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金属表面生物陶瓷材料的电化学研究

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Electrochemical Study on Bioceramic Coatings of Calcium Phosphates

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摘 要

羟基磷灰石/医用金属复合材料，既具有基底金属的强度和韧性，又具有羟基磷灰石生物陶瓷的优良生物活性和生物相容性，因而是目前最理想的植骨代用品。目前制备金属基底上羟基磷灰石陶瓷涂层主要采用的方法是等离子喷涂技术，但该技术由于等离子弧焰温度较高，羟基磷灰石生物活性陶瓷在喷涂过程中不可避免地发生相变和脆裂。另一方面，等离子喷涂为直线过程，难以在形状复杂和表面多孔的基底上制备均匀的陶瓷沉积层。

电化学沉积方法是在温和环境条件下制备羟基磷灰石涂覆层，即在接近人体生理环境条件下电沉积HAp微晶，可以获得在化学成分和晶体结构上与人体骨组织相近的羟基磷灰石涂层，从而增加植入材料表面涂层的生物相容性和生物活性。本论文对钙磷生物陶瓷沉积层的研究主要涉及电沉积实验条件对羟基磷灰石及其前驱体即电沉积产物钙磷陶瓷的组成和结构的影响、钙磷陶瓷电化学沉积机理及羟基磷灰石电沉积层生物活性等方面。主要研究结论如下：

1. 磷酸钙生物陶瓷沉积层的电化学制备及其表征

通过恒电流和恒电位两种模式，从含有钙离子和磷酸根离子的水溶液中电沉积钙磷生物陶瓷，应用扫描电子显微镜(SEM)、X射线衍射(XRD)、Raman光谱、付立叶红外光谱(FTIR)及电感耦合等离子原子发射光谱(ICP/AES)等技术研究了磷酸钙沉积层的表面形貌、化学组成和晶体结构等性质。

1.1 一般而言，恒电流模式下阴极过电位随沉积时间的增加而逐渐增大；恒电位模式下电流密度随沉积过程的进行而逐渐减小。电沉积钙磷陶瓷的重量随电流密度、阴极过电位、电解液温度、溶液浓度及电沉积时间等实验参数的变化而变化。溶液本体的pH值随电沉积过程的进行而逐渐降低。

1.2 电沉积层的表面为多孔状结构，结晶颗粒为针状晶体；当加入少量添加剂后，颗粒变成片状结构。当电流密度(或阴极过电位)较小时，能得到分布均匀且结合良好的磷酸钙沉积层；若电流密度(或阴极过电位)太大，无法得到均匀的磷酸钙沉积层，局部出现螺丝状堆积物，甚至发生沉积层脱落。

1.3 磷酸钙沉积层的化学组成和晶体结构随电沉积实验条件的改变而发生较大变化: 在25℃条件下, 控制阴极电位$E = -1.50$ — -2.30V之间, 沉积层基本由含两个水的磷酸氢钙(DCPD)组成。在60℃条件下, 恒电位沉积时, 沉积层为几种磷酸钙盐的混合物, 且随着过电位的增加, 羟基磷灰石的含量逐渐增大。在60℃、不同电流密度条件下，磷酸钙电沉积层具有不同的组成和结构:(I) $j < 1$ mA/cm^2, 沉积层由$CaHPO_4 \cdot 2H_2O$ (DCPD) 和 $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ (OCP)组成。(II) $j = 2$ mA/cm^2, 电沉积层主要为含n个水的磷酸三钙$Ca_3(PO_4)_2 \cdot nH_2O$ (TCP)。(III) $j = 3$ mA/cm^2, 电沉积层含有生物活性陶瓷羟基磷灰石$Ca_{10}(PO_4)_6 \cdot (OH)_2$(HAP)。(IV) $j > 5$ mA/cm^2, 沉积层基本上是由羟基磷灰石(HAp)组成

1.4 Raman和FTIR红外光谱实验表明：在含两个水的磷酸氢钙(DCPD)中，磷酸根PO_4的振动光谱选律没有发生变化；而在磷酸八钙（OCP）、磷酸三钙(TCP)及羟基磷灰石(HAP)中，磷酸根PO_4的振动光谱选律均发生了改变，四个振动频率谱带均具有Raman和FTIR红外光谱活性。

