学校编码：10384　　分类号_____密级 _____
学　　号：200436020　　UDC_____

厦　门　大　学

硕　士　学　位　论　文

钛表面电泳沉积羟基磷灰石及其复合涂层的研究

Investigation for the Electrophoretic Deposition of Hydroxyapatite and its Composite Coating on Titanium

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论文提交日期：　2007 年 11 月
论文答辩日期：　2007 年 12 月
学位授予日期：　2007 年　　月

答辩委员会主席：_____
评　　阅　　人：_____

2007 年 11 月

Investigation for the Electrophoretic Deposition of Hydroxyapatite and its Composite Coating on Titanium

A Dissertation Submitted for the Degree of

Master of Engineering

By

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At

Department of Materials Science and Engineering

Xiamen University

November, 2007

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摘　要

$Ca_{10}(PO_4)_6(OH)_2$（羟基磷灰石，HA）是人骨等硬组织的主要无机成分，具备高的生物活性及骨传导性能，被广泛用作为生物医学植入材料。然而，纯 HA 陶瓷材料的力学性能较差，如脆性大，限制了它在生物医学领域的应用。为此人们致力于发展各种 HA 涂层或复合材料。在医用金属上涂覆 HA 涂层是目前复合生物医学材料领域的研究热点之一。已发展了多种在医用金属钛表面涂覆 HA 生物活性涂层的方法，其中，电泳沉积法，由于其工艺灵活性，低成本以及许多其它的优点，近年来受到了广泛的关注。本论文针对钛表面电泳沉积 HA 涂层材料面临的涂层烧结及涂层－基体界面结合的问题，作了如下研究工作。

一、在以无水乙醇作为分散溶剂的分散体系中，按不同的工艺条件，如沉积电压，热处理温度及悬浮液粉体含量，在钛表面电泳沉积 HA 涂层。采用扫描电镜（SEM）、X 射线衍射（XRD）表征涂层的微观形貌及物相组成，通过黏结-拉伸实验测定涂层与基底的结合强度。结果表明，电泳沉积在 30V 电压条件下进行，可在保证涂层沉积具备一定的沉积效率的同时，获得均匀、致密的性能良好的涂层。涂层的热处理在 850℃下进行，可避免 HA 涂层在烧结过程中发生热分解。提高悬浮液的粉体含量，有助于提高电泳沉积 HA 涂层的致密性，改善其烧结性能，提高烧结致密化程度；另一方面，HA 涂层致密性的提高，有效地抑制了钛基底表面氧化反应，改善了涂层与基底的界面结合状态，使得 HA 涂层与钛基底的结合强度得到了显著的提高，从悬浮液粉体含量为 5 $g•L^{-1}$ 时对应的 4.54MPa，提高到悬浮液粉体含量为 20 $g•L^{-1}$ 时对应的 19.92MPa。

二、将反应烧结技术应用于电泳沉积 HA 生物涂层的工艺过程，在 HA 与金属 Al 粉的混合悬浮液体系中，电泳共沉积 HA/Al 复合涂层，经过适当的热处理，在钛表面制备了羟基磷灰石/氧化铝（hydroxyapatite/aluminum oxide, HA/Al_2O_3）复合涂层，与在相同条件下制备的单一 HA 涂层进行比较研究。采用 SEM 表征复合涂层的表面、横截面形貌和微观结构。采用能量散射 X 射线谱（EDS）分析复合涂层的化学组成。复合涂层的物相组成和热稳定性采用 XRD 进行表征。通过黏结-拉伸实验测定涂层与基体的结合强度。最后，通过 MTT 实验对复合涂层的生物学性能进行了初步表征。结果表明，复合涂层通过 850℃热处理后烧结

