A STUDY OF THE MECHANICAL PROPERTIES AND BIOACTIVITY OF FUNCTIONALLY GRADED TITANIUM MATRIX COMPOSITES REINFORCED WITH BIOACTIVE PARTICLES

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SUMMARY: A functionally graded material (FGM) has a progressively varying composition, structure and properties as a function of position within the material. Functionally graded titanium matrix composites with bioactive reinforcement have been fabricated from titanium, hydroxyapatite (HA), Bioglass® (Bg), and Apoceram (Ap) using a powder metallurgy route.

The mechanical properties of the FGMs were assessed, using three point bend tests to determine the bend strength and single edge notch bend tests to determine the fracture toughness. Microstructural studies were also undertaken of the fabricated materials and fracture surfaces. An improvement was observed in the toughness of the FGMs over the composites, with the FGMs showing a more “graceful” failure. The bioactivity of the FGMs were also assessed and the results obtained indicate the viability of these FGMs as medical implants.

KEYWORDS: functionally graded, biomaterials, biocompatibility, bioactive, titanium matrix

INTRODUCTION

Functionally graded materials (FGMs), a class of materials whose composition and microstructure vary continuously or discretely along a specific direction, are becoming more and more of a familiar concept.

FGMs are of increasing interest in advanced engines and airframes and in other applications such as armour, electric and dielectric devices and medical implants since the compositional gradient can be tailored towards specific requirements. The latter application is the one in which the work reported in this paper is aimed.

There is a fundamental requirement that an implant material and the tissues of the body coexist without either having an undesirable or inappropriate effect on the other. The phenomena related to this mutual coexistence are collectively referred to under the term of ‘biocompatibility’ defined as ‘the ability of a material to perform with an appropriate host response in a specific application’[1]. The properties required of a biomaterial are quite
complex, as the human body is known to be one of the most hostile environments within which a material can be placed. Titanium and titanium alloys have been used increasingly in the area of bone replacement, orthopaedic surgery and dental implantation and are regarded universally as having outstanding mechanical properties, corrosion resistance and biocompatibility.

In the early 1970s it was discovered that a certain compositional range of calcium phosphate silicate based glasses did not produce a fibrous capsule when implanted in bone, but instead produced a strongly adherent bonded interface[2,3]. The term bioactive has subsequently been used to describe all biocompatible materials which form a bond with living tissues. Subsequently certain calcium phosphate crystalline materials e.g. hydroxyapatite and fluorapatite, and some glass-ceramics were also shown to be bioactive.

The principal limitation in the use of the glass, glass-ceramic group of bioactive materials, is that to varying extents they are weak, brittle and hard to shape, thus unsuitable for most high load bearing applications.

Bioactive glasses contain SiO$_2$, Na$_2$O, CaO and P$_2$O$_5$ in specific proportions, namely:
- less than 60 mole % SiO$_2$
- high Na$_2$O and CaO content
- high Ca/P$_2$O$_5$ ratio

These features make the surface highly reactive when exposed to an aqueous medium and result in rapid formation of carbonate apatite (CA) on the surface[4]. The rate of formation of the CA layer has been shown to correlate with the bioactivity index (IB) of the material - i.e. the rate and type of bonding to tissues[5].

Bioactive ceramics, glasses and glass-ceramics have the singular advantage over other implant materials, such as titanium which is not bioactive, in that they remove the necessity for fixation and its attendant problems.

The limitations of these brittle bioactive materials were addressed by incorporating in a titanium matrix various weight percentages of bioactive reinforcement, using powder metallurgy methods[6], the aims being to obtain bioactivity from the reinforcement and superior toughness to conventional bioactive materials from the titanium matrix; with preliminary investigation of the former while the latter has been confirmed. In addition, these composite materials were studied in an attempt to first understand the mechanical behaviour of the monolithic composites, then to apply that knowledge to the study of the FGMs. Early work on titanium/hydroxyapatite FGMs was undertaken by Bishop[7]. Significantly improved mechanical properties were reported for these FGMs over the monolithic composites. Interfacial weakness between the layers however was a recurring problem. The interlayer interfacial weakness has been ameliorated in Al-SiC by providing a semi-continuous variation in composition rather than a stepwise variation by introducing a vibration stage in the pre-pressing processing [8]. The work described here builds on these earlier studies of FGMs, in particular titanium-hydroxyapatite FGMs and extends it to other bioactive reinforcement FGM systems, namely titanium - Bioglass® and titanium - Apoceram, and to the assessment of bioactivity.

The reinforcing bioactive glass-ceramic phase in the titanium matrix functionally graded composite material investigated in this paper, Apoceram, is a glass ceramic based on the
Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$ system with P$_2$O$_5$ used as a nucleating agent. It consists of interlocking spherulites of apatite [Ca$_5$(PO$_4$)$_3$OH,F] and wollastonite [CaSiO$_3$] crystal phases. The reinforcing phase of Bioglass® is also of the Na$_2$O-CaO-Al$_2$O$_3$-SiO$_2$ system and is a glass.

