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Effect of Micro-Arc Oxidation Voltage and Duration on the Morphology, Phase Structure, Chemical Composition of Calcium Phosphate Coatings

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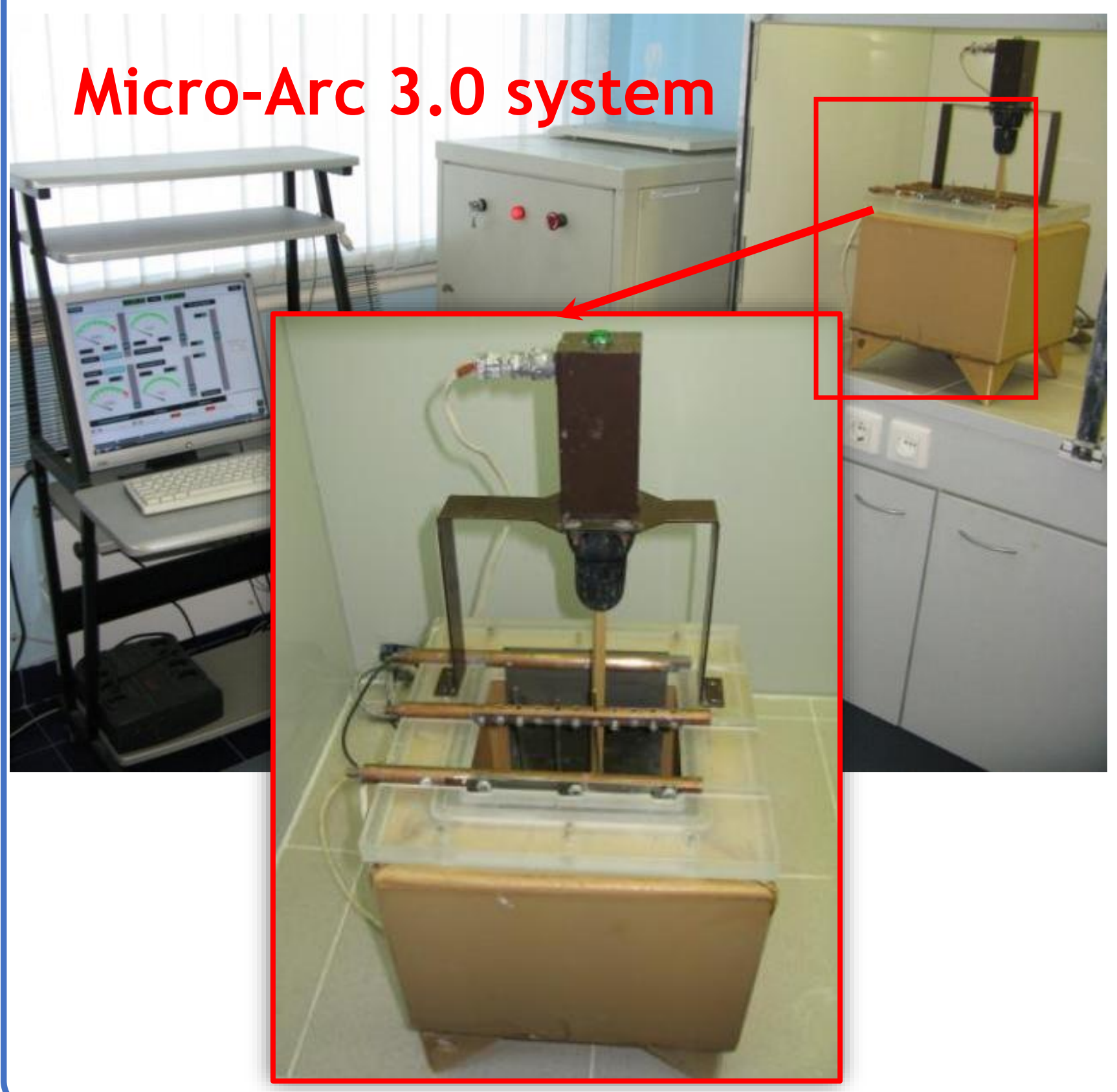
INTRODUCTION

One of the most promising approaches in the modern biomedical materials science is to modify and functionalize the surface of metallic implants, especially from titanium and its alloys, in order to provide a new complex of the performance properties. The application of bioactive ceramic coatings such as calcium phosphate (CaP) coatings can improve the osseointegration of titanium implants. One of the promising methods for depositing CaP coatings on titanium surfaces is the micro-arc oxidation (MAO) method, which makes it possible to improve the corrosion and wear resistance of titanium alloys, significantly increase their biocompatibility and biological activity, improve the bond between the substrate and the coating, and also makes it possible to cover objects of complex shape, which is a great advantage for biomedical applications. The MAO method makes it possible to obtain coatings with a hierarchically organized structure and necessary physical, chemical and biological properties by varying various process parameters, such as electrolyte composition, applied voltage magnitude, current density, coating duration, etc. The aim of the work was the study of the effect of the applied anode voltage (200 V, 350 V) and the duration (1, 2, 4 and 10 min) of the MAO process on the morphology, phase structure and chemical composition of CaP coatings on the pure titanium (Ti) substrate.

