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Materials Science and Engineering A 447 (2007) 19–26

MATERIALS SCIENCE & ENGINEERING A

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Development of titanium based biocomposite by powder metallurgy processing with in situ forming of Ca–P phases

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Received 24 May 2006; received in revised form 21 July 2006; accepted 26 October 2006

Abstract

Composites of titanium and calcium–phosphorus phases were developed by powder metallurgy processing and evaluated for bioactivity. Titanium hydride powder and precursors of calcium and phosphorus in the form of calcium carbonate and di-ammonium hydrogen orthophosphate were mixed in different proportions, compacted and calcined in different atmospheres. The calcined compacts were subsequently crushed, recompacted and sintered in vacuum. In situ formation of bioactive phases like hydroxylapatite, tricalcium phosphate and calcium titanate during the calcination and sintering steps was studied using X-ray diffraction. The effect of calcination atmosphere on density, interconnected porosity, phase composition and modulus of rupture of sintered composites was examined. The sintered composites were immersed in simulated body fluid for 7 days to observe their in vitro behaviour with XRD and FTIR spectroscopic identification of deposits. Composites with 10 wt% precursors sintered from vacuum calcined powder gave the best results in terms of bioactive phases, density and strength.

Keywords: Titanium; Calcium; Phosphorus; Hydroxylapatite; Biocomposite; Load bearing implants

1. Introduction

The metallic materials most commonly used for biomedical applications are stainless steels, cobalt based alloys, titanium and titanium based alloys. Among these, titanium and its alloys are of considerable interest in both medical and dental fields because of their biocompatibility and low density coupled with good balance of mechanical properties and corrosion resistance. These alloys are suitable for implant devices replacing hard tissue, such as artificial hip joints, artificial knee joints, bone plates, dental implants, etc. [1], as well as for repairing some soft tissues [2]. However, almost all metallic implants, including titanium, are bioinert: while not rejected by the human body, these implants cannot actively interact with the surrounding tissues and thus cannot prevent the implant from being loosened [3,4]. One of the established ways of making metallic implants bioactive is to coat with hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, which constitutes about 70% of natural bone [5,6]. More commonly, synthetic hydroxylapatite (HA) has been plasma spray coated on Ti substrates before implantation [7]. There are also other Ca–P compounds such as amorphous calcium phosphate (ACP), octa-calcium phosphate (OCP), tricalcium phosphate (TCP) and biphasic calcium phosphate (BCP) that can also impart bioactivity to implant materials [7]. Thus, coated implants offer the possibility of combining the strength of metals with bioactivity of the ceramics [8].

Coated implants have inherent weaknesses of mismatch of thermal expansion coefficient and delamination at the metal–ceramic interface [9]. In order to overcome the limitations of coated implants, the present study was undertaken to develop a biocomposite from powders containing titanium, calcium and phosphorus. Composites with varying contents of titanium, calcium and phosphorous were synthesized through powder metallurgy under different processing conditions and their in vitro bioactivity was studied. Powder metallurgy processed composites having in situ formed bioactive calcium–phosphatic phases in titanium matrix are expected to be better in anchoring to the host environment as tissues grow not only on to the surface of the implant but also into the pores present in the implant. The resultant composite combining the superior mechanical

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doi:10.1016/j.msea.2006.10.154

Table 1
Properties of titanium sponge

Properties	Values
Chemical composition (%)	
Ti	99.7
Na	0.065
Mg	N.D.
Mn	N.D.
K	0.007
Fe	N.D.
Ca	0.005
C	0.015
Size (mm)	15–25

Table 2
Properties of $TiH_{1.924}$ and dehydrided Ti metal powder

Properties	Hydride powder	Metal powder
Chemical composition (%)		
Ti	95.79	99.20
C	0.008	0.001
Na	0.080	0.030
Mg	N.D.	N.D.
K	0.009	0.004
Mn	0.004	0.010
Fe	N.D.	N.D.
Ca	0.013	0.010
Sieve analysis (%)		
$-250+180$ μm	09	10
$-180+150$ μm	13	15
$-150+106$ μm	18	18
$-106+45$ μm	36	36
-45 μm	24	21
Apparent density (g/cm^3)	1.76	1.68

properties of metals with bioactive properties of ceramics can be used as implants for load bearing applications [10].

