学校编码：10384　　分类号_____密级 _____
学　　号：200425125　　UDC_____

厦　门　大　学

硕　士　学　位　论　文

牙釉质表面 原位修复 涂层制备与表征

Preparation and characterization of the in situ repair coating on enamel surface

何 立 志

指导教师姓名：　冯　祖　德　　教授
专业名　　称：　无机化学

论文提交日期：　200　7　年　6　月
论文答辩日期：　200　7　年　6　月
学位授予日期：　200　7　年　　月

答辩委员会主席：_____
评　　阅　　人：_____

2007 年 6 月

厦门大学学位论文原创性声明

兹呈交的学位论文，是本人在导师指导下独立完成的研究成果。本人在论文协作中参考其他个人或集体的研究成果，均已在文中明确标明。本人依法享有和承担由此论文而产生的权利和责任。

声明人（签名）：

2007 年 6 月　日

厦门大学学位论文著作权使用声明

本人完全了解厦门大学有关保留、使用学位论文的规定。厦门大学有权保留并向国家主管部门或其指定机构送交论文的纸质版和电子版，有权将学位论文用于非赢利目的的少量复制并允许论文进入学校图书馆被查阅，有权将学位论文的内容编入有关数据库进行检索，有权将学位论文的标题和摘要汇编出版。保密的学位论文在解密后适用本规定。

本学位论文属于

1、保密（　），在　　年解密后适用本授权书。

2、不保密（　）

（请在以上相应括号内打“√”）

作者签名：　　日期：　　年　月　日

导师签名：　　日期：　　年　月　日

目 录

摘 要.....I

ABSTRACT.....II

第一章 绪论.....1

1.1 牙齿介绍.....1

1.1.1 牙的结构.....1

1.1.2 牙釉质的微观结构和理化性质.....2

1.1.2.1 牙釉质的微观结构.....2

1.1.2.2 牙釉质的物理性质.....3

1.1.2.3 牙釉质的化学性质.....3

1.2.龋病病因学理论.....4

1.2.1 龋病病因学.....4

1.2.2 龋病的发病机制学说.....6

1.3 目前修复材料.....8

1.3.1 口腔修复材料的分类.....9

1.3.2 复合树脂.....9

1.3.3 银汞合金.....11

1.3.4 烤瓷材料.....13

1.3.5 牙釉质美容修复材料.....14

1.4 目前的预防材料.....15

1.4.1 机械的方法.....15

1.4.2 化学的方法.....15

1.4.3 生物的方法.....17

1.5 本文的主要工作内容与意义.....18

参考文献.....19

第二章 实验仪器与方法.....27

2.1 实验方法.....27

2.2 红外吸收光谱 ……27
2.3 X 射线衍射 ……27
2.4 拉曼光谱 ……28
2.5 X 射线光电子能谱 ……28
2.6 扫描电子显微镜 ……29
2.7 透射电子显微镜 ……29
2.8 离子色谱 ……30
参考文献 ……31
第三章 不同 Ca/P 纳米缺钙羟基磷灰石微波合成与表征 ……32
3.1 前言 ……32
3.2 实验 ……33
3.2.1 纳米缺钙羟基磷灰石的合成 ……33
3.2.2 主要表征方法 ……33
3.3 结果与讨论 ……34
3.3.1 红外光谱分析 ……34
3.3.2 拉曼光谱分析 ……35
3.3.3 XRD 分析 ……35
3.3.4 EDS 分析 ……36
3.3.5 TEM 微观形貌分析 ……37
3.4 结论 ……38
参考文献 ……38
第四章 牙釉质表面 DCPD 涂层的制备与表征 ……40
4.1 前言 ……40
4.2 材料与方法 ……40
4.2.1 制备牙齿试样 ……41
4.2.2 制备糊剂与牙齿涂层 ……41
4.2.3 红外分析 ……41
4.2.4 XRD 分析 ……41
4.2.5 金相显微分析和扫描电镜分析 ……41

