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Calcium phosphate coating formed on titanium scaffold by plasma electrolytic oxidation

The article provides the results of the preparation of calcium phosphate coatings by plasma electrolytic oxidation. Calcium phosphate coatings are formed on titanium scaffolds with a porous structure. Titanium scaffolds are products of additive manufacturing equipment by selective laser melting. The morphology of the obtained coating, phase and elemental composition are described, the Ca/P ratio of the coating is determined. The surface of the scaffold is porous due to the baking of powder particles during production. XRD analysis shows the presence of calcium phosphate and oxide compounds. The resulting oxide coating is evenly distributed over the porous surface of the scaffold. Titanium, aluminum and vanadium are located in the areas of the coating free of calcium phosphate particles. The average Ca/P ratio for the resulting coating was 2.48. This value is close to the Ca/P ratio in human bone. It is concluded that the use of the PEO method is promising for the manufacture of scaffolds with a porous structure with calcium phosphate coatings for use in traumatology and orthopedics. The use of titanium scaffolds with a porous structure with calcium phosphate coatings will improve the osseointegration of implants and exclude the possibility of implant failure.

Keywords: titanium, calcium phosphate, plasma electrolytic oxidation, protective coatings, bioactivity, hydroxyapatite, implant, osteogenesis.

Introduction

Currently, artificial materials are widely used in medicine to replace joints and restore bone tissue. Titanium and titanium alloys are used for medical implants since they meet the requirements of modern medicine the most and have high biocompatibility and high corrosion resistance [1], as well as a good strength-to-density ratio. However, due to their limited biological activity, titanium-based materials cannot effectively interact with bone tissue in the early stages of implantation, which can lead to implant failure [2, 3].

To improve biological activity, one of the most effective methods is the deposition of calcium phosphate (CP) coatings on the implant surface by plasma electrolytic oxidation (PEO) [3]. The preparation of such compounds as hydroxyapatite, tricalcium phosphate, octacalcium phosphate, and calcium acid phosphates (brushite, monetite) as part of the coating is preferable because they are similar in composition and properties to the components of natural human bone tissue [4, 5].

Titanium alloys used in medicine are acceptable, but have a significant drawback — this is a discrepancy between the rigidity of the implant and bone tissue, which can lead to a shielding effect, osteoporosis and further loss of the implant [6]. One of the important parameters of bone tissue is porosity, since the porous material provides the necessary conditions for cell growth and division, and can also help to reduce the rigidity of the implant [7], which avoids the shielding effect, which leads to the destruction of bone tissue.

The advantage of the PEO method is the possibility of depositing calcium phosphate coatings on implants of various shapes, including porous ones; this method also makes it possible to obtain coatings with a given phase and elemental composition [7, 8]. In addition, Ag, Zn, and other elements can be used to form a coating with antibacterial properties. ZnO also has luminescent and photoelectric properties and can be used in other directions [9, 10]. Therefore, the optimization of coating parameters and electrolytes for the formation of calcium-phosphate coatings of materials for the replacement and restoration of bone tissue is an urgent problem.

Experimental

Titanium scaffolds with a porous structure were fabricated from titanium alloy powder (Ti-6Al-4V) DIN EN ISO 22674 Rematitan® by selective laser melting (SLM) on an MLab Cusing R (Concept Laser, Germany) additive manufacturing facility.

For coating by the PEO method, a switching power supply “PV-500V/20kW” was used. The surface layer was formed on the surface of scaffolds with a porous structure during PEO processing in an aqueous electrolyte solution using a bipolar mode. A titanium alloy bath (Ti-6Al-4V) was used as a cathode. Electrolyte composition: $Na_2HPO_4 \cdot 12H_2O$ (30-40 g/l), $Ca_3(CH_3COO)_2 \cdot 2H_2O$ (40-50 g/l). The following parameters were used for coating: pulse frequency – 50 Hz; pulse voltage – 200 V; processing time – 5 min.

The surface morphology and elemental analysis were studied using a JSM-6390LV scanning electron microscope (SEM) equipped with an INCA Energy Penta FET X3 energy dispersive microanalysis system.

X-ray diffraction analysis of the obtained coatings was performed on a PANalytical X'Pert PRO Cu Kα diffractometer with a wavelength of 1.54056 Å.

Results and Discussion

The SEM image (Figure 1) shows the surface morphology of the coating obtained by the PEO method. The sample surface has a porous structure and contains titanium particles melted during the additive manufacturing of scaffolds. It can be seen that the resulting oxide coating is evenly distributed over the surface of the sample. Due to the porous surface of the scaffold, additional porosity of the coating surface was formed. The observed coating is the result of CaP transfer from the electrolyte during PEO [11].

