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Deposition of bioactive glass-ceramic thin-films by RF magnetron sputtering

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Abstract

Thin films of bioactive glass-ceramics have been deposited on titanium and silicon substrates by RF magnetron sputtering. The crystalline phases and the microstructure of the films have been characterized using XRD and SEM analysis; the main phases present were calcium–magnesium phosphates, enstatite and forsterite. The adhesion of the films on titanium has been examined by pull-off testing; the adhesion strength for as-deposited films was around 40 MPa, but after crystallization the strength dropped to about half this value due to the presence of cracks. Samples kept in simulated body fluid showed an apatite-like layer, suggesting that the films are bioactive.

Keywords: Adhesion; Biomedical applications; Films; Glass ceramics; X-ray methods; Sputtering

1. Introduction

The use of bioactive materials to restore body functions is a growing trend in modern medicine. These bioactive materials are namely used in dental and orthopaedic implants for encouraging the ingrowth of natural bone into the prosthetic device. In this situation the material surfaces have to be accepted by the body in order to obtain a strong bond between the implant and the bone.[1–4]

For obtaining good osteointegration metallic implants are normally coated with hydroxyapatite using the plasma-spraying technique. The chemical structure and composition of hydroxyapatite is almost the same as the mineral part of bone, but there are some problems using hydroxyapatite because it is fragile and presents a very slow osteointegration rate.[5–8] Newer deposition methods and a range of other coating materials have recently been advanced.[9–12] In particular, new bioactive glass-ceramics from the SiO_2–CaO–P_2O_5 family have good mechanical properties and induce better osteointegration then hydroxyapatite; they are very flexible to process because of the glass phase and there is also the possibility to manipulate the crystalline phases in subsequent heat treatments.

When plasma spraying is used with new bioactive glass-ceramics it is very difficult to control the layer thickness, adherence, roughness and porosity of surface and the nature of crystalline phases. The RF magnetron sputtering technique has been used to deposit biomaterials and hydroxyapatite but the changes that can appear if deposition parameters are varied were not studied in great detail.[10,11,13–19] With RF magnetron sputtering, dense uniform and adherent films with similar properties as the bulk material can be obtained and the main properties of the films can be modified by varying the deposition parameters.

In this work, new bioactive glass-ceramic coatings from the MgO–CaO–P_2O_5–SiO_2 system[20,21] were deposited on titanium and silicon substrates using RF magnetron sputtering.

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2. Experimental

Two types of substrates were used: titanium disks (99.6% Ti) and Si wafers 1×1 cm^2, oxidised for 72 h at 950 °C in wet oxygen flow. The oxidised silicon substrates were covered with a sputtered Ti layer, in order to have the same underlining material.[22] The sputtering targets were both 2 inches in diameter; Ti was 99.6% pure and the bioactive glass ceramic had the composition 17.25 MgO–52.75 $3CaO{\cdot}P_2O_5$–30 SiO_2 (wt.%). The glass ceramic targets were obtained by uniaxially pressing disks made from glass powder finer than 150 μm and sintered at 1200 °C. The base pressure in the sputtering chamber was 10^{-6} mbar (10^{-4} Pa) and the RF sputtering process was carried out in Ar or $Ar+O_2$ atmosphere with a ratio between Ar and O_2 flow of 2:1. This ratio was set using mass flow controllers.

The RF power for titanium deposition was 150 W. The Ti thickness was 200 nm, measured during deposition with a quartz thickness monitor. The pressure in the chamber was 1.01×10^{-2} mbar for films made with both Ar and $Ar+O_2$. The RF powers used for sputtering the bioactive glass ceramic target were 100 and 150 W and the deposition time was kept constant at 2 h. The deposits were made either at room temperature or at 750 and 850 °C in situ at 1×10^{-2} mbar (1 Pa) Ar and $Ar+O_2$. The samples prepared at room temperature were then heat-treated in a furnace for crystallization at 900, 950 and 1000 °C for 30 min, in air. The Ti substrates were coated with bioactive glass ceramic using the same Ar pressure, and an RF power of 100 W. Deposition time was 2 h and the deposition was performed at room temperature. After deposition, the samples were heat-treated in air at 950 °C for 30 min.