4.2.6 表面硬度测试 ····42
4.2.7 溶解性测试 ····42
4.2.8 耐磨性测试 ····42
4.3 结果与讨论 ····43
4.3.1 FT-IR 分析结果 ····43
4.3.2 XRD 分析结果 ····44
4.3.3 金相显微分析和扫描电镜分析结果 ····46
4.3.4 显微硬度测试结果 ····49
4.3.5 溶解性测试结果 ····50
4.3.6 耐磨性测试结果 ····52
4.4 小结 ····52
参考文献 ····53
第五章 涂层形成机理探讨 ····55
5.1 前言 ····55
5.2 材料与方法 ····55
5.2.1 涂层形成机理模型 ····55
5.2.2 牙齿试样 ····56
5.2.3 XPS 分析 ····56
5.2.4 SEM 分析 ····56
5.2.5 TEM 分析 ····56
5.3 结果与讨论 ····57
5.3.1 SEM 和 XPS 分析 ····56
5.3.2 TEM 分析 ····59
5.3.3 pH 值影响 ····61
5.4 小结 ····62
参考文献 ····62
第六章 牙釉质表面抗菌涂层的制备与表征 ····65
6.1 前言 ····65
6.2 材料与方法 ····66

6.2.1 Cu/Zn 掺杂纳米缺钙羟基磷灰石的合成 ……66
6.2.2 Cu/Zn 掺杂 DCPD 涂层制备 ……66
6.2.3 主要表征方法 ……67
6. 3 结果与讨论 ……67
6.3.1 IR, XRD, EDS 表征 Cu/Zn 掺杂纳米缺钙羟基磷灰石 ……67
6.3.2 Cu/Zn 掺杂的 DCPD 涂层表征 ……71
6.4 小结 ……75
参考文献 ……76
主要结论与展望 ……78
攻读硕士学位期间发表的论文与专利 ……80
致 谢 ……81

Table of Contents

Abstract in Chinese ····· Ⅰ

Abstract in English ····· II

Chapter Ⅰ. Preface ····· 1

1.1Tooth introduction ····· 1

1.1.1 The structure of tooth ····· 1

1.1.2 The microstructure and the physical and chemical properties of enamel ····· 2

1.1.2.1 The microsturcture of enamel ····· 2

1.1.2.2 The physical Properties of enamel ····· 3

1.1.2.3 The chemical Properties of enamel ····· 3

1.2 The pathogenesis and the mechanism of caries ····· 4

1.2.1 The pathogenesis of caries ····· 4

1.2.2 The mechanism of caries ····· 6

1.3 The present dental restorative materials ····· 6

1.3.1 Classification of dental restorative materials ····· 9

1.3.2 Composite resin ····· 9

1.3.3 Amalgam alloy ····· 11

1.3.4 Procelain materials ····· 13

1.3.5 Restorative materials of enamel ····· 14

1.4 Preventive materials ····· 15

1.4.1 Mechanical methods ····· 15

1.4.2 Chemical methods ····· 15

1.4.3 Biological methods ····· 17

1.5 Significances and Main Content of This Dissertation ····· 18

References ····· 19

Chapter Ⅱ. Experimental methods and instruments ····· 27

2.1 Experimental methods ····· 27

2.2 FT-IR……27
2.3 XRD……27
2.4 FT-Raman……28
2.5 XPS……28
2.6 SEM……29
2.7 TEM……29
2.8 IC……30
References……31
Chapter Ⅲ. Microwave Synthesis and Characterization of nano-sized Calcium Deficient Hydroxyaptite with Different Ca/P Ration……32
3.1 Introduction……32
3.2 Experiments……32
3.2.1 Synthesis of nano-size CDHA……33
3.2.2 Characterization of methods……33
3.3 Results and discussions……34
3.3.1 IR analysis……34
3.3.2 Raman analysis……35
3.3.3 XRD analysis……35
3.3.4 EDS analysis……36
3.3.5 TEM analysis……37
3.4 Summary……38
References……38
Chapter Ⅳ. Preparation and characterization of DCPD coating on enamel……40
4.1 Introduction……40
4.2 Materials and Methods……40
4.2.1 Preparation of tooth samples……41
4.2.2 Preparation of the paste and coating samples……41
4.2.3 FT-IR……41

