n-SiO$_2$ Embedded HA/TiO$_2$ Composite Coatings Deposited on Pure Titanium Substrate by Micro-Arc Oxidation

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1. Introduction

As orthopaedic and dental metallic implant materials, titanium and titanium alloys are widely used due to their relatively low modulus, good fracture toughness, excellent strenth-to-weight ration, and superior biocompatibility and corrosion resistance (Long and Rack, 1998**)**. They have become the first choice above all other candidate metallic implant materials such as Co-Cr-Mo alloys, stainless steel in recent years. But smooth titanium or titanium alloy implants are considered to have weak bioactivity and bone-bonding in vivo (Li et al., 2004; Sul, 2003; Xie et al., 2000). Therefore, a composite system including an hydroxyapatite (HA) film on the titanium or titanium alloy implant, which combines the mechanical benefits of metal alloys with the biological properties of HA, has generated widespread interest because of the HA has excellent biocompatibility and tissue bioactivity (Tkalcec et al., 2001; Weng et al., 1997). Many techniques including plasma-spraying, pulsed laser deposition and electrophoretic deposition have been studied to produce HA films over the last 20 years, and plasma-spraying was the only one that achieved commercial success (Yang et al., 2005; Cotell et al., 1992; ZHITOMIRSKY, 1997; Liu, et al., 2002; Wen et al., 2002; Gu et al., 2003; Clèries et al., 2000; Koike & Fujii, 2001). But the film formed by plasma-spraying was easily separated from the surfaces or resorbed in the body environment because of the unstable characteristics through its rapid solidification, inhomogeneous composition, melted and decomposed phases, etc (Xu et al., 2006). The other methods such as electrophoretic deposition may produce highly crystalline coatings, which are difficult to resorb in the body (Gross & Berndt, 1994).

Recently, it was reported that hydroxyapatite-containing titania coating on titanium or titanium alloy was prepared by micro-arc oxidation (MAO) technique (Barrere et al., 2002; Chen et al., 2006; Fu et al., 2002; Han et al., 2003; Wei et al., 2009; Ni et al., 2008). The obtained coating has a porous surface and exhibits perfect biocompatibility and biological activity, which is essential for orthopaedic and dental metallic implant materials. This technique is very suitable for the bioactive surface modification of titanium and its alloy implants.

2. Micro-arc oxidation technique

Micro-arc oxidation (MAO) technique, also named plasma electrolytic oxidation , micro-plasma oxidation, or anodic spark deposition developed from anodic oxidation from the

1970s. MAO is an electrochemical, plasma chemical technology in an electrolyte to obtain ceramic coating on valve-metal surfaces such as aluminium, titanium, magnesium, et al. and their alloys. During MAO treatment, the valve metal substrate is used as anode and a stainless steel plate was used as a cathode in an electrolyte cell. Sometimes, the cathode can be the stainless cell which hold the electrolyte simultaneously. When the applied voltage to the substrate immersed in electrolyte is increased to a certain point, a micro-arc occurs on the surface and a ceramic layer is formed. The method makes it possible to obtain a new coating strongly adhering to the surface and characterized by high mechanical, heat-resistant, wear resistance and other functional properties.

2.1 Micro arc oxidation of aluminium

At its earlier development stage, MAO technique was mainly studied to enhanced friction, wearing and corrosion resistance of aluminium and its alloys. It was first reported depositing oxide coating on aluminium anode by Markov and co-work, Van and co-work in 1970s (Markov et al., 1976; Van et al., 1977). Subsequently, Dittrich et al., Krysmann et al., Kurze et al.(Dittrich et al., 1984; Krysmann et al., 1984; Kurze et al., 1987) in the 1980s, and Wirtz et al (Wirtz et al., 1991) in the early 1990s contributed to the development of the MAO process. However, the MAO process gained worldwide recognition as an eco-friendly technology for deposition the tribologically superior ceramic coatings on aluminum and its alloy by the pioneering research contribution made by Yerokhin et al. of Tula State University (Russia) in the 1990s (Voevodin et al., 1996; Yerokhin et al., 1998; Yerokhin et al., 1999). After that, more researchers from United States, United kingdom, China, et al. have contributed to the further research on the Formation and Mechanism of Ceramic Coating and its properties (Krishna et al., 2007; Lukiyanchuk et al., 2002; Mertsalo et al., 2003; Rudnev et al., Shi et al., 2004; Tianet al., 2002; 2004;Xue et al., 2001).

2.2 Micro arc oxidation of titanium

MAO technique used to modify the surface of titanium and its alloys began with 2000's on the base of research development of that on aluminium. The main purposes at incipient stage were wear resistance and corrosion resistance, and quickly turned to biomaterial modification. Micro-arc oxidation can produce a porous, relatively rough and firmly adherent titanium oxide coating on titanium surface, which is beneficial for the biological performance of the titanium implants. The obtained MAO films on titanium can be used for such applications as orthopaedic or dental implants. A large number of scientists have investigated this technology and have obtained their results.

2.3 Microstructure of MAO coating on titanium

It was reported by almost all investigators that the oxide film formed using MAO on titanium surface exhibited a porous microstructure with SEM. The holes which were regarded as discharge channels of micro-arc in electrolyte were relatively well separated and homogrneously distributed over the surface (Chen et al., 2006; Han et al., 2002a, 2002b, 2003; Li et al., 2004; Ni et al., 2008). Theoretically speaking (Akin et at., 2001; Dunn et al., 1993), this micro-porous morphology of the implant surface is beneficial to bone tissue growth and enhanced anchorage of implant to bone; furthermore, a porous surface may be valuable for bioactive constituents such as growth factors or bone morphogenic proteins and has the function of an enhanced cell proliferation. The cross-sections of the oxide layers formed with different oxidation time showed that there was no obvious discontinuity

between the film and the underlying substrate, which indicated that the film could be tightly adhered to the substrate (Han et al., 2002a, 2002b, 2003; Ni et al., 2008). The morphological difference such as diameter of the pores and the thickness of the film associated with electrolyte concentration, discharge voltage and treatment time, have been found by many investigators (Li et al., 2004; Han et al., 2002a, 2003; Kuromoto et al., 2007; Yao et al. 2008).

Ti and O are two primary elements in the MAO coating analyzed by EDX analysis, which came from substrate and component or water of electrolyte respectively. In addition, the elemental component in electrolyte can incorporate into the coating too. The contents of the elements in the coating are different with the change of oxidation time, electrolyte concentration, and so on. (Chen et al., 2006; Han et al., 2002a, 2003; Li et al., 2004; Ni et al., 2008).