EXPERIMENTAL

The Micro-Arc 3.0 installation with the DC power supply, electrolytic bath, counter electrodes and personal digital assistant to processing control was used to synthesize the MAO biocoatings. The MAO parameters to synthesize the MAO biocoatings is presented in Table 1.



Photos of samples with CaP coatings deposited during different times of the MAO at 350 V

Table 1. MAO parameters

Electrolyte composition	$Ca_{10}(PO_4)_6(OH)_2$ + H_3PO_4 + $CaCO_3$
Voltage	Static, anodic, 200, 350 V
Frequency	50 Hz
Pulsed duration	100 µs
Time	1-10 min

RESULTS AND DISCUSSION

SEM studies showed that during 1 min under the low applied voltage of 200 V, the thin coating with heterogeneous thickness (5.8-15.5 µm) and inhomogeneous morphology was formed (fig.1a, 2a). The SEM images illustrated two different surface morphologies, both predominant TiO_2 sublayer with numerous crater-like micropores and the local CaP layer with hemispherical structural elements contained internal pores. 2 min of MAO led to the formation of a uniform CaP coating with a typical surface morphology represented by the structural spheroidal elements (spheres) with internal pores (fig.2 a). Further increasing the MAO duration up to 10 min was accompanied by a linear increasing the coating's thickness from 28.6 to 55.5 µm [1] and by the following change in its elemental composition. The calcium amount in the coating increased from 3.2 to 5.5 at.%, the titanium amount decreased from 13.6 to 8.9 at.%, the phosphorus and oxygen amounts were unchanged within the ranges of 15.4 – 16.2 at.% and 67.1 – 69.7 at.%, respectively (Fig. 3 a). XRD analysis showed that CaP coatings formed at low voltage of 200 V, regardless of the MAO duration, were in an X-ray amorphous state. It was evidenced by an obvious diffuse scattering region on the XRD patterns corresponding to the amorphous CaP phase (Fig. 4).

