



## Bioactive glass coated zirconia for dental implants: A review

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### ABSTRACT

Nowadays, zirconia has been favored greatly for dental implants; however its disadvantages such as poor mechanical properties and brittleness makes it unsuitable. On the other hand, bioactive glasses coating have been utilized on tougher substrates such as zirconia. Bioactive glass coatings can decrease the healing time and hence accelerate the formation of the bond between bone and implant. Hence, in this study, we introduce the novel zirconia/bioactive glass composites with high mechanical strength and bioactivity to achieve the ideal implant in dentistry. Furthermore, a review of bioactive glass coatings (i.e., 45S5 and 58S) on zirconia as well as surface modification methods (i.e., sol-gel, laser cladding, plasma spraying, etc.) is provided.

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## 1. Introduction

In order to replace the missing teeth, oral implants can be considered a preferred option. This procedure was first proposed by Brånemark in the 1960s [1-5]. Many reports have covered the chemical and physical features of these implants including their design factor, surface structure and properties as well as implant microstructure. Moreover, many factors are believed to be important in the implant therapy prediction and clinical consequences.

Implants with good biocompatibility, sufficient corrosion and toughness can be categorized as ideal implants. Other ideal properties can be their great strength and resistance to fracture and wear [6-9]. The biological responses of dental implants as well as their chemical composition

are the main properties that are significant in the categorization of these materials. Note that the principles of design of implant should be necessarily based on the material physical features [10].

Building fillers with the more similarity to human teeth is of great importance since current fillers cannot present enough functional and reinforcing impact for dental composites. Although, in the research of monomer structures as well as filler compositions, repair failure can still happen because of reconstruction fracture and the secondary-carriers [11-13].

Ceramics lack the electric current conduction and they can be applied for the production of purification and dissociation membranes of biological fluids in medical equipment. In this regard, they can be suitable to manufacture porous components for dosage drug administration.

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In medical field, they are appropriate to make prosthesis. Ceramics enjoy excellent integration capability with the tissue of human bone that can be considered as a superiority over the implants with metallic nature. Their biological inertness and electrical passivation have made ceramics a promising material for the medical equipment. In comparison with metallic implants, zirconia-based ceramics show minimum ion release and they are biologically inert [14-32].

Modern Ti implant technologies are being introduced owing to possible combination of immunologic and aesthetic aspects of Ti and Ti alloys. Nevertheless, these characteristics should be maintained during the improvement of this technology. To sustain these properties, dental implantology started to apply Zr as a desirable alternative to Ti [29].

Ti and Zr are similar in terms of biocompatibility and osteointegration. However, since Zr is more bioinert than Ti, it is protected more against the attack by different organisms fermentation systems as well as degradation. This can present a minimum release of ion as compared with the metallic implants. It is well understood that the ion released from metallic implants can exert different unwanted effects including inflammatory, toxic, mutagenic and allergic reactions. A decrease in the lifetime and mechanical properties of the metallic implant can be made because of the in vivo corrosion of these implants [33].

The demand for zirconia dental implants is increasing recently. In comparison with the Ti dental implants, their increased esthetic feature-owing to similarity to the human tooth color is the main benefit of these implants [34-45]. To enhance the zirconia bioactivity and morphological properties for proliferation, excellent cell attachment and the acceptable differentiation during the surrounded bone cure, many efforts have been made [46, 47].

In terms of advantages, some documents have mentioned that zirconia decreases the risk of explosive reactions in surrounding peri-implant tissues, because it can reduce the biofilm aggregation and bacteria adhesion [32, 36, 48, 49]. On the other hand, titanium is grey and it can be corroded [25, 50]. These two facts about Ti, which surely can influence the appearance and health system, can provide aesthetic disadvantages that cannot be denied [46]. Both of the materials would need 3 to 6 months prior to the fixation of complete prosthetic reconstruction [18, 51-56]. This time can be reduced by applying the bioactive glass coating. Furthermore, after implantation, the bone loss rate can be decreased, which is another benefit of these coatings [57-60].

## 2. Zirconia implants

Zirconia with better optical, aesthetic, mechanical and biological qualifications is a suitable substitute to traditional Ti implant system for oral recovery [61-64]; it is produced by the oxidation of zirconium [25, 27, 65-67]. Zirconium, which is a transition metal [56, 68] with grey-white color [69-73], can be used to make zirconia implant.