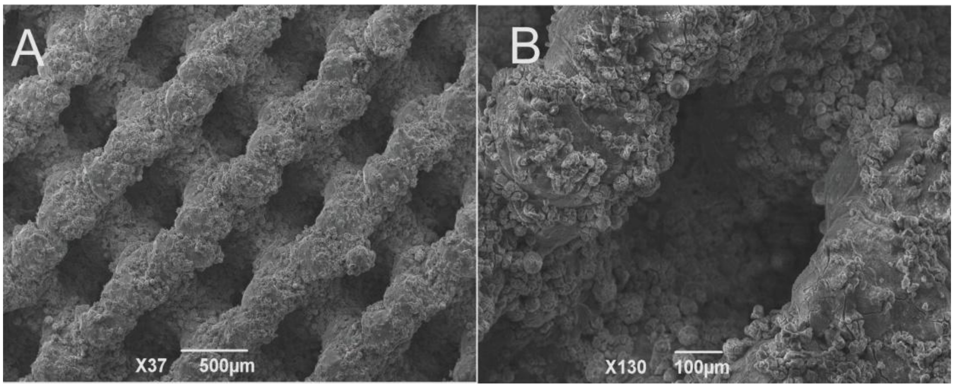

Figure 1. SEM images of the scaffolds surface after PEO

Table 1 and Figure 2 illustrate the results of the energy dispersive X-ray (EDX) analysis. Spectral lines are distinguishable. The elemental composition indicates the presence of an oxide layer, which is the main coating in PEO. According to the presented elemental analysis, it is possible to observe the content of the main elements in the coatings, such as phosphorus, calcium, oxygen, titanium. The average ratio of calcium to phosphorus is 2.48. The Ca/P ratio of the resulting coating is close to the Ca/P ratio in human bone tissue [12].

Table 1

Elemental composition of the obtained CP coatings (wt.%)

Spectrum	O	Na	Al	**P**	**Ca**	Ti	V	Total	Ca/P
Spectrum 1	61.27	0.84	2.68	**0.94**	**1.61**	31.35	1.30	100	**1.7**
Spectrum 2	33.37	0.39	1.16	**2.24**	**6.27**	53.56	3.01	100	**2.7**
Spectrum 3	55.18	0.56	2.91	**1.30**	**1.75**	36.38	1.92	100	**1.3**
Spectrum 4	41.38	0.48	1.42	**1.95**	**6.37**	46.06	2.35	100	**3.2**
Average	47.80	0.57	2.04	**1.61**	**4.00**	41.84	2.14	100	**2.48**