XRD patterns prove that the MAO coating formed by MAO is mainly composed of anatase and rutile, the peaks of which are strongly depending on the electrolyte concentration and parameter such as oxidation time, applied voltage et al (Han et al., 2003; Ni et al., 2008). The diffraction peaks of some other materials such as CaTiO$_3$, β-Ca$_2$P$_2$O$_7$ and α-Ca$_3$(PO$_4$)$_2$, which related to electrolyte composition can be detected at the same time, and this is also decided by electrolyte concentration, oxidation time, and applied voltage et al. (Chen et al., 2006; Fu et al., 2002; Ni et al., 2008, Han et al., 2003).

2.4 Properties of MAO coating on titanium

One main purpose of using MAO technique on titanium and its alloys implants is to improved its biological behavior by modifying the composition and morphology of the implant surface. So some biological and mechanical properties were measured to evaluate MAO process (Akin et al., 2001; Han et al., 2002a, 2002b, 2003; Ishizawa & Ogino, 1995; Li et al., 2004; Lim et al., 1996; Song et al., 2004 ; Sul, 2003; Wang et al., 2000; Wu et al., 2003). It also has been found that the biological behavior of the MAO samples closely related to the morphology, Elemental and phase composition, roughness, and so on.

2.4.1 Bioactivity of MAO coating on titanium-apatite-induced ability in SBF solution

The bioactivity of the MAO film can be studied by immersing the coated samples in simulated body fluid (SBF) for a period of time (Han et al., 2003; Song et al., 2004). The aim is to evaluate the apatite induction of the film in a body-analogous solution by analyzing the changes in chemistry, corrosion resistance, apatite-induced ability, and crystallinity of the coating.

In vitro bioactivity of the MAO titania-based films on titanium surface was evaluated in simulated body fluid (SBF) by Han et al. (Han et al., 2003). They found that only the film containing CaTiO$_3$, β-Ca$_2$P$_2$O$_7$ and α-Ca$_3$(PO$_4$)$_2$ could induce an apatite layer on its surface, exhibiting bioactivity. CaTiO$_3$ combined with β -Ca$_2$P$_2$O$_7$ and α-Ca$_3$(PO$_4$)$_2$ seems to be the key structural factor for MAO-formed titania-based films to be of bioactivity. Han et al. analysed the morphologies of the sample which has the apatiteinduced ability in SBF solution immersed in SBF for 40 and 50 days (Han et al., 2003). They found that after 40 days immersion, the surface of the sample exhibits the decrease of pore size and porosity, and starts to be covered with the mineralized apatite. When immersed for 50 days, original porous characterization of the sample disappears and its surface is fully covered with a dense layer of apatite. When observed at high magnification, the apatite layer is in fact composed of network structure, and the diameter of the net pores is less than 100 nm. similar results can be found in the work of others (Song et al., 2004).

Some literatures suggested that TiO_2, regardless of anatase or rutile in the MAO-formed film on titanium seems to be bioactive (Li et al., 2004; Wu et al., 2003). While others hold the view that the in vitro bioactivity is ascribed to Ti-OH group or negatively charged surface as well as to an epitaxial effect of the anatase structure (Lim et al., 1996; Wang et al., 2000; Wu et al., 2003).

2.4.2 Biocompatibility of MAO coating on titanium

Biocompatibility can be evaluated by in vitro cell tests which comprise proliferation and differentiation behavior of the cells and in vivo tests (Akin et al., 2001; Li et al., 2004). Evaluation parameters can be proliferation and differentiation behaviors (alkaline phosphatase (ALP) activity) of the cells of in vitro cell tests and the bond strength between the bone and the implant in of vivo tests.

Akin et al. found that the in vitro proliferation of human bone-derived cells (HBDC) is similar on three samples with 0.50, 16, and 50 µm diameter pores, respectively. However, higher [3H]thymidine (3H-TdR) incorporation by the HBDC is observed when they are grown on 0.50- and 16-µm pores compared to the 50-µm pores, suggesting an enhanced cell proliferation for the smaller pores(Akin et al., 2001).

In the work of Li and co-work (Li et al., 2004), the proliferation and differentiation behaviors of MAO specimens were evaluated by in vitro cell tests using MG63 and human osteosarcoma (HOS) cell lines, respectively. In their works, the proliferation behavior was determined by counting the number of cells after culturing them for 7 days. The differentiation behavior was estimated by measuring the alkaline phosphatase (ALP) activity of the HOS cells after culturing them for 10 days. The results showed Even though the proliferation rate was highest when the specimen was oxidized at the relatively low voltage of 190 V and decreased steadily with increasing voltage, the number of cells increased more than 10 times compared to the originally plated cells. However, The ALP activities of the HOS cells was not much affected by the MAO process when the applied voltage was lower than 300 V, but increased rapidly when the voltage was higher than 300 V. the result shows that the roughness and the amount of Ca and P ions incorporated into the titanium oxide layer strongly affect the cell response. Especially, the ALP activity significantly increased at higher voltages, which is deemed to be closely related to the increase in surface roughness and the increased amount of Ca and P contained in the oxide layer.

In the work of Li et al., the bond strength between the bone and the MAO-treated specimens was measured with a torque measurement device by in vivo tests on female, New Zealand white rabbits (Li et al., 2004). The removal torque of the MAO-treated Ti implants was more than three times higher than that of the as-machined Ti implant. The results showed a considerable improvement in osseointegration capability of MAO-treated specimens as compared to the pure titanium implant. This enhancement is attributable to the increase of surface roughness and to the presence of the Ca and P ions, which were incorporated into oxide layer during the MAO process.

2.4.3 Mechanical properties of MAO coating on titanium

Mechanical properties, including hardness, elastic modulus, and adhesion strength were some other important properties and were tested in some investigations (Han et al., 2002a, 2002b; Sul, 2003; Ishizawa & Ogino, 1995).