Segments of the metal implant can be uncovered by recession of gingiva and the loss of apical bone, which this can disclose a discolored overlying gingiva [74-77]. Thus, it would be possible to use the zirconia ceramics because they enjoy great aesthetic, biological and mechanical characteristics and they lack electrical corrosion. Polyethylene and Ti show more inflammatory reactions than zirconia. Less inflammatory re-

sponse along with the lack of mutagenicity and toxicity in zirconia, can be considered as the most attractive zirconia properties [58].

## 3. Bioactive glass in biomedical applications

To regenerate the tissue, many medical approaches have been employed by bioglasses or bioceramics, which are manufactured in various phases and shapes. The capability of reaction with physiological media have been seen to be slower in bioceramics than that of bioactive glasses. This can result in better bonding with alive tissues and the formation of apatite layer. Hence, bioceramics require the special coated layer to improve their biomedical applications [78].

Because of the great bioactivity of BGs, they are one of the best biomaterials for renovation and bone repair. For the first time, they were introduced by Hench's team at the late 1960s [39, 79-81]. Moreover, by combining great mechanical strength and excellent bioactivity of BGs, they can be successfully used as coatings on inert substrates [82]. Reaction with the physiological fluids and the formation of chemical bonding between bones and bioglass can be occurred when bioglasses are implanted in the body [83-87]. A bioactive surface can be considered as important agent to avoid many simultaneous reactions, which take place between the implant and the targeted tissue at the implant surface [82].

Melting process, which starts from carbonates and oxides, is the most important technique of bioactive glass preparation. Then, sol-gel method with the ability of producing bioactive glasses with high bioactivity was introduced. Their increased bioactivity, which is presented by this method, resulted from the microstructural properties and tailored composition. Furthermore, melting approach needs to be processed at higher temperature as compared with the sol-gel methodology, which can limit or avoid the flux addition for sol-gel method [88]. The bioactive glass with its composite coatings can be classified as following categorization according to the coating structure.

### 3.1. 45S5 bioglass

Ceramic 45S5 BG with 24.5% sodium oxide, 45% silicon dioxides, 24.5% calcium dioxide and 6% phosphorus pentoxide have attracted the attentions of researchers as a biomaterial substance because of its osseointegration capability, bioactive surface and the ability of healing bone damages [89-91]. It can be prepared by melt-cast method with various crystallinity including amorphous and crystalline [92]. A schematic of melting process for producing melt-prepared glasses (MPG) is provided in Fig. 1.

In order to study the impact of bioactive glass 45S5 crystallization on the degradation and constitution of apatite, Plewinski et al. [93], performed XRD analysis on the samples including samples treated by heat and amorphous samples. To guarantee the perfect amorphous sample crystallization, the heat-treatment was continued for 1 hour at 1000 °C. They found that the apatite layer could be formed on this crystallized bioglass, unlike the amorphous ones, under these conditions.

### 3.2. 58S bioglass

58S bioactive glass is a great bioactive, biodegradable glass with the capability of bone bonding. Due to these qualifications, this bioactive glass, with 33% calcium oxide, 58% silicon dioxide 9% phosphorus pentoxide, has been favored as scaffold substance [94-97]. The reaction of 58S bioactive glass with physiological fluids occurs after implantation quickly and it makes bond to the tissue of bone. This happens without inflammatory, toxicity and foreign-body reaction. The fast ionic dissolution as well as the hydroxyl-carbonated apatite layer formation was seen after the rapid in-vivo surface reactions. By release of calcium, silicon and phosphorous ions, the gene expression as well as the prolif-

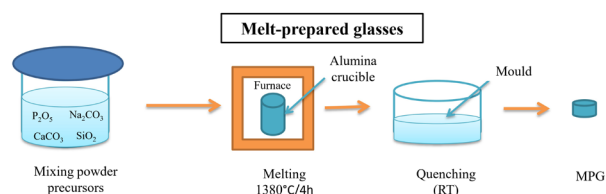


Fig. 1. Schematic of the melting process for preparing bioglass.

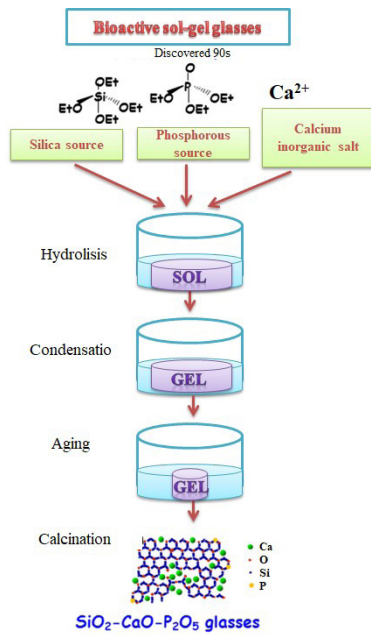


Fig. 2. Schematic illustration of the sol-gel process.

eration of osteoblast takes place to form the bone quickly.