The coatings on $Si+SiO_2$ substrates were studied by X-ray diffraction (XRD, Rigaku D/MAX-B). The coated Ti substrates (8 mm discs) were used for SEM (Hitachi S-4100), and for adhesion tests by the "pull off" method on epoxy-glued specimens (contact area was 5 mm in diameter) at 0.083 mm/s. One coated sample was immersed in tris-buffered Kokubo's simulated body fluid (SBF) for preliminary in vitro bioactivity testing.

3. Results and discussion

Fig. 1 shows the change in thickness with deposition time for films made in Ar atmosphere, at 10^{-2} mbar (1 Pa) pressure and RF powers of 100 and 150 W; the deposition rates are 0.5 and 1.1 Å/s, respectively. The deposition rate at 100 W is very low, but it cannot be increased by increasing the RF power, because the depositions made at 150W damage the targets.

Fig. 2 Shows the XRD graphs for films made at 10^{-2} mbar (1 Pa) and 100 W RF power for 2 h. The films were heat treated in air for 30 min at 900, 950 and 1000 °C. In the following legend are the symbols for all crystalline phases that appear in the diffraction pattern.

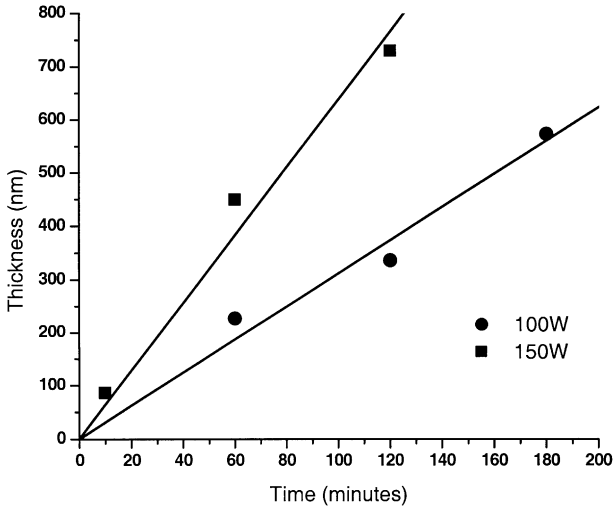

Fig. 1. Deposition rate for glasses sputtered under 10^{-2} mbar argon atmosphere.

Legend:
A- Calcium Magnesium Phosphate ($Ca_7Mg_2P_6O_{24}$);
O- Enstatite ($MgSiO_3$);
Δ- Forsterite (Mg_2SiO_4);
E- Titanium Oxide (TiO_2-brookite);
B- Titanium Oxide (TiO_2-rutile);
Γ- Silicon (Si with 100 orientation).

Graph 2′ in Fig. 2 is the same as graph 2, but at a higher magnification, because it was not possible to show all the peaks using the same scale. It can be seen that the coatings are crystallized for all heat treatment temperatures and composed of crystalline phases like enstatite, forsterite and calcium magnesium phosphate.

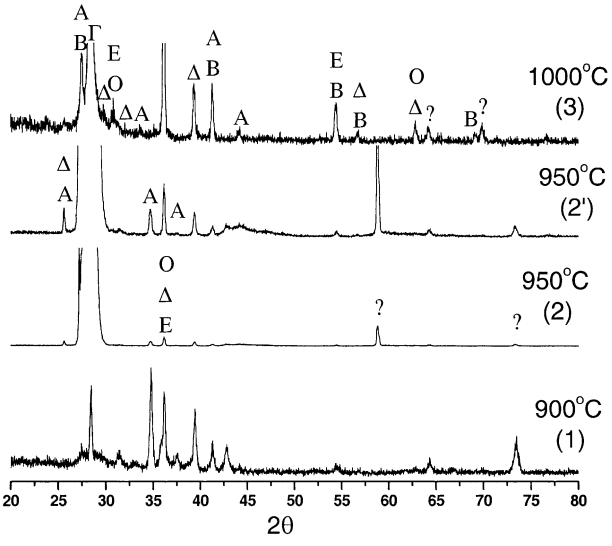

Fig. 2. XRD analysis for bioglass films heat treated in air for 30 min, at the temperatures shown.

The same figure shows the increase in the number of peaks when the crystallization temperature was raised.

