Synthesis of Sintered Titanium - Apatite for orthopedic Applications

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الخلاصة

يعتبر التيتانيوم من اكثر المعادن ملائمة للزوارع الجراحية وخاصة في حقل جراحة العظام والاسنان لامتلاكه خاصية التوافقية الحياتية مع جسم الانسان ، وهنالك المواد التي تحوي في مكوناتها الكالسيوم والفسفور كمركبات الهيدروكسي ابتايت والمشابهة في تركيبها لمادة العظم فانها في الغالب يتم طلاء السبائك الطبية بها من اجل تحسين خواصها الميكانيكية

هذه الدراسة تعرض نمطا جديدا في حقل تحضير المتراكبات المستخدمة في الحقول الطبية حيث تم تحضير عدة عينات من متراكب التيتانيوم- هيدروكسي ابتايت الملدنة بدرجة حرارة ٩٠٠م° . يحضر مركب الهيدروكسي ابتايت بالطريقة الكيمياوية الرطبة ويجري خلط نسبة معينة منه مع مسحوق التيتانيوم وبحجوم دقائقية معروفة ومن ثم يتم تلبيد العينات بدرجات حرارية مختلفة من اجل التوصل الى كثافة مقاربة لكثافة العظم.

قياسات التوافقية الحياتية تتم بغمر النماذج المحضرة في مشابهات محاليل الجسم وقد وجد من خلال البحث ان سمك طبقة الهيدروكسي ابتايت على سطوح النماذج المغمورة اكثر من ١٠٠مايكرومتر وهي ملائمة من وجهة النظر الطبية كونها تسلك سلوكا كما هو السلوك الطبيعي للعظام عندما تصاب بتشوهات نتيجة الحوادث المختلفة وعندها تستخدم تلك المواد المتراكبة المحضرة ضمن المواصفات العالمية وذات الفعالية البايلوجية لترميم تلك التشوهات.

ABSTRACT

A new system of functionally graded materials is considered in this study. The samples were obtained by sintering titanium with hydroxyapatite powders (HAP) at 900◦c. Hydroxyapatite type grains were prepared by wet chemical method by addition of H_3PO_4 to a suspension of $Ca(OH)_2$ with close control of the all process parameters like pH, reaction temperature, ageing, digestion time and sintering temperature.

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 HAP type phases developed at the sample surface after soaking for several weeks in SBF is about 100 μm and tends to form a continuous network of a new developed bioactive layer.

1. Introduction

Titanium is one of the most adequate metallic implant materials, because it is biocompatible and self-passivity. Even though the density of bulk titanium, 4.5 g/cm^3, is higher than that of bone, it is considerably lower than that of stainless steels, of approximately 8 g/cm^3 (1,2).

Materials based on calcium-phosphate, such as hydroxyapatite, have been shown to enhance bone apposition to orthopedic implants; they do not form fibrous tissues, but instead an extremely thin, epitaxial bonding layer with existing bone. These materials have an excellent bioactive behavior but due to their low mechanical

properties they are mostly used as coatings on implant surfaces of substrates such as Ti-6Al-4V and other medical alloys (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 mineralized bone tissue may be developed under *in vivo* simulated conditions (4-7). Functionally graded materials consisting of metallic and ceramic components 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 (8, 9). These found to be preferred solving to improve adhesion strength of the load bearing metallic component to the bone, resulting in shorter healing periods as well as predictable behavior of the implant for longer periods of time. There are different techniques of producing HA appropriate for these purposes (10, 11).

It has been previously reported that sintered HAP ceramics showed marked plastic deformation, the so-called superplastic deformation, at around 1050 °C under appropriate loading conditions similar to other ceramics (12, 13)

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 and Ti = balance, Fluka Co, Germany) with the grain size of 63 - 100 μm was used. Hydroxyapatite was prepared through a wet chemical method, milled to obtain a powder with the grain size of less than 40 μm. The precursor reagents were calcium hydroxide $Ca(OH)_2$ 1M as a source of calcium ions and orthophosphoric acid H_3PO_4 0.6M as the phosphorus precursors. The Ca/P molar ratio in precursors was 1.67. The preferred heating temperature was found at 60 ^oC. Then the resulting precipitate was washed at room temperature and dried for 2 hrs at 110 ^oC. The powder heat treated in air for 3 hours at 900 °C and for 1 hour at 1150 °C.

Samples with 10% weight hydroxyapatite were mixed in a tubular mixer. Powders were pressed by applying forces of 40 and 50 kN with the surface of 1.0 cm^2.

