

FABRICATION OF A BIOCOMPATIBLE COBALT BASE ALLOY WITH A BIOACTIVE (WOLLASTONITE) POROUS SURFACE THROUGH A CASTING PROCESS

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In this work, the investment casting technique was used for the fabrication of a bioactive cobalt base alloy with a porous surface. The mould was fabricated according to a design that allows the generation of an array of micrometric open pores across the surface. These pores are filled with a mixture of wollastonite and maize husk particles, which in turn generate porosity in the wollastonite when burned. After casting, the samples were immersed in simulated body fluid (SBF) for a period of 7, 14 or 21 days at a temperature of 37°C to evaluate their bioactivity. The surfaces of all of the samples were characterised via spectroscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The stereoscopy and SEM analyses of the surfaces demonstrated the presence of ceramic material inside the pores. The EDX analysis of the material inside the pores revealed the presence of the chemical components of wollastonite. Surface analysis of the samples after immersion in SBF indicated the presence of a ceramic phase at the surface of the pores, which could be identified as apatite according to its morphology and composition.

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1. Introduction

Cobalt base alloys are commonly used in the fabrication of prosthetics because of their desirable mechanical properties and adequate biocompatibility. However, these alloys are inert materials and fail to develop adherence to bone tissue [1].

For this reason, many techniques have been utilised to coat these biocompatible alloys with a variety of bioactive materials, such as bioglass [2], hydroxyapatite [3] and wollastonite [4], which promote adherence to live bone tissue. The most widely used technique in medical applications is plasma spraying of hydroxyapatite; however, the hydroxyapatite deposited through this method differs from bone apatite in both its crystallinity and composition due to the high temperatures employed during the application process [5].

Methods for incorporating particles of bioactive materials into the surfaces of biocompatible metals have been developed in recent studies. For example, it was reported that particles of different bioactive materials were successfully attached to the surface of a cobalt base alloy (ASTM F75) during the investment casting process [6, 7] and subsequently during the heat treatment [8]. Nevertheless, given that after casting, the prosthetics must undergo different surface machining processes, it is unlikely that the bioactive particles will remain attached to the surface.

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Hence, this report presents a casting-based fabrication method through which a Co-Cr-Mo-C alloy surface can be obtained in which there are pores filled with wollastonite, whose properties are advantageous for subsequent surface treatment processes.

2. Materials and methods

2.1 Sample preparation

An array of 25 pores was engraved on round wax models (20 mm diameter, 5 mm height) through penetration by metallic pins. The average depth and diameter of the pores were 736.06 μm and 807.67 μm , respectively. Then, the pores were filled with a wollastonite-maize husk (W-H) mixture consisting of 80% wollastonite (27 μm , 96%, Minerales Gosa México) and 20% maize husk. A paintbrush soaked in a suspension of 5 ml polyvinyl alcohol and 4 grams of the W-H mixture was used to deposit the mixture inside the pores, after which the samples were dried in the open air for 24 hours.

For fabrication of the investment mould, the wax models with pores saturated with the W-H mixture were adequately covered with layers of 50% SiO_2 and ZrSiO_4 and dried in the open air. Then, the wax was drained from the mould in an autoclave at 70°C for 1 hour. Next, the mould was sintered at a rate of 10°C per minute up to a temperature of 810°C, then held at that temperature for 2 hours. Finally, the Co-Cr-Mo alloy was transformed to a molten state in a high-frequency electric induction oven (InductoTherm Power Track 30) in an argon atmosphere at a pressure of 0.83 atm and cast at 1,600°C into the preheated mould at 980°C.

2.2. Immersion of the samples in SBF

For the characterisation of *in vitro* bioactivity, a solution with an ionic concentration similar to that of blood plasma (simulated body fluid, SBF) was used. The concentrations of different ions in the solution are shown in Table 1. The solution was prepared by the dissolution of appropriate amounts of NaCl, NaHCO_3 , KCl, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, Na_2SO_4 and $(\text{CH}_2\text{OH})_3\text{CNH}_2$ in deionised water, adjusting the pH to 7.25 at 37°C with HCl [9].

Table 1. Ionic concentrations of SBF, 1.5 SBF, 5 SBF and human blood plasma.