The samples were also investigated using scanning electron microscopy (SEM). Fig. 3 shows the surface of a film on titanium, heat treated for 30 min at 950 °C. The glass layer was cracked and the titanium was oxidised; the white phase in the picture is the titanium oxide crystals growing through the film. Fig. 4 shows a film made in the same conditions, but after immersion in SBF for 2 days. A white precipitate identified by EDS as being rich in calcium, magnesium and phosphorus appears on the surface of the glass layer, even after this short immersion time, suggesting that the film is potentially bioactive.

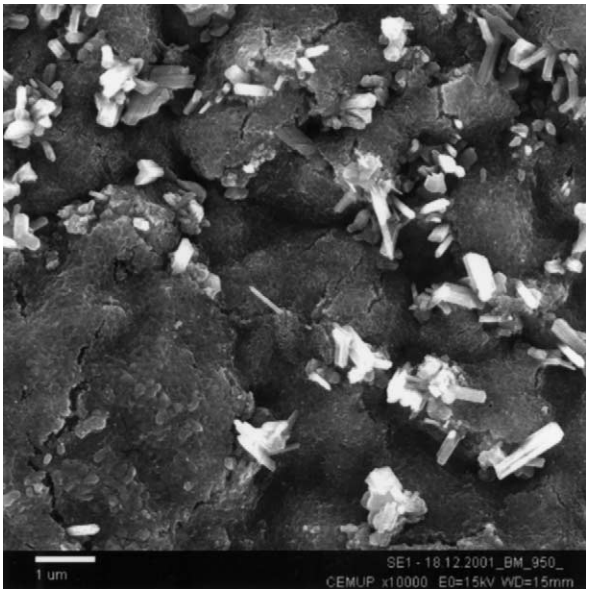

Fig. 3. Surface of bioglass film deposited on titanium and heat treated at 950 °C for 30 min, in air.

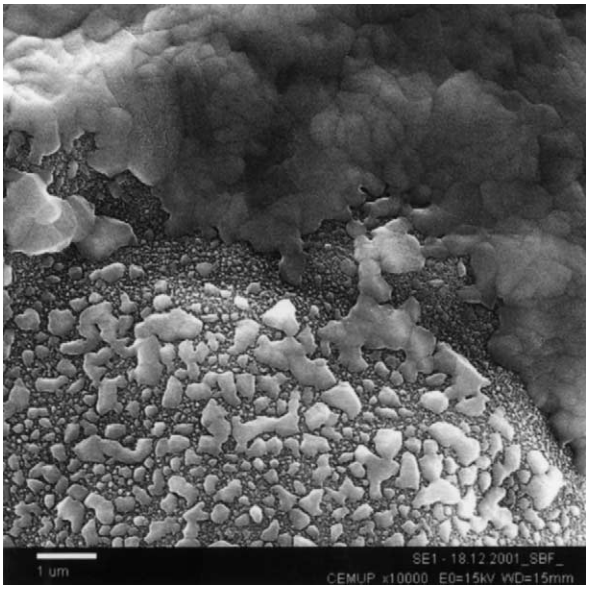

Fig. 4. Surface of film deposited on titanium, heat treated at 950 °C for 30 min in air, after immersion in SBF for 2 days.

The adhesion strength of the films deposited on titanium substrates was examined using the pull-off method. The strength of the epoxy glue used was measured as being 57.9±7.0 MPa. The tests were made on films before and after crystallization. Although the adhesion failure occurred between the film and the substrate for all samples, the values obtained for the amorphous films were high (41.1±4.5 MPa), being close to the strength of the glue for some samples. After crystallization the adhesion strength dropped to 16.3±1.9 MPa. This result can be explained by the presence of cracks appearing in the film after heat-treatment, as shown in Fig. 3.

4. Conclusion

Thin films of bioactive glass-ceramic have been deposited on titanium and titanium-covered silicon substrates by RF magnetron sputtering. The main crystalline phases after heat treatment in the 900–1000 °C range were enstatite, forsterite and calcium magnesium phosphate. The adhesion strength of the films has been examined by pull-off testing, with very good results for uncrystallized films (41.1±4.5 MPa); the values for crystallized films drop to less than half of that value, due to the presence of cracks. For in vitro experiments, one sample has been kept in simulated body fluid, and showed signs of bioactivity even after a short immersion time of 2 days.

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