1.5 应用热力学原理，其它组份的钙磷电沉积层经过低温碱液处理，可以得到结晶度较好的纯羟基磷灰石晶体。用各种实验技术对电沉积层进行研究表明，与等离子喷涂技术相比较，其化学组成和晶体结构更接近于人体硬组织中的羟基磷灰石。

2．钙磷陶瓷电化学沉积机理

2.1．本文建立了一种现场测定固/液界面pH值的实验装置。应用IrO_2/Pt为pH敏感微探针，将其嵌入到钙磷陶瓷沉积的基底钛铝钒合金中，进行电沉积过程pH值的现场检测。该实验装置确保在检测固/液界面pH值时不会影响磷酸钙陶瓷电化学沉积过程。

2.2．用阳极电化学沉积的方法，从含有$IrCl_3 \cdot nH_2O$的溶液中，在铂探针针尖上沉积二氧化铱。实验表明该方法制备的二氧化铱敏感材料具有良好氢离子响应性能，其响应斜率25℃时为61—64 mV/pH，60℃时为69—73 mV/pH。

2.3．利用所建立的实验装置，现场测定了不同电流密度（或电位）条件下，电化学沉积过程中阴极/溶液界面pH值。其基本规律为电沉积初期界面pH快速上升，到某一最高值后界面pH值呈下降趋势。根据现场pH值检测结果，结合各种谱学检测钙磷陶瓷层组成和结构的实验结果，讨论了钙磷陶瓷的电沉积机理。认为钙磷陶瓷沉积层的组成和结构主要决定于电极表面后置化学沉淀反应，而阴极/溶液界面pH值决定着钙磷陶瓷按不同化学反应沉积。

2.4．用电化学交流阻抗技术，对不同沉积时间的钙磷陶瓷沉积层进行了研究。利用双层结构物理模型，对不同沉积时间陶瓷沉积层的交流阻抗谱进行计算模拟，其结果与实验值符合得相当完美。

2.5. 根据计算得到等效电路各元件模拟值，讨论了电沉积过程中钙磷陶瓷沉积机理。认为钙磷陶瓷沉积层随着沉积过程的进行，不但厚度增加而且内层密度也在逐渐增加。另一方面，电沉积初期钙磷沉积层结构比较致密，随着电沉积时间的增加后期沉积的陶瓷层结构比较疏松。

2.6. 用AFM研究不同电结晶时间基底表面上磷酸钙晶粒形貌，发现存在两种晶体形貌结构：一种呈多边形结构，另一种呈圆柱形结构。

2.7. 从AFM图可以推测出沉积层晶粒有两种生长模式：一种是“独立生长”模式—晶粒成长过程中相互之间影响较小；另一种是“非独立生长”模式—晶粒成长过程中发生集结和重叠。磷酸钙晶粒大小不均一性说明基底表面磷酸钙电结晶是一种连续成核—生长机理，即在电极表面磷酸钙电结晶过程中，晶粒成核与生长同时进行。

3. 羟基磷灰石电沉积层生物活性的初步研究

通过体外细胞培养的方法，研究了不锈钢、电化学沉积羟基磷灰石/不锈钢、羟基磷灰石等离子喷涂层/Ti6Al4V复合材料及羟基磷灰石电沉积层/羟基磷灰石等离子喷涂层/Ti6Al4V复合材料等四种植入材料的生物相容性和生物活性。样品附近及表面细胞生长数量和形态变化的实验结果告诉我们不锈钢表面不利于细胞的生长，细胞发育不良，而电化学处理后的复合材料，在其附近及表面不但细胞的数量多，而且体形丰满，发育良好，这些结果说明电化学得到的羟基磷灰石沉积层具有良好的生物相容性和生物活性。在另外一组实验中，对羟基磷灰石等离子喷涂层/Ti6Al4V复合材料研究显示，电化学处理能提高羟基磷灰石生物陶瓷的生物活性和生物相容性。因此电化学沉积技术是一种潜在的制备羟基磷灰石/医用金属人工植入复合材料的新方法。

Abstract

Having both good mechanical properties and formability of the metal substrate and excellent bioactivity and biocompatibility of hydroxyapatite bioceramic coating, hydroxyapatite/surgical metal or alloy composite is therefore considered as the best implant material for bone substitution. Currently, the plasma spray technique is extensively used by the implant industry to produce hydroxyapatite coatings. However, there are major problems associated with the method. Because of the high temperature involved, this technique has the potential of the decomposition and phase transformation of hydroxyapatite during the spray coating process. At another hand, the plasma spray technique is a line-of -sight process that produce a non-uniform coating when applied to porous surfaces or complex substrates.

