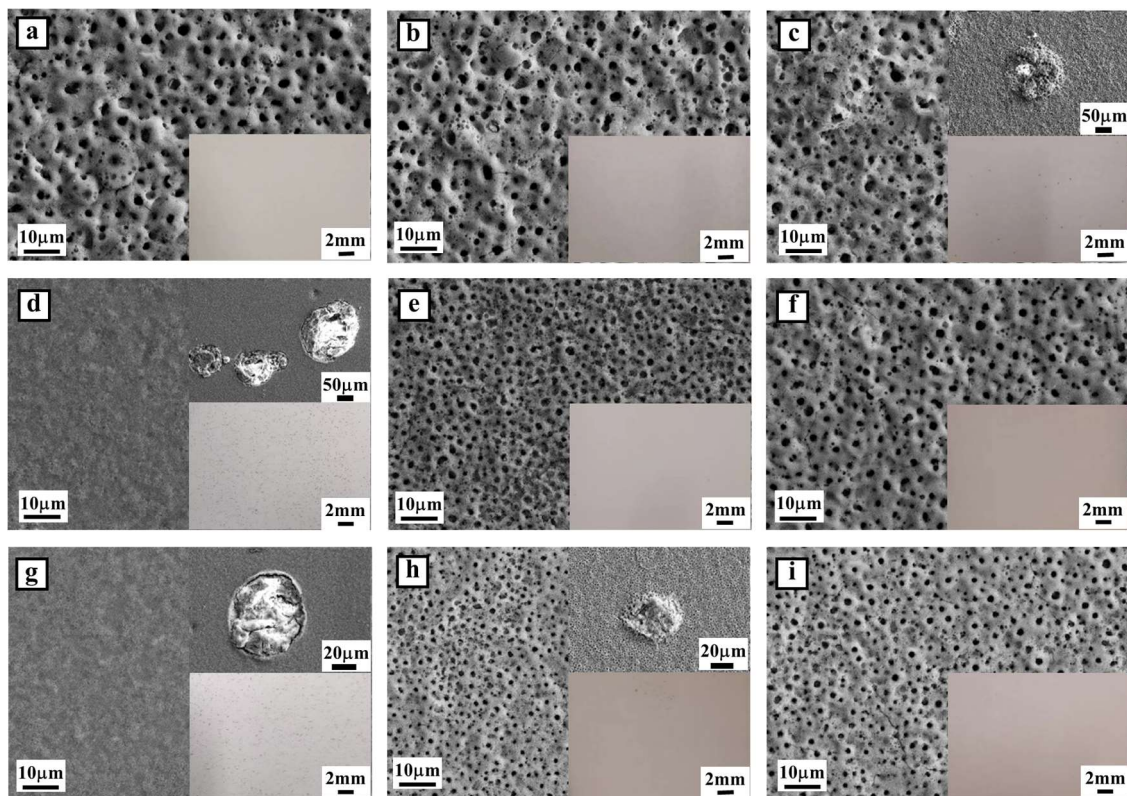


Figure 2. SEM surface morphologies, enlarged details of the defects (the top-right subfigures), and the real images (the bottom-right subfigures) of samples Nos. 1–9 prepared according to the orthogonal experiment shown in Table 1: (a) No. 1, (b) No. 2, (c) No. 3, (d) No. 4, (e) No. 5, (f) No. 6, (g) No. 7, (h) No. 8, and (i) No. 9.

The EDS spectra and chemical compositions of the nine samples are shown in Figure 3. Both of the samples No. 4 and No. 7 (Figure 3d,g) clearly exhibited low Ca, F, P, and O contents but an obviously high Mg content; more specifically, they separately contained 0.19 wt.% and 0.19 wt.% of Ca, 2.73 wt.% and 2.33 wt.% of F, 2.56 wt.% and 2.64 wt.% of P, 20.09 wt.% and 20.24 wt.% of O, but 65.90 wt.% and 66.70 wt.% of Mg, which further proved the failure of the MAO coating formation and indicated that the pits were derived from substrate corrosion. All the other seven samples were comparable with each other in terms of C, O, F, P, and Mg content but were different in Ca content; more exactly, samples No. 1 and No. 3 (Figure 3a,c) exhibited the lowest and the highest Ca contents of 3.37 wt.% and 8.08 wt.%, respectively, suggesting that the substrate and the electrolytes in the MAO solutions participated in the coating formation. It should be mentioned that some randomly distributed pits appeared on samples No. 4 and No. 7, while some microbumps appeared on samples No. 3 and No. 8. Moreover, compared with samples No. 4 and No. 7 (Figure 3d,g), samples No. 3 and No. 8 (Figure 3c,h) clearly exhibited higher O and P contents but a lower Mg content; therefore, it could be inferred that the microbumps on samples No. 3 and No. 8 were derived from the localized ablation of the MAO coating but not from substrate corrosion, as in the case of the pits on samples No. 4 and No. 7.

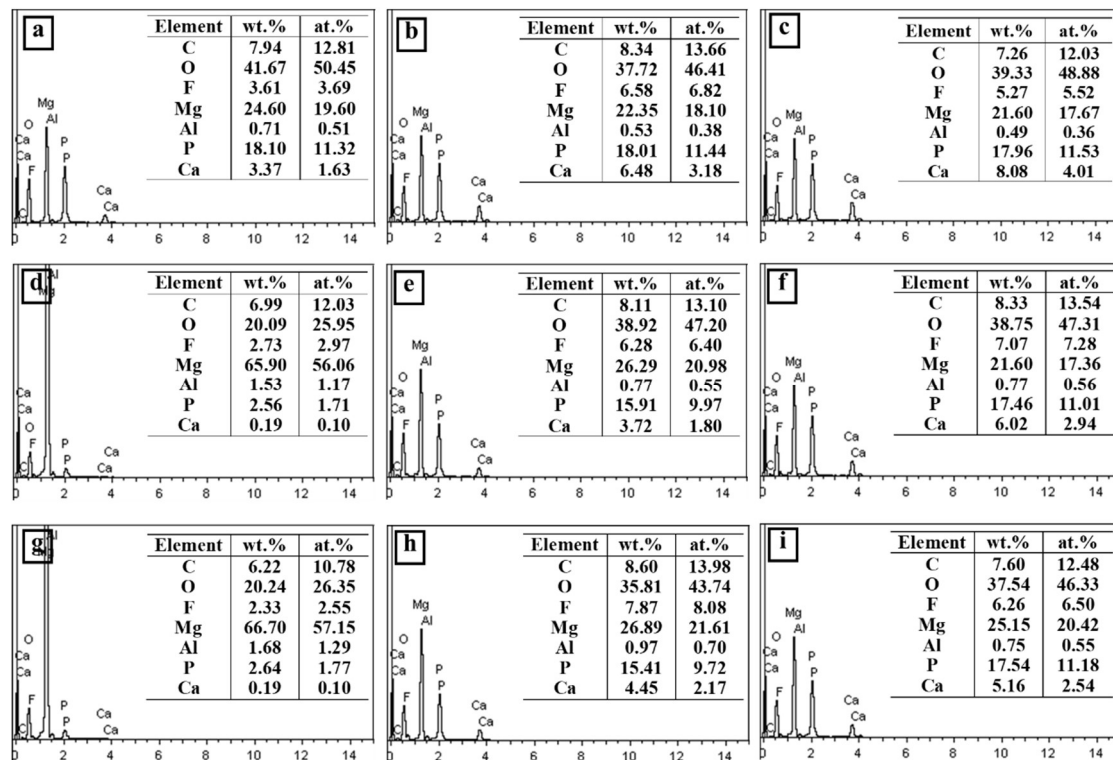


Figure 3. EDS spectra and chemical compositions of samples Nos. 1–9 prepared according to the orthogonal experiment shown in Table 1: (a) No. 1, (b) No. 2, (c) No. 3, (d) No. 4, (e) No. 5, (f) No. 6, (g) No. 7, (h) No. 8, and (i) No. 9.

