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Direct preparation of $CaTi_4\ (PO_4)_6$ coatings on the surface of titanium substrate by micro arc oxidation

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Abstract $CaTi_4\ (PO_4)_6$ coatings was prepared on the surface of CP (commercially pure) Titanium substrate via micro arc oxidation in a newly designed electrolyte system. The preparation method –micro arc oxidation, as well as its discharge characterization was described and studied. The phases, morphology, chemical composition of the coatings were characterized by XRD, EDX and SEM analysis respectively. The results show: the main phase of the prepared coating was $CaTi_4\ (PO_4)_6$ which is a bioactive coating material, the morphology of the coating was rather coarse and not like that of traditional MAO coating which was full of pores. Also the samples prepared in different electrolyte systems were studied and compared.

Introduction

Titanium and its alloys are widely used as implants for dental and orthopedic applications in contact with bone due to their excellent mechanical properties and the passive oxide's superior chemical stability [1–4]. But for the passive oxide and smooth surface, Titanium and its alloys as a rather bioinert material are lack of bioactivity and considered to have weak bone-bonding ability in vivo. Thus, their uses as implants are restricted and need to be modified by various methods [5]. On the other hand, Calcium phosphate materials [6–12], e.g. Hydroxyapatite and bioceramics such as Flouroapatite, β-TCP, bioglass and bioactive glass ceramics, $Ca(Ti,Zr)_4(PO_4)_6$, have many biological benefits as implant materials: similar composition to the inorganic proportion of bone, direct bonding to bone and enhancement of new bone formation around them. Unfortunately the bioceramics has its own drawback which being their brittleness and so restricts their use as load bearing materials.

Developing new surface modified methods to combine the favorable properties of both biomaterials classes-biometal and bioceramics-is the key to solve the existed problems. A number of different coating methods [1, 13–20], e.g. plasma spraying, thermal spraying, electrochemical deposition, sol-gel method, have been involved and developed to prepare bioceramics coatings (mainly HAP and TCP) on Titanium substrate in order to get high stability against low mechanical fracture and dissolution in living tissue. But almost all the coating methods developed in nowadays suffered from brittleness and relatively low adhesion to the metal substrate except for plasma spraying technique. Although plasma spraying technique has become a standard method of titanium surface modification and achieved success in clinic, it still has some drawbacks: ceramics coating easy to decompose at high temperatures which cause easy to dissolve and shed in the body, hard and expensive to treat complicated geometrical shapes. Seeking for new coating methods or novel bioceramics coating on titanium implants has become the focus of today's biomaterials research.

Micro Arc Oxidation (MAO), also known as anodic spark deposition, is a new surface engineering technique [21, 22]. It is an advanced coating process for producing inorganic glass- ceramic-like coating onto valve metal

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surfaces and the resulting ceramic coating has high adhesive strength to the substrate and is composed of compounds containing elements from both the anode metal and the electrolyte components. And also the coatings' wear resistance, corrosion resistance, heat resistance and micro hardness are improved dramatically. After Kurz .P research group first introduced the MAO technique to prepare ceramic coating on metal substrate in 1980s [23], it had become the research focus for surface modifying Titanium and its alloys to improve its bioactivity [24–29]. During the 20 years, the mainly researches were development of the electrolyte systems which influenced the coatings' properties, including bioactivity. But until now, almost all the researches are based on Ishizawa's electrolyte system prototype to improve the substrate's bioactivity. The obtained coatings mainly contained electrolyte composition Calcium, phosphor and substrate metal oxide TiO_2 which didn't have the expected bioactivity. In order to improve the MAO coatings' bioactivity and also other beneficial properties as implants, our research group is also focus on the development of electrolyte system; we developed a novel electrolyte system, in which a bioceramic coating was prepared on the cp (commercial pure) titanium substrate via MAO technique. Some of the research results are reported in this paper.

Materials and methods

Sample preparation

All titanium sample ($10 \times 10 \times 0.2$ mm^3) used in this work were cp titanium and before its use, it was polished used 360 waterproof abrasive paper and W10 metallographic abrasive paper (Shanghai grinding wheel factory China) successively to clean the surface natural oxide and other contaminant. After polishing the sample were rinsed by ethanol and distilled water successively to clear the contamination. And then the samples were stored in a seal box.