4.2.4 XRD·····41
4.2.5 SEM and metallic microscope·····41
4.2.6 Microhardness test·····42
4.2.7 Solubility test·····42
4.2.8 Wear resistance·····42
4.3 Results and discussions·····43
4.3.1 IR analysis·····43
4.3.2 XRD analysis·····44
4.3.3 SEM and metallic microscope analysis·····46
4.3.4 Microhardness test analysis·····49
4.3.5 Solution test analysis·····50
4.3.6 Wear resistance analysis·····52
4.4 Summary·····52
References·····53
Chapter Ⅴ. Investigation of mechanism of DCPD coating·····55
5.1 Introduction·····55
5.2 Materials and Methods·····55
5.2.1 The mode of coating mechanism·····55
5.2.2 Preparation of tooth samples·····56
5.2.3 XPS·····56
5.2.4 SEM·····56
5.2.5 TEM·····56
5.3 Results and Discussion·····56
5.3.1 XPS and SEM analysis·····56
5.3.2 TEM analysis·····59
5.3 pH Effection·····61
5.4 Summary·····62
References·····62
Chapter Ⅵ. Preparation and characterization of zinc-doped

antibacterial coating on enamel ····65

6. 1 Introduction ····65

6. 2 Materials and Methods ····66

6.2.1 Preparation of Zn/Cu doped CDHA ····66

6.2.2 Preparation of Zn/Cu doped coating ····66

6.2.3 Characterization of methods ····67

6.3 Results and discussions ····67

6.3.1 Characterization of Zn/Cu doped CDHA by IR XRD EDS ····67

6.3.2 Characterization of Zn/Cu doped coating ····71

6.4 Summary ····75

References ····76

Main conclusions and outlook ····78

Papers Published during the Study for Master Degree ····80

Acknowledgements ····81

摘 要

龋病是人类是最常见的疾病，全世界至少有 50%的居民即 30 亿多人患有龋病。龋病是一种慢性病，不会立即致人死亡，但它能引发很多急性炎症和病灶感染性或免疫性疾病，而且严重破坏人类咀嚼器官导致消化系统功能减退和疾病发生 。据世界卫生组织(WHO) 统计，因龋病而消耗的人类卫生资源是惊人的，现已将龋病列为影响人类健康的三大疾病之一。

牙科修复材料在牙齿修复中起着相当重要的作用。牙科材料发展至今，按其属性可分为金属与非金属两类。前者以银汞合金为代表，后者以复合树脂为主要代表。安全性、生物相容性成为口腔金属材料研究 和临床应用的重要问题。腐蚀与合金的生物相容性密切相关。复合树脂耐磨性能较差，不宜用于承受较大咀嚼力区的修复是其致命的弱点；聚合体积收缩导致边缘微漏，增大了继发龋的概率传统的方法涉及到机械去除受影响的部份，用树脂或者是合金材料来填充。为了使传统的修复材料粘附在牙体上，这种方法将不可避免破坏周围健康的牙齿 。针对早期的龋损或者是细小的裂隙，它不是理想的方法。最近，日本学者 Kazuo 等报到了人工合成牙釉质的方法来修复早期牙釉质的龋损 ，但是这种方法合成的牙釉质的厚度被限定在 20μm 而且合成的牙釉质没有抗菌活性。