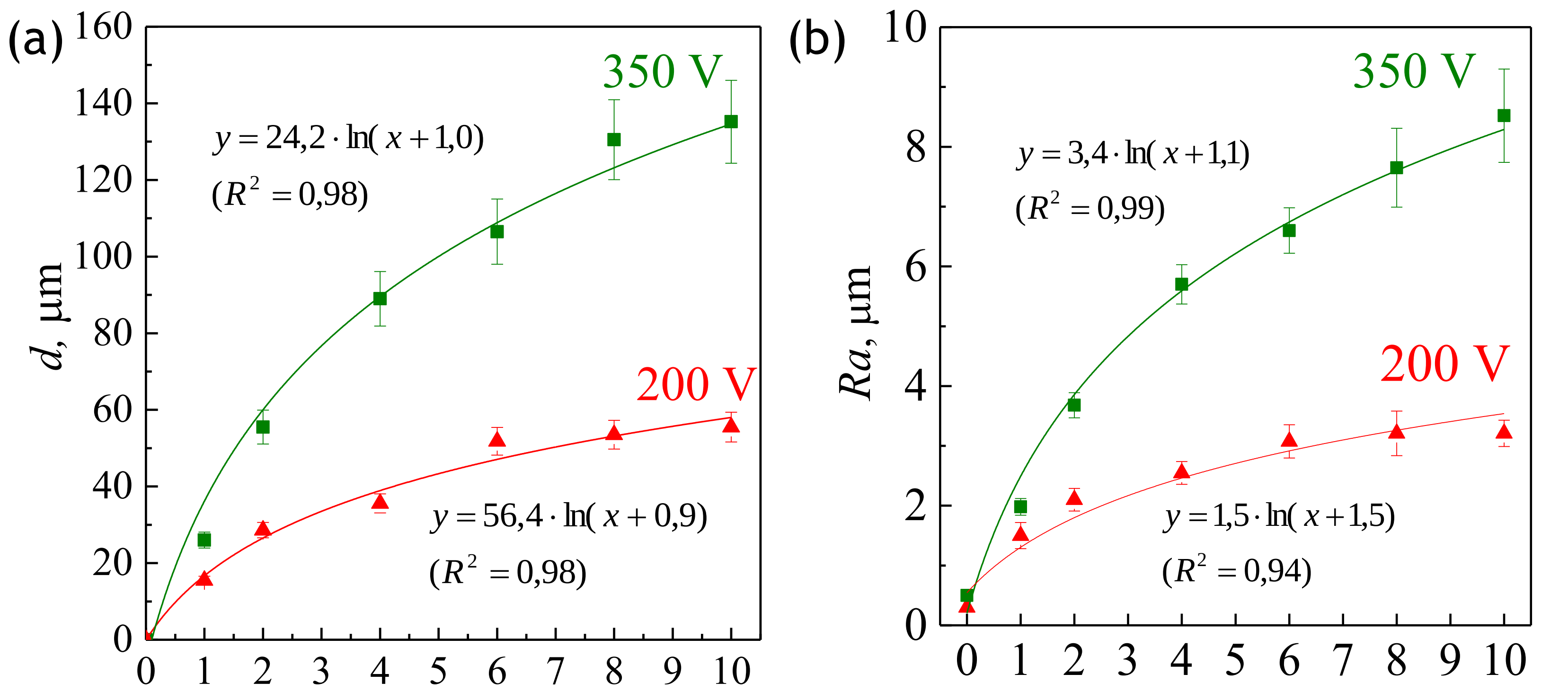


FIG. 1 *Graphs of the coating thickness (a) and roughness (b) against the MAO duration at 200 V and 350 V*

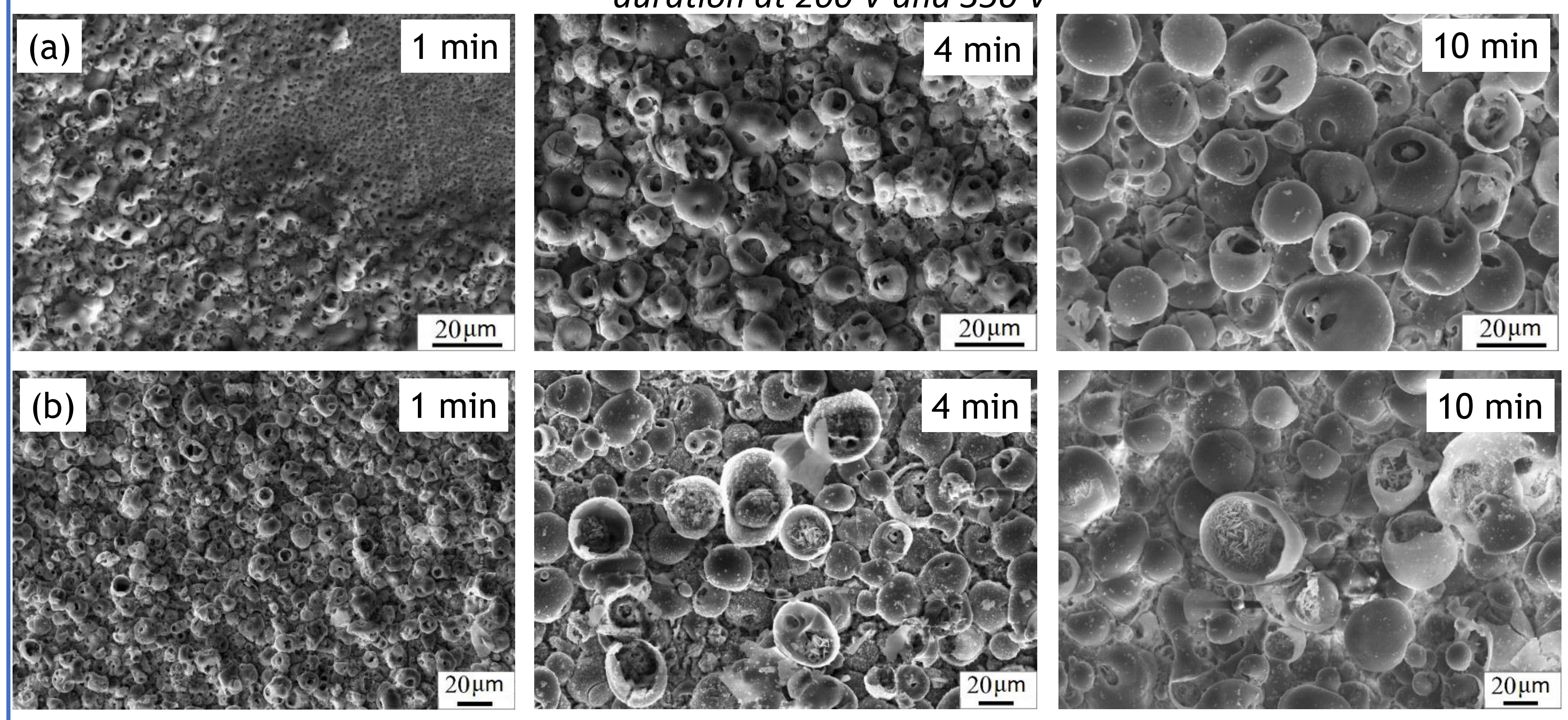


FIG. 2 *SEM-images of the coating surface deposited at 200 V (a) and 300 V (b) with different duration.*