3.1.2. XRD Analysis

Taking into account the surface morphology and Ca content, samples No. 1, No. 2, No. 4, No. 5, and No. 6 were subjected to XRD analysis, and the XRD patterns are shown in Figure 4. The diffraction peaks at 37.0° , 43.3° , 62.8° , and 78.4° could be indexed to the (111), (200), (220), and (222) planes of the MgO phase (JCPDS No. 45-0946), respectively, indicating that the coatings contained MgO. Meanwhile, the Ca- and P- species could not be detected. Combining this XRD analysis with the EDS spectra and chemical composition analyses, it could be deduced that the Ca- and P- species might exist in an amorphous state.

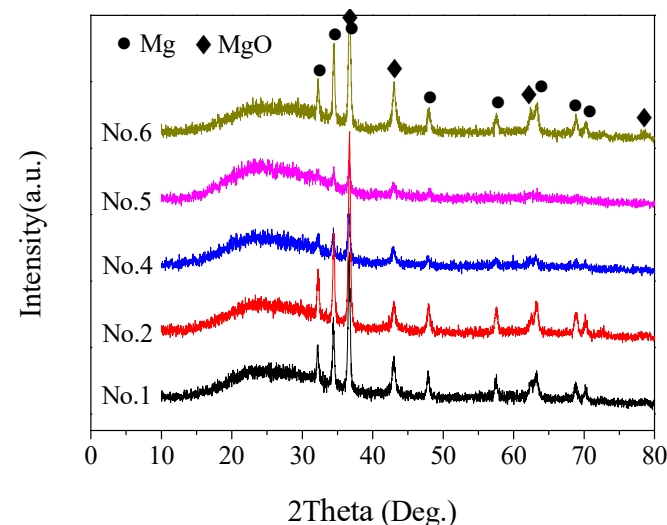


Figure 4. XRD patterns of the samples No. 1, No. 2, No. 4, No. 5, and No. 6.

3.1.3. XPS Analysis

In order to ascertain the chemical state of Ca- and P- species in the MAO coating, sample No. 2, with its typically porous MAO coating structure and the second highest Ca content of 6.48 wt.%, was subjected to XPS analysis, and the spectra are shown in Figure 5. The survey spectrum (Figure 5a) showed that elements C, O, F, P, Mg, and Ca were detected in the coating, just as in the EDS analysis results. Spectrum C 1s (Figure 5b) could be fitted into three peaks, one of which, at 284.6 eV, was assigned to the C–C bond, while the other two, at 285.9 and 288.3 eV, were separately attributed to the C–O and C=O bonds and to impurity peaks. Spectrum O 1s (Figure 5c) could be fitted into two peaks at 531.2 and 532.4 eV, corresponding to MgO [39] and PO_4^{3-} [40]. Spectrum Mg 1s (Figure 5d) could be fitted into two peaks at 1304.0 and 1304.9 eV, corresponding to MgO and $\text{Mg}_3(\text{PO}_4)_2$ [38,39]. Spectrum Ca 2p (Figure 5e) could be fitted into two peaks at 347.8 eV for Ca 2p_{3/2} and 351.4 eV for Ca 2p_{1/2}, and further attributed to $\text{Ca}_3(\text{PO}_4)_2$ [41]. Two peaks were fitted in spectrum P 2p (Figure 5f) at 132.3 eV for P 2p_{3/2} and 134.1 eV for P 2p_{1/2}, and further attributed to PO_4^{3-} and H_2PO_4^- [40]. There was one peak at 684.8 eV in spectrum F 1s (Figure 5g), which was assigned to MgF_2 [39]. All these analyses indicated that the coating was mainly composed of MgO, $\text{Mg}_3(\text{PO}_4)_2$, $\text{Ca}_3(\text{PO}_4)_2$, and MgF_2 .

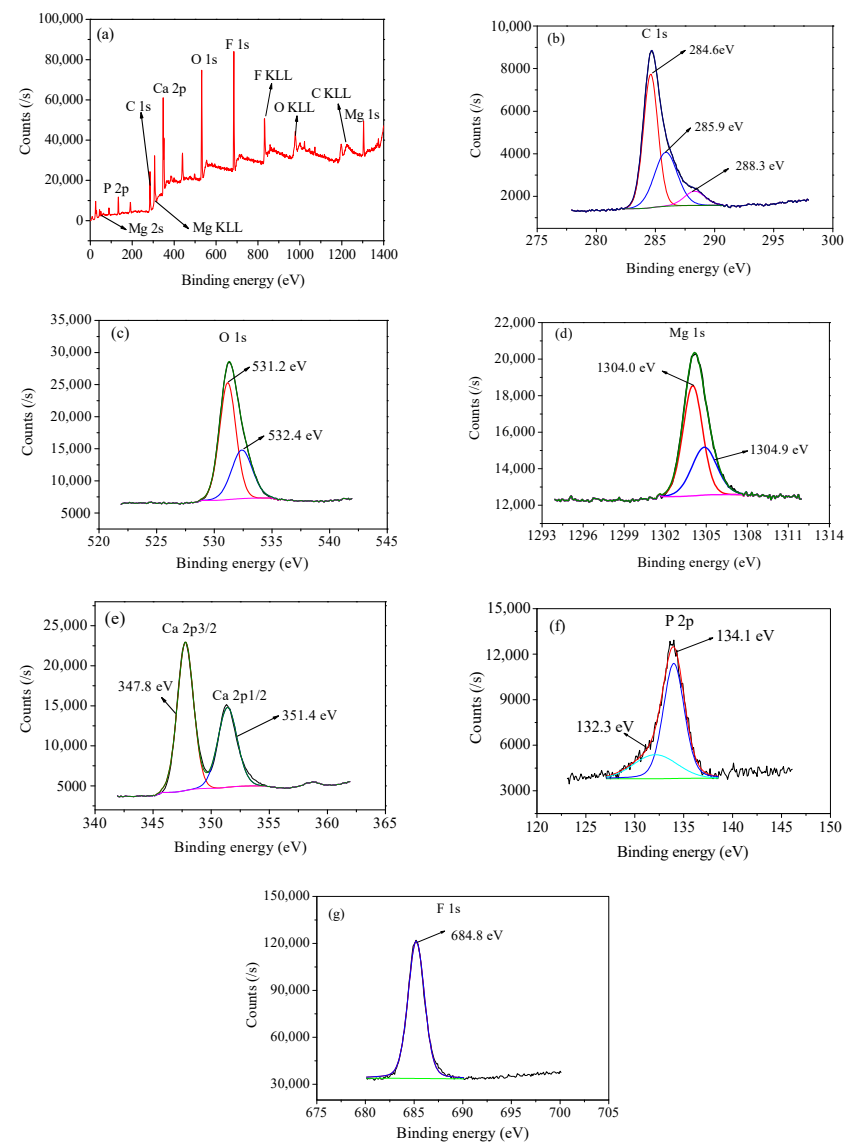


Figure 5. XPS spectra of sample No. 2: (a) survey spectrum, (b) C 1s, (c) O 1s, (d) Mg 1s, (e) Ca 2p, (f) P 2p, and (g) F 1s.

3.1.4. Electrochemical Analysis

The PDP curves of samples Nos. 1–9 in Hank's solution are shown in Figure 6a, and i_{corr} s obtained with Tafel fitting are shown in Table 1. Sample No. 1 exhibited the smallest i_{corr} of 6.89 nA/cm^2 and the best corrosion resistance; meanwhile, samples No. 7 and No. 4 showed the first- and second-largest i_{corr} s of 356 and 246 nA/cm^2 , respectively, suggesting relatively worse corrosion resistance attributed to failure in the coating preparation and the localized pits that originated from substrate corrosion. Although typical MAO coatings were successfully prepared on samples No. 3 and No. 8, their i_{corr} s were both slightly higher— 55.1 and 74.0 nA/cm^2 , respectively—due to the localized microbumps derived from the coating ablation.