According to research results of Han et al. (Han et al., 2002a), The film prepared at 350 V exhibited a low hardness and Young's modulus which were 0.9±0.2 GPa and 32±4 GPa,

respectively. The film exhibited a significant plasticity and ductility compared to the conventional coarse-grained titania ceramics which were 9 and 230 GPa, respectively. However, the adhesion of the film to the substrates was fairly strong, as high as approximately 37±3 MPa when the film prepared at 350 V (Han et al., 2002a）. Another research received by the same authors revealed that the bond strength of the films prepared at 350 V was approximately 30±2 MPa and fracture occurred inside the films but not at the interface (Han et al., 2002b). They pointed out that this adhesive strength is much higher than that of sol–gel derived titania films, which is usually less than 10 MPa.

In study of Sul (Sul, 2003), multifactorial biocompatibility of the surface of oxidized implants by MAO method resulted in significantly improved bone reactions as evaluated by biomechanical and histomorphometrical techniques after 6 weeks of implant insertion. Mechanical interlocking and biochemical interaction, separately or together, explain the primary modes of the forces acting over the bone to implant interface. The results of the P and Ca implants point to the possibility of biochemical bonding between bone and oxidized titanium implant. Another literature, wrote by Ishizawa and co-work, proved that the sample with low contents of Ca and P had a high adhesive strength after soaking in a simulated body fluid for 300 days (Ishizawa & Ogino, 1995)

2.5 Influencing factors on MAO film of titanium

The surface morphology, elemental composition, phase components and properties of the MAO coatings on the titanium and its alloys' surface are influence largely by treatment conditions. To find the relationship between them and control them freely are always the purpose of researchers. The main influencing factors are often regarded as electrolyte factors such as its composition and concentration and operation parameters as treatment time, applied voltage, current density et al.

2.5.1 Electrolyte composition and concentration

An advantage of MAO technic is the possibility of incorporating of element in the electrolyte (e.g. Ca, P ions) into the coating by changing the composition and concentration of the electrolyte (Han et al., 2002b; Ishizawa & Ogino, 1995; Li et al., 2004; Song et al., 2004; Ni et al., 2008). The salts have been used in studies include acetate monohydrate ((CH$_3$COO)$_2$Ca$\cdot$H$_2$O), sodium dihydrogenphosphate (NaH$_2$PO$_4\cdot$2H$_2$O), sodium phosphate (Na$_3$PO$_4$), sodium carbonate (Na$_2$CO$_3$), β-glycerophosphate disodium salt pentahydrate (C$_3$H$_7$Na$_2$O$_6$P$\cdot$5H$_2$O, e.g. β-GP), and calcium acetate monohydrate (CA), et.al. (Chen et al.,2006; Han et al., 2002a, 2002b, 2003 ; Ni et al., 2008; Song et al., 2004). For example, EDS spectrum of the films formed in solution containing 0.2 M calcium acetate monohydrate (Ca(CH$_3$COO)$_2\cdot$H$_2$O) by Han et al (Han et al., 2002b) proved that Ca can incorporated into the film during the MAO process and the atomic concentration was estimated to be ~3.2%.

However, there are also some opposite results emerged by Han et al (Han et al., 2002a, 2003) that the film didn't contain element in the eletrolyte which containing sodium carbonate (Na$_2$CO$_3$). The reasons for this difference may relate to other factors such as concentration of salt, applied voltage, oxidation time, et al. which have not yet been clearly studied by investigators.

As studied by EDX analysis in our previous work (Ni et al., 2008), The films contained Ca and P as well as Ti and O. Ca and P came from electrolyte composition (CH$_3$COO)$_2$Ca$\cdot$H$_2$O

and NaH$_2$PO$_4$·2H$_2$O) and the content of which increased with increase of electrolyte concentration. The conclusion is that the increase of the electrolyte concentration was in favor of the increase of relative content of Ca and P compounded into the films. The same result was obtained by Ishizawa & Ogino (Ishizawa & Ogino, 1995) too**.**
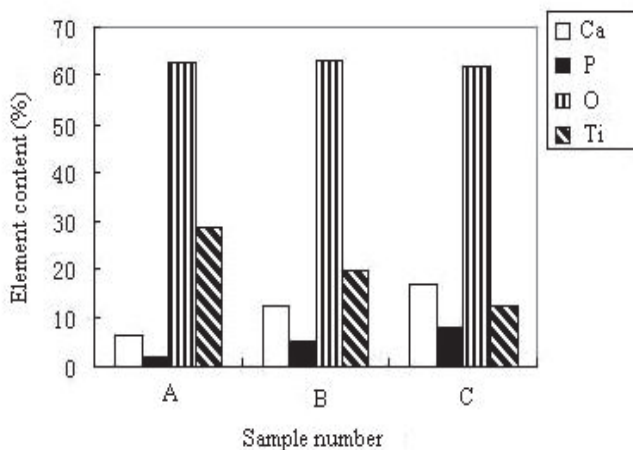

Fig. 1. The element content in coatings subjected to sample A, B, C obtained in different electrolyte concentration (A) (CH$_3$COO)$_2$Ca.H$_2$O 0.13mol/L; (NaH$_2$PO$_4$.2H$_2$O) 0.06mol/L (B) (CH$_3$COO)$_2$Ca.H$_2$O 0.26mol/L ; (NaH$_2$PO$_4$.2H$_2$O) 0.12mol/L; (C) (CH$_3$COO)$_2$Ca.H$_2$O 0.39mol/L; (NaH$_2$PO$_4$.2H$_2$O) 0.18mol/L (Ni et al., 2008)

Another effect of electrolyte composition and concentration to the obtained MAO film is the surface morphology of the surface (Han et al., 2003; Ni et al., 2008). According to Han et al. (Han et al., 2003), at the same voltage, the films formed in CA- and b-GP-containing electrolytic solution become more rough compared with the films formed in Na$_2$CO$_3$- and Na$_3$PO$_4$-containing solutions, and exhibit similar roughness to the films formed in CA-containing solution. It was observed in Fig.2 obtained in our previous work (Ni et al., 2008) that the discharge pores changed from clearer and bigger to unsharp and smaller when the electrolyte concentration increased gradually. The possible reason that the diameters of the pores tend to reduce with increasing of the electrolyte concentration may be incorporating of electrolyte concentration. The more the electrolyte concentration was, the more electrolyte deposited by sintering on the surface of the film and covered the edge of pores.