X-ray diffraction analysis (XRD, Lab X 6000 Shimadzu- Japan) was carried out on powder and sintered samples. The surfaces were characterized by optical microscopy (Nikon- Japan).

Bioactivity was investigated by an *in-vitro* test; the samples were soaked in Ringer's solution as simulated body fluid (SBF) solution Wt/ L [NaCl (9.00), $NaHCO_3$

(0.20), $CaCl_2$ (0.24), KCl (0.43)] (1). Exposure experiments in SBF of pH 7.4 were conducted between 37 and 40 °C in polystyrene vials.

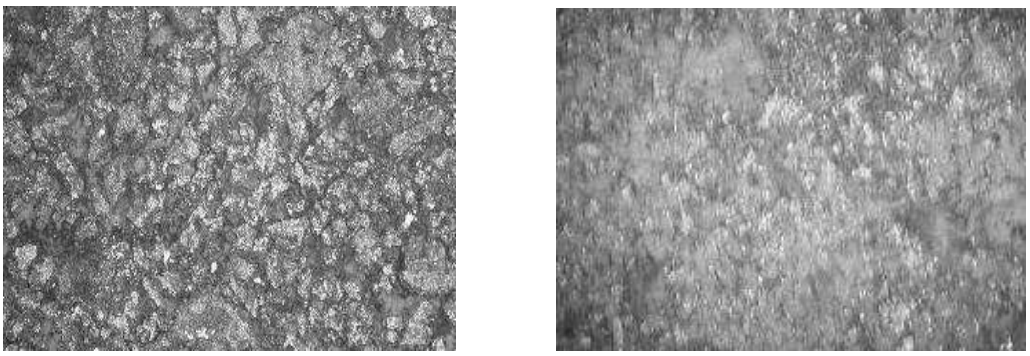
3. Results and discussion

The density of the samples sintered under 40 kN is 3.15 g/cm^3 and 3.23 g/cm^3 for those sintered under 50 kN. As mineral bone density is often inferred, the value of 2.982 g/cm^3, so that the density of the sintered Ti-HA samples is very convenient for bone implant (10, 13).

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, and for this reason such materials are also called biomimetic systems (5, 12).

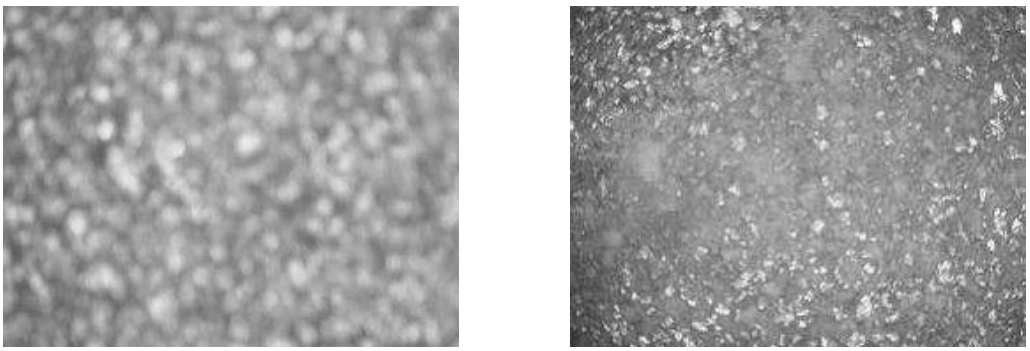
The X-ray diffraction analysis carried out on hydroxyapatite type powder shows that the as prepared samples (controlled samples) are characterized by large structural disorder degree. Relative large peaks correspond to crystalline calcium phosphate. The applied heat treatments induce the crystallization of several apatite type crystals. In order to check the bioactivity the samples were soaked for 2 weeks in SBF with pH = 7.4 at temperatures ranging between 37 and 40 ^{o}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 2 weeks an expansion of calcium phosphate phase (Fig. 1b and 2b)**.** Optical microscopy on sintered 90Ti-10HA samples (a) before and (b) after soaking in SBF. The microstructure of the surface is dominated by HA type phase.



a b

Fig. 1: Optical microscopy images on sintered 90Ti-10HA samples at 40 KN (a) before and (b) after soaking in SBF.



a **b**

Fig. 2: Optical microscopy images on sintered 90Ti-10HA samples at 50 KN (a) before and (b) after soaking in SBF.