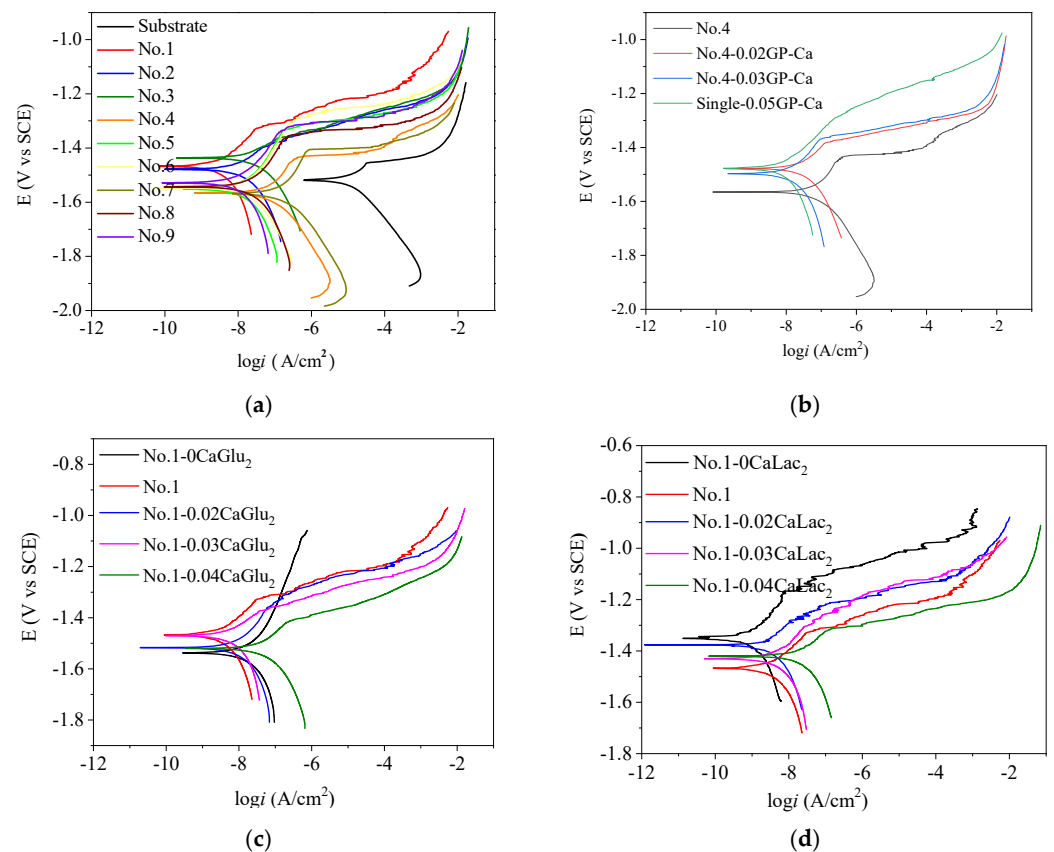


Figure 6. PDP curves of the substrate and the MAO samples: (a) the substrate and the orthogonal samples Nos. 1–9; (b) the samples No. 4, No. 4–0.02GP–Ca, No. 4–0.03GP–Ca, and Single–0.05GP–Ca; (c) the samples No. 1– $i\text{CaGlu}_2$, wherein $i = 0\text{--}0.04$; and (d) the samples No. 1– $i\text{CaLac}_2$, wherein $i = 0\text{--}0.04$.

3.2. Orthogonal Experiment Results

Considering the Ca content and i_{corr} of the MAO coatings as target variables, intuitive analysis was conducted to ascertain the influence of the four factors on each target variable. The analysis results are shown in Table 1 and Figure 7. In this figure and table, k_1 , k_2 , and k_3 are the calculated average values of each target variable at level 1, level 2, and level 3 of each factor, and the difference between the maximum and the minimum values of k_1 , k_2 , and k_3 for each factor was used to determine the importance of the factor. More exactly, the greater the difference, the more important the corresponding factor. As shown in Table 1, the descending order by importance of the four factors on the Ca content of the coatings was GP–Ca > EDTA–Ca > CaLac₂ > CaGlu₂. The order was the same for i_{corr} also, suggesting that the GP–Ca concentration and the CaGlu₂ concentration were individually the most and the least important factors for both the Ca content and the i_{corr} of the coatings.

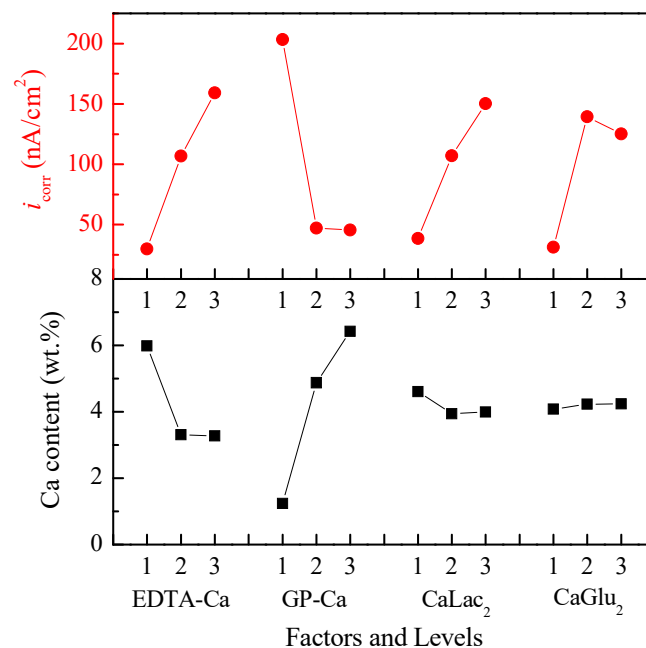


Figure 7. Effect of the four factors on the Ca content and the i_{corr} of the coatings prepared according to the orthogonal experiment shown in Table 1.

As shown in Figure 7, the impacts of the four factors on formation, structure, and properties of the coatings could be summarized as follows:

(1) The GP-Ca concentration was the most important factor. The increase in the GP-Ca concentration resulted in a significant enhancement in the Ca content but led to an L-shaped-like variation pattern of i_{corr} , i.e., first, a significant decrease and then an almost negligible decrease, suggesting that a higher GP-Ca concentration would be beneficial for the fabrication of an MAO coating with a higher Ca content and better corrosion resistance.

(2) EDTA-Ca was the second most important factor. The increase in the EDTA-Ca concentration resulted in an L-shaped-like variation pattern of Ca content but led to a dramatic increase in i_{corr} . The former finding differed from our previous research findings but the latter finding agreed with our previous findings; thus, a higher EDTA-Ca concentration was conducive to enhancing the Ca content of the MAO coatings but detrimental to their corrosion resistance [26]. Considering the orthogonal array shown in Table 1, the L-shaped decrease in Ca content with increased EDTA-Ca concentration in this research could be attributed to the failure of MAO coating fabrication on samples No. 4 and No. 7.

(3) The CaLac₂ concentration was the third most important factor, and its impacts on the Ca content and the i_{corr} were relatively slight. In particular, increasing the CaLac₂ concentration led first to a slight decrease and then to an almost negligible change in the Ca content, but led to an increase in the i_{corr} .

(4) The CaGlu₂ concentration was the least important factor, and its influence on the Ca content was extremely slight or even undetectable, though its impact on the i_{corr} showed first a decreasing trend and then a slight increase. Taking into account the surface morphology, Ca content, and corrosion resistance, sample No. 2 was preferable to the others, because it exhibited a typically porous MAO coating with a more uniform distribution of micropores, no obvious microcracks, and no localized pits generated from substrate corrosion or microbumps from coating ablation. Meanwhile, it showed the second highest Ca content of 6.48 wt.% and the second lowest i_{corr} of 27.7 nA/cm² among the nine samples.

3.3. Single-Factor Experiments

According to the orthogonal experimental results, the four different organic calcium salts revealed different impacts on the formation, the chemical composition—especially Ca content—and the corrosion resistance of the MAO coatings. Two particular performances

were worthy of further investigation. One was the failure of the MAO coating formation on samples No. 4 and No. 7, and the other was the difference between the pits derived from substrate corrosion on samples No. 4 and No. 7 and the microbumps from coating ablation on samples No. 3 and No. 8. In response to these two special performances, single-factor experiments were carried out to explore the impacts of GP–Ca, CaGlu₂, and CaLac₂.