The bioactive properties of the FGMs are assessed using Fourier Transform Infrared Spectroscopy (FTIR) and Fourier Transform Raman Spectroscopy (FT Raman). The sensitivity of FT-Raman to the changes in the vibrational modes of P-O with nucleation of the CA crystallites makes it an appropriate analysis tool for the formation of the carbonate apatite (CA) layer. The C-O vibrational modes are also very intense in Raman spectra[9].

**EXPERIMENTAL PROCEDURE**

**Material Fabrication**

Titanium powder (Deeside Titanium Ltd., Active Metals Ltd.), hydroxyapatite powder (Jesse Shirley & Son Ltd.), Bioglass® (U.S. Biomaterials Corporation) and Apoceram (fabricated at Imperial College) were used to make the functionally graded composite materials. The particle size for the titanium powder was between 30 and 84 µm. The hydroxyapatite (HA) used was found to have an agglomerate particle size of between 18 and 55 µm but the individual crystal size was submicron. The Bioglass®(Bg) had a particle size range of 10 - 55 µm while the particle size for Apoceram(Ap) was below 55 µm. The different processes employed in the fabrication of the FGM systems are schematically shown in Figures 1 and 2.
Figure 2 Fabrication using cold isostatic pressing route

Cold Compaction

The appropriate weight proportions of the titanium and bioactive reinforcement, to give 10 and 20 weight percent reinforcement, were mixed in a Turbula 3D path rotating mixer for one to one and a half hours. The powders were layered into a 60 mm steel die, pre-lubricated by zinc stearate in acetone. The die was placed in a mechanical vibrator for approximately thirty seconds, to expel air, settle the powders and make the interfaces between the layers more gradual. The powders were then compressed to produce green billets with heights between 3 and 4 cm, and approximately 70 to 80% theoretical density.

Cold Isostatic Pressing and Heat Treatment

Selected green billets were placed in a hydraulic isostatic press and pressed for a holding time of approximately two minutes at 400 MPa. The pressed billets were heated in a controlled atmosphere furnace to 850°C at a rate of 150°C/h. The billets were cooled at the same rate to approximately 200°C then removed from the furnace and allowed to cool in air to room temperature.

Hot Compaction

The green billets were lubricated and then preheated in an argon circulating electric furnace to the 750°C for the Ti-HA FGMs and 1000°C for the Ti-Ap and Ti-Bg FGMs. The heated billets were transferred to a 60 mm steel die, also lubricated, in a 5 MN hydraulic press and pressed to a maximum pressure of 1.6 GPa at approximately the preheat temperature. The billets were then transferred back to the furnace and furnace cooled to room temperature.
MATERIAL CHARACTERISATION

Structural Analysis

An automated diffractometer, with copper $K_α$ radiation, and operating at 40kV and 40mA was used to carry out X-ray analysis on the FGM samples. Microstructural studies using ion, the titanium matrix heats up when exposed to the laser, making it difficult to analyse the surface layers.

Mechanical Tests

The flexural strength of the materials was determined using a three point bend test with specimens of nominal dimensions of 45 x 5 x 10 mm. Prior to testing, specimens were ground and polished to a 1 µm diamond finish. The fracture toughness measurements were performed according to BS 7448 : 1991 for plain strain fracture toughness testing of metallic materials. The procedure ideally should include fatigue pre-cracking from a machined notch. The brittle nature the of high reinforcement content layer made this extremely difficult, so the tests were performed without fatigue pre-cracking. It was felt that if other validity criteria were met, then the difference between fracture toughness measurements in fatigue pre-cracked samples and those that were not would be minimal. Previous work done on Triballoys by Halstead[10] established that for fracture toughness values up to 19 MPa√m, there is very little difference between the data from samples with and without fatigue precracking.

Bioactivity Assessment

Immersion in Simulated Body Fluid

Samples of Ti-HA, Ti-Ap, Ti-bioglass® FGMs were cut to approximate dimensions of 10 x 10 mm and approximate thickness of and polished to a 1 µm finish on either side. They were then immersed in simulated body fluid (SBF) for varying periods (Table 1), at 37°C. The simulated body fluid was prepared by dissolving Ringers tablets in distilled water to the appropriate concentration, to yield the approximate ion concentration given in Table 2. When the samples were removed from the SBF, they were placed in a dessicator to dry off any excess moisture.