Apparently, because of changing of elements composition in the MAO coating on Ti substrate with altering of electrolyte concentration, the phase components of the coating would changed too. Fig.3 (Ni et al., 2008) affirmed this deduction using XRD patterns of MAO coatings formed in different concentration of electrolyte in our previous work. Except for Ti, anatase and rutile, the peak of hydroxyapatite was gradually appeared with increase of electrolyte concentration. The result imply us that hydroxyapatite can be prepared by controlling of electrolyte used in MAO process.
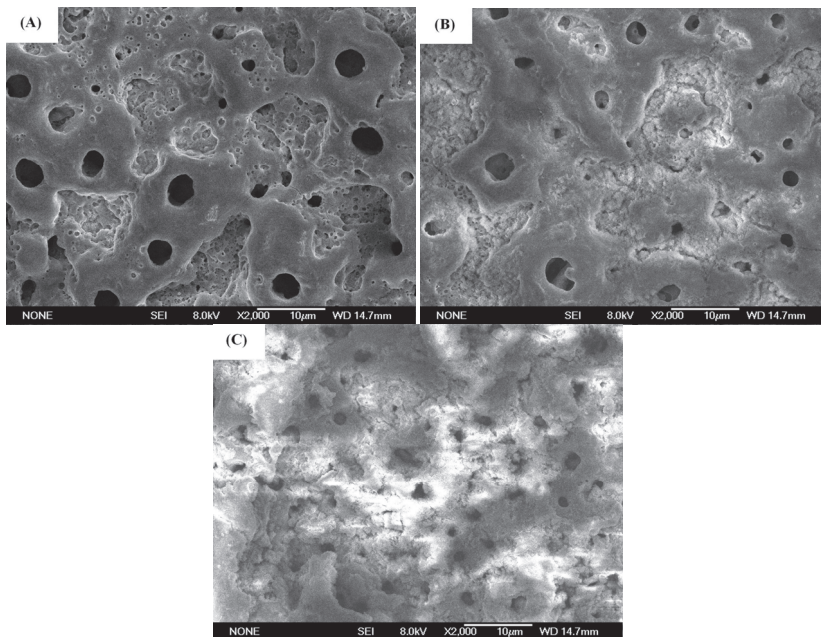
Fig. 2. SEM surface morphologies of micro-arc oxidation coatings formed in different electrolyte concentration: (A) $(CH_3COO)_2Ca.H_2O$ 0.13mol/L, $(NaH_2PO_4.2H_2O)$ 0.06mol/L; (B) $(CH_3COO)_2Ca.H_2O$ 0.26mol/L, $(NaH_2PO_4.2H_2O)$ 0.12mol/L; (C) $(CH_3COO)_2Ca.H_2O$ 0.39mol/L, $(NaH_2PO_4.2H_2O)$ 0.18mol/L (Ni et al., 2008)
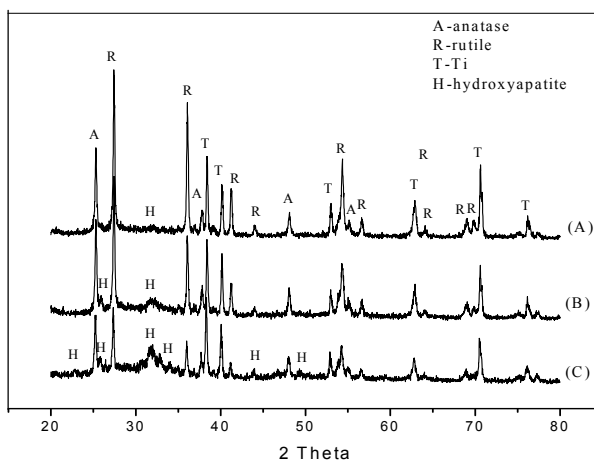

Fig. 3. XRD patterns of the MAO samples formed in different electrolyte concentration for 10min. (A) $(CH_3COO)_2Ca.H_2O$ 0.13mol/L, $(NaH_2PO_4.2H_2O)$ 0.06mol/L ;(B) $(CH_3COO)_2Ca.H_2O$ 0.26mol/L ,$(NaH_2PO_4.2H_2O)$ 0.12mol/L ; (C) $(CH_3COO)_2Ca.H_2O$ 0.39mol/L , $(NaH_2PO_4.2H_2O)$ 0.18mol/L (Ni et al., 2008)

2.5.2 Process parameters

Beside influence of electrolyte to the MAO film, process parameters such as oxidation time, applied voltage, power supply mode, and current density et al. are other factors that should not be ignored. The uppermost process parameters are oxidation time and applied voltage which can be controlled from several min to several quarters and from dozens volts to several hundred volts, respectively (Han et al. 2002a, 2002b, 2003; Ishizawa & Ogino, 1995; Kuromoto et al., 2007; Li et al., 2004; Ni et al. 2008; Song et al., 2004; Sul et al., 2002). The phase, element content, morphology, and thickness of the films were strongly dependent on the treatment time and applied voltage.

The morphological difference associated with treatment time and discharge voltage have been found by many investigators (Han et al. 2002a, 2003; Ishizawa & Ogino, 1995; Kuromoto et al., 2007; Li et al., 2004; Ni et al. 2008;; Sul et al., 2002). On the surface of MAO coating on titanium, the diameters of discharge pores tend to increase with treatment time prolonged within certain period time, and it will not increase in the time that upon the time bucket. The periods of time are not stationary because it is influenced by others process of MAO and sometimes it would not appear. The roughness of the coating also increased with increasing of voltage (Kuromoto et al., 2007; Li et al., 2004).
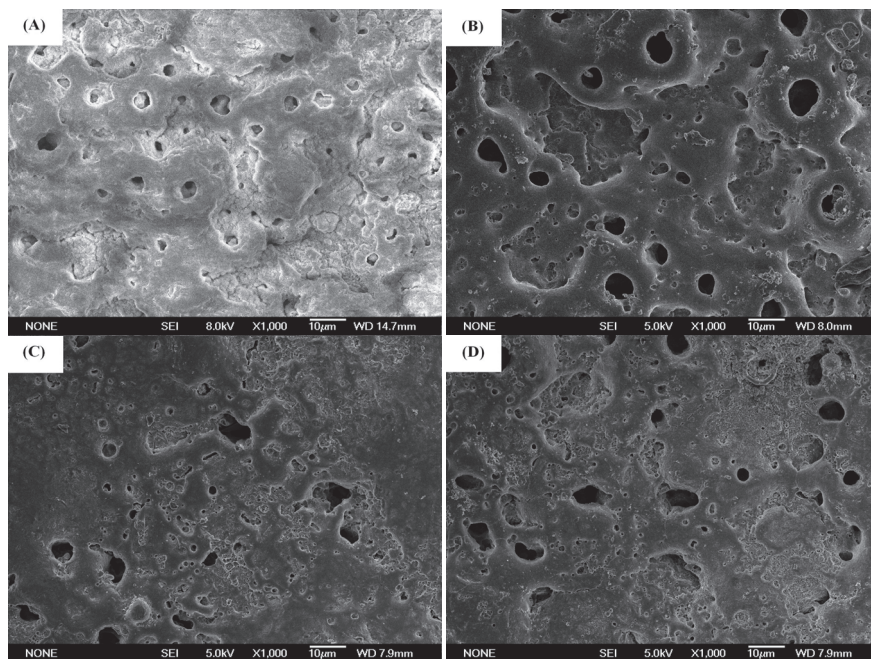

Fig. 4. SEM surface morphologies of micro-arc oxidation coatings treated for different oxidation time.(A) 10min;(B) 20min;(C) 30min;(D) 40min (Ni et al. 2008).