3.3.1. Effect of GP–Ca Concentration

On the one hand, the orthogonal experiment had determined that GP–Ca concentration was the most important factor for Ca content and corrosion resistance. In particular, a lower GP–Ca concentration had resulted in lower Ca content and worse corrosion resistance of the MAO coating. On the other hand, it had not been possible to develop MAO coatings on samples No. 4 and No. 7, since the solutions contained a somewhat low GP–Ca concentration of 0.01 mol/L. Therefore, it could be inferred that the failure of the MAO coatings on samples No. 4 and No. 7 was highly related to the rather low level of GP–Ca concentration. To confirm this inference, another two samples were prepared by increasing the GP–Ca concentration to 0.02 and 0.03 mol/L but maintaining all other parameters, consistent with the sample No. 4. The two samples were named as No. 4–0.02GP–Ca and No. 4–0.03GP–Ca, respectively, and their operation parameters, surface morphologies, and chemical compositions are shown in Table 2 and Figure 8.

Table 2. Operation parameters, coating features, and Ca content of the samples prepared according to the single-factor experiments.

Sample	Concentration of Calcium Salt (mol/L)					Coating Feature	Ca Content (wt.%)
	EDTA–Ca	GP–Ca	CaLac ₂	CaGlu ₂	[Ca] _T		
No. 4	0.02	0.01	0.02	0.03	0.08	corrosion pits	0.19
No. 4–0.02GP–Ca	0.02	0.02	0.02	0.03	0.09	localized ablation	5.86
No. 4–0.03GP–Ca	0.02	0.03	0.02	0.03	0.10	localized ablation	6.89
Single–0.05GP–Ca	0	0.05	0	0	0.05	typically porous	0.11
No. 1–0CaGlu ₂	0.01	0.01	0.01	0	0.03	typically porous	2.18
No. 1–0.01CaGlu ₂ (No. 1)	0.01	0.01	0.01	0.01	0.04	typically porous	3.37
No. 1–0.02CaGlu ₂	0.01	0.01	0.01	0.02	0.05	typically porous	3.87
No. 1–0.03CaGlu ₂	0.01	0.01	0.01	0.03	0.06	typically porous	4.31
No. 1–0.04CaGlu ₂	0.01	0.01	0.01	0.04	0.07	localized ablation	4.68
No. 1–0CaLac ₂	0.01	0.01	0	0.01	0.03	typically porous	2.66
No. 1–0.01CaLac ₂ (No. 1)	0.01	0.01	0.01	0.01	0.04	typically porous	3.37
No. 1–0.02CaLac ₂	0.01	0.01	0.02	0.01	0.05	typically porous	3.86
No. 1–0.03CaLac ₂	0.01	0.01	0.03	0.01	0.06	typically porous	3.92
No. 1–0.04CaLac ₂	0.01	0.01	0.04	0.01	0.07	localized ablation	4.05

It could be seen that the increase in the GP–Ca concentration led to the following details: (i) an MAO coating could not be developed on sample No. 4 (Figure 2d), but samples No. 4–0.02GP–Ca and No. 4–0.03GP–Ca exhibited typically porous MAO coating characteristics (Figure 8(a1,b1)); (ii) the Ca content was only 0.19 wt.% for sample No. 4 (Figure 3d) but increased to 5.86 wt.% and 6.89 wt.% for samples No. 4–0.02GP–Ca and No. 4–0.03GP–Ca (Figure 8(a3,b3)), respectively; (iii) it was notable that some localized microbumps with an average size of about 150 µm also appeared on samples No. 4–0.02GP–Ca and No. 4–0.03GP–Ca (Figure 8(a2,b2)), which were similar in morphology to those on samples No. 3 and No. 8 (Figure 2c,h). The elemental mapping of microbumps on sample No. 4–0.03GP–Ca is shown in Figure 8(c1–c6). This mapping revealed that the microbumps were mainly composed of P, O, Mg, and Ca, which further proved that the microbumps were derived from the MAO coating ablation, just like those on samples No. 3 and No. 8. The PDP curves and the Tafel fitting results for samples No. 4–0.02GP–Ca, No. 4–0.03GP–Ca, as well as No. 4 are shown in Table 3 and Figure 6b. The i_{corr} s were separately 54.1 and 64.9 nA/cm² for No. 4–0.02GP–Ca and No. 4–0.03GP–Ca, one order

of magnitude smaller than that of sample No. 4 (246 nA/cm^2 shown in Table 1), but the same order of magnitude as the samples No. 3 and No. 8 (55.1 and 74.0 nA/cm^2 , also shown in Table 1). The polarization resistance R_p exhibited a similar change pattern. These details proved that the GP–Ca concentration played a more decisive role in the coating formation in this near-neutral solution system. In other words, in the solution system using a combination of GP–Ca and other calcium salts as the Ca source, a higher GP–Ca concentration was beneficial for MAO coating formation with higher Ca content and better corrosion resistance.

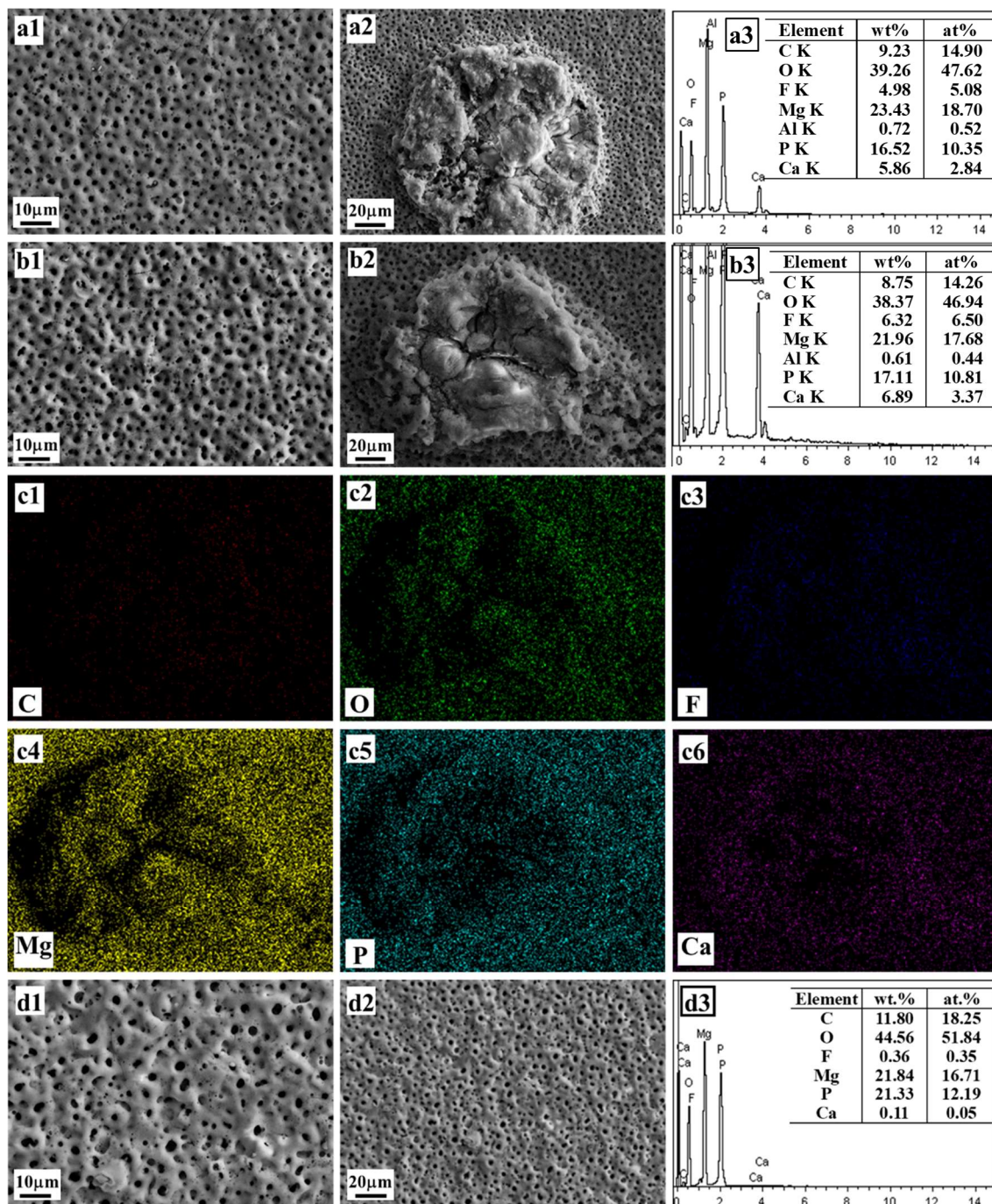


Figure 8. Surface morphologies and enlarged detail of localized microbumps, EDS spectra and chemical compositions, and elemental mapping of microbumps for the samples: (a1–a3) No. 4–0.02GP–Ca, (b1–b3) No. 4–0.03GP–Ca, (c1–c6) element mapping of microbumps on b2, (d1–d3) Single–0.05GP–Ca.