Concentration (mM/dm ³)								
	Na ⁺	K ⁺	Mg ⁺²	Ca ⁺²	Cl ⁻	HCO ₃ ⁻	HPO ₄ ⁻²	SO ₄ ⁻²
SBF	142	5.0	1.5	2.5	147.8	4.20	1.0	0.5
Human blood plasma	142	25.0	1.5	2.5	103.0	27.0	1.0	0.5

Each sample was placed at the bottom of a plastic container with 150 ml of SBF at 37°C. The containers with the samples were kept in an incubator at 37°C for 21 days, and the SBF was replaced every 7 days. Then, the samples were removed from the containers, carefully rinsed with deionised water, dried at room temperature and stored in a desiccator.

2.3. Characterisation methods

After casting and immersion in SBF, the surfaces of the metallic samples were analysed via stereography (SG), scanning electron microscopy (SEM) (Philips, model XL 30 ESEM), and energy dispersive X-ray spectroscopy (EDX) (software package: EDAX Genesis).

3. Results and discussion

Fig. 1 shows stereoscopic images of the surface of a sample after the casting process. In the first image (Fig. 1a), the pore array on the surface can be observed, as can the ceramic material inside the pores. At a higher magnification (Fig. 1b), the porosity of the ceramic material caused by the evaporation of the maize husk flakes mixed with the wollastonite can also be observed.

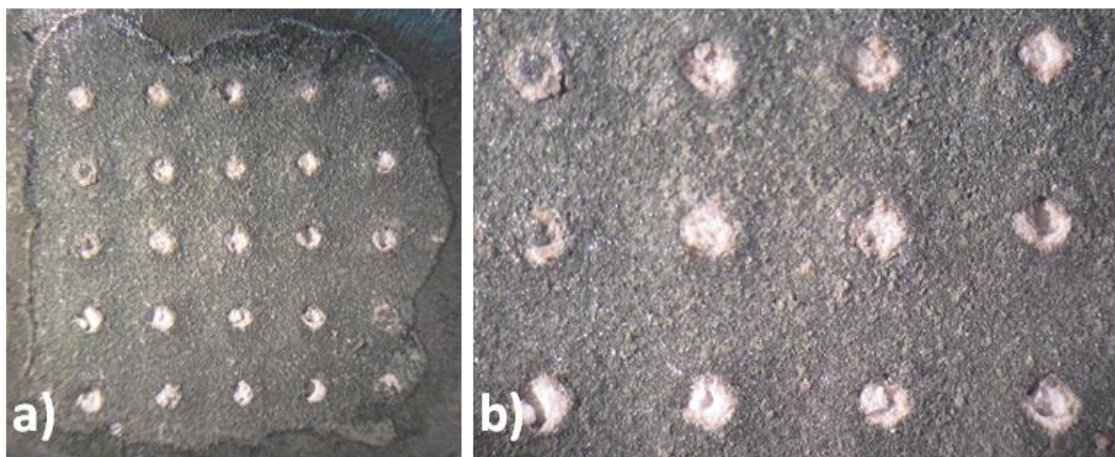


Fig. 1. SG analysis of the samples after the casting process

Fig. 2 presents the SEM and EDX results obtained after the casting process. In Fig. 2a, the ceramic particles inside one of the pores can be clearly appreciated; it can also be observed that these ceramic particles have undergone incipient fusion due to the high temperatures used in the casting process. Furthermore, under these conditions, it is likely that a portion of the wollastonite has transformed into pseudo-wollastonite. Nevertheless, it has been demonstrated that both of these phases are bioactive.⁴ The obtained EDX spectrum (Fig. 2b) indicates that the particles inside the pore contain mainly Si, Ca and O elements of wollastonite, as well as Zr and Al elements of the investment in which the mould was fabricated.

