Bond degradation at the plasma-sprayed HA coating/Ti–6Al–4V alloy interface: an *in vitro* study

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The successful use of the plasma-sprayed HA-coated Ti–6Al–4V system requires strong adhesion between the ceramic coating and the underlying metal substrate. The aim of this study was to evaluate the bond strength at the HA coating (HAC)/Ti–6Al–4V interface, for specimens that had and had not been subjected to immersion in a pH-buffered, serum-added simulated body fluid (SBF). Moreover, coating characteristics affecting the mechanical stability after having been immersed in SBF were clarified. The results showed that bonding degradation of approximately 25–33% of the original strength was measured after immersion in SBF, and that this predominantly depended on the characteristics of the HAC and the period of immersion. Since the surface morphologies of HACs have dissolved in the SBF, it is suggested that the interlamellar structure of the HAC was weakened and, therefore, the bond strength degraded. As both the crystallinity and impurity phases of the HAC increased with immersion time, it can be concluded that the dissolution of the HAC resulting from the initial microstructure has overtaken that of the coating crystallinity and phase purity. A denser microstructure is required to ensure a satisfactory HAC/Ti–6Al–4V interface.

1. Introduction

Plasma-sprayed hydroxyapatite (HA)-coated Ti alloy implants, exhibiting excellent biocompatibility and satisfactory mechanical properties, are currently being investigated as an approach to achieving reliable implant-to-bone fixation, both in animal [1–10] and human clinical studies [11, 12]. In the majority of previous studies, the biological and biomechanical behaviours at the HA coating (HAC)/bone interface have favoured an encouraging result. However, in evaluating the performance and stability of HAC in the load-bearing situation after long-term follow-up, special consideration should be given to the HAC/Ti alloy interface.

Although there is evidence of a chemical reaction observed at the HAC/Ti alloy interface [13, 14], research suggests the presence of a potentially weak HAC/Ti alloy interface [13, 15–18], which may compromise the function of this device, particularly while the HACs are used as the primary means of fixation (i.e. no micro- or macro-textured bond coat enhancing the interfacial strength between HAC and Ti alloy substrate). In a study by Spivak et al. [17], the failure mode of bone-HAC interfacial tensile testing was observed to occur consistently at the HAC–Ti interface, indicating clearly that it was difficult to develop reliable HAC/Ti alloy bonding. Recently, using a modified short-bar technique for interfacial fracture toughness determination, Filiaggi et al. [13] showed that there existed relatively low fracture toughness values in an HA coated Ti 6Al 4V implant system. Therefore, emphasis must be given to the promotion of bonding at the HAC/Ti alloy interface.

To improve HAC/Ti alloy bonding, some general guidelines have been proposed: (1) a denser microstructure (less porosity) would result in higher bonding strength [19]; (2) by overcoming the problems of stress concentration and low cohesive strength among interlamellar structure, thinner HAC (50–75 μm) displayed higher bonding strength [19, 20]; (3) bonding could be improved after heat treatment *in vacuo* by the formation of a titanium–phosphate phase at the interface [21]. Nevertheless, for clinical applications, the question arises whether the HAC/Ti alloy interface...
would degrade with time in a physiological medium. Since signs of resorption of HACs have been documented [7, 9, 12, 22-23], the influence of the dissolution of HACs on the mechanical stability remains to be determined. Furthermore, changes in the coating characteristics after immersion in a physiological medium have not yet been fully evaluated.

In this study, HACs that were quite different in microstructure, concentration of impurity phase, and index of crystallinity were used to evaluate bonding at the HAC/Ti alloy interface. Testing was done with and without simulated body fluid (SBF) immersion. The SBF employed was a pH value buffered, serum added physiological medium, different from the traditional salt medium. After 1, 2, 3, and 4 weeks of immersion, the bond strength at the HAC/Ti alloy interface was calculated by means of the adhesive test (ASTM C-633). Moreover, the changes in coating characteristics that influenced the stability in SBF were studied. This work expands upon the results of a previous study [24].

2. Materials and methods

2.1. Preparation of plasma-sprayed HACs

The feedstock HA powders and spraying conditions used have been reported elsewhere [24]. Three HACs with different coating characteristics were prepared (Table I) according to our previous work [24]: (1) H1-HAC with the most dense and molten microstructure, the highest concentration of impurity phases (CIP), and middle index of crystallinity (IOC); (2) H2-HAC with dense and molten microstructure, middle CIP, and the least ICO; (3) H3-HAC with the least dense and partially molten microstructure, the lowest CIP, and the best IOC. The surface morphologies of HACs with different degrees of melting are shown in Fig. 1. The CIP of HACs was defined as follows [24]:

\[
\text{CIP} = \left( \frac{I_{\text{imp}}}{I_0} \right) \times 100\%
\]

where \( I_{\text{imp}} \) was the sum of the main peak intensity of all impurity phases in each HAC and \( I_0 \) was the main peak intensity of HA phase in the HA powders. The IOC of HACs was defined as follows [24]:

\[
\text{IOC} = \left( \frac{I_c}{I_e} \right) \times 100\%
\]

where \( I_c \) was the main peak intensity of the HA phase in each HAC. More detailed descriptions of the terms CIP and IOC are contained in a previous work [24].

As illustrated by X-ray diffraction patterns in Fig. 2, the phase purity and the crystallinity of HACs used in this study differed from one another.

Two shapes of bioinert Ti-6Al-4V (ASTM F-136) were used as substrates: cylindrical rods, measuring 2.54 cm in diameter and 7.62 cm in length were used for bonding strength measurements. Plate specimens (1 x 1 x 0.3 cm) were employed for coating characterization.

2.2. Adhesion testing at the HAC/Ti-6Al-4V interface

2.2.1. Bond strength measurements in situ

The bond strength at the HAC/Ti-6Al-4V interface was tested using the adhesion test (ASTM C-633) which was especially designed for plasma-sprayed coatings. Each test specimen was an assembly comprising a substrate rod to which the HAC was applied.