Under 350 V voltage, regardless of the MAO duration, the thick homogeneous CaP coating with similar surface morphology represented by the spheres, destructed hemispheres, pores inside the spheres, pores between the spheres and plate-like crystals was formed (fig. 1b, 2b) [2]. At the same time, an increase in the MAO process duration from 1 to 10 min led to the increase of the thickness from 37.2 to 135.2 µm. Duration of 1 min allowed the formation of coating in an X-ray amorphous state, similar to the coatings formed at a low voltage of 200 V. An increase in the MAO duration from 2 to 10 minutes led to the formation of an amorphous-crystalline structure of the coatings. This was evidenced by the increased intensity of reflections corresponding to the $CaHPO_4$ phase, β-$Ca_2P_2O_7$ phase, and a diffuse scattering region corresponding to the amorphous CaP phase (Fig. 4). The volume fraction of $CaHPO_4$ phase in the coatings was increased from 51 to 80 % in the amorphous-crystalline coatings. The coating structural-phase transformation from the X-ray amorphous state to the amorphous-crystalline one was attended by the following change in its elemental composition: the calcium amount was increased from 4.0 to 9.7 at.%, the titanium amount was decreased from 12.0 to 6.5 at.%, the phosphorus and oxygen amounts were unchanged in the ranges of 14.6 – 16.1 at.% and 64.6 – 70.4 at.%, respectively (fig. 3b).

