

## MICROSCOPIC ANALYSIS OF SINTERED TITANIUM-HYDROXYAPATITE IMPLANT MATERIALS

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A new system of functionally graded materials is considered in this study. The samples were obtained by sintering titanium with hydroxyapatite powders. Hydroxyapatite type grains were prepared by sol-gel method. The sintering conditions lead to convenient values of samples density as compared with bone density. The bioactivity was tested in simulated body fluid (SBF). The size of hydroxyapatite type phases developed at the sample surface after soaking for a week in SBF is about hundreds of micrometers and tend to form a continuous network of the new developed bioactive layer.

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### 1. Introduction

Titanium is one of the most adequate metallic implant materials, because it is biocompatible and self-passivating. Even though the density of bulk titanium,  $4.5 \text{ g/cm}^3$ , is higher than that of bone, it is considerably lower than that of stainless steels, of approximately  $8 \text{ g/cm}^3$ . In order to improve the bone attachment, bioactive hydroxyapatite layer deposition is often used for coating of titanium implant. Biologically active hydroxyapatite similar to the mineralised bone tissue may be developed under *in vivo* simulated conditions [1].

Functionally graded materials consisting of metallic and ceramic components [2] are well known to improve the properties of several systems such as medical implant devices. Hydroxyapatite is known to be both biocompatible and bioactive material, however, due to its poor mechanical properties and design limitations is not suitable for applying as a load bearing implant. This could be overcome by using appropriate metallic enforcer with hydroxyapatite [3,4,5]. These solutions allow improved adhesion strength of the load bearing metallic component to the bone, resulting in shorter healing periods as well as predictable behaviour of the implant for longer periods of time. There are different techniques of producing HA appropriate for these purposes. Sol-gel technology offers an alternative technique for producing bioactive surfaces for improved bone attachment [6,7].

This study is focused on microscopic analysis of the graded layer structure before and after immersion in a simulated body fluid as the development of an active layer is expected.

### 2. Experimental

Titanium powder (0.01%Fe; 0.01%Al; 0.001%Si; 0.05%Mg) with the grain size of 63 - 100  $\mu\text{m}$  was used. Hydroxyapatite was prepared through a sol-gel technique, burnt and milled to obtain a powder with the grain size of less than 40  $\mu\text{m}$ . The precursor reagents were calcium

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nitrate  $\text{Ca}(\text{NO}_3)_2$  as a source of calcium ions and ammonium phosphate  $(\text{NH}_4)_2\text{HPO}_4$  as the phosphorus precursors. The Ca/P molar ratio in precursors was 1.67. The distilled water solution of phosphorus precursor was added to the calcium nitrate solution heated at  $90^\circ\text{C}$ . After mixing the sol-gel was washed at room temperature and dried for 2 hrs at  $110^\circ\text{C}$ . The dried sol-gels were heat treated in air for 3 hours at  $900^\circ\text{C}$  and for 1 hour at  $1150^\circ\text{C}$ . Samples with 10 weight % hydroxyapatite were mixed in a tubular mixer. Powders were pressed by applying forces of 30 and 35 kN in a rigid die with the surface of  $0.5\text{ cm}^2$ , without the use of any lubricant. The compacts were subsequently vacuum sintered ( $10^{-6}$  Torr) at  $1160^\circ\text{C}$  for 60 minutes, with dwelling stages at 200, 600 and  $800^\circ\text{C}$ . The bulk density of the sintered samples was determined using Archimedes method. X-ray diffraction analysis (DRX) was carried out on powder and sintered samples using a Bruker Avance diffractometer.

Bioactivity was investigated by an in-vitro test. The samples were soaked in simulated body fluid (SBF) solution [8]. SBF contains NaCl,  $\text{NaHCO}_3$ , KCl,  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 1N-HCl,  $\text{CaCl}_2$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NH}_2\text{C}(\text{CH}_2\text{OH})_3$  (trishydroxymethylaminomethane- as buffer). Exposure experiments in SBF of pH 7.4 were conducted between  $37$  and  $40^\circ\text{C}$  in polystyrene vials. The surfaces were characterized by optical microscopy. The SBF volume to sample surface area was around 30 ml. The surfaces were characterized by optical microscopy. The microstructure on randomly selected areas was observed with a stereo optical microscope Nikon Eclipse E200 equipped with CCD camera Nikon Kooply X995.

### 3. Results and discussion

The density of the samples sintered under 30 kN is  $3.05\text{ g/cm}^3$  and  $3.10\text{ g/cm}^3$  for those sintered under 35 kN. As mineral bone density is often inferred [9] the value of  $2.982\text{ g/cm}^3$ , so that the density of the sintered Ti-HA samples is very convenient for bone implant.

An essential requirement for an artificial material to bond to living bone is the formation of a biologically active HA-like layer on its surface in a body environment [10] and for this reason such materials are also called biomimetic systems [11,12].

The X-ray diffraction analysis carried out on sol-gel hydroxyapatite type powder shows that the as prepared samples are characterised by large structural disorder degree. Relative large peaks correspond to crystalline calcium phosphate. The applied heat treatments induce the crystallisation of several apatite type crystals.