Electrolyte preparation

As aforementioned, the electrolyte systems influence the coatings' properties. In our study, we use the polyphosphate as complexant to complex Ca ions.

First, sodium hexametaphosphate was dissolved in the pure water, and the concentration was controlled at 25 g/L, and the detected pH value was 5.4. After the completely dissolve, then the calcium acetate or calcium chloride were introduced to the prepared solution. During the solution preparation, some white floccules could be seen and then dissolved in the excessive sodium hexametaphosphate. The Ca/P ratio of the solution was controlled between 0.17 and the pH value was adjusted to the desired value (10 in this research) by sodium hydroxide. Hereinafter we name the prepared solution as PCaE (polyphosphate acetate calcium electrolytes) system for easy writing.

At the same time, other two kinds of electrolyte systems were prepared in order to compare the effect of electrolyte systems according to literature's directions: (i) Which contains 0.12 mol l-1AR grade Ca $(H_2PO_4)_2$ and hereinafter we name it as BC (basic electrolyte) [26], (ii) which contains 0.025 M Ca $(H_2PO_4)_2$, 0.075 M Ca $(OOCCH_3)_2$, 0.12 M EDTA·Na_2 and 0.9 M NaOH and the Ca/P ratio of the solution is up to 2, the pH value was controlled at about 10, hereinafter we name it as EBSO according to the literature[27]. Also the Ca $(H_2PO_4)_2$ in EBSO system substituted by hexametaphosphate was studied. All chemicals are of chemical purity grade. All the prepared solutions were stirred with a magnetic force stirrer at least 6 h before their use.

MAO coating procedure

Coatings were prepared in aforementioned electrolytes by micro arc oxidation. A DC voltage stabilized current stabilized power (YJ901 type 0–600V/0–0.5A Huguang instrument co. Shanghai China) was utilized to supply power for the procedure. The treated cp titanium substrate was connected to the anode and the cathode also used cp titanium sheet whose surface was about the same as the surface of anode. For the measurement of voltage variation between anode and cathode at stable current, a digital video imaging was used and then read the value every second from the video. And also the anodic phenomena were recorded. After coating, the samples were thoroughly rinsed with distilled water, dried in the air and stored in a sealed box.

In the research, six samples which name as 1A, 2A, 1B, 2B, 3A and 1C respectively were treated by MAO in the aforeprepared solution and the parameters sets are listed in Table 1. The letter (A, B and C) means the electrolyte system with different type phosphate and the numeric means different treated samples.

Surface characterization

The phase and composition of the coating were analyzed by X-ray diffraction (XRD; Cu Kα 1, 50 kV, 100 mA) analysis and energy dispersive spectroscope (EDX) respectively. The morphology of the coating was characterized by scanning electron microscopy (JEOL, JSM-5600).

Table 1 Parameters used for the MAO production of coatings

Sample	Electrolyte	Current	Duration(min)	Ratio of Ca and P
1A	Polyphosphate and calcium acetate (pH = 10)	100 mA	20	0.167
2A	Polyphosphate and calcium chloride (pH = 10)	100 mA	20	0.167
1B	EBSO (pH = 10)	100 mA	10	2
2B	EBSO (pH = 14)	100 mA	20	2
3A	EBSO polyphosphate as (pH = 10)	100 mA	10	2
1C	$Ca(H_2PO_4)_2$	100 mA	7	0.5

Results and discussion

Discharge characterization in micro arc oxidation of titanium

Through the captured voltage variation of anode and anodic surface appearance, a typical discharge characteristic during electrolysis in the PCaE system was studied. The current of the process was fixed at 100 mA and the pH value of the solution was about 10. The corresponding time-dependence of the voltage during the coating process was obtained as shown in Fig. 1. Understanding this diagram contributes to understanding the processes that take place at the anode. The MAO process can be divided three corresponding stages just like the curve shown in Fig. 1.