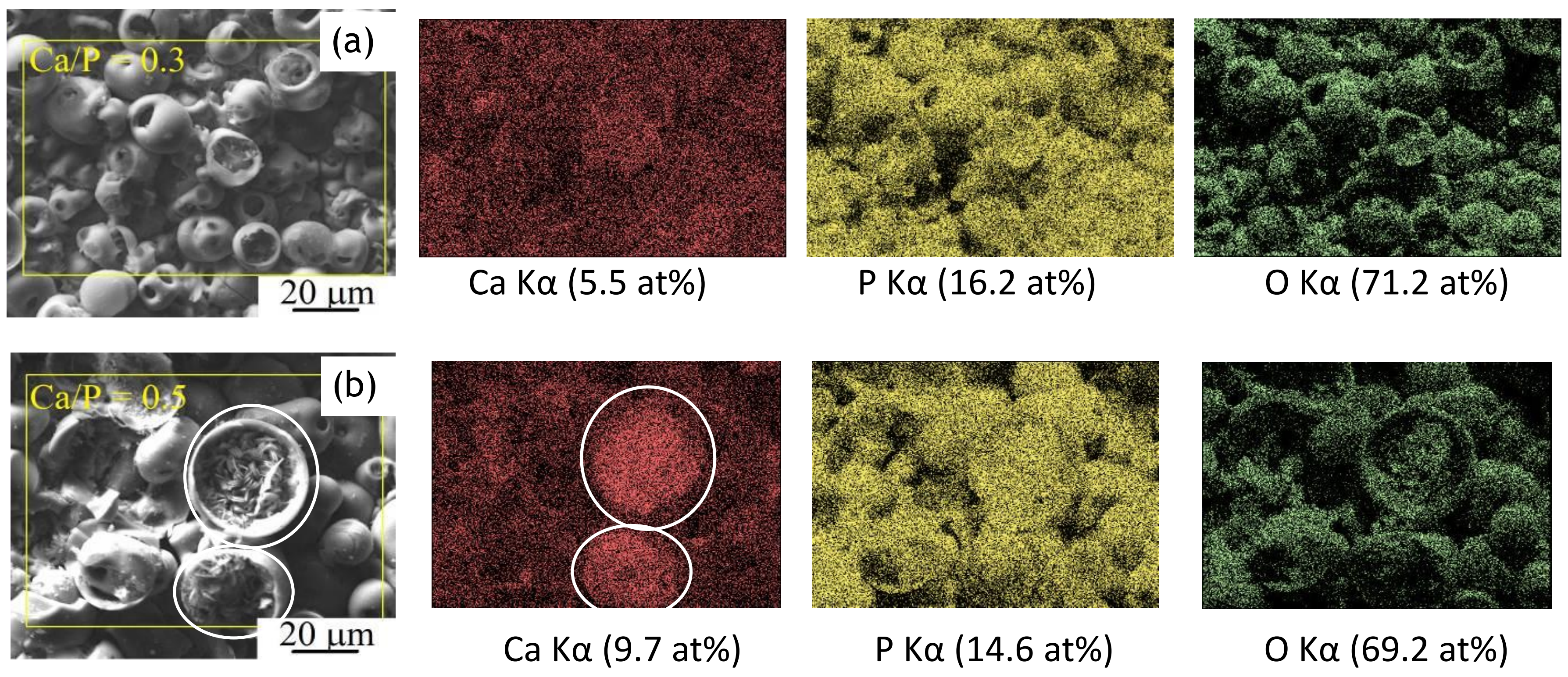


FIG. 3 *SEM-images of the coating surface and EDX maps of the Ca, P and O distribution in the coatings deposited at 200 V (a) and 300 V (b).*

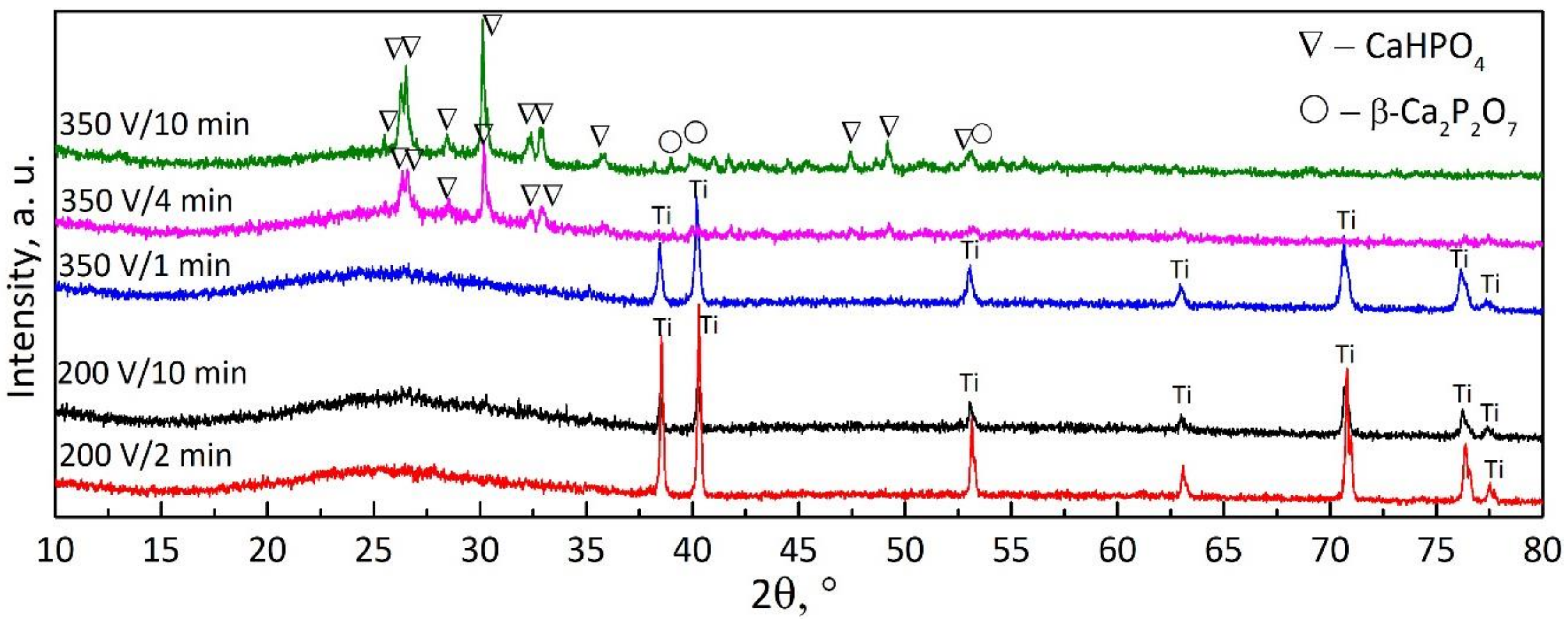


FIG. 4 *XRD patterns of CaP coatings deposited at different voltages with different duration*

Thus, this work revealed that the MAO applied voltage and the duration have a significant influence on the formation of a multilevel hierarchical structure, morphology, phase and elemental compositions of the CaP coatings on Ti surface.

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