In the early growth stage (short treatment time) of the MAO, micro arc occurs to the fresh metallic surface or to the thinner dielectric layer (obtained at low discharge voltage) where the less accumulated electrical charge is required to activate an arc and therefore extensive small micro-arcs over the surface are facilitated. Numerous homogenously distributed tiny

pores with thin layer thickness were thus found for the specimens, as opposed to those specimens prepared at high discharge voltages or extended treatment times, where less but large arc events occur. Fig.4 demonstrated the morphological difference between coatings obtained for different treatment time in our previous work (Ni et al. 2008).

The phases of the oxide layers formed by MAO process characterized by XRD analysis are dependent on oxidation time and applied voltage, too. Generally, with increase of oxidation time, the crystal of TiO$_2$ become better and diffraction peaks of hydroxyapatite in the coatings were stronger. In other words, a shorter treatment time favor the growth of anatase in the MAO film. Anatase formation requires much lower activation energy than the rutile polymorphism as had been reported (Shibata et al., 1993). Under a short treatment time, the available energy is only sufficient to overcome the activation energy for the formation of anatase and the film is thus exclusively composed of this form. A longer treatment time thermodynamically favors the stable rutile phase. Fig.5 showed this tend for us by work of our previous work (Ni et al. 2008). And it agrees well with the results revealed by Lie et al (Li et al., 2004).
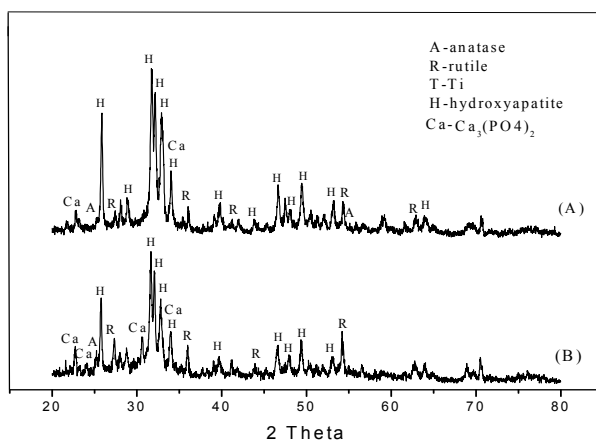

Fig. 5. XRD patterns of the MAO samples treated for (A) 30 min and (B) 40 min (Ni et al., 2008)

The same trend as treatment time was seen in discharge voltage, and the reasons can be same too (Han et al., 2003; Li et al., 2004; Shibata et al., 1993). XRD patterns of the films obtained by Han et al (Han et al., 2002a) showed that at low applied voltage, the film was composed of rutile and a small amount of anatase and with increasing the applied voltage, anatase phase gradually disappeared and rutile phase gradually increased. Sometimes, other Ca- and P-containing compounds such as Ca$_3$(PO$_4$)$_2$, CaTiO$_3$, b-Ca$_2$P$_2$O$_7$ and a-Ca$_3$(PO$_4$)$_2$ could be observed also (Ni et al., 2008; Han et al., 2003; Song et al., 2004). The possible reason for which may be higher applied voltage used (Han et al., 2003; Song et al., 2004).

As discussed above, the thickness, pore size and the content of Ca and P tended to increase with the applied voltage. And the morphology of the oxide layer was dependent on the treatment time and voltage applied during the oxidation treatment. On the other hand, the thickness and elements content changes of the MAO coating with oxidation time are not same with each other in different investigators' works. Sometimes, the thickness sostenuto thickened with the time increase (chen et al., 2006), and sometimes it thickened first and

then decreased at a certain value time (Ni et al., 2008). The tendency may be influenced by some other factors. The same condition can be seen in element content of the coating (chen et al., 2006; Ni et al., 2008).

There are also many other factors than affect the MAO film on titanium surface, such as power mode, current density, electrolyte temperature, substrate material, and so on. They all influence the microstructure, properties and of course application of the MAO coating formed on titanium and its alloy.

2.6 Summary of MAO on titanium

In a word, MAO is a simple, controllable, and cost-effective method of forming a porous TiO_2 layer on the titanium implant surface. The microstructure of the oxide layer such as amount and diameter of the pores, thickness, and roughness are easily controllable by adjusting the electrolyte concentration, voltage, processing time, current during the MAO process. Moreover, the element concentration in the coating such as Ti, O, Ca and P can also be regulated by above factors. Thus, phase composition of coating will regulate with it regulately to meet biological performance of the materials. In order to obtain HA in the coating to improve biocompatibility and biological activity of the sample, many investigators employed two-step approach such as Microarc Oxidization-Hydrothermal synthesis, hybrid treatment of micro-arc discharge oxidation (MDO) and electrophoretic deposition (Fu et al., 2002; Han et al., 2002b; Wei & Yang, 2009; Xie et al., 2000; Xu et al., 2006). Whereas, a composite film of HA and TiO_2 also can be prepared directly by MAO in Ca- and P- containing electrolyte by regulating process parameter (Chen et al., 2006; Han et al., 2003; Li et al., 2004; Ni et al., 2008).

3. n-SiO2 embedded HA/TiO2 composite coatings deposited on titanium by micro-arc oxidation

As reported, silicon plays an important role in bone mineralization and formation and is therefore incorporated into a wide variety of medical implants and bone grafts used today. The addition of silicon to HA causes a decrease in grain size that subsequently affects surface topography, dissolution–reprecipitation rates and the bone apposition process (Porter, 2006; Porter et al., 2004). In our present work, based on our preliminary works (Chen et al., 2006; Ni et al., 2008) and the function of silicon in bone mineralization and formation, a novel thought that nano-silicon dioxide particles are added to the composite coating of HA/TiO2 formed by MAO is produced, and the primary experiment was carried out.