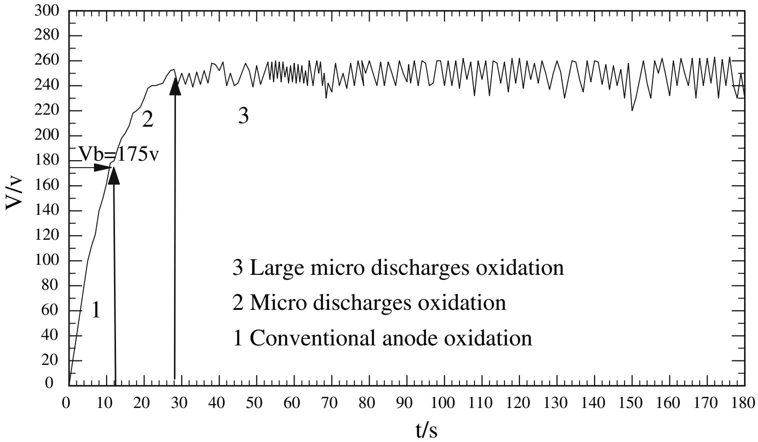
During the Stage 1 (first 5–30 s, mainly depending on the current), the oxidation process is analogous to conventional anodizing where voltages increase with time linear and a conventional oxide layer which is amorphous is formed on the substrate metal. The insulation character of this layer causes a significant increase in the voltage and also anodic surface color change and gas liberation are observed.

Stage 2: After the voltage reaches certain value (V_b = 175 ± 10 V, mainly depending on the electrolyte condition, e.g. concentration and composition), the process enters Stage 2. A feint glow is observed surrounding the test piece and discrete micro discharges appear on the anodic surface with voltage increasing. Those micro discharges can only occur because of the dielectric properties of the barrier oxide layer formed in the Stage 1 and the anodic oxidation layer started electrolytic breakdown. A layer of very even film is observed on the sample when the process is over as the breakdown often occurred in the weakest place. We defined this stage as micro discharges oxidation for the feint discharge.

Stage 3: After the voltage reaches at about 250 ± 10 V (also mainly depending on the electrolyte condition), the process enters Stage 3, which characterized by a constant cell voltage fluctuation. Phenomenologically, the anodic surface discharge becomes fiercely and large micro discharge events occurring appear associated with the emission of sparks and sounds. The crystalline phase depending on the electrolyte composition mainly via coordinated electrolyte's hydrolysis is formed on the anodic substrate and after the process, a layer of very coarse coating on the substrate metal is observed. We defined this stage as large micro discharges oxidation for its fierce discharge and large spark.

Finally, when the process duration is long enough, the cell voltage stays steadily and the discharge starts breakdown locally. Extra-large micro discharges are observed

Fig. 1 The typical voltage versus time curve in MAO of titanium (I = 100 mA, Vb means the discharge voltage)



and believed to contribute to the ceramic layer destroy. This stage defined as extra-large micro discharges oxidation should be avoided in the process.

Phase and structure of ceramic coatings

In order to study the phase and structure of the ceramic coatings treated by MAO process in different electrolyte system, the XRD spectra of the micro arc oxidized samples obtained in different electrolyte systems are shown in Fig. 2a–d.

As we can see from the XRD spectra of the coatings which were treated in different electrolyte systems, they are evidently different from each other. (a) the samples were treated in PCaE electrolyte system. According to the diffraction spectra of 1A and 2A samples, the coating phase was predominantly $CaTi_4\ (PO_4)_6$ (JCPDS chart number 81–2176) which is a bioactivity coating materials [30] and its bioactivity will be further discussed in the following part. Metal titanium diffraction was weakened dramatically and no anatase or rutile phase (TiO_2) was detected by XRD. The XRD spectra of the samples indicate that the oxidized coating was mainly composed of crystal $CaTi_4\ (PO_4)_6$ and maybe also exist some amorphous Ca- and P-containing compounds which cannot be detected by XRD. In addition, compared 2A sample's XRD spectra with 1A sample, the intensity of $CaTi_4\ (PO_4)_6$ phase is much higher and the metal titanium phase is much lower, which indicate that the relative content of $CaTi_4\ (PO_4)_6$ phase in coating of 2A sample is higher than that in coating of 1A sample. (b, c, d) the sample 1B and 2B were treated by MAO process in the EBSO electrolyte system at different pH value (b:10, c:14). For comparison the phosphate effect, the EBSO electrolyte's phosphate was substituted by polyphosphate in sample 3A (d). According to the XRD spectra of 1B and 3A samples, the coating phase was predominantly consisting of substrate metal titanium, anatase and rutile phase TiO_2. No Ca- or P-containing phases are detected even the electrolyte had high Ca/P ratio up to 2 and also the phosphate has no effect on the phase composition of the coating. Compared the 1B and 2B samples which treated in different pH value condition, the XRD spectra of 2B sample (c) are not only consisting of substrate metal titanium, anatase and rutile phase TiO_2(JCPDS chart number 75–1537), but also consisted of $CaTiO_3$ phase(JCPDS chart number 89–0056). It indicates that the coating of sample 2B has $CaTiO_3$ and so pH condition of the electrolyte has effect on the coating phase. Because at different pH value, the electrolyte system properties are different for the different reaction maybe happened in the solution. (e) the sample was treated in BC electrolyte system. According to the XRD spectra of 1C sample, the coating phase was predominantly the substrate titanium phase. Neither titanium oxide phase's (anatase or rutile) nor Ca- and P-containing phase has found on the coating phase. So the coating of 1C sample is mainly composed of titanium and amorphous TiO_2. The result is agreement with Schrecken -bach's study [26], they also only found metal titanium phase on the coating treated by MAO process.

