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# Characterization of fabricated cobalt-based alloy/nano bioactive glass composites

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ABSTRACT

In this work, cobalt-based alloy/nano bioactive glass (NBG) composites with 10, 15 and 20 wt% NBG were prepared and their bioactivity after immersion in simulated body fluid (SBF) for 1 to 4 weeks was studied. Scanning electron microscopy images of two- step sintered composites revealed relatively dense microstructure. The results showed that density of composite samples decreased with increase in NBG amount. The microstructure analysis as well as energy dispersive X-ray analysis (EDX) revealed that small amount of calcium phosphate phases precipitates on the surface of composite samples after 1 week immersion in SBF. After 2 weeks immersion, considerable amounts of cauliflower-like shaped precipitations were seen on the surface of the composites. Based on EDX analysis, these precipitations were composed mainly from Ca, P and Si. The observed bands in the Fourier transform infrared spectroscopy of immersed composites samples for 4 weeks in SBF, were characteristic bands of hydroxyapatite. Therefore it is possible to form hydroxyapatite layer on the surface of composite samples during immersion in SBF. The results indicated that prepared composites unlike cobalt-based alloy are bioactive, promising their possibility for implant applications.



## 1. Introduction

Metals and metallic alloys have many applications in dentistry, orthopedics and bone fractures as an artificial implant or restored materials. Orthopedic implants are mainly made of metals to suffer mechanical stresses in application. Titanium and its alloys, cobalt-based alloys and stainless steel are most common metals which could be used for orthopedic implants applications. Their main characteristic is proper mechanical properties but their corrosion resistance in physiological fluids and their weak bioactivity are two concerns about using them as implants [1]. In general, metallic alloys are not bioactive, i.e. they are not able to bond to living tissue without cementation or external fixation devices [2–4].

In the late 1960s Professor Hench developed bioglass as new biocompatible material using silica as base material that could be mixed with other ingredients such as calcium to joint fractured bones. Bioglass imitates natural bone and enhances the growth of new bone between the fractures [5,6]. Bioglass shifts the trend of implant materials to stimulate body's own regenerative capabilities. Dissolution of this material in normal physiological environment activates genes controlling osteogenesis and growth factor production [6–8]. The amount of trabecular bone growth is much more than that of produced by synthetic hydroxyapatite [9,10]. Implanted bioglass in bone tissue resists against removing from its position which was coined as “bonded to bone” by Hench [11,12]. Hench used “bioactive glass” phrase to describe this attachment [5,13,14].

A bioactive material is defined as a material that shows a special biological response at its surface, resulting formation of a bond between the tissue and the material [15,16]. The unique advantages of bioglass than hydroxyapatite and any other allograft are gene activation, bone regenerative capability with better quality and quantity of bone equivalent to normal bone and high level of bioactivity. These properties encourage the use of bioglass. The other advantages of bioglass than synthetic hydroxyapatite are the biological fixation, and the capability of bonding to both hard and soft tissues, whereas hydroxyapatite binds only to hard tissues [17].

The original bioglass (45S5) is composed of 45% silica ($SiO_2$), 24.5% calcium oxide (CaO), 24.5%sodium oxide ($Na_2O$), and 6% phosphorous pentoxide ($P_2O_5$) in weight percentage. When a bioglass implant is exposed to an aqueous solution or body fluids its surface converts to a silica-CaO/$P_2O_5$-rich gel layer that subsequently mineralizes into hydroxycarbonate in a few hours [18–20]. This gel layer simulates hydroxyapatite matrix so much that osteoblasts were differentiated and new bone was deposited [21].

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The bioactivity level of any material is reported in terms of bioactivity Index ($I_B$). Bioactivity Index of a material is the required time for more than half of the interface to bond, i.e., $t_{0.5bb}$.

$$I_B = 100/t_{0.5bb}$$

Materials with the $I_B$ higher than 8, like 45S5, could bond to both soft and hard tissues while materials such as synthetic hydroxyapatite with $I_B$ value <8 will bind only to hard tissue [22].

Besides their bioactivity, unfortunately bioglasses are not strong enough to be used for load-bearing applications [23–26]. Therefore bioglasses cannot be used in load-bearing applications, where metallic alloys are still the materials of choice.

In order to benefit from both good mechanical properties and bioactivity, it is reasonable to fabricate composite from a metallic biomaterial and a bioactive ceramic. Cobalt- based alloys in the Co-Cr-Mo system have been widely used as implant components due to their mechanical properties, good wear and corrosion resistances as well as biocompatibility [27–29]. One of the most important bioactive ceramics is bioglass and the most representative bioactive glass is the so-called 45S5 Bioglass®, which its composition particularly rich in sodium and calcium oxides and characterized by a high calcium-to-phosphorous ratio makes the glass surface very reactive in aqueous media, both in vitro and in vivo [30].

