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Mini Review
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Surface Coatings of Titanium and Zirconia

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Abstract

Titanium and zirconia are the biomaterials used in medicine and dentistry for restorations and implants. However, the adhesion of zirconia to other materials is weak. The implant fixation of titanium and zirconia is slow. This is due to the chemical and bio-inertness. The performance can be improved by coating with other materials. This mini review will discuss the coating methods with zirconia to improve adhesion in dental restorations and bioactive coating in titanium and zirconia implants to enhance the rate of bone healing at early implanation times.

Keywords: Titanium; Zirconia; Implants; Coatings; Bioactive materials

Introduction

Nowadays, the world population is increasing dramatically for the past few decades. This presents many public health challenges. One of the challenges is to restore the damaged and lost bone tissues due to accidents and aging. Zirconia and titanium and its alloys are the two most important biomaterials used in medicine and dentistry to restore, repair and regenerate the bone tissues [1,2]. Titanium and its alloys are widely used for medical and dental implants because of the excellent biocompatibility, good mechanical properties and high corrosion resistance. They are also used in dentistry as bridges, crowns and over dentures [3]. The rate of osseo integration of titanium implant fixation to bone tissue is slow. It takes a longer period for the strong bond formation between titanium and bone tissue cells [4]. This lengthens the clinical treatment duration. Zirconia is used in dentistry as orthodontic brackets, ceramic restorations and also a substitute for titanium as implant material because of the excellent mechanical, biocompatibility, tooth-like colour and minimal ion release [5]. However, zirconia is chemically inert and bonding to other materials such as resin composites is difficult. As an implant material, bone healing process is slow owing to the biological inertness [6]. Surface coatings of zirconia and titanium are one of the best approaches to improve the adhesion to other materials in restorations and rate of implant fixation to bone tissues. After surface coatings, there is a change of both (or one of) physical and chemical properties of the surface. On the one hand, it alters the surface topography such as increasing the surface roughness to enhance micro-mechanical interlocking. On the other hand, it alters the surface chemistry. This result is an activation of the surface towards the adhesion to other materials and enhancement of the biological activity to implant fixation.

Surface Coatings

Coatings for adhesion promotion in restorations

Grit blasting: In dental laboratories, the standard procedures for zirconia restorations are grit-blasting with alumina or silica-coated alumina sand particles under an air pressure (Figure 1). After grit-blasting, the surface roughness is increased which enhances the adhesion by micro-mechanical interlocking. Moreover, a silica-coated alumina or alumina thin layer is formed. This is followed by an application of silane coupling agent before cementation by light curing [7]. The silane coupling agent which contains two functional groups connects the resin composite and the zirconia. One functional group, -SiOR, which forms silanol, -SiOH, after activation reacts with the surface silica or alumina layer to form strong siloxane, -Si-O-Si-, or -Si-O-Al-linkages. The other functional group, -C=C-, reacts with the resin monomers containing -C=C- to form -C-C- bond by a free radical reaction [8].

Sol-gel coatings: The grit-blasting method used has a main drawback: it would cause surface defects or crack formation because of high energy sand particles impacting the surface. The surface damage also depends on the sand particle size, e.g. 30 vs 110 μm, of the sand powder used and the blasting pressure applied. That results in affecting the long term clinical performance [9]. Therefore, other methods are developed to promote resin zirconia bonding without any surface cracks formed.

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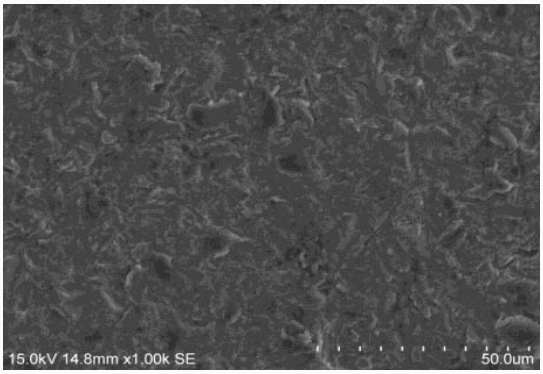

Figure 1: SEM micrographof grit-blasted zirconia surface using silica-coated alumina sand particles.

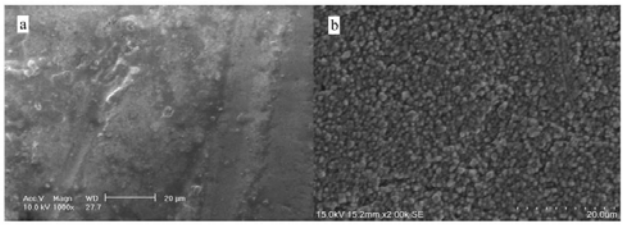

Figure 2: Sol-gel coatings on zirconia surface: a. tetraethoxysilane hydrolysis and b. silicon nitride hydrolysis. A silica coating is formed.