Table 3. Tafel fitting results of the samples prepared according to the single-factor experiments.

Sample	β_a (mV/dec)	β_c (mV/dec)	i_{corr} (nA/cm ²)	E_{corr} (V)	R_p (M Ω /cm ²)
Substrate	0.7271	0.1435	4670	−1.55	0.1114
No. 4	0.5382	0.2855	246	−1.56	0.3293
No. 4–0.02GP–Ca	0.2382	0.590	54.1	−1.45	1.362
No. 4–0.03GP–Ca	0.3237	0.3833	64.9	−1.49	1.174
Single–0.05GP–Ca	0.1549	0.3380	17.4	−1.45	2.651
No. 1–0CaGlu ₂	0.5972	0.639	10.3	−1.54	13.014
No. 1–0.01CaGlu ₂ (No. 1)	0.2050	0.4192	6.89	−1.47	8.676
No. 1–0.02CaGlu ₂	0.501	0.7346	35.0	−1.52	3.659
No. 1–0.03CaGlu ₂	0.2394	0.5887	37.1	−1.47	1.992
No. 1–0.04CaGlu ₂	0.3206	0.3112	135	−1.52	0.508
No. 1–0CaLac ₂	0.3538	0.786	4.82	−1.35	21.979
No. 1–0.01CaLac ₂ (No. 1)	0.2050	0.4192	6.89	−1.47	8.676
No. 1–0.02CaLac ₂	0.4691	0.7658	19.7	−1.38	6.412
No. 1–0.03CaLac ₂	0.3596	0.8103	20.7	−1.43	5.225
No. 1–0.04CaLac ₂	0.2647	0.5521	75.1	−1.42	1.034

However, this did not mean that the higher the GP–Ca concentration, the better the MAO coating performance. A sample, prepared through dissolving 0.05 mol/L of GP–Ca alone in the base solution and named as Single–0.05GP–Ca, exhibited a totally typical MAO coating without localized pits or microbumps but clearly exhibited a low Ca content of 0.11 wt.%, an i_{corr} of 17.4 nA/cm², and an R_p of 2.651 M Ω /cm², as shown in Table 3 and Figures 6b and 8(d1–d3). All these findings demonstrated convincingly that the combinations of GP–Ca with other calcium salts were more effective than GP–Ca alone, and, furthermore, that increasing the GP–Ca concentration and controlling the total concentration of the four calcium salts, which was abbreviated as $[Ca^{2+}]_T$, should be simultaneously considered to ensure preferable surface morphology, Ca content, and corrosion resistance of the MAO coatings. Otherwise, too low a GP–Ca concentration and too high $[Ca^{2+}]_T$ would produce negative impacts on the formation and properties of the MAO coatings.

3.3.2. Effect of CaGlu₂ Concentration

According to our more recent research about HA-containing MAO coatings on titanium alloys [32], the introduction of CaGlu₂ could effectively increase the Ca content of the coating in a base solution composed of 3.0 g/L sodium phytate (Na₁₂Phy) and 1.0 g/L H₃PO₄, which was totally different in its chemical composition and pH value from the one featured in this research. Meanwhile, when the same electrolyte CaGlu₂ was added into different MAO solution systems, it would have a different impact on the formation and performance of the MAO coating [1,3]. In addition, the aforementioned results concerning the effect of the GP–Ca concentration showed that too high $[Ca^{2+}]_T$ might produce a negative impact on the formation and performance of the MAO coating. To verify the effects of CaGlu₂ concentration and $[Ca^{2+}]_T$, four samples were prepared by varying the CaGlu₂ concentration from 0 to 0.02, then to 0.03, and then to 0.04 mol/L and maintaining all other parameters consistent with sample No. 1. The corresponding samples were named as No. 1–0CaGlu₂, No. 1–0.02CaGlu₂, No. 1–0.03CaGlu₂, and No. 1–0.04CaGlu₂, respectively. The operation parameters of these samples are also shown in Table 2.

Figure 9 presents the surface and cross-sectional morphologies, surface chemical composition, and thicknesses of the four samples as well as sample No. 1. As shown in Figure 9(a1–e1), MAO coatings were successfully developed on all the samples. However, with the CaGlu₂ concentrations increasing from 0 to 0.04 mol/L, the average pore size decreased from 1.75 ± 0.15 , to 1.73 ± 0.13 , 1.56 ± 0.08 , and 1.54 ± 0.21 , and then increased to 2.32 ± 0.27 μ m, with the result that the size of the micropores on the coating surface

became increasingly uneven. In particular, when the CaGlu_2 concentration was 0.03 mol/L, some small areas formed by rapid melting/cooling became apparent (Figure 9(d1)). When the CaGlu_2 concentration was as high as 0.04 mol/L, the number and size of these small areas formed by rapid melting/cooling significantly increased, and eventually some microbumps with an approximate size of 150 μm appeared on the surface of No. 1–0.04 CaGlu_2 (Figure 9(e1)). The microbumps were similar in morphology to those on samples such as No. 4–0.03GP–Ca, suggesting the localized ablation of the MAO coating. The Ca content of the coatings gradually increased from 2.18 wt.% to 4.68 wt.%, with CaGlu_2 concentration increasing from 0 to 0.04 mol/L (Figure 9(a2–e2)). The cross-sectional morphology shown in Figure 9(a3–e3) indicates that each coating was porous and with an inner–outer layer structure. Moreover, with the CaGlu_2 concentration increasing from 0 to 0.01, 0.02, and 0.03 mol/L, the coatings became thicker in their inner dense layer; therefore, the thicknesses decreased from 10.71 ± 0.43 to 9.98 ± 0.39 , 9.10 ± 0.16 , and 8.20 ± 0.26 μm , respectively. In comparison, due to the localized microbumps, No. 1–0.04 CaGlu_2 was a little more rough, loose, and porous, and finally achieved a thickness of 9.36 ± 0.39 μm . Figures 6c and 9(a4–e4) and Table 3 present the PDP curves and the Tafel fitting results of the series samples. The i_{corr} s for No. 1–0 CaGlu_2 , No. 1, No. 1–0.02 CaGlu_2 , and No. 1–0.03 CaGlu_2 fluctuated from 10.3 to 6.89, 35.0, and 37.1 nA/cm^2 ; however, they were slightly different from or even comparable to each other within one order of magnitude. However, the i_{corr} for No. 1–0.04 CaGlu_2 was as large as 135 nA/cm^2 , and obviously larger than the others, indicating a worse corrosion resistance. As shown in Table 3, the polarization resistance R_p of the samples gradually decreased from 13.014 to 0.508 $\text{M}\Omega/\text{cm}^2$ with CaGlu_2 concentration increasing from 0 to 0.04 mol/L. All these findings showed that increasing the concentration of CaGlu_2 did not always produce a positive impact on coating formation and performance. Too high a CaGlu_2 concentration was actually harmful to the morphology and the resulting corrosion resistance of the coating, although it was beneficial in increasing the Ca content of the coating. From another view of point, these findings also further verified that too high $[\text{Ca}^{2+}]_T$ was not conducive to the ideal surface morphology and better corrosion resistance of the coating.