DCPD 在生物体内作为最终向羟基磷灰石转化的中间过渡相，因此被认为是具有好的生物活性陶瓷之一，它还是所有磷酸钙盐在酸性条件下最稳定的物相 。缺钙羟基磷灰石在适当的温度和酸性环境下，在短时间内很快转变为 DCPD，而且结晶性很好。针对现代饮食习惯，接触偏酸性食物或饮料机会越来越多，而酸性物质对牙釉质硬度有较大的影响，因此利用 DCPD 来修复早期龋陨有一定的优势。利用 CDHA 在酸性条件下在牙釉质表面转变成 DCPD，进一步形成涂层，涂层厚度约为 60~80μm。涂层借助 IR、XRD、EDS、SEM、TEM 等手段表征涂层，其显微硬度值约为 125 (VHN)是正常牙釉质的 40%左右，涂层能够与牙釉质较好地结合，其间无明显缝隙。大量的文献也曾报道了 Zn^{2+}、Cu^{2+}等具有一定的抗菌性，对于牙菌斑形成有一定的作用。在 DCPD 涂层的基础上，改进加入 Zn^{2+}/Cu^{2+}掺杂，形成 Zn^{2+}/Cu^{2+}掺杂的抗菌 DCPD 涂层。其抗菌活性被测试，抗菌率都接近 100%。

关键词 涂层；缺钙羟基磷灰石；二水磷酸氢钙

ABSTRACT

Dental caries is one of the most common diseases. At least 50% of the population of the whole world, that is more than 30 hundred million, is suffering caries. Caries can give rise to acute inflammation, focal infection or immunological disease. In the meantime, it seriously destroys the masticator, decreases the function of the digestive system and causes the disease of the system. According to the statistics of WHO, the depletion of human hygienic resources due to caries is astonishing. Caries is listed as one of the top three diseases which badly influence the human health.

The widely accepted theories available for the pathogenesis of caries are the "chemico-bacterial theory" suggested by Miller in 1890 and the "proteolysis theory" suggested by Gottlieb, Frisbin in 1947 and Pincus *et al* in 1950. Those theories all involve bacteria destroying and acid demineralization.

It is important that to develop dental restorative materials to repair tooth. Up to now, there are two types of dental restorative materials according to their properties. One is the metallic restorations, the other is non-metallic restorations. Dental amalgam is one of the metallic restorations; resin composite material is one of the non-metallic restorations. Amalgam restorations may be preferable to resin composite materials for the restoration of the portion of a posterior tooth subject to considerably greater bitting forces because of strength and wear resistance considerations. But amalgam restorations are subject to the effect of corrosion when exposed to conditions present in the ora cavity. Resin composite restorations are usually chosen for restorative task, but resin composite materials are weaker than metals. Applying these repair materials require mechanical removing of the affected part and filling of the hole with a resin or alloy. These methods will inevitably destroy surrounding healthy tooth to facilitate the adhesion of the filler. So it is not an ideal method in the case of tiny gap and early caries. Recently, K. Onmua *et al* developed a synthetic enamel method to repair the enamel, but the thickness of this synthetic enamel was limited to 20 μm and the repair layer did not have antibacterial activity.

A number of studies had reported the relationship between dental erosion and

acidic foodstuffs. In addition, a report indicated that the mechanisms of DCPD growth and dissolution were of interest because of the importance of this calcium phosphate in the development of dental caries under acidic condition. DCPD is the most stable calcium phosphate under acidic condition. The aim of this study was the preparation and characterization of an antibacterial and highly crystalline zinc-doped DCPD coating on enamel. DCPD coating was prepared on enamel surface by the rapid growth of high crystalline DCPD crystal under strong acidic condition. The microstructure and hardness of the coating were characterized. The formation of the coating was characterized by FT-IR, XRD SEM, TEM, and EDS. Inhibition of the formation and metabolism of dental plaque by zinc salts has been documented. It has been previously reported the mechanism of inhibition of zinc ions on S. mutans, studies suggested that free zinc ions were responsible and that the inhibition of acid production was corrected with adsorption of zinc on the bacterial. Moreover, zinc ions have been included in several dental products, unlike other potential anti-plaque agents, zinc ions tend to cause no unpleasant clinical side-effects.The antibacterial activity against *E. coli* was examined and the microhardness was tested.

Keywords: Coating; CDHA; DCPD