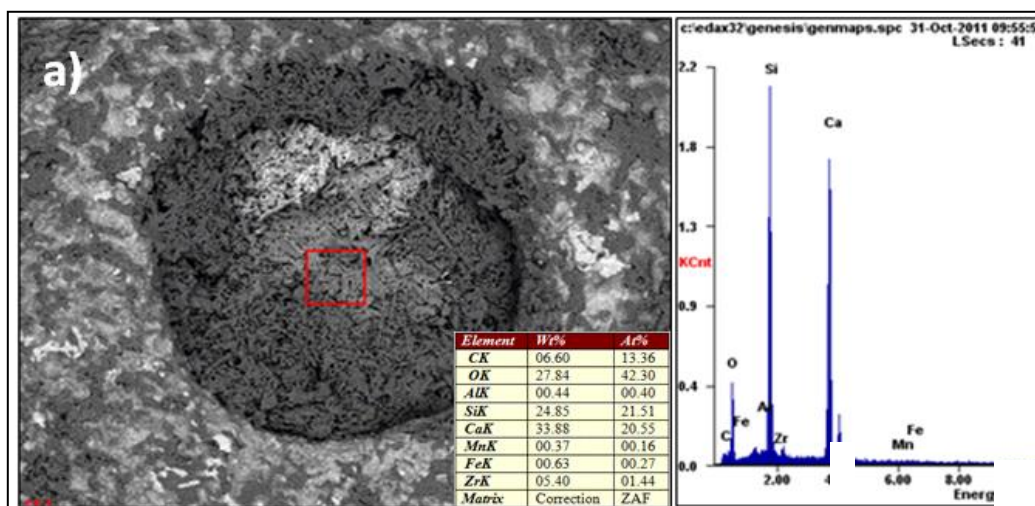


Fig. 2. SEM and EDX analyses of a sample after the casting process

Fig. 3 shows the results of the SEM and EDX analyses of the samples submerged in SBF for 7, 10 and 21 days.

Fig. 3a shows a low-magnification micrograph of the surface of a pore in one of the samples after 7 days of immersion, where the formation of ceramic agglomerates can immediately be observed. These agglomerates exhibit a different morphology than the ceramic material trapped inside the pores during the casting process. The EDX spectrum (Fig. 3b) indicates that the main elements present are Ca and Si from the wollastonite, Zr and Al from the mould, and the alloy elements Co, Cr and Mo. This analysis indicates that the new ceramic phase on top of the pores is too thin to be detected by the EDX spectrometer.

After 14 days of immersion, the samples presented significant differences with respect to their state after 7 days of immersion: Fig. 3c presents a low-magnification micrograph in which it can be observed that the formed layer completely covers the surface of the pore. The morphology of the particles of the layer is similar to that of bioactive systems where apatite coatings have developed, which have been reported in the literature [10]. The EDX analyses (Fig. 3d) reveal that the predominant elements in this coating are Ca, P and O. It is important to mention that none of the predominant elements in the alloy, such as Cr and Co, nor Si from the wollastonite was detected. This indicates that the coating shows a considerable thickness, which prevents the other phases from being detected.