3.3.3. Effect of CaLac_2 Concentration

Meanwhile, to discover the impact of the CaLac_2 concentration on the formation and performance of the MAO coating, and to clarify the mutual impact between CaGlu_2 and CaLac_2 , four samples were prepared by varying the CaLac_2 concentration from 0 to 0.02, to 0.03, and then to 0.04 mol/L and maintaining all other parameters consistent with sample No.1. The samples were separately named as No. 1–0 CaLac_2 , No. 1–0.02 CaLac_2 , No. 1–0.03 CaLac_2 , and No. 1–0.04 CaLac_2 , and their operation parameters, surface and cross-sectional morphologies, and chemical compositions are shown in Table 2 and Figure 10. It can be seen that the impact of the CaLac_2 concentration on the Ca content differed slightly from that of CaGlu_2 , while an extremely similar situation occurred with the sample No. 1–0.04 CaLac_2 , which had, once again, localized microbumps appear on its surface. To provide more detail, as shown in Figure 10(a1–e1), all the samples showed typically porous MAO coating features, and the average pore sizes were 1.95 ± 0.14 , 1.73 ± 0.13 , 1.82 ± 0.08 , 1.81 ± 0.11 , and 2.32 ± 0.27 μm , when the CaLac_2 concentration increased from 0 to 0.04 mol/L. However, when the CaLac_2 concentration was 0.04 mol/L, the small areas formed by rapid melting/cooling began to become apparent, leading to an uneven distribution of micropores. More importantly, there were also some microbumps of an approximate size of about 90 μm on the surface of No. 1–0.04 CaLac_2 (Figure 10(e1)), just like those on No. 1–0.04 CaGlu_2 , suggesting a similar localized ablation of the MAO coating. With the CaLac_2 concentration increasing from 0 to 0.04 mol/L, the Ca content of the coatings obviously increased from 2.68 wt.% for No. 1–0 CaLac_2 to 3.86 wt.% for No. 1–0.02 CaLac_2 , but then slightly increased to 3.98 wt.% for No. 1–0.03 CaLac_2 and 4.05 wt.% for No. 1–0.04 CaLac_2 (Figure 10(a2–e2)). This suggested that CaLac_2 was not as efficient as CaGlu_2 in increasing the Ca content. The cross-sectional morphology of the

samples showed that with the CaLac_2 concentration increasing from 0 to 0.01, 0.02, 0.03, and 0.04 mol/L, the thickness of the coating decreased from 10.59 ± 0.26 to 9.98 ± 0.39 , 9.18 ± 0.16 , 8.50 ± 0.16 , and $8.39 \pm 0.14 \mu\text{m}$, respectively (Figure 10(a3–e3)). This suggested that the No. 1– $i\text{CaLac}_2$ ($i = 0$ to 0.04) series exhibited almost equal values and a similar variation tendency in coating thickness compared to the No. 1– $i\text{CaGlu}_2$ ($i = 0$ to 0.04) series. The PDP curves and the Tafel fitting results for the samples are shown in Figures 6d and 10(a4–e4) and Table 3. With the CaLac_2 concentration increasing from 0 to 0.04 mol/L, the i_{corr} increased from 4.82 to 75.1 nA/cm^2 , and the R_p decreased from 21.979 to 1.034 $\text{M}\Omega/\text{cm}^2$, respectively, indicating a deterioration in corrosion resistance. These findings indicated that, similarly to the case of CaGlu_2 , too high a CaLac_2 concentration and too high $[\text{Ca}^{2+}]_T$ were harmful to the surface structure and consequently deteriorated the corrosion resistance of the coating. In addition, when CaGlu_2 and CaLac_2 were kept at an equal concentration, the No. 1– $i\text{CaGlu}_2$ ($i = 0$ to 0.04) series exhibited a higher Ca content, while the No. 1– $i\text{CaLac}_2$ ($i = 0$ to 0.04) series showed smaller localized microbumps, lower i_{corr} , higher R_p , and, therefore, better corrosion resistance, suggesting that CaGlu_2 was a little more efficient in increasing the Ca content of the coatings, while CaLac_2 was a little more efficient in improving their corrosion resistance.

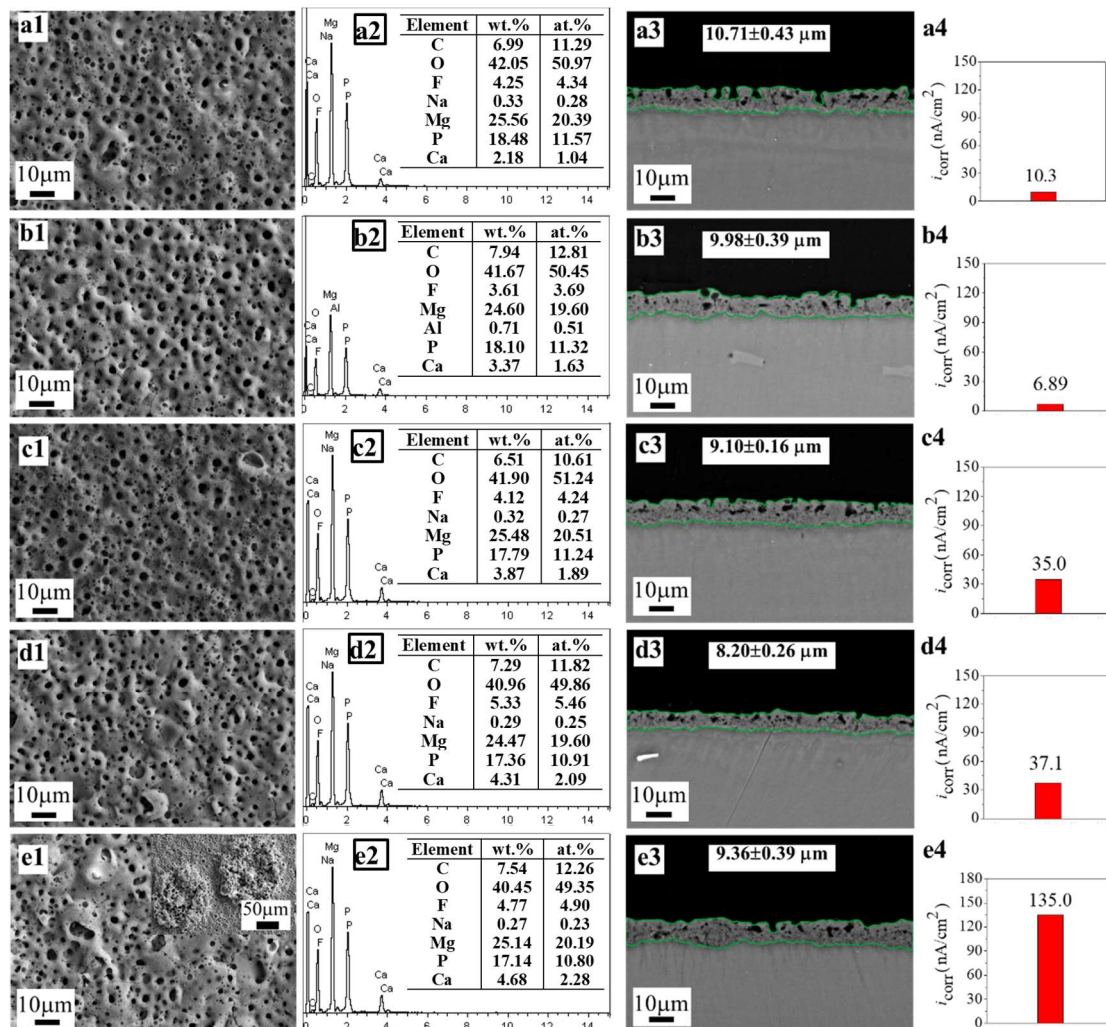
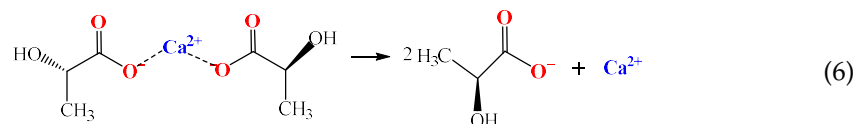
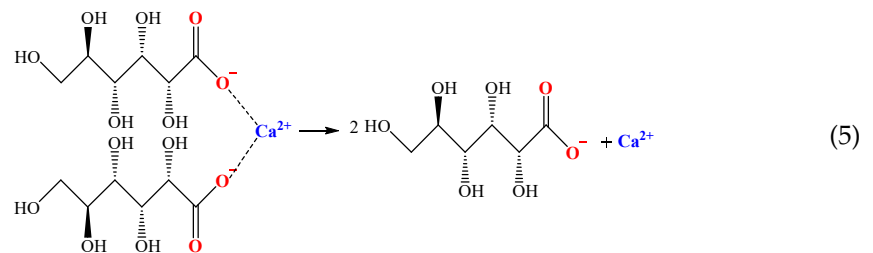
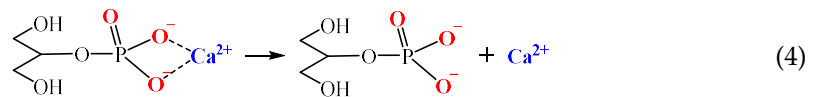
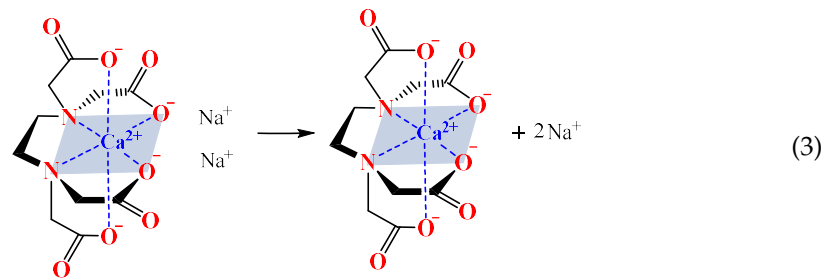