<table>
<thead>
<tr>
<th>Sample &amp; Composition</th>
<th>Immersion Period (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0/10wt%HA Ti-HA FGM</td>
<td>✔</td>
</tr>
<tr>
<td>0/10/20wt%HA Ti-HA FGM</td>
<td></td>
</tr>
<tr>
<td>0/10/20wt%BgTi-Bioglass® FGM</td>
<td>✔</td>
</tr>
<tr>
<td>0/10/20wt%ApTi-Apoceram FGM</td>
<td>✔</td>
</tr>
<tr>
<td>Ti-20%Bioglass</td>
<td>✔</td>
</tr>
</tbody>
</table>
Table 2: Ion Concentration (mM) of SBF and Human Blood Plasma[11]

<table>
<thead>
<tr>
<th>Ion</th>
<th>Simulated Body Fluid</th>
<th>Blood Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>142.0</td>
<td>142.0</td>
</tr>
<tr>
<td>K⁺</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>147.8</td>
<td>103.0</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>4.2</td>
<td>27.0</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Spectroscopic Analysis

The dried samples were analysed using Fourier Transform Infra Red Spectroscopy (FTIR) and Fourier Transform Raman Spectroscopy (FT-Raman). The FTIR was performed using a Nicolet 800 spectrometer in conjunction with a Nic-palnoe® microscope. The spectra were obtained at 4cm⁻¹ resolution averaging 256 scans. The FT Raman spectra were recorded using a Nicolet 910 spectrophotometer, equipped with an Nd:YVO₄ near-infrared laser, which eliminates the problems of sample flourescence and photo-decomposition characteristic of conventional Raman instruments with high power lasers.

RESULTS AND DISCUSSION

Microstructure

Generally the HA containing FGMs fabricated at the lower processing temperature (750⁰C) were found to have a partially sintered Ti matrix with some porosity and unsintered agglomerate reinforcement (Figure 3). The microstructure of the Ap and Bg containing FGMs fabricated at 1000⁰C, contained less porosity in the titanium matrix (Figure 4). There was evidence of some crystallisation in the Bioglass® (confirmed in the XRD trace) and further crystallisation in the Apoceram glass-ceramic. In the Ti-HA FGM the percentage of porosity, both micro porosity and macro porosity, was higher in the reinforcement than in the titanium. Plasma spraying of metal substrates with HA has been reported as problematic because of the thermal decomposition reactions which occur at the high temperatures required[12]. It has also been reported that the decomposition of hydroxyapatite can be induced at significantly lower temperatures (850⁰C) than previously described in literature (∼1300⁰C) through the presence of Ti [13]. The XRD results confirmed that the HA remained as HA, suggesting that little or no thermal decomposition of HA had taken place, despite the presence of Ti. There is also, little in the microstructural examinations to suggest the presence of reaction products with HA. It is surmised that the starting powder of titanium must have contained a thin layer of oxide which served as a passivating layer and prevented reaction between the hydroxyapatite and the titanium. The presence of titanium oxide was confirmed through secondary ion mass spectroscopy on the Ti-HA FGM. Although no quantitative analysis was available through this technique, it was concluded that the % volume content of the TiO₂ was
minimal and was not detected by XRD. There is evidence however of a reaction layer
between the Ti and Apoceram (Figure 4) and Bioglass®. Theoretical thermodynamic
calculations, taking into account the higher processing temperature for the Ti-Ap and Ti-Bg
FGMs suggest that reactions with the phases present in Apoceram and Bioglass® are
thermodynamically more favourable and may thus account for the reaction layers observed.

![Secondary electron image of the 10% layer in a double layer (10/20%) titanium-hydroxyapatite FGM](image1)

*Figure 3: Secondary electron image of the 10% layer in a double layer (10/20%) titanium-hydroxyapatite FGM*

![Back scattered electron image of the 20% layer in a triple layer (0/10/20%) titanium-apoceram FGM](image2)

*Figure 4: Back scattered electron image of the 20% layer in a triple layer (0/10/20%) titanium-apoceram FGM*

**Fractography**

Examples of the fracture surfaces of the samples investigated indicated that the mode of micro
fracture for all the composite FGMs was predominantly brittle fracture. The titanium regions
had undergone mainly cleavage fracture (Figure 5, Figure 6) although some localised ductile fracture is observed (Figure 5). Crack propagation in the composite region occurred predominantly through the reaction layer at the reinforcement/matrix interface in the Ti-Bg and Ti-Ap FGMs (Figure 6). In the Ti-HA FGM some intergranular fracture was also observed through the reinforcement. The contributory factors therefore to the improvement in fracture toughness and work of fracture (Table 3) as one moved from composite to FGM are not due to major changes in the micro fracture mechanism but are almost certainly related to crack retardation as described in the next section.