Morphology of ceramic coatings

The surface morphologies of the Ti samples which treated in different electrolyte systems by MAO process are shown in Fig. 3a–f.

As we can see, the morphologies are different from each other when treated in different electrolyte systems. The cp Ti sample (A) was treated in the electrolyte only containing hexametaphosphate, the morphology of the coating was a typical MAO ceramic layer morphology which is full of pores caused by discharge and gas evolution as shown in Fig. 3a. The dimension of the pores were about 0.5–5 μm. Very coarse and porous ceramic coatings which maybe benefit to its bioactivity were formed on the 1A and 2A samples treated in PCaE systems, as shown in Fig. 3b, c (B:1A and C:2A). Depositions are clearly observed on the both surface, which may be Ca-, Ti- and P-containing compounds and almost no cracks were found on both surface. That maybe improves the integrity of the ceramics coating. Besides, there are also some pores on the surface coating but not as much and regular as the typical MAO coating shown in Fig. 3a. The samples 1B and 3A treated in EBSO systems surface morphologies were also shown in Fig. 3d, e (D: 1B and E: 3A). The ceramic coatings were even and had more regular pores on the surface. The regular pores' diameters are about 0.1–1 μm. And there are many cracks on the surface of sample 1B which maybe cause shed if it is implanted as biomaterials in the body. When the phosphate was substituted by polyphosphate in EBSO system, the integrity of the coating was improved as compared 3A with 1B for the cracks was no longer observed on sample 3A. Figure 3f is the titanium metals without MAO treatment but treated by anode pretreatment.

Surface chemical composition of ceramic coatings

The chemical composition of the ceramics coatings treated in different electrolyte systems by MAO process were evaluated by EDX analysis and atom percentage of elements titanium, calcium and phosphor of the coatings are shown in Table 2.

The sample A is treated in the electrolyte only containing polyphosphate. So the chemical composition of the ceramic coating only contains Ti and P elements, and no Ca element was detected. The samples 1A and 2A treated