3.1 Experimental procedure

The material oxidized was commercially pure titanium (TA$_2$), the element composition of which was shown in Table 1.

The titanium plates ($30\times15\times2$ mm^3) were polished progressively using 200, 400, 800, and 1000-grit silican carbon paper and ultrasoniclly cleaned with acetone and deionized water respectively. The cleaned Ti plate was oxidized as an anode in an electrolyte containing sodium phosphate monobasic dehydrate ($NaH_2PO_4.2H_2O$, AR), calcium acetate monohydrate (($CH_3COO)_2Ca.H_2O$, AR), a little ethylene glycol ($C_2H_6O_2$, AR) as dispersant and a small quantity of SiO_2 nano-particles. The electrolyte was treated with ultrasonic in order that the solute was dissolved sufficiently and the n-SiO_2 particles were dispersed in the electrolyte uniformly. While a stainless steel plate was used as a cathode in an

electrolytic cell. After the MAO treatment, the sample was washed with water and dried with a blower.

TA$_2$	Fe	O	C	N	H	Ti
Contents of impurities (<wt%)	0.30	0.20	0.10	0.05	0.015	remains

Table 1. Element composition of the pure commercial titanium

For the MAO treatment, a pulse power supply was employed. The pulse parameters (e.g. voltage, current, and duty cycle) can be adjusted independently. In this study, MAO was carried out at current density of 22~25A/dm^2 for different oxidation time as 10 min and 20 min at room temperature, and the duty cycle was 15%. The final voltage was 450V and 500V.

The surface and cross-sectional morphologies of the films were observed by scanning electron microscopy (SEM, JSM-6700F, Japan). The elemental composition was examined with energy dispersive X-ray spectrometer (EDX, INCA, Oxford) incorporated into the scanning electron microscope. The phase components of the coatings were analyzed using X-ray diffraction (XRD, D/max-γB, Japan) using CuKα radiation at 40 KV and 150mA with a scanning speed of 9°/min and a step size of 0.02^o.

According to ISO7405:1997(E)standard (ISO 7405:1997(E)), 3-[4,5-dimethylthiazol-2-yl]-2-5-diphenyl-tetrazolium bromide (MTT) assay method was used to preliminarily evaluate the cylotoxicity of the films on L-929 mouse fibroblast. After sterilization of the samples, the extracted liquid of the films, pure titanium substrates was prepared respectively by adding the samples together with DMEM with 10% fetal bovine serum in aseptic test tube and then cultivated at 37℃ in CO$_2$ standing-temperature incubator for 24 h. L-929 cell suspension of 5×10^3 cells/ml was made by diluting the cells with DMEM with 10% fetal bovine serum. Aliquots of 200 uL of the cell suspension were seeded into each well of 96-well plate and cultivated at 37℃ in CO$_2$ standing-temperature incubator for 24 h. And then, the extracted liquid was added into the well with 200μl per well after removing the previous culture medium and washing twice with PBS. DMEM with 10% fetal bovine serum was added for negative group and 1% solution of phenol was added for positive group. After the 96-well plate was cultured at 37℃ in CO$_2$ standing-temperature incubator for 2d, 4d and 7d respectively, about 20μl MTT solution（5mg/ml）was added in each well for 4h at 37℃ in the CO$_2$ standing-temperature incubator. After washing with PBS twice, about 150μl dimethyl sulfoxide (DMSO) was added to dissolve crystals. After shaking at room temperature for 10 min and appearing of bluish violet crystals, absorbance (Optical density - OD) of each well was determined at 490 nm using a microplate reader. Cylotoxicity grade of the samples was converted by relative growth rate (RGR) according to table 2.

$$RGR = \frac{\text{average value of the samples}}{\text{average value of the negative group}} \times 100\% \qquad (1)$$

RGR(%)	≥100	75~99	50~74	25~49	1~24	0
cytotoxicity grade	0	1	2	3	4	5

Table 2. Relation between cytotoxicity grade and RGR

3.2 Results and discussion
3.2.1 Morphology of the coatings

Fig.6 showed SEM micrographs of the surfaces of the MAO coatings formed at different oxidation time. In Fig.6 (A), there were micro-pores and snaky apertures on the surface of the film when the treated time was 10min. The higher magnification images indicated that there was a reticular structure at the edge of the pores while the network structure was not observed on the other area of the surface (in Fig.6 (B) and Fig.6 (C)). When the treated time extended to 20 min, the pores and the snaky apertures on the surface disappeared and the surface was covered by many micron-sized globules whose size was about 5~10μm.(in Fig.6 (D)). In the higher magnification the coating was a coralloid structure on the surface of the micro-sized globules (in Fig.6 (E) and Fig.6 (F)).
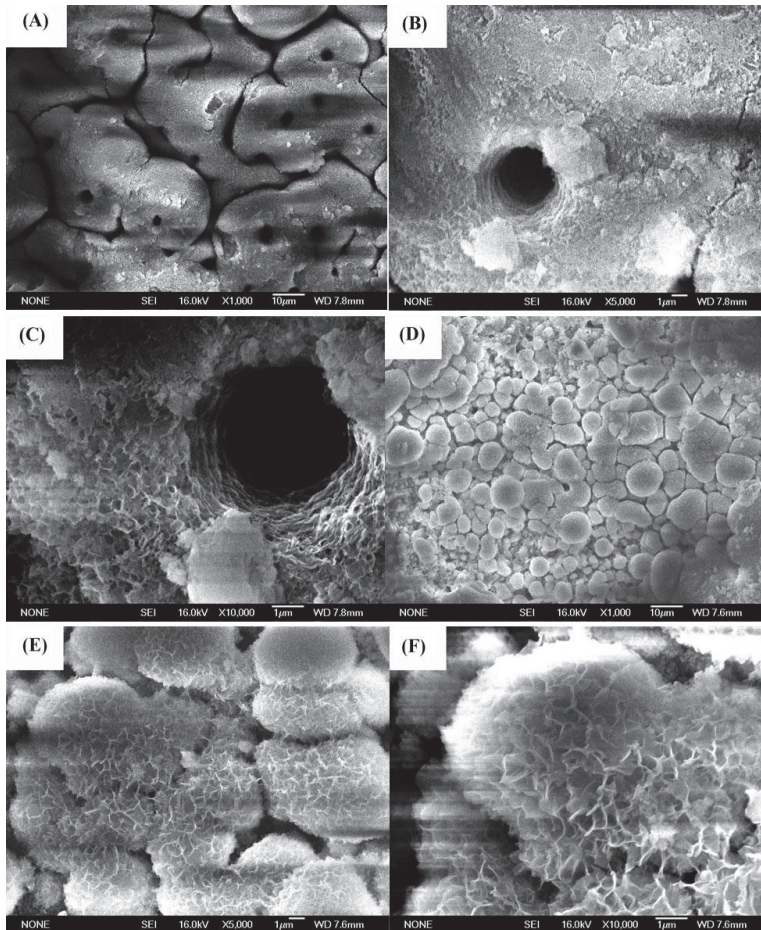
Fig. 6. SEM surface morphologies of micro-arc oxidation coatings treated for 10min (A) low magnification (×1000); (B) local magnification of (A) (×5000); (C) local magnification of (B) (×10000) and for 20min (D) low magnification (×1000); (E) local magnification (D) (×5000); (F) local magnification of (E) (×10000)