Figure 9. Surface morphologies and enlarged detail of localized microbumps, EDS spectra and chemical compositions, cross-sectional morphologies, and i_{corr} s for the samples: (a1–a4) No. 1–0CaGlu₂, (b1–b4) No. 1–0.01CaGlu₂ (No. 1), (c1–c4) No. 1–0.02CaGlu₂, (d1–d4) No. 1–0.03CaGlu₂, and (e1–e4) No. 1–0.04CaGlu₂.

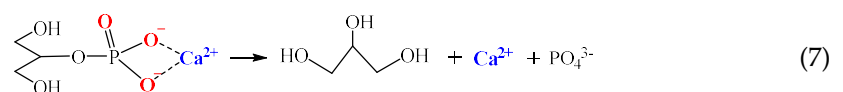


As shown in Equations (2)–(6), the anions, separately abbreviated as Phy^{12-} , $[\text{EDTACa}]^{2-}$, GP^{2-} , Glu^- , and Lac^- , contained amine ($-\text{N}=\text{}$), hydroxyl ($-\text{OH}$), and/or carboxylic ($-\text{COO}^-$) groups which were capable of coordination; therefore, the anions would coordinate with Ca^{2+} to form negatively charged complex ions, such as $\text{Ca}_x\text{Phy}^{(12-x)-}$, $[\text{EDTACa}]^{2-}$, $\text{CaGlu}(\text{OH})_2^-$, and $\text{CaLac}(\text{OH})_2^-$. During the MAO process, the negatively charged complex ions, together with the anions from the base electrolytes in the solution, such as F^- , PO_4^{3-} , migrated to the anode surface and then to the depths of the spark discharge channel under the electrical field. Additionally, Mg^{2+} originated from the substrate would migrate through the spark discharge channel towards the anode surface. Under the joint action of the two aspects, the MAO coating was finally formed, and the key chemical composition was determined to be MgO , $\text{Mg}_3(\text{PO}_4)_2$, $\text{Ca}_3(\text{PO}_4)_2$, and MgF_2 , just as in the results of the XRD and XPS analyses.

4.2. Effects of the Calcium Salts Concentration

4.2.1. Effect of GP–Ca Concentration

The orthogonal experiment indicated that the GP–Ca concentration was the most important factor for the Ca content and corrosion resistance of the coatings; meanwhile, the single-factor experimental results found that GP–Ca was more vital to the MAO coating formation in spite of not being effective in increasing the Ca content of the coatings. It was already established that GP–Ca in an aqueous solution would dissociate to give glycerophosphate ions and would hydrolyze further into glycerol [42,43], as shown in Equation (7).



A glycerol molecule contains three alcoholic $-\text{OH}$ groups that can form inter- and intramolecular hydrogen bonds, which made glycerol an effective adsorption-type corrosion

inhibitor to effectively adsorb on a metal surface and to help to slow down metal corrosion. Furthermore, the inhibition efficiency of glycerol showed a trend of proportionally increasing with the concentration [44]. In the same way, in this research, GP–Ca might dissociate into glycerol under the high temperature of MAO treatment and then adsorb onto the surface of the samples, providing protection from corrosion; consequently, the GP–Ca concentration played a more vital role in the coating formation. This was why the coating could not be successfully fabricated and was affected by substrate corrosion pits on sample No. 4 (Figure 2d), wherein the GP–Ca concentration was at a low level of 0.01 mol/L, but could be successfully fabricated on samples No. 4–0.02GP–Ca and No. 4–0.03GP–Ca (Figure 8(a1,b1)), wherein the GP–Ca concentration increased to 0.02 and 0.03 mol/L, respectively.

As for the effect of the GP–Ca concentration on the Ca content of the coating, it could be explained as follows. On the one hand, in the MAO solution wherein GP–Ca alone was a Ca source, Ca^{2+} could chelate with the Phy^{12-} that originated from the base electrolyte H_{12}Phy to form negatively charged complex ions, i.e., $\text{Ca}_x\text{Phy}^{(12-x)-}$ and then migrate to the anode surface under the electric field and participate in coating formation. However, the large molecular structure of Phy^{12-} , as shown in Equation (2), made it difficult for $\text{Ca}_x\text{Phy}^{(12-x)-}$ to effectively migrate to the anode surface. On the other hand, GP–Ca would dissociate to give glycerol under the high temperature during MAO treatment. However, it was difficult for the alcoholic –OH groups to ionize into anions and then to coordinate with Ca^{2+} , forming negatively charged complexes in a neutral solution [34,35]. These two aspects made it difficult for most of the Ca^{2+} in the solution to be incorporated into the coating. As a result, sample Single–0.05GP–Ca exhibited a clearly low Ca content of 0.11 wt.% (Figure 8(d3)).

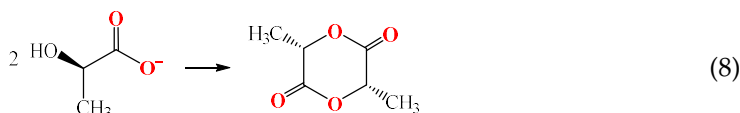
On the contrary, in the MAO solution wherein the combination of GP–Ca and EDTA–Ca, CaGlu_2 , and CaLac_2 were used as the Ca sources, EDTA–Ca would dissociate to release EDTA^{4-} with two –N= and four – COO^- groups, and, similarly, CaGlu_2 and CaLac_2 would separately release Glu^- and Lac^- , both containing –OH and – COO^- groups. The anchoring effects of – COO^- groups made EDTA^{4-} , Glu^- , and Lac^- , especially EDTA^{4-} , easily chelate with Ca^{2+} to form highly stable six-membered complexes [$\text{EDTACa}]^{2-}$, $\text{CaGlu}(\text{OH})_2^-$, and $\text{CaGlu}(\text{OH})_2^-$ [34,35,45,46], ultimately assisting in the migration of Ca^{2+} to the anode surface and then participation in the MAO coating formation. As a result, there was a synergistic effect between GP–Ca and EDTA–Ca, CaGlu_2 , and CaLac_2 in increasing the Ca content of the coatings.