Sol-gel method is an alternative technique. It is a mild method with relative low processing temperature, more economic and energy saving. The basic principle is the formation of a silica network by hydrolysis of silica precursors under acidic and basic medium. The silica particles react and deposit on the surface to form a silica layer. A silane coupling agent is applied and followed by a cementation. Some methods reported include tetraethoxysilane hydrolysis and silicon nitride hydrolysis under basic medium (Figure 2). These coating methods would not induce any surface flaws. However, the resin zirconia bond strengths reported are lower than the grit-blasting method after thermo cycling aging [10, 11].

Other coating methods: Different coating methods have been investigated and reported. These include: 1, selective infiltration etching, 2.nano-structured alumina coating, and 3. chemical vapor deposition have been studied to assess the resin zirconia bonding [8]. They have different mechanisms to modify the zirconia surface by coating different materials.

Coatingsto enhance implant ossteo integration

Bioactive materials such as hydroxyapatite and bioactive glass are used for coating zirconia and titanium implants to improve the biological interactions with tissue cells. Many studies have been reported these coating materials are able to enhance osseo integration and promote rapid and early implant stabilization.

Bioactive glass coatings: The bioactive glass, silicate-based (SiO_2-CaO-P_2O_5), has been reported to be able to bond to tissue cells because of the formation of a hydroxyapatite surface layer. It can elicit a specific biological response between the implant material and the tissue cells [12]. Coating with the bioactive glass on metallic implants has been reported to improve the rate of osseo integration [13-15]. Several techniques are used for bioactive glass coating: enameling, sol-gel, plasma spraying, and electrophoresis deposition [16].

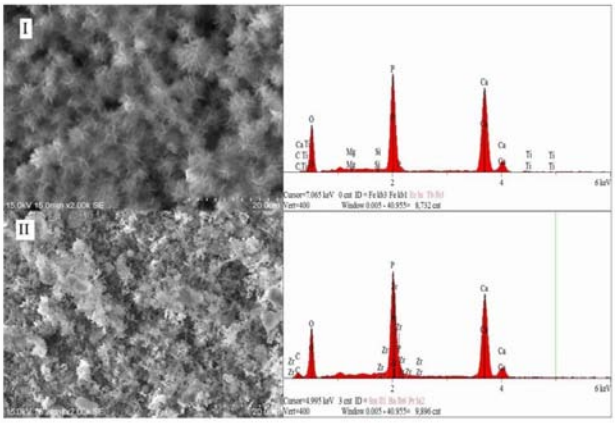

Figure 3: SEM micrographs (2000x) and EDX analysis of hydroxyapatite coating: I. titanium surfaceand II. zirconia surface modified with a novel silane coupling agent.

Hydroxyapatite coatings: Hydroxyapatite is the most widely used biomaterials in implant coating due to the chemical similarity to human bone and teeth. It has excellent biocompatibility, good ossteo conduction and osseo integration. There are numerous studies reported the improved osseo integrationat the early stage after implantation of hydroxyapatite coatings on titanium implants [17-19]. Several methods have been studied for hydroxyapatite coating on a zirconia and titanium implant surface to promote implant fixation. Some examples are plasma spraying, sol-gel, electrochemical deposition and biomimetic coatings [20]. The biomimetic coating method is based on the nucleation and growth of bone-like hydroxyapatite on a metal, ceramic or polymer surface by immersing in a simulated body fluid (SBF). It produces a uniform and homogenous coating on various shapes of implant objects. Biomimetic coating on zirconia and titanium by applying a novel silane coupling agent is being developed (Figure 3) [21].

Future Developments

The bioactive glass and hydroxyapatite used in implant coating have drawbacks such as brittleness, low mechanical strengths and bacterial infection of implants. Therefore, it is in need to modify these materials or search for other new biomaterials. Several strategies are explored: i. development of bioactive composite and hybrid coatings. Basically, the coating contains both inorganic (ceramic or glass) and organic (polymer) components which combines the advantages of both components; ii. Incorporation of antibacterial materials such as silver and chitos an into the coatings; and iii. Multifunctional coatings that combine multiple functional components. The future trend of implant coating design will not be only to improve osseo integration and prevent bacterial infection but also to extend the long term implant performance.

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