58S-BG, produced by sol-gel approach, was used by Mokhtari et al. [98], to investigate the coatings of Chitosan-58S on nanotube of Titanium dioxide. A schematic illustration of sol-gel derived BGs is shown in Fig. 2. Based on the XRD results, the crystallization process of 58S-BG, which includes calcium silicate, calcium phosphate and Calcium Metasilicate, took place after the calcination at 1100 °C. This was continued by the structure transformation from amorphous to crystalline. Calcium Metasilicate was as the principal crystalline phase in the prepared powder. This demonstrated the intense interaction between osseous tissue and wollastonite.

To improve the bioactivity and mechanical properties of 58S bioglass, Haftbaradaran et al. [99], examined the use of sol-gel prepared 58S bioglass on fabricated-vitallium alloy. Based on the anticipations, the uncoated sample displayed a lower bioactivity as compared with the coated sample.

Faure et al. [100], used an organic acid catalyst to synthesize the 45S5 bioactive glass by a novel sol-gel approach. Instead of the conventional  $\text{HNO}_3$  with high concentration,  $\text{C}_6\text{H}_8\text{O}_7$  solution with a low concentration can be applied as a catalyst for hydrolysis reaction in the 45S5 bioactive glass preparation. Nevertheless, in this study, the bioactivity of the bioglass seems to be less than sol-gel bioactivity. In fact, sol-gel derived BG grains display extremely rough surfaces with great porosity. This, surely can present excellent exchange surface in physiological medium. Therefore, the sol-gel bioglass exchange surface can be more important than the exchange surface of the produced bioglass by the melting method.

In a study by Bui et al. [101], 58S-BG was prepared via a novel sol-gel technique. In this new approach, a quick transformation process of sol to gel, was conducted by the addition of ammonia solution. Next, the freeze-drying method was applied to dry prepared gel after 6 h. During the *in vitro* evaluations, after 2 days, a clear dense HA layer was formed. This produced layer was as the bioactivity evidence of prepared bioglass.

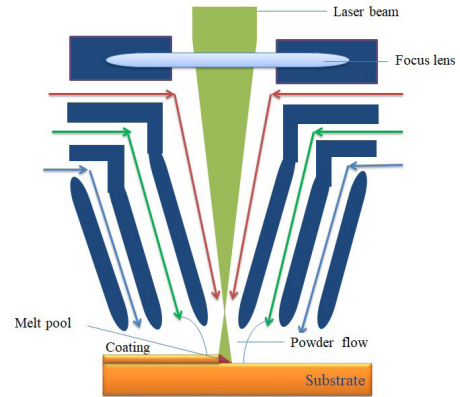


Fig. 3. Laser cladding process schematic for coating.

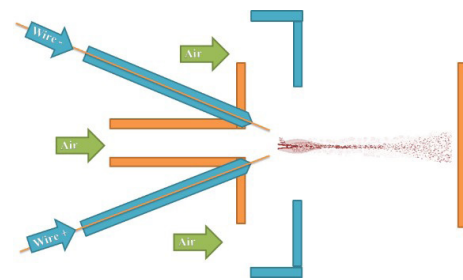


Fig. 4. Plasma spraying technique schematic illustration for deposition of BG coatings.

## 4. Bioactive glass coating

Considering the investigations by many researchers, bioactive glasses possess potential of many wide applications such as the formation of HCA and bone, but their use as materials for coating, is more attractive than other applications, especially when they are used as an implant. Their mechanical integrity becomes important [102-105] when they are used as coating on tougher substrate [106-108]. The studies about coatings have proved that depending on the approach of coatings and deposition, the main chemical and physical characteristics will change [109-113]. It was understood that chemical properties like long-term stability can also affect the bioactive glass coating performance [82].

Ceramics including  $\text{Ca}_3(\text{PO}_4)_2$ , Zr,  $\text{Al}_2\text{O}_3$  and BGs have gained more attentions recently for medical applications, since ceramic-based prostheses may provide a good opportunity to obtain more effective biometric properties [88].

### 4.1. Laser cladding

Diverse materials can be bonded together by laser cladding technique, which can be defined as a deposition method. The principal of this method is the coating of a substrate by a laser melted powder substance. However, various profiles from this method can be applied. Industrially, a coating can be produced by the powder injection onto the substrate and the melting of it by laser beam [82].