良好，且没有热分解发生。反应烧结提高了涂层的烧结致密化程度和降低基底钛表面的氧化程度。与单一 HA 涂层相比，HA/Al_2O_3 复合涂层与基底间的结合强度得到明显提高，由单一 HA 涂层的 19.92 MPa 提高到了复合涂层的 30.83 MPa。MTT 实验结果表明，尽管复合涂层的生物相容性略低于单一 HA 涂层，但二者的制备均在一定程度上改善了基底金属钛的生物相容性。

三、采用多步沉积的方式，依次在不同 HA 和金属 Al 粉含量的悬浮液中沉积，并经过适当的热处理，制备了 HA/Al_2O_3 复合梯度涂层。利用 XRD、SEM 和 EDS 等表征手段对涂层物相组成、形貌、微结构及化学组成进行表征，利用黏结—拉伸实验测试涂层与基体的结合强度。结果表明，梯度涂层经 850℃热处理后，由 HA 及 γ-Al_2O_3 两相组成。涂层内部的化学组成呈现出明显的梯度变化，梯度涂层逐渐由氧化膜、界面扩散层、HA/Al_2O_3 复合梯度层过渡到单一 HA 外层。Al 含量较高的梯度涂层内层具备相对比较致密的结构，由内往外，涂层中的 Al 含量逐渐减少，致密度不断下降，最外层为结构疏松、多孔的单一 HA 涂层。梯度涂层与基底的平均结合强度高达 23.56MPa，明显高于在同样厚度下的 HA 单一涂层(7.05MPa)。

关键词：电泳沉积，羟基磷灰石，复合涂层

Abstract

$Ca_{10}(PO_4)_6(OH)_2$ (Hydroxyapatite, HA), a major inorganic component of human bone and other hard tissues, has been used extensively for biomedical implant applications and bone regeneration due to its bioactive and osteoconductive properties. However, the poor mechanical properties of pure HA ceramic, such as its brittleness, have limited its clinical applications. For this reason, a great deal of research concentrates on the development of HA coatings and/or composites. Deposition of HA coatings onto the surface of metal implants is a relatively recent development in clinical orthopaedics and has been achieved by a number of methods. Among these methods, electrophoretic deposition (EPD) has recently gained great interest due to its flexibility, low-cost and many other characteristics. Focusing on the problems of the sintering of the coating and coating-substrate interfacial bonding associated with the preparation of HA coating on titanium substrate by EPD technique, researches were done as summarized below.

First of all, with the absolute alcohol based suspension, HA coatings were deposited on titanium substrate by EPD under varying conditions, such as deposition voltage, heat treatment temperature and suspension powder content. Scanning electronic microscope (SEM) and X-ray diffraction (XRD) were employed to characterize the morphologies and phase composition of the as-prepared coatings. Bonding strength between the coating and substrate was tested by shear strength testing experiment. The results show that, EPD under 30V makes suitable deposition efficiency and produces coating with good properties as well. Heat treatment under 850℃ avoids the thermal decomposition of HA. The increase in the suspension powder contents is beneficial in increasing the deposition density of the HA coating, improves its sintering ability and increases its decification degree; On the other hands, the increase in density of the HA coating effectively restrains the surface oxidation of the titanium substrate during heat treatment and improved the interface between the coating and substrate; As a result, bonding strength between the HA coating and

titanium substrate was significantly enhanced, from 4.54MPa when the suspension powder content is as low as 5 g/L to 19.92MPa when the suspension powder content is as high as 20 g/L.

To be next, reaction bonding process was applied to the preparation of HA coating by EPD. HA/Al composite coating was deposited in the HA, Al mixed suspension. After a suitable heat treatment, HA/Al_2O_3 composite coating was formed. At the same time, monolithic HA coating was also prepared in the same conditions as comparison. SEM was employed to characterize the surface and cross-sectional morphologies of the as-prepared coatings. Chemical compositions of the composite coating were analyzed through EDS. Phase composition and thermal stability of the composite coating were characterized by XRD and FTIR. Bonding strengths between the coating and substrate were tested by shear strength testing experiment. Preliminary characterization of the biological property was also done by MTT test. The results show that the composite coating can be sintered with no decomposition at 850℃ heat treatment. The reaction bonding process enhances the coating's densification degree and lowers the substrate's oxidation degree during the heat treatment. In comparison with the HA monolithic coating (19.92 MPa in average), the HA/Al_2O_3 composite coating exhibits much higher bonding strength (30.83 MPa in average). Results of MTT test show that, although the biocompatibility of HA/Al_2O_3 composite coating is relatively lower than the monolithic HA coating; preparation of these two kinds coatings both improved the biocompatibility of the titanium substrate.