Hydroxyapatite coatings were prepared by electrochemical deposition method in a warm condition, that is hydroxyapatite is electrocrystalized in the condition close to human physiological environment, so the hydroxyapatite coatings are much similar to the main inorganic component of human hard tissues in the chemical composition and crystal structure and it's bioactivity and biocompatibility is increased. In this thesis, the effect of electrodeposition experimental conditions on the chemical constitutes and crystal structures of electrodeposition products, the electrodepositon mechanism of calcium phosphate ceramic coatings, and the bioactivity and biocompatibility of electrodeposition hydroxyapatite coatings are studied by various experiment methods. The major results and conclusions are summarized as follows:

1. Electrochemical Deposition and Characterization of Calcium Phosphate Ceramics (CPCs)

In potentiostat or galvanostat mode, calcium phosphate bioceramic coatings are fabricated by the electrodeposition technique from aqueous electrolytes containing Ca- and P-bearing ions. Surface morphologies, chemical compositions and crystal structures of electrodeposition coatings of CPCs are studied using various modern analytical techniques, such as scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman Spectroscopy, fourier transform infrared (FTIR), and inductive coupled plasma atomic emission spectroscopy(ICP/AES).

1.1 In general, the cathodic overpotential will increase with electrodeposition time in galvanostat mode, and the current density will decrease during the electrodeposition process in potentiostat mode. The weights of electrodeposition coatings of CPCs are markedly dependent on the applied current density, cathodic overpotential, electrolyte temperature, deposition solution's concentration, and so on. The pH value in the bulk of deposition solution will gradually decrease with the electrodeposition process.

1.2 Surface morphologies of electrodeposition coatings of CPCs have a characterization of porous structure. The coating is composed of an interlocking network of non-oriented crystals that are needle-like. The crystal structure is changed into plate-like when a few additions are added in electrodeposition solutions. While the current density or cathodic overpotential is small, uniform and adherent coatings could be obtained. If the current density or cathodic potential is too large, electrodeposition coatings are non-uniform, spiral-like in local area, and even are divorced from the cathodic surface.

1.3 The influence of experimental conditions on the chemical constitutes and crystal structures of electrodepositon coatings of CPCs is investigated in the thesis. The electrodeposition coating is basically composed of dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$, DCPD) at cathodic potentials in the range -1.50 — -2.30 V and at room temperature. In potentiostat mode and at 60℃, the coatings consist of several calcium phosphates, and the content of hydroxyapatite will be increased as the cathodic overpotential rises. The chemical component and crystal structure of electrodeposition coatings of CPCs will change with the current density at 60℃: (I) when the current density (j) is smaller than 1 mA/cm^2, the electrodepositon coatings are composed of DCPD and octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$, OCP); (II) The electrodeposits are mainly tricalcium phosphate hydrate ($Ca_3(PO_4)_2 \cdot nH_2O$, TCP) at j=2 mA/cm^2; (III) the electro-deposition products will contain bioactive ceramic hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) when the applied current density is equal to 3 mA/cm^2; (IV) while the current density larger than 5 mA/cm^2 is applied, the coating is basically composed of HAp.

1.4 The experiments about Raman and FTIR spectroscopies show that vibration absorptions of phosphate group PO_4 are usual in DCPD, but all four absorptions of phosphate group PO_4 are Raman and IR active in OCP, TCP and HAp.

1.5 According to thermodynamic theory, the electrodeposition coatings of other calcium phosphates are treated in alkaline solution, and then could be transformed to good crystals of pure hydroxyapatite. Using various modern analytical methods, Studies of the electrodeposition hydroxyapatite coating give

the result that its chemical composition and crystal structure, comparing to by the plasma spray technique, is much similar to the main inorganic component of human bone.