There is a possibility to introduce variability by the operator during the coating preparation. Laser cladding is able to remove them by increasing the products quality, because it can enhance the fabrication process speed automatically (Fig. 3) [39, 114-116].

Great pores interconnectivity in the outer layer of porous layer and the desirable joining quality at the interface of substrate and coating observed by micro-computed tomography in the study by Baino et al.

[114]. They studied the laser cladding fabricated bioactive glass coating. The fabrication process was applied on the ceramic acetabular cups and the coatings can be made in a porous or pore-free form. The desired glass/ceramic joining was confirmed by indentation analysis.

To promote the osteointegration physiologically, a valuable technique is proposed, in which a bioactive coating deposition is applied on the surface of implant to make contact with bone. Baine et al. [117], used two dissimilar approaches (i.e. laser cladding and sponge replication) to produce the porous coatings of bioactive glass on the  $Al_2O_3$ - $ZrO_2$  composite implant. The key for bone binding is the good ability of hydroxyapatite formation. An early evidence of modern porous glass coating biocompatibility and bioactive features was proved in this study.

Laser cladding process, which is believed to be effective in bioactive glass coatings, was applied by Montealegre et al. [118], to coat the bioactive glass on alumina/zirconia composite for orthopedic applications. Besides, for two different BGs, the technology could coat macroporous bioactive glass on alumina/zirconia composite. Moreover, the laser cladding process provides a possibility to achieve dense and homogeneous BG coating. The structure and formulation of the powders of BGs are easily translated to the BG coatings.

#### 4.2. Sol-gel

The wet chemical technique of sol-gel shows high reactivity because of providing a high surface area [119-121]. This high possibility of reactivity, surely provides a low temperature for this process. This means that the process does not need high temperature sintering. Moreover, it does not need high values of pH [122-124].

Sol-gel, as an affordable process, have become favorite technique of coating for glass-ceramic composite or bioactive glass, since it has various benefits i.e. coating layer uniformity, fairly great adhesion power on complex substrate, high composition accommodation [125-127], and desirable purity [128]. This method can be combined with other approaches easily. To fix the bioactive coating on the substrate of ceramic, a high temperature is needed after heat-treatment. Thus, in spite of the convenience of this method, a high temperature can involve the mismatch of the thermal expansion coefficient that can occur between the coating and substrate. This can be continued by the residual stress accumulation on interface or the change of coated glasses composition [129].

The fabrication of a broad bioactive glass range is possible by sol-gel method that has increased the success of this process. Besides, this benefit provides a possibility to make an improvement in cell adhesion and protein absorption, because the sol-gel process can give a high specific surface porous microstructure to the bioactive glass coating.

In vitro behavior of porous zirconia was investigated by Mesquita-Guimarães et al. [130] via MG-63 cells. During the condensation, the optimization of 58S BG coating was followed by changing the number of immersions as well as controlling the sol-gel solution viscosity. In the 423-Z.BG structures, the improvement in the cell proliferation was occurred in the presence of 58S BG bioactive glass. This enhancement, which was continued to maximum level, may reveal that the coating

affects the activity of cells positively to make the extracellular matrix.

Araujo et al. [33], used a novel bioactive glass layer including a low ratio of Ca/P on a Zirconia-3% Ytria substrate to prepare the extremely bioactive glass coating. The prepared coatings in this study, had thickness of 345  $\mu m$  with crack-free surface, which are the representative of great glass/substrate biocompatibility in terms of the matching of expansion coefficient.

In another study, Lin et al. [131], produced mesoporous bioglass (MBGs), which were coated by  $ZrO_2$  using dip-coating method to apply in the engineering process of bone tissue. To remove the excess sols, immersed-samples were centrifuged (30 s and 500 rpm). The results showed desired cell viability and biocompatibility and no cytotoxicity.

The dip-coating method consists of three steps: (i) samples dipping, (ii) withdrawing them and (iii) drying. After immersing the samples in the solution, they should be withdrawn in a constant speed. In order to guarantee the spread of equal thickness all over the substrate surface, it is important to have a steady speed.

The application of the dip-coating technique under extreme conditions as well as surface thickness distribution was studied by Faustino et al. [132] by making some models. The study and optimization of sol-gel method is required, since preparation, curing as well as aging time of sol-gel approaches are time consuming. Moreover, during heat-treatment process, there is the possibility of phase separation. Thus, industrially, these can make limitations in production process.

