Design and characterization of bioceramic coating materials for Ti6Al4V

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Abstract Novel bioceramics used as coating materials for Ti6Al4V were designed and characterized by adjusting the thermal expansion coefficient. The results show that the thermal expansion coefficient (α) of 6PM-B5-F4 coating is 10.1 × 10⁻⁶/°C, which matched that of Ti6Al4V. The bonding strength between the alloy and 6PM-B5-F4 coating was further measured by the longitudinal pull-off test. The in vitro response of the bioceramic was studied by immersing the specimens in simulated body fluid (SBF). The bioceramic morphology and structure were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transformed infrared spectroscopy (FTIR).

Keywords Ti6Al4V, bioceramic, bonding strength, thermal expansion coefficient, bioactivity

1 Introduction

Ti6Al4V has been widely used as an orthopedic implant due to its excellent mechanical properties [1]. However, the alloy is bioinert and noxious, which can result in implant failure and toxicosis in the body [2]. The metallic implants with bioceramic layers have excellent bioactive performance, and the design is a good solution for the problems above. It should be noted that physical properties, especially the thermal expansion, are discontinuous at the interface between the alloy substrate and the bioceramic, which weakens the interface bonding strength. Consequently, this remarkable study focuses on the design of the bioceramic coating materials used for titanium alloys.

There are several key design criteria that should be necessary [3,4]: (i) the thermal expansion of the bioceramic should be tailored to match that of Ti6Al4V. (Typically, it is preferred that the thermal expansion of the bioceramic be slightly lower than that of metals, resulting in small compressive stresses). (ii) The softening point of the bioceramic (Ts) should be low enough to keep the firing temperature below the α → β transformation temperature of Ti6Al4V (955°C–1010°C). (iii) The hydroxycarbonate (HCA) can be deposited on the surface of the bioceramic in SBF.

Previous studies [4,5] have shown that the simplest way of reducing the thermal expansion coefficient of bioceramics is to increase the SiO2 content. However, bioceramic bioactivity will be diminished by this method. The composition of the bioceramic in this research was derived from 6PM [3,4] (originally developed by Gomez-Vega et al.) by partially substituting B2O3 for SiO2 and adding CaF2. The purpose of this work was to design and fabricate a kind of novel bioceramic, which is used as coating material for Ti6Al4V, to meet the requirements of thermal expansion and bioactivity.

2 Experimental

Three kinds of bioceramics derived from 6PM were prepared by substituting 5 wt.%–12 wt.% B2O3 for SiO2 and adding 4 wt.% CaF2, which aimed at tailoring the thermal expansion coefficient of the bioceramic to match that of Ti6Al4V (10.8 × 10⁻⁶/°C⁻¹). According to the different contents of B2O3 in the coating, the three kinds of bioceramics were respectively named as 6PM-B5-F4, 6PM-B8-F4, 6PM-B11-F4. The composition and thermal expansion coefficient (α) of the bioceramics are designed and summarized in Table 1. The thermal expansion coefficient was calculated by the following equation [6]:

...
\[
\alpha = \sum a_i p_i \times 10^{-7}
\]  
(1)

Here, \(\alpha\) is the linear expansion coefficient; \(a_i\) is the empirical coefficient of each oxide; \(p_i\) is the percent of each oxide.

These bioceramics were prepared by mixing appropriate \(\text{SiO}_2\), \(\text{P}_2\text{O}_5\), \(\text{Na}_2\text{CO}_3\), \(\text{K}_2\text{CO}_3\), \(\text{CaO}\), \(\text{MgO}\), \(\text{Na}_2\text{B}_4\text{O}_7\) and \(\text{CaF}_2\) in ethanol using a high-speed stirrer. After drying at 80°C for 12 h, the mixtures were fired in air at 850°C, holding for 1 h in order to make the carbonate decompose enough, and then heating to 1350°C, holding for 3 h. After furnace cooling, the bioceramic bulks were obtained. The thermal expansion coefficient value \(\alpha_1\) and softening temperature \(T_{s1}\) of these bioceramics were measured by a dilatometer (DIL402C, Netzsch Co., Germany). The bioceramic bulks were milled into powders in a planetary agate mill for 4 h using ethanol as medium. The powders were coated on the Ti6Al4V surface using ethanol as medium. After drying, the alloy coated bioceramic was sintered at softening temperature for 30 min. The bonding strength between alloy and ceramic was measured by a longitudinal pull-off test on the electronic universal testing machine, and the tensile speed was 2 mm/min. The bioceramic morphology and structure were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transformed infrared spectroscopy (FTIR). The in vitro responses of these bioceramics were studied by immersing the specimens in simulated body fluid (SBF).