4.2.2. Effect of CaGlu_2 and CaLac_2 Concentrations

Being typical hydroxycarboxylates, CaGlu_2 and CaLac_2 possess medium aqueous solubility and their solubility product constants (K_{sp}) are $(7.1 \pm 0.2) \times 10^{-4}$ and $(5.8 \pm 0.2) \times 10^{-3}$ [33], respectively; therefore, they would dissociate to give Glu^- and Lac^- ions containing both –OH and – COO^- groups as shown in Equations (5) and (6). Two types of functional groups, especially the anchoring group – COO^- , enable Glu^- and Lac^- ions to coordinate with Ca^{2+} , to carry Ca^{2+} to the anode surface, and to incorporate Ca^{2+} into the MAO coating. As a result, the Ca content of No. 1– $i\text{CaGlu}_2$ and No. 1– $i\text{CaLac}_2$, wherein i was 0, 0.01, 0.02, 0.03, and 0.04, separately increased from 2.18 wt.% to 4.68 wt.% and from 2.66 wt.% to 4.05 wt.% with CaGlu_2 and CaLac_2 concentrations increasing from 0 to 0.04 mol/L, respectively.

Nevertheless, there are also minor differences between Glu^- and Lac^- in both structure and properties. More specifically, the Glu^- ion contains five –OH groups, one – COO^- group, and a C_6 backbone chain, while the Lac^- ion has one –OH group and one – COO^- group; therefore, Glu^- ions exhibit better ligand flexibility and stronger coordination ability than Lac^- ions. For example, it was found that the association constant ($\log K_{1,1}$) was about 1.7–1.9 for Glu^- and Ca^{2+} forming the complex ion CaGlu^+ [33,34], while the association constant was 1.23 ± 0.04 for Lac^- and Ca^{2+} forming the complex ion CaLac^+ in the near-neutral medium of 4.0 M NaCl solution [35]. In addition, the bifunctionality and

the orientation of $-OH$ and $-COO^-$ groups allow the Lac^- ions to self-esterify to form a dimer with the six-membered heterocyclic ring structure, as shown in Equation (8). This to some extent reduced the ability of Lac^- to carry Ca^{2+} to the anode surface during the MAO process and thus attenuated the ability of $CaLac_2$ to increase the Ca content of the coating. As a result, as shown in Figures 9(c1–e1) and 10(c1–e1), at equal concentrations of $CaGlu_2$ and $CaLac_2$, the No. 1– $iCaGlu_2$ series exhibited a higher Ca content than the No. 1– $iCaLac_2$ series. Moreover, the Ca content of the No. 1– $iCaLac_2$ series increased distinctly but then slightly, i.e., from 2.66 wt.% to 3.86 wt.% with the $CaLac_2$ concentration increasing from 0 to 0.02 mol/L and from just 3.86 wt.% to 4.05 wt.% with the $CaLac_2$ concentration increasing from 0.02 to 0.04 mol/L.



4.2.3. Effect of Total Concentration of the Four Calcium Salts ($[Ca^{2+}]_T$)

Generally, a higher concentration of the electrolytes in an MAO solution suggests a higher ionic strength of the solution and a higher electronic field strength under a constant current mode, which helps to achieve lower breakdown voltage and thus more efficient deposition and better corrosion resistance in an MAO coating [1,3,18]. However, too high an electronic field strength and energy would promote intensive, large-sized and unevenly distributed spark discharges on the sample surface, resulting in increased reaction intensity, the formation of MAO coatings with large micropores, and even the localized ablation of the coating [1,3,18,23,32,47,48]. In this study, coating ablation microbumps appeared on samples No. 3, No. 8, No. 4–0.02GP–Ca, No. 4–0.03GP–Ca, No. 1–0.04 $CaGlu_2$, and No. 1–0.04 $CaLac_2$ (Figures 2c,g, 8(a2,a3), 9(e1) and 10(e1)), all of which were prepared in the solutions with higher $[Ca^{2+}]_T$, accompanied by more violent spark discharging and a higher final voltage of over 480 V. To be precise, as shown in Tables 1 and 2, the $[Ca^{2+}]_T$ was 0.10 mol/L for No. 3 and No. 4–0.03GP–Ca, 0.09 mol/L for No. 8 and No. 4–0.02GP–Ca, and 0.07 mol/L for No. 1–0.04 $CaGlu_2$ and No. 1–0.04 $CaLac_2$. Additionally, although the $[Ca^{2+}]_T$ was equal for No. 1–0.04 $CaGlu_2$ and No. 1–0.04 $CaLac_2$, the average size of ablation microbumps and the i_{corr} for No. 1–0.04 $CaLac_2$, about 90 μm and 75.1 nA/cm^2 , were smaller than those for No. 1–0.04 $CaGlu_2$, which were about 150 μm and 135 nA/cm^2 , a result which could also be attributed to the self-esterifying of $CaLac_2$, and then to the reduced ionic strength of the solution and the lower electronic field strength.

The samples No. 1, No. 1– $iCaGlu_2$, and No. 1– $iCaLac_2$ ($i = 0\text{--}0.03$) (Figures 2a, 9(a1–d1) and 10(a1–d1)) were prepared in solutions with lower than 0.06 mol/L of $[Ca^{2+}]_T$ and exhibited a typical MAO coating with no microbumps. Therefore, it was convincing that too high $[Ca^{2+}]_T$ would lead to the localized microbumps and, further, to the larger i_{corr} and the worse corrosion resistance of the samples. Of course, it also should be noted that four samples, No. 2, No. 5, No. 6, and No. 9 (Figure 2b,e,f,i), which were prepared in solutions with as high as 0.07–0.08 mol/L of $[Ca^{2+}]_T$ but 0.02–0.03 mol/L of GP–Ca, exhibited a typical MAO coating without localized microbumps. This proved that the positive impact of a higher GP–Ca concentration was a more decisive factor in coating formation, and one which would compensate for the negative impact of too high $[Ca^{2+}]_T$ that would lead to coating ablation.

Finally, taking into account all of the factors mentioned above, the sample No. 2, prepared in the solution containing 0.01 mol/L EDTA–Ca, 0.02 mol/L GP–Ca, 0.02 mol/L $CaGlu_2$, and 0.02 mol/L $CaLac_2$, was the most preferable among the tested samples and exhibited the second highest Ca content of 6.48 wt.% and an i_{corr} as low as 27.7 nA/cm^2 , meaning a better corrosion resistance. Further investigation will be carried out in the future to elucidate the comprehensive performance of sample No. 2.

5. Conclusions

In a near-neutral solution, Ca–P MAO coatings were prepared using a combination of EDTA–Ca, GP–Ca, CaGlu₂, and CaLac₂ as a Ca source, and their mutual impacts on the formation and properties of the coatings were investigated. The conclusions can be summarized as follows:

(1) GP–Ca was a coating-forming agent and played a more vital role in the formation of the coatings, but GP–Ca alone could not effectively incorporate Ca²⁺ ions into the coatings, resulting in the rather low Ca content of the coating, 0.11 wt.%, even when the GP–Ca concentration of the MAO solution was as high as 0.05 mol/L.

(2) The similarity between CaGlu₂ and CaLac₂ in the main molecular structure, containing the hydroxyl group and the carboxylic group with an anchoring effect, enables them to effectively incorporate Ca²⁺ ions into the coating. However, the minor difference between CaGlu₂ and CaLac₂ in functional group orientation made CaGlu₂ a little more efficient in increasing the Ca content of the coatings, while CaLac₂ was a little more efficient in improving their corrosion resistance. For instance, when CaGlu₂ and CaLac₂ were kept at an equal concentration of 0.04 mol/L, the Ca content, *i*_{corr}, and *R*_p were 4.68 wt.%, 135 nA/cm², and 0.508 MΩ/cm² for sample No. 1–0.04CaGlu₂, but 4.05 wt.%, 75.1 nA/cm², and 1.034 MΩ/cm² for sample No. 1–0.04CaLac₂.

(3) There was a synergistic effect between GP–Ca and EDTA–Ca, CaGlu₂, and CaLac₂ in increasing the Ca content of the coatings, because the last three calcium salts had a bifunctional molecular structure, especially the carboxylic group with its anchoring effect. However, a too high total concentration of the four calcium salts, [Ca²⁺]_T, would cause localized ablation microbumps on the coatings, and eventually deteriorate their corrosion resistance.

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