#### 4.3. Plasma spray

Recently, the deposition of bioactive glass coatings, has been applied by standard spray technique in various studies (Fig. 4). The suspension plasma spray (a modern spray method, SPS) is newly introduced, in which a liquid suspension can be applied as a substitute of a dry powder, as feedstock [133].

Cattini et al. [133], investigated the processing parameters of SPS on mechanical properties, in-vitro condition and microstructure. Micro-size powder suspension was used to produce a bioactive coating. A preliminary screening of processing parameters displayed that the spray distance, the flow rate of  $H_2$  and the inputs of plasma electric power may affect the microstructure. The optimum and suitable hydrogen flow rate, power and spray distance were 7.5 slpm, 36-40 kW and 50-70 mm, respectively, for biomedical applications.

Calvo et al. [134], melt-quenched the powders of 45S5 bioactive glass consisting of 24.5% calcium oxide, 45% silicon dioxide, 6% phosphorus pentoxide and 24.5 % sodium oxide. They investigated the use of atmospheric plasma spraying (PS) on the coatings of 45S5 bioactive glass. They milled the obtained frit via two dissimilar methods including wet and dry milling. To achieve a powder, consisting of porous agglomerates, the primer method was continued by spray drying while the latter should be followed by sieving.

Great surface properties, which can guarantee the effective contact with body fluid and excellent adhesion power to the substrate, was obtained by prepared coatings through atmospheric PS. All of the feed-

**Table 1**

Various techniques used for bioactive glass coating on zirconia substrates.

Methods	Pros.	Cons.
Plasma spray	A low probability of compromising glass bioactivity, a wide range of coating materials	Weak adhesion between substrate and glass
Laser cladding	The possibility of flat coating on surfaces with curved geometry	Need surface pre-treatment, lack of uniformity
Sol-gel	Multilayer coating, porous microstructure, versatile, large compositional range of bioactive glasses, controlled composition, and homogeneity	Due to the difference in CTE between substrate and coating, post heat treatment introduces internal stress
Enameling	Large range of thickness, versatile, cheap simple	Thermal residual stress, the formation of chemical by-product, metal degradation, glass crystallization, compositional gradient

stocks showed amorphous phase.

Jouliia et al. [135], studied the mechanisms of deposition in solution precursor plasma spray (SPPS) and SPS for yttria stabilized zirconia (YSZ). They investigated the mechanisms of deposition in suspension and solution precursor plasma spraying by studying the characteristics of individual YSZ lamellae and of complete coatings. They found that plasma-spraying using liquid feedstock could be a promising method for depositing finely structured ceramic coatings. Table 1 summarizes various techniques used for bioactive glass coating on zirconia substrates

#### 4.4. Enameling

Enameling is a kind of conventional treatment of surface, with the benefits of facile operation, inexpensive processing system that can provide the optimization possibility via altering the processing parameters [136-138]. Although this technique can involve the glass frit layer fusing, the applied metal substrate for coating can control the introduction of a lower melting frit. The combination of the tailored-composite glass and the enameling method has been proved to be a suitable option for the fabrication process of a bioactive glass layer. This can be done onto a bioinert substrate of metal, which has the great adherence, bioactivity and thermal expansion coefficient.

The enameling approach is facile and affordable, and it is usually used for coating a ceramic or metal by a glass. In this technique, the deposition of a suspension of powder glass or a thin glass layer onto a substrate of metal or ceramic could be followed by glazing the glass by a suitable heat treatment.

In the zirconia, alumina and ceramic composites coating, the enameling by the substrates, which are made by ceramic, has showed more promising results compared to the metal substrates. Moreover, the proper engineering of processing system and glass structure can transfer the surface layer to a coating with functionally graded and enhanced mechanical properties [82].

## 5. Conclusions and future insights

The bioactive glasses are favored greatly due to their potential for biomedical applications such as improving the bond strength in formation of bone, accelerating healing time, etc. these characteristics have made them good candidates to be used as coating on appropriate substrate such as ZrO<sub>2</sub>-based dental implants. This is because of poor mechanical properties and brittleness of zirconia. Thus, the composite of BGs and ZrO<sub>2</sub>-based material would be great for biological applications. Hence, a thorough review was performed about these implant composites. It was found that, through coating of BGs on zirconia substrate, reinforcing properties especially in dental implants would be obtained.

Coatings are the advantageous and extensive field for medical applications. Therefore, we can fabricate special coatings to promote the zirconia implants advantages and also decrease the risk factors and possibility of dental implant failure.

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