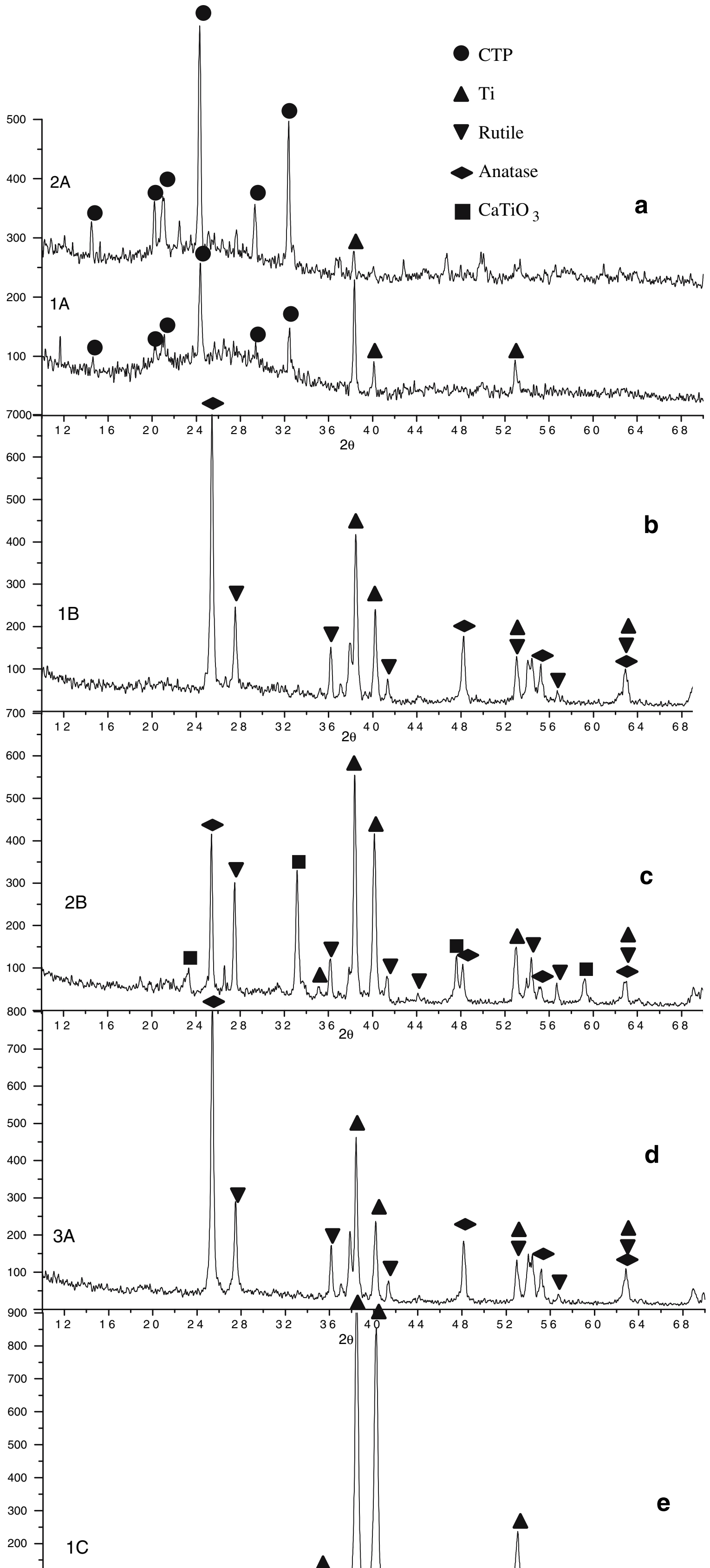


Fig. 2 XRD patterns of titanium samples treated in different electrolyte systems (**a**: XRD results of samples 1A and 2A; **b**: XRD results of samples 1B; **c**: XRD results of samples 2B; **d**: XRD results of samples 3A; **e**: XRD results of samples 1C)

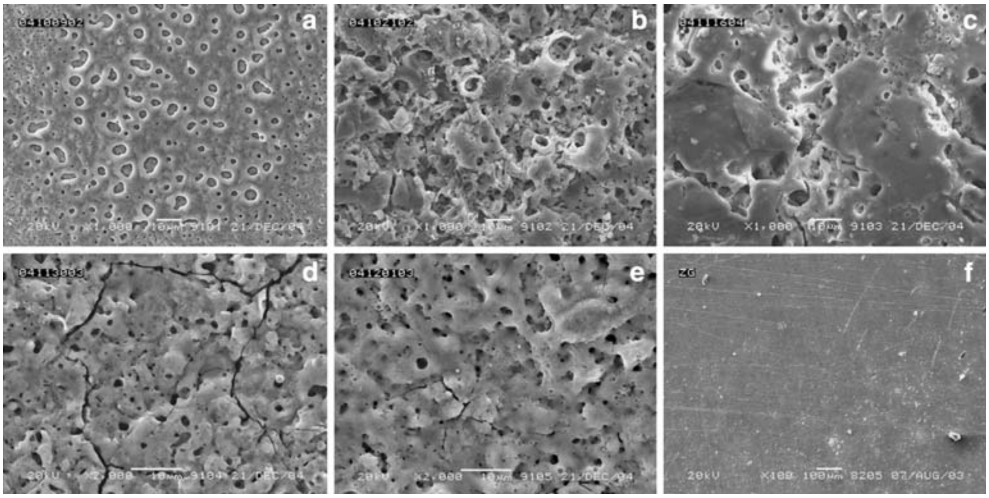


Fig. 3 SEM photographs of titanium treated by MAO in different electrolyte systems (**a**: SEM results of samples treated in the electrolyte system only containing hexametaphosphate; **b**, **c**: SEM results of samples 1A and 2A; **d**, **e**; SEM results of samples 1B and 3A; **f**: SEM result of sample without MAO treatment but treated by anode pretreatment)