In order to check the bioactivity the samples were soaked for 7 days in SBF with pH = 7.4 at temperatures ranging between  $37$  and  $40^\circ\text{C}$ . At the surface of the samples the Ti and HA type phases are relative homogeneous (Fig. 1a and 2a). After immersion in SBF one can observe after 7 days an expansion of calcium phosphate phase (Fig. 1b and 2b).

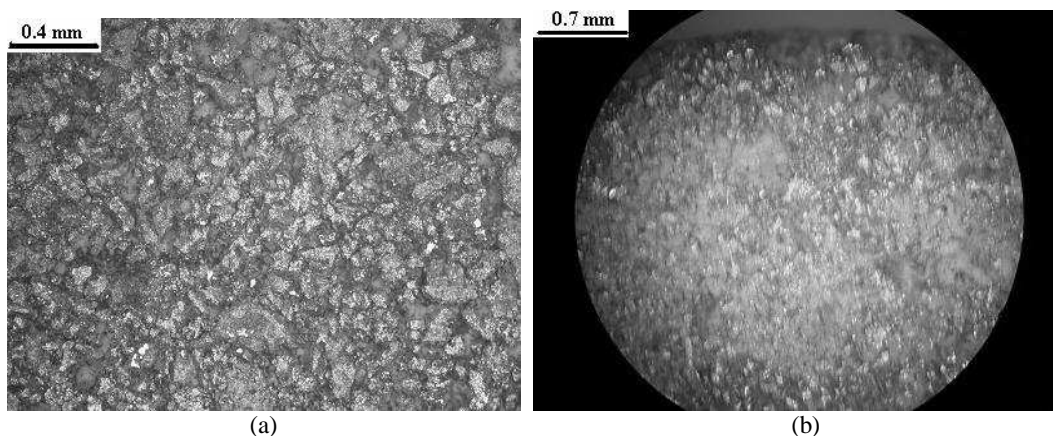


Fig. 1. Optical microscopy on sintered 90Ti-10HA samples (a) before and (b) after soaking in SBF. The samples were pressed by applying a force of 30 kN.

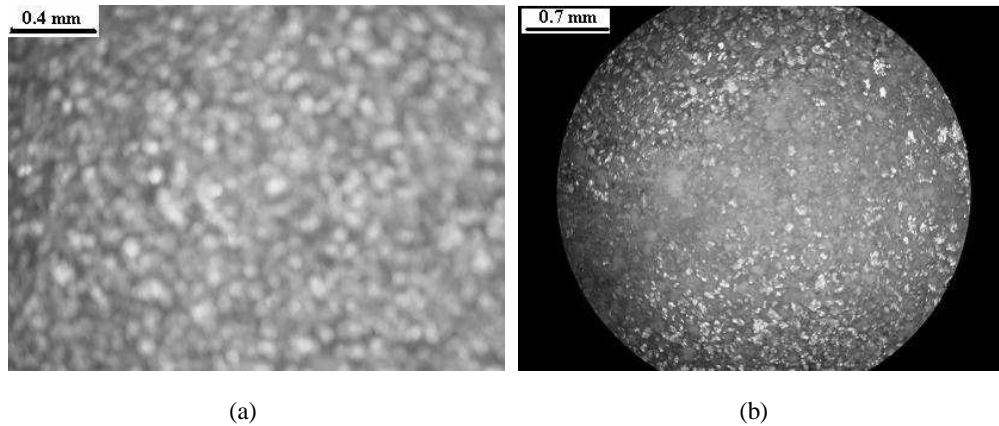


Fig. 2. Optical microscopy images on sintered 90Ti-10HA samples (a) before and (b) after soaking in SBF. The samples were pressed by applying a force of 35 kN.

The microtexture of the surface is dominated by HA type phase. After immersion in SBF, one observes that the bioactive phase is extended at the expense of titanium phase. The HA type phases developed at the surface of Ti-HA sintered samples after seven days immersion in SBF have the size up to 0.35 mm for samples sintered under 30 kN. Increase of sintering force from 30 to 35 kN leads to a finer phase distribution at the surface (Fig. 2a) and after SBF soaking the HA type phases have the size up to 0.50 mm. At the same time, in both cases, one remarks the tendency to form a continuous network of the new bioactive layer developed in interaction with the SBF as result of interface interactions and cations exchange, primary with the HA type phase.

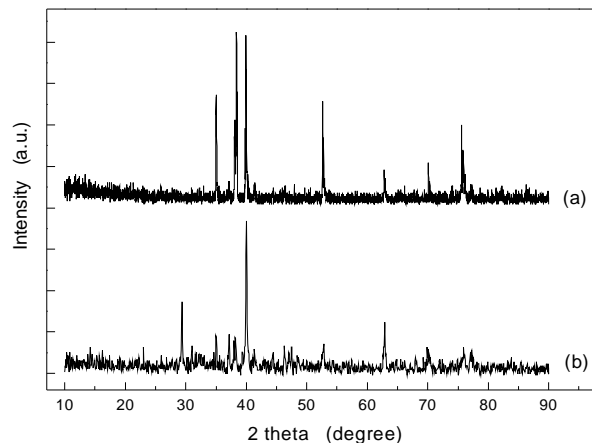


Fig. 3. DRX patterns of the 90Ti-10HA samples sintered under 30 kN (a) before and (b) after soaking in SBF.