**Mechanical Properties**

The fracture toughness values showed a significant improvement for the FGMs over the composites and monolithic reinforcement. The FGMs demonstrated a much more graceful failure with some load carrying capacity after failure had commenced. The load-time curves presented in Figure 7 and Figure 8 are typical for both SENB fracture and three point bend tests. The graceful nature of the material failure is clearly demonstrated, leading to much greater values for the work of fracture for the FGMs. Modelling work using finite element analysis on Ti-HA FGMs [7] has shown that the high reinforcement content surface layers are under residual compressive stress.

![Figure 5: Secondary electron image of the fracture surface of the titanium (0%) layer in a double layer (0/10%) titanium-Bioglass® FGM](image)

![Figure 6: Secondary electron image of the fracture surface of the 10% layer in a triple layer (0/10/20%) titanium Apoceram FGM](image)
Table 3 Mechanical Properties

This accounts for the higher $K_{IC}$ of the FGMs compared to their conventional composites counterparts. Furthermore the interface between the layers in an FGM hindered primary crack propagation. This was particularly noticeable at the 0/10 wt%HA interface where propagation into the 0% layer usually took place after some delamination. Another feature often associated with propagation through an interface was crack branching (Figure 9) which effectively reduces $K_I$ at the crack tip. For these reasons the FGMs have superior values for the work of fracture.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Toughness(MPa$^{1/2}$)</th>
<th>Work of Fracture(J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-HA$_{10}$ FGM triple layer (10/20/30 wt%HA)</td>
<td>13</td>
<td>1.2</td>
</tr>
<tr>
<td>Ti-HA$_{10}$ FGM triple layer (0/10/20 wt%HA)</td>
<td>11</td>
<td>0.9</td>
</tr>
<tr>
<td>Ti-Bioglass®$_{10}$ FGM triple layer (10/20/30 wt%Bioglass®)</td>
<td>12</td>
<td>0.1</td>
</tr>
<tr>
<td>Ti-Bioglass®$_{10}$ FGM double layer (0/10 wt%Bioglass®)</td>
<td>21</td>
<td>3.0</td>
</tr>
<tr>
<td>Ti-Bioglass®$_{10}$ FGM double layer (0/10 wt%Bioglass®)</td>
<td>11</td>
<td>0.1</td>
</tr>
<tr>
<td>Ti-Ap$_{10}$ FGM triple layer (0/10/20 wt%Ap)</td>
<td>9</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Figure 7: Load-time curve for a hot pressed Ti-HA FGM triple layer (0/10/20%) in SNEB fracture toughness testing

Figure 8: Load time curve for a cold isostatically pressed double layer (10/20%) Ti-Bg FGM in SNEB fracture toughness testing
Bioactivity Assessment

FTIR Analysis

The phosphate peak in the carbonate apatite layer is detected in the high reinforcement containing layer (20% Bg) and the monolithic Ti-20% Bg composite after 24 hours immersion. The peak increases with immersion time and is well defined at 120 hrs. The phosphate peak is centred at 1040 cm\(^{-1}\). A small peak, due to the C-O vibrational modes is also observed at 907 cm\(^{-1}\). The FTIR spectra for the high reinforcement containing layer in the titanium-bioglass FGM is shown in Figure 10. Figure 11 shows the FTIR spectra for the titanium-20% Bg composite. No discernible peaks of formation of carbonate apatite are observed in the spectra for the high reinforcement containing triple layer Ti-Ha and Ti-Ap FGMs prior to 72 hours exposure. After 72 hours exposure to SBF however there is an increase in the phosphate peak in the Ha containing FGM, indicating possibly, some deposition of carbonate apatite (Figure 12). The results obtained are consistent with the bioactive behaviour of Bioglass® which is known to be more bioactive than hydroxyapatite, with carbonate apatite peaks detected as...
early as after 30 minutes exposure to SBF. The spectra for the 20%Ha layer in the Ti-Ha FGM is shown in Figure 12.

**FT - Raman Analysis**

This technique did not yield any additional information on the formation of carbonate apatite in the samples investigated. This is believed to be due to a number of reasons. One of these is that the layer is not yet crystalline and as a result does not possess a very good Raman signal.

*Figure 11*  **FTIR spectra for the 20% layer in the Titanium-hydroxyapatite triple layer FGM for various SBF exposure periods**

*Figure 12: FTIR spectra for the Titanium-20%Bioglass® composite for various SBF exposure periods*

In addition, the titanium matrix heats up when exposed to the laser, making it difficult to analyse the surface layers.
CONCLUSIONS

Titanium matrix composite FGMs with bioactive reinforcement were successfully produced using powder metallurgy routes, with adequate mechanical properties and “graceful” fracture behaviour. The preliminary bioactivity studies undertaken show that these functionally graded titanium matrix composites with bioactive reinforcement show promise. Further work needs to be done on assessing their performance in vivo. With optimum reinforcement compositions however, these FGM materials could herald a new and exciting future in biomedical implants.

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REFERENCES