### 3 Results and conclusions

#### 3.1 Bioceramic characterization

Table 2 shows the measured thermal expansion coefficient value, \(\alpha_1\), and softening temperature, \(T_{s1}\), of these bioceramics. The values of \(T_{s1}\) of all bioceramics are well below the \(\alpha \rightarrow \beta\) transformation temperature of Ti6Al4V (955°C–1010°C). The thermal expansion coefficient of 6PM-B5-F4 is \(10.1 \times 10^{-6}\text{°C}^{-1}\), which is slightly lower than that of Ti6Al4V (10.8 \(\times 10^{-6}\text{°C}^{-1}\)). From Table 1, it can be observed that increasing the \(\text{B}_2\text{O}_3\) content can reduce the calculated value of \(\alpha\). Additionally, the difference between calculated values (Table 1) and measured values (Table 2) can be attributed to the loss of materials during firing.

The bonding strength was done after sintering a ceramic coating on the alloy surface, and is shown in Fig. 1. The results show that the bonding strength between the alloy and the 6PM-B5-F4 bioceramic was about 9 MPa, obviously higher than those of 6PM-B8-F4 and 6PM-B11-F4 owing to the adjustment of the thermal expansion coefficient by inducing \(\text{B}_2\text{O}_3\) in the bioceramics. This trend agrees well with the measured thermal expansion coefficient listed in Table 2. Therefore, the 6PM-B5-F4 is the best design composition in this experiment.

#### 3.2 Morphology and structure analysis

Figure 2 shows the SEM images of the surface of the bioceramic coating (6PM-B5-F4) sintered on the Ti6Al4V alloy before and after being eroded by HF acid. It can be seen from Fig. 2(a) that before erosion by HF acid, the bioceramic coating was smooth. After HF acid erosion, many particle structures appeared on the coating surface.

![Fig. 1 The bonding strength between Ti6Al4V alloy and bioceramics](image-url)

### Table 1 Composition and calculated values of thermal expansion coefficient of bioceramics in this study (wt. %)

<table>
<thead>
<tr>
<th></th>
<th>SiO2</th>
<th>Na2O</th>
<th>K2O</th>
<th>CaO</th>
<th>MgO</th>
<th>P2O5</th>
<th>B2O3</th>
<th>CaF2</th>
<th>(\alpha/10^{-6}\text{°C}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>6PM-B5-F4</td>
<td>59.1</td>
<td>9.8</td>
<td>2.7</td>
<td>7.1</td>
<td>6.3</td>
<td>6.0</td>
<td>5</td>
<td>4</td>
<td>9.5</td>
</tr>
<tr>
<td>6PM-B8-F4</td>
<td>56.1</td>
<td>9.8</td>
<td>2.7</td>
<td>7.1</td>
<td>6.3</td>
<td>6.0</td>
<td>8</td>
<td>4</td>
<td>9.3</td>
</tr>
<tr>
<td>6PM-B11-F4</td>
<td>53.1</td>
<td>9.8</td>
<td>2.7</td>
<td>7.1</td>
<td>6.3</td>
<td>6.0</td>
<td>11</td>
<td>4</td>
<td>9.2</td>
</tr>
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</table>

### Table 2 Measured thermal coefficient \(\alpha_1\) (20°C–500°C) and softening temperature \(T_{s1}\) of the bioceramic

<table>
<thead>
<tr>
<th></th>
<th>(\alpha_1/10^{-6}\text{°C}^{-1}) (20°C–500°C)</th>
<th>(T_{s1}) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>6PM-B5-F4</td>
<td>10.1</td>
<td>598</td>
</tr>
<tr>
<td>6PM-B8-F4</td>
<td>7.8</td>
<td>629</td>
</tr>
<tr>
<td>6PM-B11-F4</td>
<td>8.5</td>
<td>636</td>
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