2. Mechanism of Electrodeposition Coatings of CPCs

2.1 In this work, a novel pH microsensor system is designed for in situ measuring the pH change at the electrode/solution interface. The microsensor IrO_2/Pt, embedded into a round sample of Ti6Al4V surgical alloy as the substrate for electrodepositon of calcium phosphate ceramic coatings, is used to monitor the interfacial pH value for the first time during the electrodeposition process of calcium phosphate coatings. This system can ensure that the in-situ measurement of the solid/solution interfacial pH value doesn't influence on the electrodeposition process of CPCs.

2.2 By electrodeposition technique, the pH sensing material, iridium oxide (IrO_2), is coated on platinum probe from the electrolyte containing iridium chloride hydrate ($IrCl_3 \cdot H_2O$). The calibration experiments show that the sensing material IrO_2 prepared by the electrodeposition technique responds well to pH changes in the measured solution. The respond potential will decrease linearly with increasing of pH over the entire range by a slope of 61 - 64 mV/pH unit at room temperature and 69 - 73 mv/pH unit at 60℃.

2.3 Using the experiment apparatus made by ourselves, the pH value of the cathode/solution interface is in-situ monitored during the electrodeposition process at various current densities. The results indicate that the interfacial pH will increase with the applied current density, first jump to a maximum, then slowly decrease at the controlled current density during the electrodeposition process.

The mechanism of electrochemical deposition of calcium phosphate coatings is discussed according to the in-situ pH measurements and the chemical components and crystal structures of precipitates. The electrodeposition process includes electrochemical reactions, acid-base reactions, and precipitation reactions. The current density may determine the pH value at the cathode/solution interface, and the precipitation reactions and the electrodeposition products on the substrate.

2.4 Electrodeposition coatings of calcium phosphate ceramics prepared in various deposition times are studied by electrochemical impedance spectroscopy (EIS). A two-layer mode of ceramic films can be used for simulating electrodeposition coatings of CPCs fabricated in various deposition times. The high quality of fitting are readily seen from the good match between the measured and the simulated spectra.

2.5 The result from the spectra fitting to the circuit is used to discuss the electrodeposition mechanism of calcium phosphate ceramic coatings. It is thought that both the thickness of the electrodeposition coating and the density of the electrodeposition inner coating are increased with the electrodeposition process. At another hand, the electrodeposition coatings of CPCs precipitated in initial period are relatively compact, and the density of CPC coatings will step-by-step decrease with the electrodeposition time.

2.6 Atomic force spectroscopy (AFM) is used to study surface imagines of the electrodeposition coatings of CPCs produced in various deposition time. Two crystal structures, trapezoid and cylinder, are found on the substrate. Two modes for the crystal growth on the cathodic surface are inferred according to the crystal AFM. One is a "dependent mode", in which the crystal growth doesn't influence each other during electrocrystalization process, and another one a "non-dependent mode" which will result in the crystal coalescence and overlaping during the crystal growth process. The crystal non-uniformity on the substrate indicates that the electrocrystalization process is a progressive nucleation and growth mechanism in which nuclei are being born continuously and growing with time.

3. Biocompatibility and Bioactivity of Hydroxyapatite electrodeposition coatings

The biocompatibility and bioactivity of four materials, 18-8 stainless steel (SS), hydroxyapatite-electrodeposited 18-8 stainless steel, hydroxyapatite-plasma sprayed coating/Ti6Al4V composite, and hydroxyapatite-electrodeposited coating/ hydroxy-apatite-plasma sprayed coating/Ti6Al4V composite, is studied by in vitro method. The morphological and number changes of cells show that 18-8 SS presents obviously cytotoxicity, but no signs of cytotoxicity are apparent on the surface of electrodeposition hydroxyapatite, and their surfaces are suitable for cell growth and can promote cells to reproduce. After the electrochemical treatment of hydroxyapatite-plasma sprayed coating/Ti6Al4V composite material, the biocompatibility and bioactivity is improved. These results reveal that the electrodeposition hydroxyapatite coating has excellent bioactivity and biocompatibility, and the electrodeposition technique is a novel potential method in preparation of the bone substitute, hydroxyapatite/surgical metals or alloys composite materials.