2. Experimental work

High purity titanium sponge lumps having composition as given in Table 1 were hydrided, crushed to obtain titanium hydride and subsequently dehydrided to titanium metal powder. The properties of the powders obtained are given in Table 2. Calculated quantities of calcium carbonate [$CaCO_3$] and di-ammonium hydrogen *ortho*-phosphate [$(NH_4)_2HPO_4$] with a calcium to phosphorus ratio of 1.3:1 were blended with titanium metal or hydride powders in separate experiments. The proportion of Ca and P precursor mix in the blend was varied from 10 to 30 wt%. The compositions of different blends are given in Table 3. Each powder blend was mixed for 30 min in a ball mill, with a ball to powder ratio of 1:1, followed by 30 min of mechanical milling at 250 rpm in Fritsch planetary mill Pulverisette 5 under inert argon atmosphere. Stainless steel balls and vials were used for the purpose of milling with a ball to powder ratio of 15:1. The milled powder (−250 μm) was characterized using Cilas 920 laser diffraction analyzer for particle size distribution, Bruker's D8 Advance XRD for phase content and Jyobin Vyon JY 38S inductively coupled plasma atomic emission spectroscopy (ICP-AES) for Ca and P concentrations.

The powders were compacted without any lubricant addition at 250 MPa, calcined at 1000 °C for 1 h and reground to powder (−250 μm) for subsequent processing. The atmosphere of calcination was selected from among hydrogen, argon and vacuum. These calcined powders were compacted without any lubricant addition at 600 MPa to specimens of size 10 mm diameter and 6 mm height. All calcined specimens were sintered at 1150 °C in a vacuum of 1×10^{-2} Pa (1×10^{-4} mbar). The green and sintered densities of compacts from powders calcined in different atmospheres are given in Table 3. Density of sintered composites was obtained both from dimensions and by Archimedes principle. Interconnected porosity of the samples was also computed from impregnation by xylene. Rectangular specimens (31.5 mm × 12.5 mm × ~4 mm thickness) were also compacted and sintered from calcined powders and tested for modulus of rupture (MOR) using three-point bend test in an Instron universal testing machine. MOR values were calculated by means of formula:

$$\text{MOR (MPa)} = \frac{3PL}{2bd^2} \quad (1)$$

where P is the breaking load in N, L the span length (26.3 mm), b the specimen width in mm and d is the specimen thickness in mm. The composites were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and inductively coupled plasma atomic emission spectroscopy.

For bioactivity studies, simulated body fluid (SBF) was prepared according to Tas's method [11]. Sintered composites were immersed in 50 ml of SBF and weight change of composites, recorded at the end of 7 days. Initial and final concentrations of Ca, P, Mg, Na and K in SBF were determined using ICP-AES analyzer. Morphology of the samples before and after immersion in SBF was studied using JEOL scanning electron microscope

Table 3
Green and sintered densities of composites from powders calcined in different atmospheres

Sample	$TiH_{1.924}$ powder (wt%)	Precursor mix of Ca and P (wt%)	Sintered density of H_2 calcined powder (g/cm^3)		Sintered density of Ar calcined powder (g/cm^3)		Sintered density of vacuum calcined powder (g/cm^3)	
			Green	Sintered	Green	Sintered	Green	Sintered
PA	90	10	2.84	3.05	3.44	3.85	3.83	3.91
PB	80	20	2.88	2.93	2.92	2.96	2.76	2.94
PC	75	25	2.90	2.82	2.81	2.75	2.35	2.61
PD	70	30	2.29	2.23	2.74	2.62	2.38	2.4