Based on literature [31–33], nano bioactive glass compared to micro one differs in properties such as specific surface area, pores size, wettability and surface energy, which promotes reactions with vivid texture. Therefore, using nanobioglass as reinforcement phase, it is expected to accelerate apatite formation on the composite surface and strengthen its bonding to bone. As a result the implant would be fixed at its position. Therefore in this study cobalt-based alloy/nano bioactive glass composites with different amounts of bioglass were prepared and their microstructure, before and after immersion in simulated body fluid (SBF) were investigated. The SBF solution after immersion was also analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) in order to study the variation of calcium, phosphor and silicon ions concentration.

## 2. Experimental procedures

Cobalt- based alloy powder was purchased from CARPENTER Powder Products. Its composition is reported in Table 1. Nano bioactive glass (NBG) particles with chemical composition close to 45S5 Bioglasss® containing 45% $SiO_2$, 24.5% $Na_2O$, 24.5 CaO and 6% $P_2O_5$ in weight percentages were prepared by sol-gel technique as described in detail by Fathi and Doostmohammadi [34]. Transmission electron microscopy (TEM) image of synthesized NBG powder is shown in Fig. 1, which proves that its particle size is <100 nm. The particle size of purchased metallic alloy powder and synthesized NBG powder was in the range 75–180 μm and <100 nm, respectively. In order to fabricate the Co- based alloy/NBG composites, three different compositions containing 10, 15 and 20% NBG powder were weighed. Homogenous mixture of metallic alloy and ceramic component was obtained by mixing in a planetary ball mill for 1 h under argon atmosphere to avoid oxidation. Mixed powders were uniaxially pressed under 700 MPa to prepare green pellets of composites. Because of advantages of two- step sintering compared to conventional sintering (lower sintering temperature as well as higher obtainable density) [35] green samples were sintered via two- step sintering. The studied temperature range for first step and second step was 900–1100 °C and 700–900 °C, respectively and their corresponding soaking time were 10 min and 2–14 h, respectively. For each sintering cycle, five samples were used and after measuring density of sintered ceramics via Archimedes method, the optimum sintering temperature of each composition was determined.

**Table 1**
Composition of cobalt-based alloy.

| Element | Co | Cr | Mo | Ni | Fe | Si | Mn | Others |
|---|---|---|---|---|---|---|---|---|
| Weight percent | 60.80 | 27.60 | 5.30 | 2.76 | 1.40 | 0.88 | 0.87 | 0.39 |

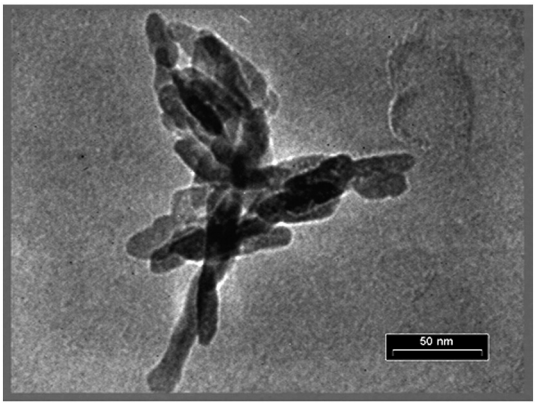


**Fig. 1.** The TEM image of agglomerated NBG powder.

Simulated body fluid (SBF) soaking was used to evaluate the in vitro bioactivity of prepared composites samples. The composition of this buffer, described by Kokubo et al. [36], has an ionic composition similar to that of human blood plasma. Sintered composites were immersed in SBF solution and stored in plastic flasks, maintained at 37 °C in an incubator for 7, 14, 21 and 28 days. The formation of the apatite layer on the composites samples were recognized, analyzed and confirmed using Fourier transform infrared spectroscopy (Bomem, MB-100) in the range 4000-600 $cm^{-1}$ with 2 $cm^{-1}$ scan rate.

The microstructure of optimally sintered composites samples before and after immersion in SBF solution was investigated by scanning electron microscopy (Phillips XL 30). In order to estimate the composition of the formed layer on samples after immersion in SBF solution, energy dispersive X-ray (EDX) analysis was carried out. The pH variations of SBF solution during 1 to 4 weeks of sample immersion were measured by using a pH-meter. The SBF solution after immersion was also analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) in order to study the variation of calcium, phosphor and silicon ions concentration.

## 3. Results and discussion

### 3.1. Determination of optimum sintering temperature

Based on measuring density by Archimedes method, the optimum sintering time and temperature for all compositions were found to be 1000 °C for first step and 800 °C for second step with 10 h soaking time. These sintering conditions resulted in relative density of sintered composite samples higher than 96, 94 and 91% for samples containing 10, 15 and 20% NBG, respectively. That is, higher amount of NBG, lower density of sintered composite. A possible explanation of this behavior is that with increasing the volume fraction of bioglass particles, internal friction of the composite powder increases which hinder consolidation of the material. It was described by Dai et al. [37] that a small amount of the reinforcing phase fills easier inter particles voids of metallic matrix and therefore can be easier compacted due to a lower friction. Higher volume fraction, however, intensifies bridging effects during single-action pressing and effectively suppresses densification.

### 3.2. SEM images and EDX analysis of sintered composites

The SEM images of optimally sintered composite samples containing 10, 15 and 20% NBG are compared in Fig. 2 and their corresponding EDX