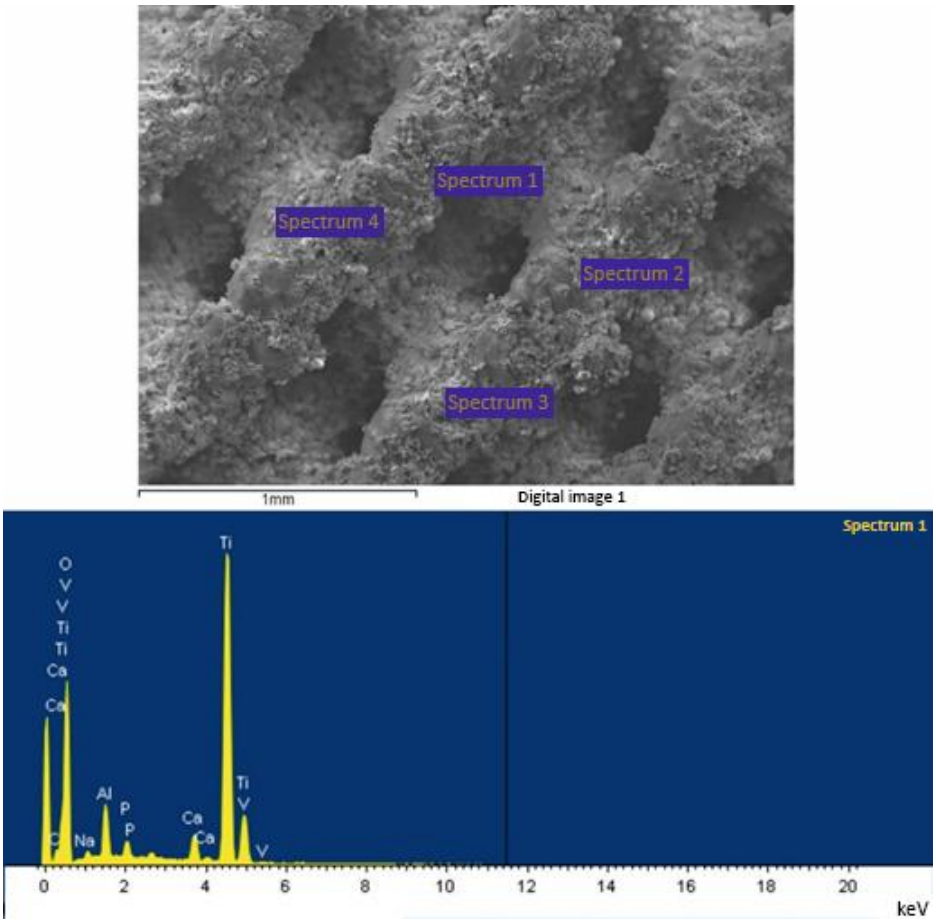

Figure 2. EDX analysis of the obtained CP-coating

On the maps of the distribution of elements, one can observe that phosphorus and calcium are concentrated mainly in the particles that form the surface relief. Titanium, aluminum, and vanadium are located in the areas of the coating free of calcium phosphate particles (Figure 3).

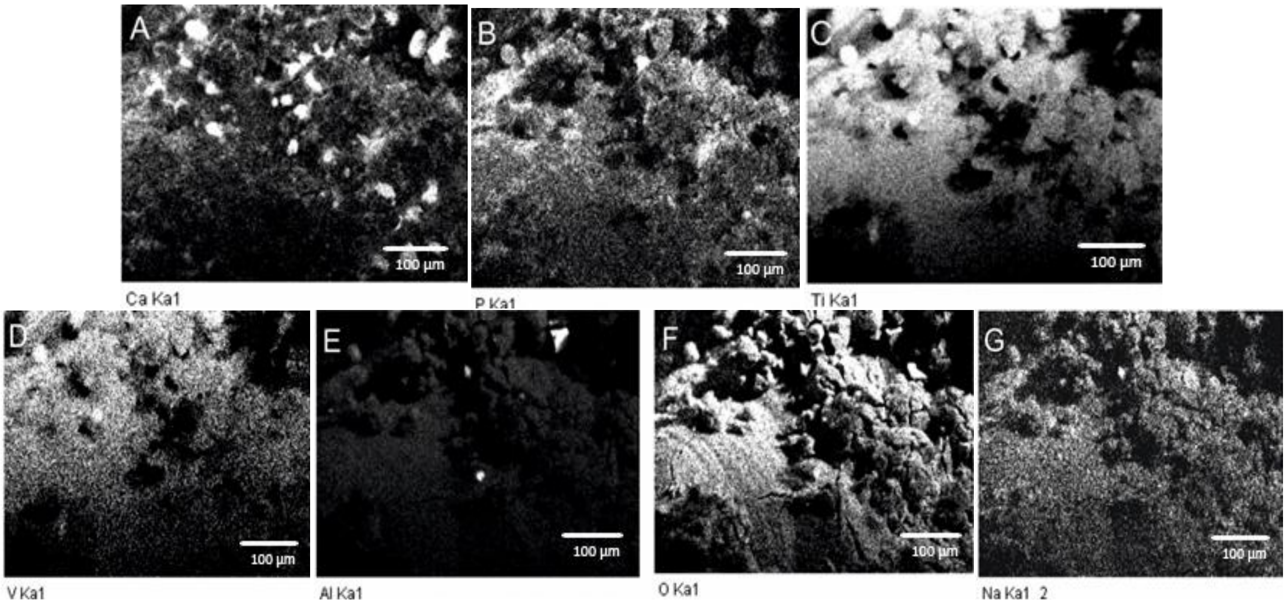

Figure 3. Elements distribution SEM images: (A) - Cl, (B) - P, (C)-Ti, (D)-V, (E)-Al, (F)-O, (G)-Na

Analysis of the XRD pattern (Figure 4) of the resulting coating shows the presence of calcium phosphate and oxide compounds. When analyzing the obtained data, the ICSD databases were used. The presence of a calcium cyclotetraphosphate phase and a titanium oxide coating is confirmed.

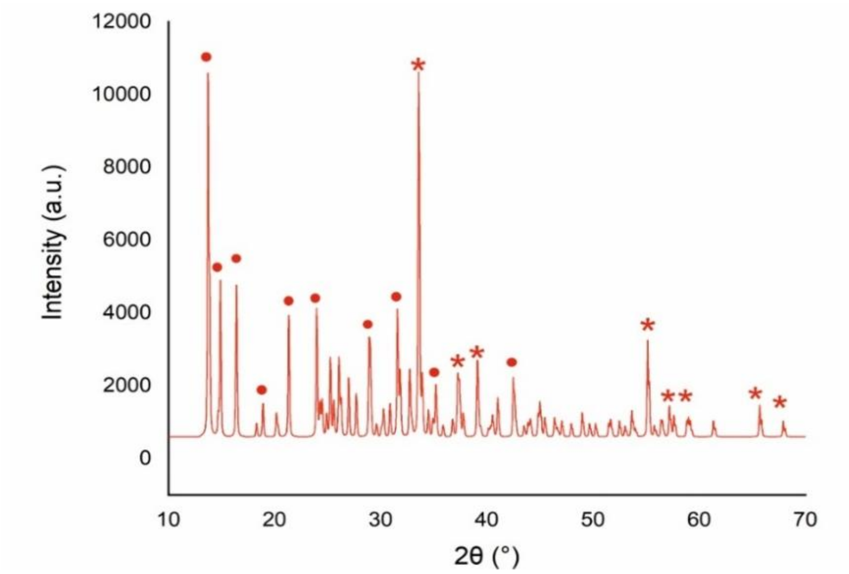

Figure 4 XRD pattern of the resulting coatings
* $Ca_2[P_4O_{12}]\ 4H_2O$; ● TiO_2