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 2 weeks immersion in SBF have the size up to 0.35 mm for samples sintered under 40 kN. Increase of sintering force from 40 to 50 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 cautions exchange, primary with the HA type phase. Fig. 3; XRD patterns of the 90Ti-10HA samples sintered under 40 kN (a) before and (b) after soaking in SBF.

Due to the fact that in XRD patterns (Fig. 3a and 4a) only titanium lines of metallic phase (2, 11) have been identified, one can assume that the second phase consists of vitreous calcium phosphate or much 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 (1150 ^{o}C) and high pressure used for samples processing. Haydroxyapatite type polycrystalline phases developed at the surface of Ti-HA powder sintered samples after 2 weeks immersion in SBF confirmed in XRD pattern (Fig. 3b and 4b).

Another effect of the SBF soaking is observed on the titanium microcrystal orientation on the sample surface that are after 2 weeks 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 (5, 6).

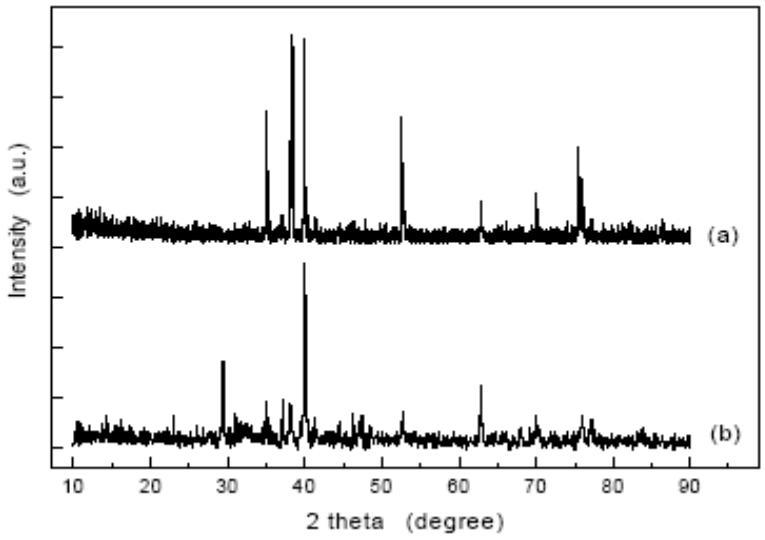


Fig. 3: XRD patterns of the 90Ti-10HA samples sintered at 30 kN (a) before and (b) after soaking in SBF.

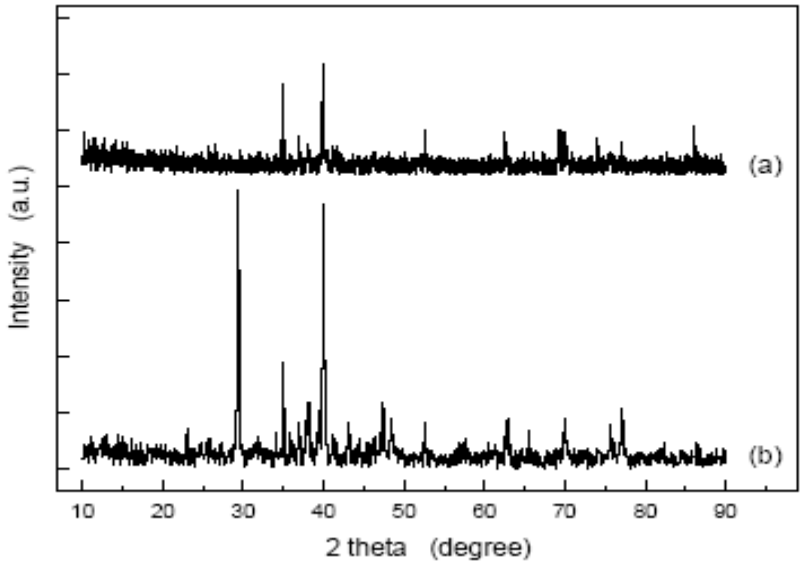


Fig. 4: XRD patterns of the 90Ti-10HA samples sintered at 35 kN (a) before and (b) after soaking in SBF.

4. Conclusions

The density of the sintered Ti-HA samples is very convenient for bone implant. *In vitro* these materials proved to have bioactive behavior. The development of a bioactive phase on the surface of Ti-HA sintered samples was evidenced by microscopic analysis after soaking for 2 weeks in simulated body fluid.

The size of HAP type phases developed at the sample surface is about hundreds of micrometers and depends on the pressing force applied during sintering process.

HAP 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.

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