The cross-sections of the typical coating were shown in Fig.7 When the oxidation time was 10min, the thickness was about 25μm. The thickness of the film increased with the oxidation time increasing. The thickness was nearly 40μm when the oxidation time reached 20min. There was no obvious discontinuity between the deposited film and the substrate. That indicated that the film can be tightly adhered to the substrate.
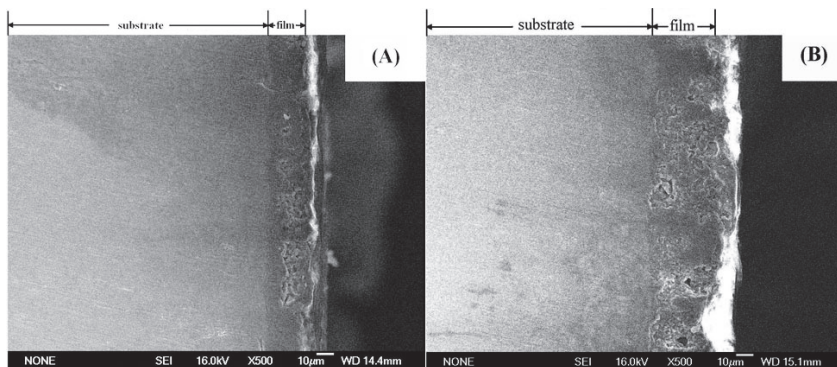

Fig. 7. SEM cross-sectional views of micro-arc oxidation coatings treated for (A) 10min and (B) 20min

3.2.2 Elemental composition of MAO coatings

The coating formed by MAO contained Ca, P, and Si as well as Ti and O, as shown in Fig.8 and in Fig.9. The atomic content of silicon was 0.74% and 1.31% respectively in films treated for 10min and 20min. It was suggested that the elemental compositions in an electrolytic solution could be compounded into the coating during MAO process. As shown in Fig.9 the content of Ca, P, Si and O were gradually reduced from the surface of the coating to the titanium substrate, while the content of Ti was gradually increased.
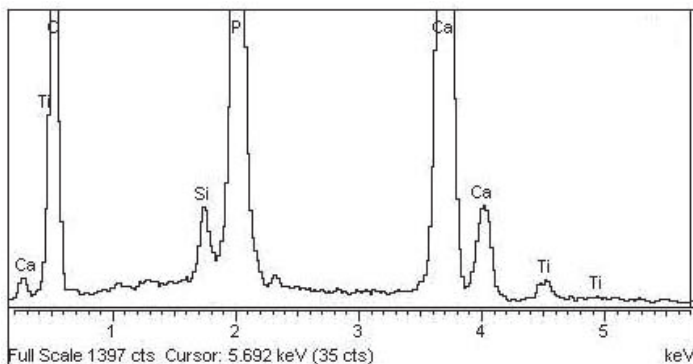

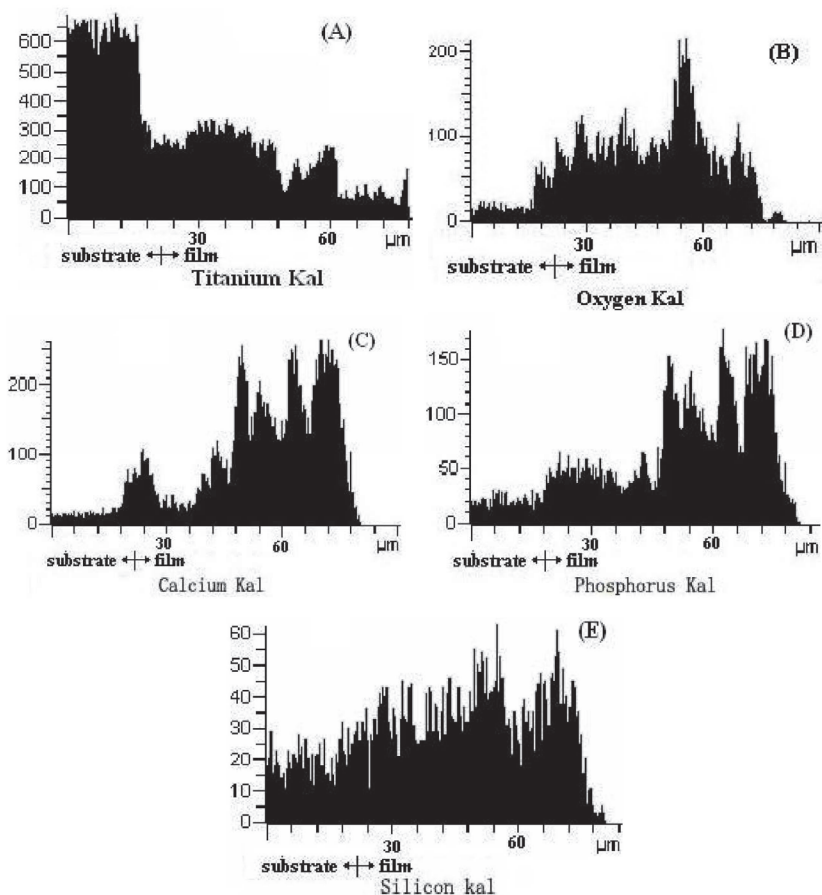Fig. 8. EDX spectrum of Ti specimens treated with MAO