Due to the fact that from XRD patterns (Fig. 3a and 4a) only  $\alpha$ -titanium lines of metallic phase [13] have been identified one can assume that the second phase consists of vitreous calcium phosphate or very distorted crystals. The titanium metallic phase seems to be formed by crystals preferentially oriented to the sample surface. These effects on the both phases are due to the relatively high sintering temperature (1160 °C) and high pressure used for samples processing. HA type polycrystalline phases developed at the surface of Ti-HA powder sintered samples after seven days immersion in SBF confirmed in XRD pattern (Fig. 3b and 4b) by appearance of new intense lines at  $2\theta = 29.5^\circ$  and  $35^\circ$ . An other effect of the SBF soaking is observed on the titanium microcrystals orientation on the sample surface, that are after seven days immersion in SBF randomly oriented.

The formation of the bioactive phase could be also induced by the Ti-OH groups, which reveals negative charge to interact with calcium ions in the SBF. The amorphous calcium titanate is postulated to reveal positive charge, thereby interacting with the phosphate ions in the fluid to form the amorphous calcium phosphate, which eventually crystallized into HA-like phase [1].

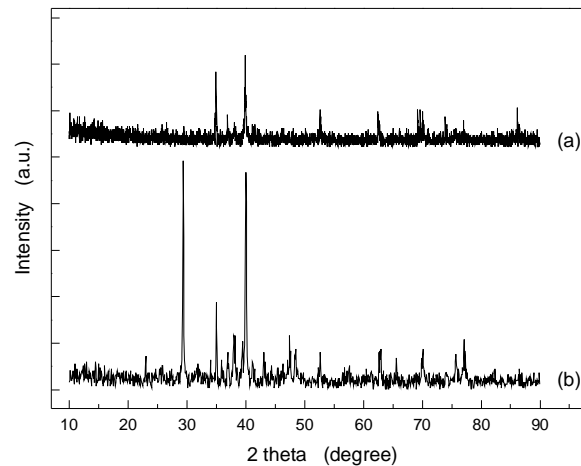


Fig. 4. DRX patterns of the 90Ti-10HA samples sintered under 35 kN (a) before and (b) after soaking in SBF.

#### 4. Conclusions

The density of the sintered Ti-HA samples is very convenient for bone implant. *In vitro* these materials proved to have bioactive behaviour. The development of a bioactive phase on the surface of Ti-HA sintered samples was evidenced by microscopic analysis after soaking for seven days in simulated body fluid. The size of HA type phases developed at the sample surface is about hundreds of micrometers and depends on the pressing force applied during sinterisation process. HA type phases trend to form a continuous network of the new developed bioactive layer. Before SBF immersion in the titanium metallic phase occur crystals preferentially oriented to the sample surface, but as a result of the interface processes with SBF titanium metallic grains become more randomly oriented.

#### References

- [1] L. L. Hench, Mater. Sci. Forum **293**, 37 (1999).
- [2] J. Aboudi, M.-J. Pindera, S. M. Arnold, J. Appl. Mech. **68**(5), 697 (2001).
- [3] T. Miyazaki, H. M. Kim, F. Miyaji, T. Kokubo, T. Nakamura, Bioceramics **10**, Elsevier Science LTD, 1997.
- [4] H. M. Kim, F. Miyaji, T. Kokubo, T. Nakamura, J. Ceram. Soc. Jpn. **105**(2), 111 (1997).
- [5] D. A. Cortes, J. C. Escobedo, A. Nogiwa, A. Munoz: Mater. Sci. Forum **442**, 61 (2003).
- [6] D. M. Liu, T. Troczynski, W. J. Tseng, Biomaterials **22**, 1721 (2001).
- [7] V. Simon, D. Muresan, C. Popa, S. Simon, Int. Conf. on Biomaterials BiomMedD'2004, Bucharest, 5-7 Nov. 2004.
- [8] T. Kokubo, S. Ito, Z. T. Huang, T. Hayashi, S. Sakka, T. Kitsugi, T. Yamamuro, J. Biomed. Mater. Res. **24**, 331 (1990).
- [9] E. M. Evans, B. M. Prior, S. A. Arngrimsson, C. M. Modlesky K. J. Cureton, J. Appl. Physiol. **91**(5), 2166 (2001).
- [10] T. Kokubo, H.-M. Kim, M. Kawashita, Biomaterials **24**, 2161 (2003).
- [11] Y. Abe, T. Kokubo, T. Yamamuro: J. Mater. Sci.: Mater. Med. **1**, 233 (1990).
- [12] J. F. Shackelford: Mater. Sci. Forum **293**, 99 (1999).
- [13] R. Sailer, G. McCarthy, JCPDS 44-1294, Int. Centre for Diffraction Data (1993).