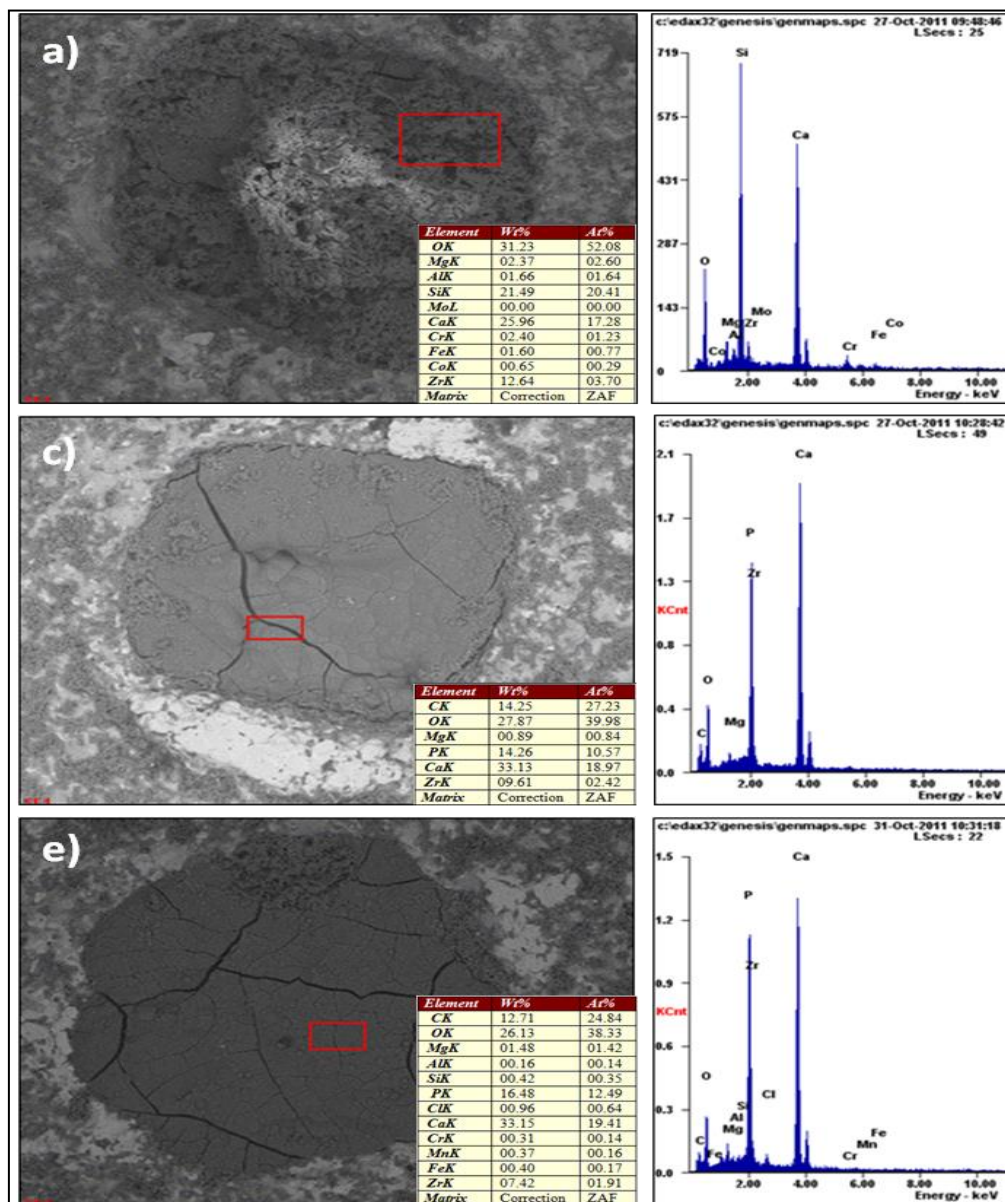


Fig. 3. SEM and EDX analyses of the samples after immersion in SBF for a) 7 days, c) 14 days, and e) 21 days. b), d) and f) show the corresponding EDX spectra

After 21 days of immersion (Fig. 3e), the same type of agglomerates are observed to be distributed throughout the pore surface until a layer is formed, very similar to that found in the sample that was immersed for 14 days. The EDX analyses reveal that the predominant elements in the coating are Ca, P and O in this case as well. Once again, none of the elements from the alloy, such as Cr or Co, nor any of the Si from the wollastonite inside the pore was detected, which may indicate that the layer formed has a considerable thickness.

Finally, it is worth mentioning that previous investigations have shown that the formation of apatite on the surface of wollastonite and pseudo-wollastonite stems from the dissolution of these two compounds, which results in the exchange of Ca^{2+} for H^+ ions in the solution. This process leads to the transformation of the surface wollastonite crystals (as well as pseudo-wollastonite in this case) into an amorphous silica phase. In parallel, the ionic exchange produces an increase in pH and saturation of calcium ions in the SBF solution around the substrate. Finally, this set of conditions leads to nucleation of the apatite phase due to the incorporation of calcium and phosphate ions from the SBF solution into the amorphous silica [11].

4. Conclusions

This work presents a method for the fabrication of a biocompatible cobalt base alloy with a porous surface, which allows the incorporation of a bioactive material during the casting process. This procedure successfully traps a portion of the bioactive material mixed with maize husks to generate porosity within the material and facilitate the nucleation and growth of apatite when in contact with SBF. This method was successfully generated a biological response with the formation of a homogeneous ceramic layer, which according to its morphology and composition, may be apatite.

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