Table 2 EDX chemical composition analysis results of samples treated in different electrolyte systems

Sample No	Ti atom%	P atom%	Ca atom%
A	22.91	8.91	0
1A	6.08	17.94	7.70
2A	7.52	17.83	6.21
2B	24.55	2.28	8.21
3A	27.88	2.41	3.74

in the PCaE electrolytes possess higher phosphor content and give a lower content of titanium and calcium element. According to the foregoing XRD results, the mainly crystalline phase of the ceramic coating is $CaTi_4$ $(PO_4)_6$. But according to the element atom ratio which is non-stoichiometry, there should be some amorphous TiO_2 in the ceramic coating. The samples 2B and 3A treated in EBSO electrolyte possess high titanium content and it indicates that the coating consists primarily of a composite of TiO_2 and is agreement with the aforementioned result of XRD. And also the coating possesses high calcium to phosphor ratio up to about 3, which is the result of high Ca/P ratio of the EBSO system. The Ca/P ratio in the coating is much higher than V.M. Franchiger's study [27] which applied the same electrolyte (in his study, the Ca/P ration only reached 1.2). The reason may be attributed to the treating time and different electrical parameters.

The potential bioactivity of the bioceramics $CaTi_4$ $(PO_4)_6$

$CaTi_4$ $(PO_4)_6$ is a bioceramics which first proposed by Szmukler-Moncler .S in the 9th European conference on biomaterials in the paper ''a new coating biomaterial?'' in 1991 [30]. And then in 1992, he definitely pointed out ''Calcium-metallic-phosphate: A new coating biomaterial'' and studied its physicochemical properties and biocompatibility [31]. The good results were achieved. There are also some other literatures [12, 32–34] which studied the bioceramics properties including its solubility, bioactivity and in vivo experiments. It also shows that $CaTi_4$ $(PO_4)_6$ is one kind of ideal material that being [32]:

I. Bioactive and bind directly with bone without connective tissue at the interface;
II. With the same thermal expansion coefficient as titanium alloy;
III. Chemically stable comparable to Hydroxyapatite.

In fact, as one can read in ref [35, 36], $CaTi_4$ $(PO_4)_6$ can even resist hydrochloride acid.

As far as the authors know, $CaTi_4$ $(PO_4)_6$ coatings can only be deposited by plasma spraying. But preparing $CaTi_4$ $(PO_4)_6$ powders needs a series of a long and tedious procedure, as declared in [12]. This is the first report on direct preparing $CaTi_4(PO_4)_6$ coatings on titanium substrate by micro arc oxidation in a newly prepared electrolyte system. The obtained bioceramic coating has potential bioactivity and better stability. Compared with other researches, the electrolyte system use polyphosphate complexant to complex Ca ions and then react with substrate titanium to form $CaTi_4$ $(PO_4)_6$, while other researches can not obtain bioactivity coatings.

In our laboratory, the bioactivity of the coatings is on research and some other physicochemical properties of the coating are studying. The results will be reported in the following papers.

Conclusion

A ceramics coating can be cost effectively produced by MAO technique on substrate cp titanium in the newly prepared electrolyte system. The coating's mainly crystalline phase is $CaTi_4(PO_4)_6$ which is a bioceramic coating material and have potential favorable bioactivity. The coating is porous and the coating is with excellent adhesion to the substrate for MAO process characteristic. The chemical compositions of the ceramic coatings contain elements from both the anode metal Titanium and the electrolyte components Calcium and phosphate. Also the results treated in different electrolyte systems were compared and the conclusion is that the electrolyte system has strongly effect on the phase, surface morphology and chemical composition of the treated samples. In different electrolyte system, different phase and composition are produced by MAO technique.

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