At last, with a stepwise deposition mode, HA/Al_2O_3 functionally gradient coating (FGC) was sequentially deposited in suspensions with different HA and Al content followed by a suitable heat treatment. XRD, SEM and EDS were employed to characterize the phase composition, morphology, microstructure and chemical composition of the FGC. Bonding strengths between the FGC and substrate were tested by shear strength testing experiment and compared with the monolithic HA coating. Results show that, the 850℃ sintered FGC was composed of highly crystallized HA and γ-Al_2O_3 with no decomposition was found. Chemical composition in the FGC exhibits obvious gradually variation. The composition of the

FGC gradually changes from the oxide layer, interface diffusion layer, HA/Al_2O_3 gradient layer to the top pure HA layer. The inner layer the HA/Al_2O_3 gradient coating, which contains the highest content of element Al, is the densest. From the inner to the outer layer, content of element Al gradually decreases while the porosity increases. The top layer of the FGC is a porous pure HA coating. The average bonding strength of the as-prepared FGC was about 23.54MPa, much higher than that of monlithic HA coating with the same thickness.

Keywords: electrophoretic deposition; hydroxyapatite; composite coating

第一章 绪 论

1.1 生物医用材料的定义及分类

生物医用材料（Biomedical materials）又称生物材料（Biomaterials），是对生物体进行诊断、治疗和置换损坏的组织、器官或增进其功能的材料[1]。随着社会文明的进步和生活水平的提高，人类迫切需要新的生物材料以对人体内发生病变、损伤或老化的组织器官进行替代、修补和校正，为此长期以来，科技工作者一直在不懈地研制和开发适合于人体器官使用的生物材料。

生物医用材料的应用已经有很长的历史[2]，早在公元前 3500 年，古埃及人就利用棉花纤维、马鬃作缝合线缝补伤口；墨西哥的印第安人用木片修补受伤的颅骨；19 世纪，金，银，铂等贵金属开始用作人体硬组织修复物；20 世纪 70 年代，玻璃陶瓷，羟基磷灰石等进入临床应用以后，将生物材料的研究推向了一个新的阶段；80 年代以来，各种复合材料的出现使生物材料的研究与开发更为深入和广泛。当前，生物医用材料研究开发的主要趋势是致力于提高材料的生物相容性、生物功能性、仿生性以及赋予材料生命活性，适应临床对各种组织和器官修复的高级要求，为临床医学的发展提供新的物质基础[3]。

人工植骨材料，即替代人体硬组织（骨骼、牙齿等）的生物材料，是重要的生物医用材料之一。由于在使用过程中与人体生理环境相接触，因而与其它功能材料相比，植骨生物材料还必须具备某些特殊要求。一般来说，植骨生物医用材料应满足如下基本要求[4]：

1．植入人体后，无毒性、不致癌、不致畸、无不良刺激、无过敏、不引起感染等症状。

2．具有与天然组织相适应的力学性能。

3．稳定的理化特性。

4．优良的生物活性。

生物医用材料种类繁多，到目前为止，被详细研究过的生物材料已经超过 1000 种，在医学临床上广泛应用的也有几十种，涉及材料学科各个领域[4]。按材料的组成和性质可分为生物医用金属材料，生物医用陶瓷材料，生物医用高分子材料以及由它们组合而成的复合材料等[5-7]。生物医用金属材料、生物医用陶瓷