Conclusions

Using the PEO method, calcium-phosphate and oxide coatings were formed on titanium scaffolds with a porous structure obtained by selective laser melting equipment. The phase and elemental compositions, surface morphology were studied, and the Ca/P ratio was determined. It is confirmed that the parameters used for the formation of the coating and the composition of the electrolyte make it possible to obtain an oxide coating with the inclusion of particles of calcium cyclotetraphosphate. The results show the possibility of using the PEO method for modifying titanium scaffolds for subsequent use in medicine, and in particular in traumatology and orthopedics. Modification of the surface of titanium scaffolds will ensure to create bioactive implants, which will positively affect their osseointegration and lead to a decrease in failure rates in the early postoperative periods.

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Плазмалық-электролиттік тотығуы әдісімен қалыптасқан титан скаффолдындағы кальций фосфатты жабын

Мақалада плазма-электролиттік тотығу (ПЭТ) әдісімен кальций-фосфатты жабындарды алу нәтижелері берілген. Кальций фосфатының жабындары кеуекті құрылымы бар титан скаффолдтарында қалыптасты. Титан скаффолдтары селективті лазерлік балқыту әдісімен аддитивті өндіріске арналған жабдықта жасалды. Алынған жабынның морфологиясы, фазалық және элементтік құрамы сипатталған, жабынның Ca/P қатынасы анықталған. Өндіріс процесінде ұнтақ бөлшектерінің қақталуынан скаффолдың беті кеуекті болады. Рентгендік фазалық талдау кальций фосфаты қосылыстары мен оксидті жабынның болуын көрсетеді. Алынған оксид жабыны скаффолдтың кеуекті бетіне біркелкі үлестірілді. Титан, алюминий және ванадий жабынның кальций фосфаты бөлшектері жоқ аймақтарында орналасқан. Алынған жабын үшін орташа Ca/P қатынасы 2,48 болды. Бұл көрсеткіш адам сүйегіндегі Ca/P қатынасына жақын. Травматология және ортопедияда қолдану үшін кальций фосфатты жабындары бар кеуекті құрылымы бар матрицаларды өндіру үшін ПЭТ әдісін қолданудың болашағы туралы қорытынды жасалды. Кальций-фосфат жабыны бар кеуекті құрылымның титан қаңқаларын пайдалану имплантаттардың остеоинтеграциясын жақсартады және олардың қабылданбау мүмкіндігін болдырмайды.

*Кілт сөздер***:** титан, кальций фосфаты, плазманың электролиттік тотығуы, қорғаныш жабындары, биоактивтілігі, гидроксиапатит, имплант, остеогенез.

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Кальций-фосфатное покрытие, сформированное на титановом скаффолде методом плазменно-электролитического оксидирования

В статье приведены результаты по получению кальций-фосфатных покрытий методом плазменно-электролитного оксидирования (ПЭО). Покрытия из фосфата кальция формировались на титановых скаффолдах с пористой структурой. Титановые скаффолды были изготовлены на оборудовании для аддитивного производства методом селективного лазерного плавления. Описаны морфология полученного покрытия, фазовый и элементный состав, определено соотношение Ca/P покрытия. Поверхность скаффолда пористая из-за спекания частиц порошка в процессе производства. Рентгенофазовый анализ показывает наличие соединений фосфата кальция и оксидного покрытия. Полученное оксидное покрытие равномерно распределяется по пористой поверхности скаффолда. Титан, алюминий и ванадий располагаются на участках покрытия, свободных от частиц фосфата кальция. Среднее отношение Ca/P для полученного покрытия составляло 2,48. Это значение близко к соотношению Ca/P в кости человека. Сделан вывод о перспективности использования метода ПЭО для изготовления матриксов с пористой структурой с кальций-фосфатными покрытиями для применения в травматологии и ортопедии. Использование титановых каркасов пористой структуры с кальций-фосфатными покрытиями улучшит остеоинтеграцию имплантатов и исключит возможность их отторжения.

*Ключевые слова***:** титан, фосфат кальция, плазменно-электролитическое оксидирование, защитные покрытия, биоактивность, гидроксиапатит, имплантат, остеогенез.