Fig. 9. Depth profiles of the elements in the oxidized coating of titanium (A) titanium; (B) oxygen; (C) calcium; (D) phosphorus and (E) silicon

3.2.3 Phase components of MAO coatings

The XRD patterns of the micro-arc oxidized samples obtained at different oxidation time was shown in Fig.10. When the oxidation time was 10 min, the film (in Fig. 10 (A)) was mainly composed of rutile, anatase and Ti, especially the peaks of rutile were strong. The peaks of hydroxyapatite could be observed, but the peaks were broad and weak, which implied that the crystallization of the formed hydroxyapatite was poor. When the treatment time was 20 min (in Fig. 10 (B)), the diffraction peaks of hydroxyapatite in the coatings were strong and became a predominant component in the films. It is shown that in the experiment with increasing treatment time, the applied voltage increased, the working energy increased, the HA coating formed under the effects of thermochemistry, electrochemistry and plasma-chemistry. On the contrary, the peaks of rutile weakened and the peaks of anatase and Ti were hardly observed. But the diffraction peaks of silicon or silicon oxide was not observed. It could be inferred that silicon in the coating by MAO was little.
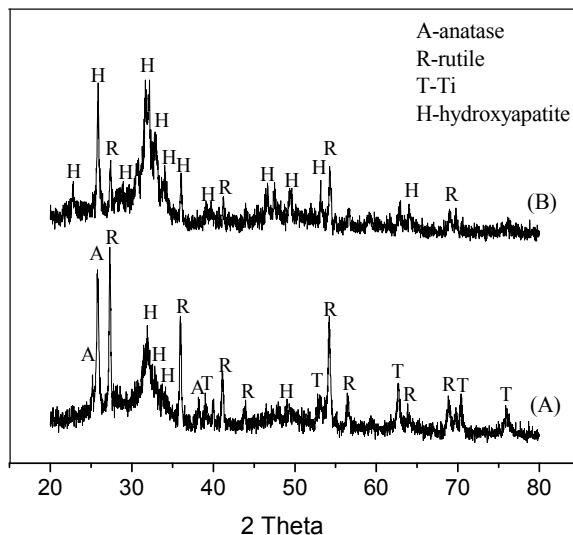
Fig. 10. XRD patterns of the MAO samples treated for (A) 10 min and (B) 20 min

3.2.4 Cytotoxicity of MAO films

The average OD-value, RGR and cytotoxicity grade of each tested group for different cultivation days were listed in table3, table 4 and table 5 respectively. The OD value increased with the increase of the cultivation time and presented its dependence on ultivation time. The cytotoxicity grade of each MAO sample was 0 and the cytotoxicity grade of titanium substrates was 0 or 1. But every cytotoxicity grade for that of the positive groups was 4. The biocompatibility of MAO films is better then that of the titanium substrate because there are HA, rutile and anatase in the film. The OD—value of each tested group were similar to the negative group and significantly different from positive group which indicated that the materials tested were safe to L-929 cells.

groups	MAO samples		titanium substrates	negative groups	positive groups
	treated for 10 min	treated for 20 min			
OD	0.275±0.026	0.281±0.028	0.256±0.031	0.235±0.025	0.055±0.007
RGR(%)	117.02	119.57	108.94	100	23.40
cytotoxicity grade	0	0	0		4

Table 3. Average values of OD， RGR and cytotoxidty grade for the tested groups at 2 days

groups	MAO samples		titanium substrates	negative groups	positive groups
	treated for 10 min	treated for 20 min			
OD	0.393±0.039	0.409±0.028	0.379±0.037	0.383±0.031	0.050±0.004
RGR(%)	102.61	106.79	98.95	100	13.05
cytotoxicity grade	0	0	1		4

Table 4. Average values of OD, RGR and cytotoxidty grade for the tested groups at 4 days

groups	MAO samples		titanium substrates	negative groups	positive groups
	treated for 10 min	treated for 20 min			
OD	0.835±0.023	0.852±0.021	0.817±0.022	0.832±0.024	0.072±0.005
RGR(%)	100.36	102.40	98.20	100	8.65
cytotoxicity grade	0	0	1		4

Table 5. Average values of OD，RGR and cytotoxidty grade for the tested groups at 7 days

4. Conclusion and remarks

According to above study, nano-silicon embedded HA/TiO_2 composite coatings can be prepared by micro-arc oxidation in Ca- and P- containing electrolyte by adding a little n-SiO_2 nano-particles in it. The surface of the coatings on titanium substrate produced a network structure without apparent interface to the titanium substrates. The thickness of the film could reach about 40μm. The film contained Ca, P, and Si along with Ti and O. As the treatment time increased, the hydroxyapatite became a predominant component in the film when the treatment time was 20min. the cytotoxicity grade of the coatings was 0 according to the MTT test and that of titanium substrate was 0 or 1，meaning that the films and substrate all had no cytotoxicity. The coatings' biocompatibility became better with increase of treatment time and were better than biocompatibility of substrate.

Based on the preparation of the composite coating of HA and TiO_2, the new work introduced a novel idea adding silicon to the composite coating in order to improve the bioactivity of the coating, and the results also proved the realizability. But, there are also many works needed to be done in depth. Although the EDS spectrum of the films revealed that the deposited coatings were composed of Ti, O, Ca, P and Si, but no siliceous crystalline was detected by XRD. The chemical status and location of the silicon are not clearly understood yet. Does silicon existe as an ion, atom, or other valence state in the HA and TiO2 coating? Or, does it constitute the structure of Si-HA? Further studies are needed to answer these questions. Primary cylotoxicity of the films on L-929 cell was evaluated and the results were perfect. However, detailed mechanical behavior and bioactivity of the coating such as apatite induction and corrosion resisting of the film in simulated body fluid (SBF), in vitro cell tests, and in vivo tests need to be researched. Furthermore, more efforts needed to pay for the optimization and mechanism study of MAO technique on titanium.

5. Acknowledgements

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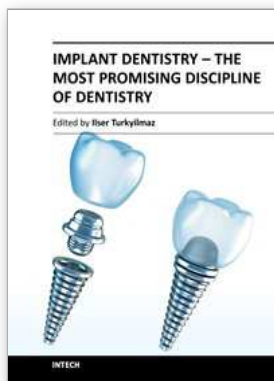
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